QUANTUM LIQUIDS AND QUANTUM CRYSTALS

Propagation of fourth sound in a solution of two superfluid liquids taking the drag effect into account

S. I. Vilchinsky

Taras Shevchenko University, 252022 Kiev, Ukraine*

The propagation of fourth sound waves in a solution of two superfluid liquids ^{3}He–^{4}He is considered by taking into account the effect of reciprocal drag of superfluid motions. It is shown that the inclusion of the drag effect leads to a change in the ratio of intensities of second and first fourth sound waves. © *1998 American Institute of Physics.* [S1063-777X(98)00101-7]

INTRODUCTION

The interest in the possibility of a superfluid transition in the system of ^{3}He impurity atoms in a ^{3}He–^{4}He solution grew after the experimental discovery of the transition of ^{3}He to the superfluid state at temperatures of the order of a few millikelvins.[1,2] Hydrodynamic equations for solutions of two superfluid liquids were derived for the first time by Khalatnikov.[3] The effect of drag by each superfluid motion by the other superfluid component of the solution was taken into account in relevant equations in Refs. 4–7, while the influence of this effect on the dynamic parameters of solutions of superfluid liquids was discussed in Refs. 8–12. The propagation of sounds in such systems was considered in Refs. 13 and 14 without taking the drag effect into account, while the propagation of first, second, and third sounds as well as one more type of vibrations taking the drag effect into account, was analyzed in Refs. 4, 15, and 16. The dispersion equation for determining the velocities of two fourth sounds taking the drag effect into consideration was derived by Volovik et al.[16] who observed that the velocities of the two fourth sounds coincide with the velocities of first and second sounds, respectively for $T \rightarrow 0$. This research aims at deriving expressions for velocities of fourth sound waves in a solution of two superfluid liquids taking into account the drag effect, and at obtaining the ratio of wave intensities for the first and second fourth sounds. We shall solve this problem without taking into account possible gap anisotropy in the ^{3}He spectrum and consider the case of isotropic superfluidity.

We shall write the hydrodynamic equations for solutions of two superfluid liquids, which will be required for further analysis and which take into account the effect of reciprocal drag of superfluid liquids,[4] namely, two continuity equations for each component of the solution:

$$\dot{\rho}_1 + \text{div}\{\rho_1 \mathbf{u}_n + \rho^s_{11}(\mathbf{v}_1 - \mathbf{u}_n) + \rho^s_{12}(\mathbf{v}_2 - \mathbf{u}_n)\} = 0,$$

$$\dot{\rho}_2 + \text{div}\{\rho_2 \mathbf{u}_n + \rho^s_{21}(\mathbf{v}_1 - \mathbf{u}_n) + \rho^s_{22}(\mathbf{v}_2 - \mathbf{u}_n)\} = 0. \quad (1)$$

Here, ρ_1 and ρ_2 are the densities of ^{3}He and ^{4}He particles, respectively (the density ρ of the solution is equal to the sum $\rho_1 + \rho_2$), $\mathbf{v}_1$ and $\mathbf{v}_2$ are the superfluid velocities,

$\rho^s_{11}, \rho^s_{22}, \rho^s_{12} = \rho^s_{21}$ are the superfluid densities, the densities ρ^s_{21} and ρ^s_{12} describing reciprocal drag of superfluid motions, $\mathbf{u}_n$ is the velocity of normal motion, and

$$\rho_1 = c\rho; \quad \rho_2 = (1 - c)\rho, \quad (2)$$

where c is the ^{3}He concentration.

We supplement these equation with two equations of superfluid motions

$$\frac{\partial \mathbf{v}_1}{\partial t} + \nabla \left(\mu_1 - \frac{1}{2} \mathbf{u}_n^2 + \mathbf{v}_1 \cdot \mathbf{u}_n \right) = 0,$$

$$\frac{\partial \mathbf{v}_2}{\partial t} + \nabla \left(\mu_2 - \frac{1}{2} \mathbf{u}_n^2 + \mathbf{v}_2 \cdot \mathbf{u}_n \right) = 0, \quad (3)$$

where μ_1 and μ_2 are the chemical potentials defined by the identity for energy:

$$d\varepsilon = T dS + \mu_1 d\rho_1 + \mu_2 d\rho_2 + [\rho^s_{11}(\mathbf{v}_1 - \mathbf{u}_n) + \rho^s_{12}(\mathbf{v}_2 - \mathbf{u}_n)] \cdot d(\mathbf{v}_1 - \mathbf{v}_n) + [\rho^s_{21}(\mathbf{v}_1 - \mathbf{u}_n) + \rho^s_{22}(\mathbf{v}_2 - \mathbf{u}_n)] \cdot d(\mathbf{v}_2 - \mathbf{v}_n). \quad (4)$$

The equations of conservation of total momentum and entropy have the form

$$\mathbf{j} = \rho_n \mathbf{u}_n + (\rho^s_{11} + \rho^s_{21})\mathbf{v}_1 + (\rho^s_{12} + \rho^s_{22})\mathbf{v}_2,$$

$$j_i + \partial \Pi_{ik} / \partial x_k = 0, \quad (5)$$

where $\rho_n \equiv \rho - \rho^s_{11} - \rho^s_{22} - 2\rho^s_{12}$ is the density of the normal component, and Π_{ik} is the tensor of the momentum flux, defined as

$$\Pi_{ik} = \rho^s_{11} v_{1i} v_{1k} + \rho^s_{22} v_{2i} v_{2k} + \rho^s_{12}(v_{1i} v_{2k} + v_{1k} v_{2i}) + \rho_n u_{1i} u_{1k} + P \delta_{ik}, \quad (6)$$

while pressure is defined as

$$P = -\varepsilon + TS + \mu_1 \rho_1 + \mu_2 \rho_2; \quad (7)$$

$$\dot{S} + \text{div}(S\mathbf{u}_n) = 0. \quad (8)$$

FOURTH SOUND IN SOLUTIONS OF TWO SUPERFLUID LIQUIDS

It is well known[17] that fourth sound in an ordinary superfluid liquid can be visualized as oscillations of the superfluid component in narrow capillaries, such that the normal component is stationary, and the penetration depth for a viscous wave is larger than the capillary diameter.[18] In order to solve the problem formulated above, we linearize the hydrodynamic equations (1), (3), and (8) under the condition $\mathbf{u}_n = 0$:

$$\dot{\rho}_1 + \rho_{11}^s \operatorname{div} \mathbf{v}_1 + \rho_{12}^s \operatorname{div} \mathbf{v}_2 = 0,$$

$$\dot{\rho}_2 + \rho_{21}^s \operatorname{div} \mathbf{v}_1 + \rho_{22}^s \operatorname{div} \mathbf{v}_2 = 0,$$

$$\frac{\partial \mathbf{v}_1}{\partial t} + \nabla \mu_1 = 0, \quad \frac{\partial \mathbf{v}_2}{\partial t} + \nabla \mu_2 = 0, \quad \dot{S} = 0. \tag{9}$$

It is convenient to introduce, instead of μ_1 and μ_2, new chemical potentials

$$\mu = c\mu_1 + (1-c)\mu_2, \quad \xi = \mu_1 - \mu_2.$$

In this case, we obtain from (6) and (7) $(\sigma = S/\rho)$

$$\rho^{-1} dP = \sigma dT + d\mu - \xi dc. \tag{10}$$

Using this notation and relations (2), we can write the system (9) in the form

$$c\dot{\rho} + \dot{c}\rho + \rho_{11}^s \operatorname{div} \mathbf{v}_1 + \rho_{12}^s \operatorname{div} \mathbf{v}_2 = 0,$$

$$(1-c)\dot{\rho} - \dot{c}\rho + \rho_{21}^s \operatorname{div} \mathbf{v}_1 + \rho_{22}^s \operatorname{div} \mathbf{v}_2 = 0,$$

$$\frac{\partial \mathbf{v}_1}{\partial t} + (1-c)\nabla\xi - \sigma\nabla T + \rho^{-1}\nabla P = 0,$$

$$\frac{\partial \mathbf{v}_2}{\partial t} - c\nabla\xi - \sigma\nabla T + \rho^{-1} P = 0,$$

$$\dot{\sigma}\rho + \sigma\dot{\rho} = 0. \tag{11}$$

We shall consider a plane acoustic wave in which all variables are proportional to $\exp[i\omega(t - x/u)]$. Denoting by prime the varying components of relevant quantities, we obtain from (11) a system of algebraic equations, in which we go over to the variables P, c, and T by using the following equations:

$$\rho' = \left(\frac{\partial \rho}{\partial P}\right) P' + \left(\frac{\partial \rho}{\partial c}\right) c',$$

$$\sigma' = \left(\frac{\partial \sigma}{\partial T}\right) T' + \left(\frac{\partial \sigma}{\partial c}\right) c',$$

$$\xi' = -\frac{1}{\rho^2}\left(\frac{\partial \rho}{\partial P}\right) P' - \left(\frac{\partial \sigma}{\partial T}\right) T' + \left(\frac{\partial \xi}{\partial c}\right) c'. \tag{12}$$

In these equations, we have used the relations between derivatives of thermodynamic quantities, following from identity (10), as well as the smallness of the thermal expansion coefficient $(\partial \rho/\partial T)$.[14] The compatibility condition for a system of algebraic equations together with (12) leads to the following equation for the velocity of sound:

$$u^4 - u^2 \beta^{-1}\left(\frac{\partial P}{\partial \rho}\right)\left\{\left[c^2 \frac{(\rho_{22}^s + \rho_{21}^s)}{\rho} - (1-c)^2 \frac{(\rho_{11}^s + \rho_{12}^s)}{\rho}\right]\right.$$

$$\times [DC - AF] + \left[c \frac{(\rho_{22}^s + \rho_{21}^s)}{\rho} - (1-c) \frac{(\rho_{11}^s + \rho_{12}^s)}{\rho}\right]$$

$$\times \left[\frac{D}{\rho} + \sigma A + \rho(\alpha F - \beta C) + \rho(\rho_{11}^s + \rho_{12}^s + \rho_{21}^s + \rho_{22}^s)(\alpha\sigma\right.$$

$$\left. - \beta)\right] - \left[\frac{(\rho_{12}^s + \rho_{21}^s)}{\rho}\right][DC - AF] + \rho(\rho_{11}^s + \rho_{12}^s + \rho_{21}^s$$

$$\left. + \rho_{22}^s)(\alpha\sigma - \beta)\right\} + \beta^{-1}(\rho_{11}^s \rho_{22}^s - \rho_{12}^s \rho_{21}^s)\left(\frac{\partial P}{\partial \rho}\right)$$

$$\times \left\{\sigma\left[\frac{\alpha}{\rho}\left(\frac{\partial \xi}{\partial c}\right) - \frac{1}{\rho^3}\left(\frac{\partial \rho}{\partial c}\right)\right] + \frac{\beta}{\rho}\left(\frac{\partial \xi}{\partial c}\right) - \frac{1}{\rho}\left(\frac{\partial \sigma}{\partial c}\right)\right\} = 0. \tag{13}$$

Here

$$A \equiv \left(\frac{\partial \rho}{\partial P}\right) + \alpha\left(\frac{\partial \rho}{\partial c}\right), \quad C \equiv \alpha\left(\frac{\partial \xi}{\partial c}\right) - \frac{1}{\rho^2}\left(\frac{\partial \rho}{\partial c}\right),$$

$$D \equiv \beta\left(\frac{\partial \rho}{\partial c}\right), \quad F \equiv \beta\left(\frac{\partial \xi}{\partial c}\right) - \left(\frac{\partial \sigma}{\partial c}\right),$$

$$\alpha \equiv -\left\{\left(\frac{\partial \rho}{\partial c}\right)\left(\frac{\partial P}{\partial \rho}\right) + \frac{\rho}{\sigma}\left(\frac{\partial \sigma}{\partial c}\right)\left(\frac{\partial P}{\partial \rho}\right)\right\}^{-1},$$

$$\beta \equiv -\left\{\left(\frac{\partial \sigma}{\partial c}\right)\left(\frac{\partial T}{\partial \sigma}\right) + \frac{\sigma}{\rho}\left(\frac{\partial \rho}{\partial c}\right)\left(\frac{\partial T}{\partial \sigma}\right)\right\}^{-1}.$$

We shall solve this equation bearing in mind that one root is much smaller than the other root in the concentration parameter $c \ll 1$ and taking into account the fact that the terms of the order of ρ_n/ρ are small for temperatures under investigation in view of the smallness of c. This gives

$$(u_4')^2 = \frac{\rho_{21}^s + \rho_{22}^s}{\rho}\left(\frac{\partial P}{\partial \rho}\right), \quad (u_4'')^2 = \frac{\rho_{11}^s + \rho_{12}^s}{\rho}\left(\frac{\partial \xi}{\partial c}\right). \tag{14}$$

For a certain redefinition, this result coincides with solutions of a biquadratic equation for the fourth sound velocities, which were obtained in Ref. 16. For $\rho_{12}^s = \rho_{21}^s = 0$, expressions (14) are transformed into the corresponding equations obtained by Mineev.[14] Thus, the drag effect in this approximation leads to the emergence of sums of densities in the numerators of expressions for velocities and does not affect qualitatively the form of fourth sound waves which can be regarded as joint oscillations of density and concentration. Besides, for $T \to 0$, the expressions for the velocities of two fourth sounds coincide with the expressions for velocities of first and second sound, respectively, which were derived by Andreev and Bakshin.[4] This in accord with the result obtained by Volovik et al.[16]

Mineev[14] obtained the ratio of intensities of the second and first fourth sounds in the radiation emitted by a wall vibrating in the direction perpendicular to its plane in the absence of drag effect, which contains the concentration parameter to a power of 3/2. Let us calculate this ratio taking into account reciprocal drag of superfluid components and

compare it with the result obtained in Ref. 14. Let us suppose that the wall vibrates in the direction perpendicular to its plane with the velocity $v_0 \exp(-i\omega t)$. The velocities of the first superfluid component in the emitted first and second fourth sounds are given by

$$v_1' = A_1 \exp\left(-i\omega\left(t - \frac{x}{u}\right)\right),$$

$$v_1'' = A_2 \exp\left(-i\omega\left(t - \frac{x}{u}\right)\right), \qquad (15)$$

while the velocities of the second component are given by

$$v_2' = A_1 a_1 \exp\left(-i\omega\left(t - \frac{x}{u}\right)\right),$$

$$v_2'' = A_2 a_2 \exp\left(-i\omega\left(t - \frac{x}{u}\right)\right). \qquad (16)$$

Here

$$a_1 = v_2'/v_1', \quad a_2 = v_2''/v_1''. \qquad (17)$$

The values of v_1 and v_2 at the surface of a solid must coincide with the velocity of the surface:

$$A_1 + A_2 = v_0, \quad A_1 a_1 + A_2 a_2 = v_0,$$

whence

$$\frac{A_2}{A_1} = -\frac{(1 - a_1)}{(1 - a_2)}.$$

The average density of energy emitted in each of sounds can be obtained from (15) and (16):

$$E = \rho_{11}^s \overline{v_1^2} + (\rho_{12}^s + \rho_{21}^s)\overline{(v_1 - v_2)^2} + \rho_{22}^s \overline{v_2^2} = \frac{1}{2} A^2 (\rho_{11}^s$$
$$+ (\rho_{12}^s + \rho_{21}^s)(1 - a)^2 + \rho_{22}^s a^2), \qquad (18)$$

while the ratio of intensities I_2 and I_1 of the emitted waves of second and first fourth sounds is given by

$$\frac{I_2}{I_1} = \frac{u_4''}{u_4'}\left(\frac{A_2}{A_1}\right)^2 \frac{\rho_{11}^s + (\rho_{12}^s + \rho_{21}^s)(1 - a_2)^2 + \rho_{22}^s a_2^2}{\rho_{11}^s + (\rho_{12}^s + \rho_{21}^s)(1 - a_1)^2 + \rho_{22}^s a_1^2}$$

$$= \frac{u_4''}{u_4'}\left(\frac{1 - a_1}{1 - a_2}\right)^2 \frac{\rho_{11}^s + (\rho_{12}^s + \rho_{21}^s)(1 - a_2)^2 + \rho_{22}^s a_2^2}{\rho_{11}^s + (\rho_{12}^s + \rho_{21}^s)(1 - a_1)^2 + \rho_{22}^s a_1^2}. \qquad (19)$$

Thus, in order to find the required ratio of intensities, we must determine a_1 and a_2. Relations (12) lead to

$$\frac{v_2}{v_1} = \left\{-(\rho_{11}^s + \rho_{12}^s)\left\{(1 - c)^2\left[\left(\frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^2 + \frac{\partial\rho}{\partial P}\left(\frac{\partial\sigma}{\partial c}\right)^2\frac{\partial T}{\partial\sigma}\right.\right.\right.$$

$$+ \frac{\partial\rho}{\partial P}\frac{\partial\xi}{\partial c}\bigg] + 2(1 - c)\left[\frac{\partial\rho}{\partial P}\frac{\partial\sigma}{\partial c}\sigma\frac{\partial T}{\partial\sigma} - \frac{1}{\rho}\frac{\partial\rho}{\partial P}\right]$$

$$+ \sigma^2\frac{\partial\rho}{\partial P}\frac{\partial T}{\partial\sigma} + 1\bigg\} + u^2\rho\frac{\partial\rho}{\partial P}\bigg\}\left\{-(\rho_{21}^s + \rho_{22}^s)\bigg\{c(1$$

$$- c)\left[\left(\frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^2 + \frac{\partial\rho}{\partial P}\left(\frac{\partial\sigma}{\partial c}\right)^2\frac{\partial T}{\partial\sigma} + \frac{\partial\rho}{\partial P}\frac{\partial\xi}{\partial c}\right]$$

$$+ 2c\left[\frac{\partial\rho}{\partial P}\frac{\partial\sigma}{\partial c}\sigma\frac{\partial T}{\partial\sigma} - \frac{1}{\rho}\frac{\partial\rho}{\partial P}\right] - \frac{\sigma}{\rho}\frac{\partial\sigma}{\partial c}\frac{\partial\rho}{\partial P}\frac{\partial T}{\partial\sigma}$$

$$+ \frac{1}{\rho}\frac{\partial\rho}{\partial c} - \sigma^2\frac{\partial\rho}{\partial P}\frac{\partial T}{\partial\sigma} - 1\bigg\}\bigg\}^{-1}.$$

Retaining only the principal terms in concentration, we obtain

$$a_1 = \frac{v_{s2}'}{v_{s1}'} = (u_4')^2\frac{\rho(\partial\rho/\partial P)}{(\rho_{22}^s + \rho_{21}^s)[1 - (1/\rho)(\partial\rho/\partial c)]},$$

$$a_2 = \frac{v_{s2}''}{v_{s1}''} = \left\{(u_4'')^2\rho\frac{\partial\rho}{\partial P} - (\rho_{12}^s + \rho_{11}^s)\left[\frac{\partial\rho}{\partial P}\frac{\partial\xi}{\partial c}\right.\right.$$

$$+ \left.\left(1 - \frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^2\right]\bigg\}\left[(\rho_{22}^s + \rho_{21}^s)\left(1 - \frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)\right]^{-1}. \qquad (20)$$

Using relations (14), we can write the obtained expressions in the form

$$a_1 = \left(1 - \frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^{-1}, \quad a_2 = -\frac{(\rho_{11}^s + \rho_{12}^s)}{(\rho_{22}^s + \rho_{21}^s)}\left(1 - \frac{1}{\rho}\frac{\partial\rho}{\partial c}\right). \qquad (21)$$

Substituting (21) into (19), we obtain

$$\frac{I_2}{I_1} = \left(\frac{\partial\xi}{\partial c}\frac{\partial\rho}{\partial P}\right)^{1/2}\left(\frac{\rho_{11}^s + \rho_{12}^s}{\rho_{21}^s + \rho_{22}^s}\right)^{1/2}(A + B)\left(\frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^2, \qquad (22)$$

where

$$A \equiv \left\{\left(\frac{\rho_{11}^s}{\rho_{22}^s}\right)\left[1 + \left(\frac{\rho_{11}^s}{\rho_{22}^s}\frac{(1 + \rho_{12}^s/\rho_{11}^s)^2}{(1 + \rho_{21}^s/\rho_{22}^s)^2}\left(1 - \frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^2\right]\right]\right\}$$

$$\times\left[1 + \left(\frac{\rho_{11}^s}{\rho_{22}^s}\right)\frac{(1 + \rho_{12}^s/\rho_{11}^s)}{(1 + \rho_{21}^s/\rho_{22}^s)}\left(1 - \frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)\right]^{-2}$$

$$\times\left[1 + \frac{\rho_{11}^s}{\rho_{22}^s}\left(1 - \frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^2 + \frac{(\rho_{12}^s + \rho_{21}^s)}{\rho_{22}^s}\left(\frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^2\right]^{-1};$$

$$B \equiv (\rho_{12}^s + \rho_{21}^s)\left[\rho_{22}^s + \rho_{11}^s\left(1 - \frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^2 + (\rho_{12}^s + \rho_{21}^s)\right.$$

$$\times\left.\left(\frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^2\right]^{-1}.$$

Using relations (14) and assuming that $\rho_{12}^s/\rho_{22}^s \ll 1$, we obtain the following expression for $A + B$ in the main order in concentrations:

$$A + B = \frac{\rho_{11}^s}{\rho_{22}^2} + \frac{\rho_{12}^s + \rho_{21}^s}{\rho_{22}^s + \rho_{11}^s}.$$

Consequently, we can finally write

$$\frac{I_2}{I_1} = \left(\frac{\partial\xi}{\partial c}\frac{\partial\rho}{\partial P}\right)^{1/2}\left(\frac{\rho_{11}^s + \rho_{12}^s}{\rho_{21}^s + \rho_{22}^s}\right)^{1/2}\times\left(\frac{\rho_{11}^s}{\rho_{22}^s} + \frac{\rho_{12}^s + \rho_{21}^s}{\rho_{22}^s + \rho_{11}^s}\right)\left(\frac{1}{\rho}\frac{\partial\rho}{\partial c}\right)^2. \qquad (23)$$

CONCLUSIONS

The ratio of intensities of the two fourth sounds emitted by a wall vibrating in the direction perpendicular to its plane, which was obtained by taking into account the effect of re-

ciprocal drag of superfluid motions, differs from the corresponding equation obtained without taking the drag effect into consideration. This is due to the fact that the inclusion of drag effect leads to a change in the average density of energy emitted by each sound: the expression (18) for energy density acquires the term

$$(\rho_{12}^s + \rho_{21}^s)\overline{(v_1 - v_2)^2},$$

which is absent in the corresponding relation in Ref. 14. Comparing (23) with the corresponding result obtained in Ref. 14, we conclude that the effect of reciprocal drag of superfluid motions leads to a change in the concentration dependence of the intensity ratio for both fourth sounds, i.e., to the emergence of a new term proportional to the sum of the densities ρ_{12}^s and ρ_{21}^s. This allows us to estimate experimentally the value of the density ρ_{12}^s describing the drag effect.

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*E-mail: sivil@popper1.isf.kiev.ua

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Dynamics of small-angle domain walls in external oscillating magnetic field

K. I. Primak and A. L. Sukstanskiĭ

*A. Galkin Physicotechnical Institute, National Academy of Sciences of the Ukraine, 340114 Donetsk, Ukraine**

The dynamics of small-angle domain walls existing in an easy-axis ferromagnet in the vicinity of spin-reorientation phase transition in an external in-plane magnetic field is studied. The dependence of the drift velocity on the amplitude, frequency, and polarization of the oscillating field is obtained. © *1998 American Institute of Physics.* [S1063-777X(98)00401-0]

In the huge number of publications devoted to experimental and theoretical study of the dynamics of domain walls (DW) in various magnetically ordered media, main attention is paid to analysis of two principal types of DW movements: translational motion in a constant magnetic field and vibrational motion in an oscillating external field. However, there exists one more type of DW movement, which can be induced by an external oscillating field, viz., DW drift, i.e., the emergence of a constant component in the velocity of the wall. The DW drift was observed experimentally in Refs. 1 and 2, while a similar effect for another type of topological solitons (Bloch lines) was observed by Gornakov et al.[3,4]

The phenomenon of DW drift in ferromagnets was predicted theoretically by Schlomann and Miln[5] on the basis of energy considerations. A more consistent approach to the solution of this class of problems on the basis of the specific theory of perturbations was proposed by Iordanskii and Marchenko[6] who studied the drift of Bloch lines. At the present time, the DW drift in an external oscillating magnetic field has been studied in detail for virtually all basic types of magnets.[7–10] In addition, the possibility of DW drift in ferroelectric magnets in an external oscillating electric was analyzed in Ref. 11, while the DW drift under the action of a high-intensity acoustic wave was predicted in Ref. 12.

However, the authors of all these publications studied the drift of only 180° domain walls existing far away from the regions of spin-reorientation phase transitions. It is well known that the structural and dynamic properties of DW in the vicinity of such transitions differ considerably from the properties of ordinary 180° domain walls. A typical example of a spin-reorientation phase transition is the well-known phase transition in a ferromagnet with an ''easy-axis'' type magnetic anisotropy in an in-plane magnetic field close to the anisotropy field. In the vicinity of this phase transitions, the component of the magnetization vector **M** that is collinear to the anisotropy axis (z-axis) is small in view of the closeness to the phase-transition point, and the angle of rotation of the vector **M** in the DW separating domains with opposite values of M_z is also small (such DW will be henceforth referred to as small-angle walls). It was proved in Ref. 13 that the dynamics of a small-angle DW can be described

by using the ''Lorentz-invariant'' model Φ^4 (see below) in contrast to conventional 180° DW in ferromagnets whose dynamics does not possess such an invariance. In this connection, it would be interesting to study the dynamics of small-angle DW in an external oscillating magnetic field; this forms the subject of the present publication.

Let us consider a ferromagnet with an ''easy-axis'' type magnetic anisotropy in an external in-plane constant magnetic field $\mathbf{H}_0$ and in a varying field $\widetilde{\mathbf{H}}(t)$ oriented in the DW plane. We choose the Cartesian system of coordinates in such a way that the anisotropy axis coincides with the z-axis and the direction of the constant in-plane field $\mathbf{H}_0$ coincides with the y-axis.

We proceed from the expression for the energy of the ferromagnet written in the standard form

$$W = \int d\mathbf{r} \left\{ \frac{\alpha}{2} (\nabla \mathbf{M})^2 - \frac{\beta}{2} M_z^2 - \mathbf{H} \cdot \mathbf{M} \right\}, \qquad (1)$$

where **M** is the magnetization vector, α and β are the exchange interaction and anisotropy constants, respectively, and $\mathbf{H} = \mathbf{H}_0 + \widetilde{\mathbf{H}}(t)$ is the applied magnetic field. In formula (1), we disregard the magnetic dipole interaction since the effect of this interaction on the dynamic properties of DW in the vicinity of a spin-reorientation phase transition is small and can be neglected.[13,14]

The static and dynamic properties of a ferromagnet are determined by the equations of motion for the magnetization vector **M** (the Landau–Lifshitz equations):

$$\dot{\mathbf{M}} = -g[\mathbf{M} \times \mathbf{H}_e] + \frac{\lambda_r}{M_0} [\mathbf{M} \times \dot{\mathbf{M}}], \quad \mathbf{H}_e = -\frac{\delta W}{\delta \mathbf{M}}, \qquad (2)$$

where $M_0 = |\mathbf{M}|$ is the saturation magnetization, g the gyromagnetic ratio, λ_r the relaxation constant, and the dot indicates differentiation with respect to time.

Parametrizing the magnetization vector **M** by two independent angular variables θ and φ,

$$\mathbf{M} = M_0 (\cos \theta \sin \varphi, \cos \theta \cos \varphi, \sin \theta), \qquad (3)$$

we can write the equations of motion (2) in the form

$$\frac{\dot{\varphi}}{g M_0} \cos \theta + \alpha \Delta \theta + (\beta + \alpha \varphi'^2) \sin \theta \cos \theta + h_z \cos \theta$$

$$\dot\varphi rx\cos\theta+\alpha\Delta\theta+(\beta+\alpha\varphi'^2)\sin\theta\cos\theta+h_z\cos\theta-h_y\sin\theta\cos\theta \quad (4)$$

$$\frac{1}{\omega_0^2}\ddot\Phi-\frac{\lambda_r}{gM_0}\dot\Phi-x_0^2\Phi''-2(\Phi^3-\Phi)-h_1(t)-2h_2(t)\Phi-\frac{\lambda}{\omega_0}\dot\Phi=0,$$

$$(9)$$

$$-\frac{\dot\theta}{gM_0}\cos\theta+\alpha(\varphi'\cos^2\theta)'-h_y\cos\theta\sin\varphi$$

$$=\frac{\lambda_r}{gM_0}\dot\varphi\cos^2\theta \tag{5}$$

where $h_y(t)=[H_0+\widetilde{H}_y(t)]/M_0$, $h_z(t)=\widetilde{H}_z(t)/M_0$, and the prime indicates differentiation with respect of the coordinate x (henceforth, we shall confine our analysis only to one-dimensional solutions of the equations of motion). While writing Eqs. (4) and (5), we have taken into account the fact that the plane of the wall in the chosen geometry coincides with the (yz) plane, and the varying external field oriented in this plane has two nonzero components $\widetilde{H}_y(t)$ and $\widetilde{H}_z(t)$. We shall assume that $\widetilde{\mathbf{H}}(t)$ is a monochromatic field of frequency ω with a certain phase shift χ between the components (it will be proved below that the DW drift velocity we are interested in depends significantly on the quantity χ):

$$\widetilde{H}_z(t)=H_{z0}\cos\omega t, \quad \widetilde{H}_y(t)=H_{y0}\cos(\omega t+\chi). \tag{6}$$

If the constant external magnetic field is smaller than the anisotropy field ($H_0<H_a=\beta M_0$), and the varying field is zero, the magnetization vector $\mathbf{M}$ in the equilibrium homogeneous state lies in the (yz) plane ($\varphi=0$) and forms the angle $\theta_*=\pm\arccos(H_0/\beta M_0)$. with the y-axis. For $H_0=\beta M_0$, a second-order phase transition to a phase with the in-plane orientation of the vector $\mathbf{M}$ takes place ($\theta_*=0$). The static one-dimensional solution of Eqs. (4) and (5) describing a DW separating two domains with $M_z=M_0\sin\theta_*$ and $M_z=-M_0\sin\theta_*$ can be written in the form[15]

$$\sin\theta(x)=\sin\theta_*\frac{\sinh[(x/x_0)\sin\theta_*]}{\cosh[(x/x_0)\sin\theta_*]+\cos\theta_*}. \tag{7}$$

It is impossible to obtain the exact distribution of magnetization in a moving DW in the presence of an in-plane field in analytic form, but a number of peculiarities typical of a moving DW have been analyzed qualitatively.[13,14] Among other things, the effective mass of a DW as a function of the applied in-plane field was determined, and the limiting velocity of the steady-state motion of DW was calculated. It was shown[13] that in a strong in-plane field close to the anisotropy field, i.e., in the case when the parameter $\varepsilon=(1-H/H_a)^{1/2}\ll1$, the DW dynamics can be described in the main approximation in this small parameter by using the well-known Φ^4 model. Indeed, if $\varepsilon\ll1$, the angle θ in DW is small, $|\theta|\leqslant\theta_*\approx\sqrt2\varepsilon\ll1$. Retaining in Eq. (5) only the terms linear in the parameter ε, we can express the angle φ in terms of the angle θ:

$$\varphi\approx-\frac{\dot\theta}{gH_0}. \tag{8}$$

Substituting (8) into Eq. (4), we obtain the following expression in the main approximation in the parameter ε:

where the following notation has been introduced:

$$\Phi=\frac{\theta}{\sqrt2\varepsilon}, \quad x_0^2=\frac{2\alpha}{\beta\varepsilon^2}, \quad \omega_0^2=\frac{g^2H_0H_a\varepsilon^2}{2},$$

$$\lambda=\frac{\lambda_r}{\varepsilon}\left(\frac{2H_0}{H_a}\right)^{1/2}, \quad h_1(t)=-\frac{\sqrt2\,\widetilde{H}_z(t)}{H_a\varepsilon^3},$$

$$h_2(t)=\frac{\widetilde{H}_y(t)}{H_a\varepsilon^2}.$$

It can be easily verified that Eq. (9) is the Euler–Lagrange equation for a system described by the Lagrange function L typical of the Φ^4 model in the external field, i.e.,

$$L=\int dx\left\{\frac{1}{2\omega_0^2}\dot\Phi^2-\frac{x_0^2}{2}\Phi'^2-\frac{1}{2}(\Phi^2-1)^2-[h_1(t)\Phi\right.$$

$$\left.+h_2(t)\Phi^2]\right\}, \tag{10}$$

and by the dissipative function Q defined as

$$Q=\frac{\lambda}{2\omega_0}\int dx\dot\Phi^2. \tag{11}$$

It should be noted that, although the dynamics of a ferromagnet is described in the general case by Eqs. (4) and (5) that do not possess the Loretz or Galilean invariance, the Φ^4 model, which is suitable at the phase-transition point, is Loretz-invariant with the characteristic velocity $c=x_0\omega_0=g(\alpha M_0H_0)^{1/2}$. Consequently, in contrast to the general case, we can easily construct dynamic solutions of the equations of motion if the corresponding static solution is known. For example, the static solution of Eq. (9) in the absence of an external oscillating field and damping, which satisfies the boundary conditions $\Phi_0(\pm\infty)=\pm1$, $\Phi_0'(\pm\infty)=0$ and describes a stationary DW, has the form

$$\Phi_0(x)=\tanh\left(\frac{x}{x_0}\right), \tag{12}$$

where x_0 has the meaning of the DW thickness (kink).

The corresponding dynamic solution for a wall moving at a constant velocity V can be obtained from (12) by using the standard ''relativistic'' substitution $x\to(x-Vt)/(1-V^2/c^2)^{1/2}$. The limiting velocity of steady-state motion of DW is equal to c.

If we take into account the interaction with the varying external field and damping, the ''Loretz invariance'' of Eq. (9) is naturally violated, and hence we can obtain its solution, following Refs. 7–10, by using a version of the perturbation theory for solitons assuming that the amplitude of the external magnetic field [and hence the ''fields'' h_1 and h_2 in Eq. (9)] is small. For this purpose, we define the collective

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variable $X(t)$ as the coordinate of the DW center at an arbitrary instant of time t and seek the solution of Eq. (9) in the form

$$\Phi(x,t) = \Phi_0(\xi) + \psi_1(\xi,t) + \psi_2(\xi,t) + \dots , \qquad (13)$$

where $\xi = x - X(t)$, and the indices $n = 1, 2, \dots$ indicate the order of smallness of the quantity in the amplitude of the external oscillating field ($\psi_n \sim h^n$). The function $\Phi_0(\xi)$ describes the motion of a nondistorted kink and has the same structure as in the static solution (12) (in view of the smallness of the external oscillating field, the amplitude of variation of the kink velocity is also small, $V \ll c$, and hence we can neglect the ''Loretz'' contraction of the kink thickness). The terms $\psi_n(\xi,t)(n=1,2,\dots)$ describe the distortion of the DW shape and the excitation of spin waves during the DW motion.

The DW drift velocity is defined as the value of the DW instantaneous velocity $V(t) = \dot{X}(t)$ averaged over the period of oscillations, $V_{dr} = \overline{V(t)}$, where the bar indicates averaging over the period of oscillations of the applied field. The DW velocity V can also be represented in the form of a series in the external field amplitude, bearing in mind that we are interested only in the forced motion of the DW:

$$V = V_1 + V_2 + \dots, \quad V_n \sim h^n. \qquad (14)$$

Substituting expansions (13) and (14) into Eq. (9) and singling out the terms of various orders of smallness, we obviously obtain an equation in the zeroth approximation describing a stationary DW and having a solution of the form (12). The first-order equation in the perturbation theory can be represented in the form

$$\left(\hat{L} + \frac{1}{\omega_0^2} \frac{\partial^2}{\partial t^2} + \frac{\lambda}{\omega_0} \frac{\partial}{\partial t} \right) \psi_1(\xi,t)$$
$$= \left(\frac{\dot{V}_1}{\omega_0^2} + \frac{\lambda V_1}{\omega_0} \right) \Phi_0'(\xi) - [h_1(t) + h_2(t)\Phi_0(\xi)], \qquad (15)$$

where the operator $\hat{L}$ has the form of a Schrödinger operator with a reflectionless potential:

$$\hat{L} = -x_0^2 \frac{d^2}{d\xi^2} + 4 - \frac{6}{\cosh^2 \xi/x_0}. \qquad (16)$$

The spectrum and wave functions of the operator $\hat{L}$ are well known. In contrast to the models of magnets analyzed in Refs. 7–12, the operator $\hat{L}$ possesses not one but two discrete levels with the eigenvalues λ_1 and λ_2, corresponding to the localized wave functions $u_1(\xi)$ and $u_2(\xi)$:

$$u_1(\xi) = \frac{A_1}{\cosh^2(\xi/x_0)}, \quad \lambda_1 = 0, \quad A_1 = \left(\frac{3}{4x_0} \right)^{1/2};$$

$$u_2(\xi) = \frac{A_2 \sinh(\xi/x_0)}{\cosh^2(\xi/x_0)}, \quad \lambda_2 = 3, \quad A_2 = \left(\frac{3}{2x_0} \right)^{1/2}, \qquad (17)$$

as well as the continuous spectrum $\lambda_k = 4 + (kx_0)^2$ with the eigenfunctions u_k:

$$u_k(\xi) = A_k[3\tanh^2(\xi/x_0) - 3ikx_0 \tanh(\xi/x_0)$$
$$- (1 + k^2 x_0^2)]\exp(ik\xi),$$

$$A_k = [(1 + k^2 x_0^2)(4 + k^2 x_0^2)L]^{1/2}, \qquad (18)$$

where L is the length of the crystal.

The functions $\{u_1, u_2, u_k\}$ form a complete orthonormal set, and it is natural to seek solutions of Eq. (15) in the form of an expansion in this set. For a monochromatic external field of frequency ω, we put

$$\psi_1(\xi,t) = \mathrm{Re} \left\{ e^{i\omega t} \left[c_1 u_1(\xi) + c_2 u_2(\xi) + \sum_k c_k u_k(\xi) \right] \right\}. \qquad (19)$$

Here it is appropriate to make the following important remark. Equation (15) describes the excitation of linear spin waves agaist the background of DW. The first term in the expansion of the function $\psi_1(\xi,t)$ corresponds to the shear (Goldstone) mode, i.e., the motion of DW as a single whole. However, the corresponding degree of freedom has been already taken into account by introducing the collective coordinate $X(t)$ in the definition of the variable ξ. For this reason, the shear mode should be omitted in expansion (19), i.e., we must put $c_1 = 0$ (a detailed discussion of this question can be found in the monograph[16]). This condition leads to the requirement of orthogonality of the function $u_1(\xi)$ on the right-hans side of Eq. (15), which in turn defines the equation for the DW velocity $V_1(t)$ in the approximation that is linear in the external oscillating field:

$$\dot{V}_1 + \lambda \omega_0 V_1 = \frac{3}{2} c\omega_0 h_1(t). \qquad (20)$$

The solution of this equation describes DW vibrations in an oscillating external field, these vibrations being excited only by the z-component of the field. It can easily be seen that $\overline{V_1(t)} = 0$, i.e., the DW drift is absent in the approximation linear in the external field.

The coefficients c_2 and c_k in expansion (19), that define the amplitudes of the spin wave localized at DW and nonlocalized (intradomain) spin waves, can be found by the standard procedure by multiplying the right-hand side of Eq. (15) by $u_2^*(\xi)$ or $u_k^*(\xi)$ and integrating with respect to the variable ξ. After simple calculations, we obtain

$$c_2 = -\frac{\pi x_0 A_2}{3 - \Omega^2 + i\lambda\Omega} h_{20},$$

$$c_k = -\frac{\pi x_0 A_k}{4 + k^2 x_0^2 - \Omega^2 + i\lambda\Omega} \left[4\delta(kx_0)h_{10} \right.$$
$$\left. - \frac{i(4 + k^2 x_0^2)}{\sinh(\pi k x_0/2)} h_{20} \right], \qquad (21)$$

where $\Omega = \omega/\omega_0$, $h_{10} \sim H_{z0}$ and $h_{20} \sim H_{y0}$ are the amplitudes of the corresponding fields, and $\delta(x)$ is the Dirac δ-function.

It can be seen that the y-component of the oscillating field leads to excitation of spin waves localized at DW as well as intradomain spin waves, while the z-component excites only intradomain spin waves with $k = 0$.

Let us now analyze the equation in the second approximation in the applied field amplitude. After averaging over the period of oscillations, the corresponding equation for the function $\psi_2(\xi,t)$ can be represented in the form

$$\hat{L}\Phi_2(\xi) = -\frac{1}{\omega_0^2}\overline{V_1^2(t)}\Phi_0''(\xi) - 6\Phi_0(\xi)\overline{\psi_1^2(\xi,t)}$$

$$-2\overline{h_2(t)\psi_1(\xi,t)} + \frac{\lambda}{\omega_0}\overline{V_2(t)}\Phi_0'(\xi), \qquad (22)$$

where $\Phi_2(\xi) = \overline{\psi_2(\xi,t)}$.

As in the first-approximation equation (15), we require that the expansion of the function $\Phi_2(\xi)$ in the eigenfunctions of the operator $\hat{L}$ contains no shear mode, i.e., we require that the right-hand side of Eq. (22) be orthogonal to the function $u_1(\xi)$ (17). This leads to the following expression for the drift velocity $V_{dr} = \overline{V_2(t)}$:

$$V_{dr} = \frac{9x_0\omega_0}{\lambda}\int_{-\infty}^{+\infty}d\xi\left[\Phi_0(\xi)\overline{\psi_1^2(\xi,t)}\right.$$

$$\left. + \frac{1}{3}\overline{h_2(t)\psi_1(\xi,t)}\right]\Phi_0'(\xi). \qquad (23)$$

Substituting $\Phi_0(\xi)$ from (12) into this expression, using expansion (19) for the function $\psi_1(\xi,t)$ with the coefficients from (21), and carrying out averaging over the period of vibrations and integration in (23), we obtain

$$V_{dr} = \mu_{12}h_{10}h_{20}, \quad \mu_{12}(\Omega,\chi)$$

$$= \mu_{12}^0\left\{3\pi\frac{[(3-\Omega^2)(4-\Omega^2)+\lambda^2\Omega^2]\cos\chi + \lambda\Omega\sin\chi}{[(3-\Omega^2)^2+\lambda^2\Omega^2][(4-\Omega^2)^2+\lambda^2\Omega^2]}\right.$$

$$+ \frac{1}{(4-\Omega^2)^2+\lambda^2\Omega^2}[I_1(\Omega,\lambda)\cos\chi$$

$$\left. + I_2(\Omega,\lambda)\sin\chi]\right\}, \qquad (24)$$

where the quantity μ_{12} has the meaning of nonlinear DW mobility:

$$\mu_{12}^0 = \frac{9\pi x_0\omega_0}{2^7\lambda},$$

$$I_1(\Omega,\lambda)$$

$$= \int_{-\infty}^{\infty}\frac{x^4(4+x^2)[(4-\Omega^2)(4-\Omega^2+x^2)+\lambda^2\Omega^2]}{(1+x^2)[(4-\Omega^2+x^2)^2+\lambda^2\Omega^2)]\sinh^2\left(\frac{\pi x}{2}\right)}dx,$$

$$I_2(\Omega,\lambda)$$

$$= \lambda\Omega\int_{-\infty}^{\infty}\frac{x^6(4+x^2)}{(1+x^2)[(4-\Omega^2+x^2)^2+\lambda^2\Omega^2]\sinh^2\left(\frac{\pi x}{2}\right)}dx.$$

The dependence of the function μ_{12} on the dimensionless frequency Ω for various values of the phase shift χ is shown in Fig. 1.

Formula (24) defines the DW drift velocity in the Φ^4 model described by the Lagrange function (10). Going over to the initial dimenional parameters of the magnet, we can write the small-angle DW drift velocity in the form

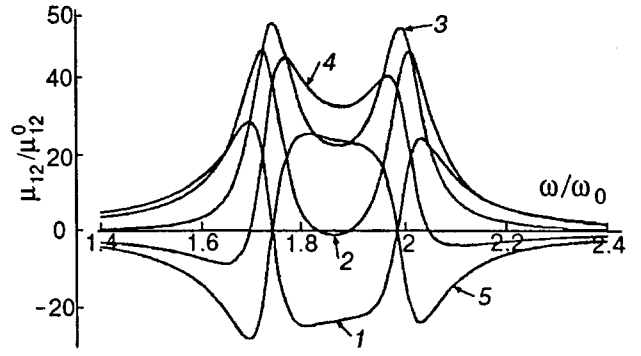$$V_{dr} = \mu_{yz}(\omega,\chi)H_{z0}H_{y0}, \qquad (25)$$

FIG. 1. Frequency dependence of nonlinear mobility for $\lambda = 0.1$ and various values of phase shift χ: 0 (curve *1*), $\pi/4$ (curve *2*), $\pi/2$ (curve *3*), $3\pi/4$ (curve *4*), and π (curve *5*).

where the nonlinear DW mobility $\mu_{yz}(\omega,\chi)$ is defined by an expression similar to (24) with the characteristic value μ_{yz}^0 given by

$$\mu_{yz}^0 = -\frac{9\pi g}{2^3\lambda_r H_a\varepsilon^4}\left(\frac{\alpha}{\beta}\right)^{1/2}. \qquad (26)$$

Using the parameters typical of ferromagnets, i.e., $g \sim 2\times10^7\ \text{s}^{-1}\text{Oe}^{-1}$, $\lambda_r \sim 10^{-2}$, $(\alpha/\beta)^{1/2} \sim 10^{-6}$ cm, and $H_a \sim 5\times10^3$ Oe and putting $\varepsilon = 10^{-1}$, we obtain the drift velocity $V_0 = |\mu_{yz}^0|H_{y0}H_{z0} \sim 10$ m/s for fields of the order of $H_{z0} \sim H_{y0} \sim 1$ Oe.

It should be noted that the values of the coefficient of the nonlinear DW mobility μ_{yz}^0 (26) is much larger (by 1–2 orders of magnitude) than the corresponding coefficient determining the drift velocity of ordinary 180° DW existing in ferromagnets far away from the phase-transition point.[7] As we approach the phase-transition point, i.e., for decreasing parameter ε, the nonlinear mobility coefficient increases, in accordance with (26), in proportion to ε^{-4} due to a decrease in the mass of a small-angle DW.[13] However, it should be borne in mind while obtaining a numerical estimate of the drift velocity that the perturbation theory used above is valid only for h_{10}, $h_{20} \ll 1$, i.e., in a weak oscillating magnetic field, $H_{z0} \ll H_a\varepsilon^3$, $H_{y0} \ll H_a\varepsilon^2$. Consequently, the characteristic value of the DW drift velocity V_0 which can be described adequately in the perturbation theory developed above is proportional to the small parameter ε. Obviously, a DW can also drift with a higher velocity, but in this case a more general theory should be developed for analyzing the DW dynamics.

*E-mail: sukstan@purr.dipt.donetsk.ua

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Second-order nuclear magnetic relaxation in samples with two-level tunneling systems

L. Zh. Zakharov and L. L. Chotorlishvili

Institute of Physics, Georgian Academy of Sciences, 380077 Tbilisi, Georgia

A. I. Tugushi

Tbilisi State University, 380028 Tbilisi, Georgia

Second-order nuclear magnetic relaxation associated with electric quadrupole interaction between paramagnetic centers and two-level systems is studied. First- and second-order relaxation times are compared. It is shown that second-order relaxation prevails in relatively low magnetic fields. © *1998 American Institute of Physics.* [S1063-777X(98)00501-5]

Physical properties of disordered systems whose low-temperature ($T < 1$ K) properties are determined by tunneling two-level systems (TLS) have been studied intensely in recent years.[1] A characteristic property of TLS is that their density of states depends weakly on energy. Nuclear magnetic resonance (NMR) is one of many methods used for studying the physical properties of disordered bodies. The effect of tunneling TLS on nuclear magnetic relaxation associated with paramagnetic centers (PC) and called the first-order relaxation was studied in Ref. 2. In this publication, the magnetic field modulation at a nucleus occurs due to a change in the distance between the nucleus and a PC. (It is assumed that a fraction of nuclei form TLS, and the separation between the nucleus and the PC varies due to tunneling of the nucleus between two equilibrium positions.)

In addition to the first-order relaxation, the second-order relaxation in which magnetic field modulation at a nucleus occurs due to fluctuation of electron magnetic moments without a change in the separation between the nucleus and the PC also exists. In order to study second-order relaxation, Lepsveridze[3] proposed phenomenologically the following Hamiltonian of interaction between PC and TLS:

$$\hat{H}_{Sd} = \sum_{nm} B_{nm} \left(S_n^z d_m^z + \frac{1}{2} (S_n^+ d_m^- + S_n^- d_m^+) \right),$$

where $S_n^{\pm}$ and S_n^z are the PC spin components, d_m^z and $d_m^{\pm}$ the TLS pseudospin components, and B_{nm} is the phenomenological constant of interaction.

In this research, we consider a specific mechanism of second-order relaxation. In particular, we assume that a PC has a spin, and hence possesses a quadrupole moment. The presence of TLS leads to a change in the electric field gradient at PC due to the tunneling of a nucleus between two equilibrium positions, causing fluctuations of electron magnetic moments responsible for nuclear relaxation.

Let us derive the Hamiltonian of interaction between PC and TLS. We write the Hamiltonian of quadrupole interaction between PC and the electric field gradient[4]:

$$\hat{H}^Q = P_{\parallel} \left[\left\{ (S^z)^2 - \frac{1}{3} S(S+1) \right\} + \frac{1}{3} \eta ((S^+)^2 + (S^-)^2) \right],$$

$$P_{\parallel} = -\frac{3e^2 Q \langle r_2^{-3} \rangle}{4S(2S-1)} \langle J\|\beta\|J \rangle \langle |3J^z - J(J+1)| \rangle,$$

$$\eta = \frac{3 \langle (J^{\pm})^2 \rangle}{|\langle 3J^z - J(J+1)| \rangle|},$$

S being the PC spin, J the spin of the nucleus forming the TLS, and r the separation between the PC and the nucleus.

Taking into account the fact that the nucleus can be in a nonsymmetric potential well, we can write the electric field gradient in the form

$$e\hat{Q} = \begin{pmatrix} eV_{zz}^1 & 0 \\ 0 & eV_{zz}^2 \end{pmatrix} = eV_{zz}^1 \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + eV_{zz}^2 \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

$$= e \frac{V_{zz}^1 + V_{zz}^2}{2} \hat{I} + e \frac{V_{zz}^1 - V_{zz}^2}{2} \sigma^z, \tag{1}$$

where V_{zz}^1 and V_{zz}^2 are the values of electric field gradient corresponding to two different states of the TLS, $\hat{I}$ is the unit matrix, and σ^z the Pauli matrix.

The second term in Eq. (1) describes the change in the electric field gradient due to the jumps of the TLS between two equilibrium positions. An order-of-magnitude estimate of this term gives

$$e(V_{zz}^1 - V_{zz}^2)d^z \sim \frac{d}{a} eV_{zz}d^z \sim 0.1 eV_{zz}d^z,$$

where d is the distance between minima of the TLS and a the separation between the TLS and PC.

Taking into account the above arguments, we can write the Hamiltonian of interaction between a PC and a tunneling TLS in the form

$$\hat{H}_{Sd} = \sum_{kn} A_{kn} \left[\left\{ (S_k^z)^2 - \frac{1}{3} S_k(S_k+1) \right\} + \frac{1}{3} \eta [(S_k^+)^2 + (S_k^-)^2] \right] d_n^z.$$

In the representation of TLS which is accomplished through a unitary transformation by the operator

$$U = \exp(i\varphi d^y),$$

where $\tan\varphi = \Delta_0/\Delta$; Δ_0 is the tunneling parameter and Δ the potential well asymmetry,[1] $\hat{H}_{Sd}$ assumes the form

$$\hat{H}_{Sd} = \sum_{kn} A_{kn} \left[\left\{ (S_k^z)^2 - \frac{1}{3} S_k(S_k+1) \right\} + \frac{1}{3}\, \eta[(S_k^+)^2 \right.$$
$$\left. + (S_k^-)^2] \right] \left\{ \frac{\sqrt{\varepsilon_n^2 - \Delta_{0n}^2}}{\varepsilon_n}\, d_n^z + \frac{1}{2}\frac{\Delta_{0n}}{\varepsilon_n}\,(d_n^+ + d_n^-) \right\},$$

$$(2)$$

where ε_n is the TLS energy.

Thus, we shall henceforth assume that interaction (2) is responsible for the time correlation of PC spins.

Let us write the total Hamiltonian of the system:

$$\hat{H} = -\hbar\omega_I \sum_i I_i^z + \hbar\omega_S \sum_j S_j^z + \hat{H}^{IS} + \sum_n \varepsilon_n d_n^z + H_{Sd},$$

where $\hbar\omega_I$ is the Zeeman energy of the nucleus, I the nuclear spin, $\hbar\omega_S$ the Zeeman energy of the electron, and $\hat{H}^{IS}$ the Hamiltonian of the dipole–dipole interaction between a paramagnetic center and a nucleus.

In order to derive the expression for nuclear magnetic relaxation time, we shall use the Kubo formula.[5] It is well known that the relaxation time is determined by the correlation function of the paramagnetic impurity, which in turn is due to the interaction $\hat{H}_{Sd}$, i.e.,

$$\langle S_j^z S_j^z(t) \rangle = \langle S_j^z e^{i\hat{H}_{Sd}t} S_j^z e^{-i\hat{H}_{Sd}t} \rangle.$$

Using perturbation theory (treating $\hat{H}_{Sd}$ as a perturbation), we can prove that the contribution to the correlation function comes only from even terms of the expansion, and hence the correlation function can be approximated by a Gaussian curve. Consequently, we can write

$$\langle S_j^z S_j^z(t) \rangle = \langle S_j^z S_j^z \rangle e^{-(\alpha+\gamma)t^2},$$

$$(3)$$

where

$$\alpha = \frac{\eta^2}{9} \sum_{jn} |A_{jn}|^2 \frac{\varepsilon_n^2 - \Delta_{0n}^2}{\varepsilon_n^2} \langle d_n^z d_n^z \rangle (\langle S_j^+ S_j^- \rangle + \langle S_j^- S_j^+ \rangle - 1)$$

$$(4)$$

and

$$\gamma = \frac{\eta^2}{9} \sum_{jn} |A_{jn}|^2 \frac{1}{4}\frac{\Delta_{0n}^2}{\varepsilon_n^2} (\langle d_n^+ d_n^- \rangle + \langle d_n^- d_n^+ \rangle)[\langle S_j^+ S_j^- \rangle$$
$$+ \langle S_j^- S_j^+ \rangle - 1].$$

In formula (4), we replace d_n^z by the corresponding fluctuation and go over from the summation over n and j to integration with respect to TLS parameters. After simple calculations, we obtain

$$\alpha = \frac{\eta^2}{18}\left(\ln\frac{\varepsilon_{\max}}{e\Delta_{0m}} \right) \bar{P} C \overline{A^2} (\langle S^+ S^- \rangle + \langle S^- S^+ \rangle - 1) T,$$

$$\gamma = \frac{\eta^2}{36}\, \overline{A^2}\, \varepsilon_{\max} \bar{P} C,$$

where $\bar{P}$ is the density of states of the TLS, $\bar{P} \sim N_D/\varepsilon_{\max}$, $C = N_{PC}/N$, where N_D and N_{PC} are the TLS and PC concentrations, respectively, A is the mean value of the constant A_{jn}, $A_{jn} \sim (d/a) P_\parallel$, $\varepsilon_{\max}$ the maximum value of the TLS energy, and Δ_{0m} the minimum value of the tunneling energy. Substituting (3) into the expression for relaxation time, we finally obtain

$$\frac{1}{T_1} = 4\frac{N_{PC}}{N}\frac{\sqrt{\pi}}{\hbar^2 \sqrt{\alpha+\gamma}}\, e^{-\omega_I^2/[4(\alpha+\gamma)]} \langle (S^z)^2 \rangle \overline{U^2},$$

where $\bar{U}$ is the mean value of interaction between a nucleus and a PC.

It can be easily seen that since $\varepsilon_{\max} \ll T$, we can state that $\gamma \gg \alpha$, and hence

$$\frac{1}{T_1} \sim 4c\frac{\sqrt{\pi}}{\hbar^2\sqrt{\gamma}}\, e^{-\omega_I^2/4\gamma} \langle (S^z)^2 \rangle \overline{U^2}.$$

Let us compare the expression obtained for the rate of second-order relaxation with the expression for the rate of the first-order relaxation obtained in Ref. 2. The latter expression contains two terms: a term proportional to temperature and a constant term. At temperatures

$$T > \frac{\hbar}{k_B}\frac{(1+\tau^2\omega_I^2)}{\tau}$$

(τ is the time of correlation of the pseudospin correlation function $\langle d^z d^z(t)\rangle$, which is determined by the interaction between TLS for high TLS concentrations and attains the value $\tau \sim 10^{-9}$ s[6] for TLS concentrations $N_D = 10^{27}$ m^{-3}), the term proportional to temperature will dominate for $T > 10^{-2}$ K if we put $\omega_I \tau < 1$. Confining our analysis to temperatures $T > 10^{-2}$ K, we can write

$$\frac{1}{T_1} : \frac{1}{T_1'} \sim \frac{4C}{\hbar^2}\sqrt{\pi/\gamma}\,\overline{U^2}\langle(S^z)^2\rangle e^{-\omega_I^2/4\gamma} : \frac{9d^2}{a^2} z\,\frac{\overline{U^2}}{\hbar^2}$$

$$\times C\frac{n(\varepsilon)}{N_I}\frac{1}{8}\ln\frac{\varepsilon_{\max}}{e\Delta_0}\frac{\tau}{1+\omega_I^2\tau^2}\, k_B T, \qquad (5)$$

where $n(\varepsilon) = N_D \bar{P}$, z is the number of nearest neighbors of PC, and $d \sim 0.1\,a$.

From formula (5) we obtain

$$\frac{1}{T_1} : \frac{1}{T_1'} \sim \sqrt{\pi/\gamma}\, e^{-\omega_I^2/2\gamma} : z\bar{P}\frac{N_D}{N}\tau k_B T$$

$$= \frac{\sqrt{\pi/\gamma}\, e^{-\omega_I^2/2\gamma}}{z\bar{P}(N_D/N_I)\tau k_B T}.$$

For $N_D/N_I \sim 10^{-3}$, where N_I is the concentration of pseudospins, $\tau \sim 10^{-9}$ s, $\bar{P} \sim 10^{19}$ J, and $z \sim 10$,[1] we have

$$\frac{1}{T_1} : \frac{1}{T_1'} \sim \frac{10^{15} e^{-\omega_I^2/2\gamma}}{\sqrt{\gamma T}}.$$

$$(6)$$

It can be seen from formula (6) that for

$$T < \frac{10^{15} e^{-\omega_I^2/2\gamma}}{\sqrt{\gamma}}$$

the second-order relaxation rate $1/T_1$ is higher than the first-order relaxation rate $1/T_1'$.

Let us estimate the value of T for U nuclei. The substitution of the standard value of $\gamma \sim 2.5 \times 10^{10}$ Hz for the Zeeman frequency $\omega_I \sim 10^6$ Hz gives $T < 1$ K.

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On thermodynamics of supercooled liquids and glasses

A. S. Bakai

National Science Center ''Kharkov Institute of Physics and Technology, 310108 Kharkov, Ukraine*

Thermodynamics of glass-forming liquids and glasses is considered taking into account the contribution of heterophase fluctuations to the free energy. The role of heterophase fluctuations in liquids and glasses is played by nuclei of noncrystalline solids and nuclei of the liquid phase respectively. Crystalline solid state is not considered. Free energy is described on the bases of the droplet model and the model of mixed state. It is shown that three regions of stability of different structural states of the system exist on the (P,T) plane. Two of them are stability regions for droplet structural states, while the mixed state is stable in the third region in which heterophase fluctuations have the form of isolated drops. In this state, two infinite percolating clusters (liquid and noncrystalline solid) coexist. The width of the temperature interval $[T_{t1},T_{t2}]$ in which the mixed state is stable increases with configuration entropy (complexity) of the noncrystalline solid fraction. In the approach used, weak first-order phase transitions are observed at $T=T_{t1}$ and $T=T_{t2}$. It is shown that first- and second-order phase transitions are possible in the mixed state. The criteria for the existence of these phase transitions are obtained. Equations of state and expressions for thermodynamic parameters (entropy, heat capacity, compressibility, and thermal expansion coefficient) are derived for the droplet and mixed states. © *1998 American Institute of Physics.* [S1063-777X(98)00601-X]

INTRODUCTION

This publication aims at the description of thermodynamics of glass-forming liquids and glasses, taking into account heterophase fluctuations. The contribution of heterophase fluctuations to the free energy of the system is usually small down to the phase-transition temperature due to a comparatively large work of nucleation. It will be proved that the situation is different in the case of glasses and glass-forming liquids. Over wide ranges of temperatures and pressures, these systems are essentially heterophase structures, i.e., the volume fractions of two phases are comparable. The main reason behind this phenomenon is the multiplicity of structural states (SS) of glasses.

The SS multiplicity for glasses follows if only from the fact that, in view of its random nature, the structure has an infinitely large number of possible forms (for an infinitely large number of atoms and molecules in the system). A more detailed analysis[1] shows that the number of SS for glasses with virtually the same value of free energy is exponentially large in the general case [$\sim\exp(\zeta N)$, where $\zeta>0$, N is the number of atoms in the system]. Glasses are formed as a result of cooling of a liquid which also possesses SS multiplicity, and the phase trajectory of the system has time to ''visit'' various regions of the phase space belonging to different SS. As regards glasses, the overwhelming majority of SS in them are separated by very high or infinitely large barriers so that the system is in the region of phase space occupied by only one or a few possible SS during the time of observation. For this reason, glasses are phases with broken ergodicity, while liquids are ergodic. The violation of structural ergodicity in glasses was discussed in greater detail in Refs. 2 and 3.

The properties of a system in different structural states are close but not identical. For this reason, glasses are usually studied by considering ensembles with different structural forms and by using their statistical description, although experimental samples can be in one or negligibly small number of states from the possible SS during measurements. The structural state assumed by the system upon cooling the high-temperature phase is determined by the details of phase transformation, i.e., by the kinetics of the process. At the same time, the equilibrium state and relaxation rate are determined by thermodynamic properties (free energy) of the system. These properties depend to a considerable extent on whether the ergodicity is violated jump-wise, as during a transition from the paramagnetic to the ferromagnetic state, or we are dealing with a gradual (continuous) contraction of the region of the phase space accessible for the phase trajectory. A considerable difficulty in the description of the system thermodynamics in the phase-transition region is associated with a consistent consideration of ergodicity breaking during a transition from the high-temperature to the low-temperature phase.

Phenomena associated with heterophase fluctuations near the phase-transition point were considered by Frenkel[4,5] and studied experimentally.[6] Frenkel proposed the droplet approach that makes it possible to describe the equilibrium size distribution function for nuclei and to take into account their contribution to the free energy. Fisher[7] modified this approach to a description of thermodynamic states of the system in the vicinity of the critical point. Among other things, we managed to obtain relations between critical indices and to derive the equation of state of the system near the critical point. In spite of the drawbacks of the droplet approach associated with rather strong simplifying assumptions, it proved to be quite adaptable and effective for describing heterophase fluctuations in kinetics of nucleation. It

is important that this model gives correct results when the volume fraction of heterophase fluctuations is small. For this reason, the results obtained by using other approaches can be verified by comparing with those obtained on the basis of the droplet model. In this paper, we propose a version of the droplet model with less stringent simplifying assumptions as applied to the description of thermodynamics of liquids and glasses as well as the so-called droplet states in which heterophase fluctuations can be regarded to a high degree of accuracy as isolated nuclei with a nearly spherical shape.

Thermodynamic properties of glass-forming liquid have not been investigated so far by using the droplet approach. For example, Adam, Gibbs, and DiMazio[8] who described the thermodynamics and relaxation processes of a supercooled liquid, assumed that the configurational entropy of the liquid decreases upon cooling as a result of formation of blocks with a small number ($W \geq 2$) of SS. The number W is assumed to be constant, and the size of blocks increases upon cooling. If $N(T)$ is the number of molecules in a block, the configuration entropy per molecule is $\zeta(T) \approx \ln 2/N(T)$. Adam, Gibbs, and DiMarzio[8] also introduces the concept of block structure of glass-forming liquids, which was widely used later by other authors in an analysis of various properties of glass-forming liquids (see, for example, Refs. 9–11). In this case, the contribution of liquid domains was disregarded, and the possibility of ergodicity breaking in the system was ignored.

A certain advance in the description of thermodynamic properties of glass-forming liquids was made by using the two-level model or the two-state model (TSM). The two-level model was introduced for the first time by Vol'kenshtein and Ptitsyn[12] for describing relaxation processes in a glass-forming liquid. Later, this model was used for the description of thermodynamic properties of supercooled liquids (see Chap. 4 in Ref. 13 and the references cited therein). Macedo, Capps, and Litovitz[14] proposed (apparently, independently) the TSM (we shall use this name of the model for definiteness) as applied to the description of the temperature dependence of specific volume of liquid B_2O_3. Later, Angel *et al.*[15,16] proposed the lattice bond model which is essentially a version of the TSM.

The basic assumptions of the TSM can be formulated as follows. A supercooled liquid is regarded as a one-phase system. At the same time, each molecule can be in two states to which different values of enthalpy, entropy, and specific volume are ascribed. Molecules are assumed to be statistically independent. Under these assumptions, we can easily construct the partition function of the system and determine the probabilities of finding a molecule in each possible state. We put aside a more detailed discussion of the TSM to Sec. 5, observing here that, in spite of the lack of appropriate substantiation, the TSM provides a correct qualitative description of the behavior of thermodynamic quantities over comparatively wide temperature intervals.[13,14,17]

Thermodynamic properties of supercooled liquids were also considered partially in Refs. 18 and 19 devoted to a description of first-order phase transitions of the liquid–liquid type, whose existence follows from a number of experimental observations (see Refs. 18–20). The model of frustration-limited domains[18,21] as well the modified Van der Waals model[19] provide qualitative descriptions for the observed phenomena. At the same time, the conditions of applicability for such types of models remain unclear.

Cohen and Grest[22,23] considered liquids and glasses as heterophase states (containing liquid and solid fractions) on the basis of the free-volume model. In this approach, it is shown that a first-order phase transition of the glass–liquid type occurs as a result of a rapid increase in the communal entropy during the formation of an infinite (percolating) liquid cluster. This result will be considered in greater detail in Sec. 5.

The structure of a supercooled liquid affects significantly its dynamics; it is generally accepted that this structure is heterogeneous. Denser structural elements characterized by a higher degree of local ordering alternate with less dense liquid-like elements. The scales of structural heterogeneities vary from values smaller than a nanometer to several hundred nanometers. The methods of light scattering in organic liquids revealed the existence of dense clusters with characteristic spatial scales up to 10^2 nm (Fischer clusters).[24–28] In addition, the observed 'ultraslow' modes appear as a result of diffusion-induced rearrangements of Fischer clusters.[25,26] These results can be regarded as a direct evidence of the fact that glass-forming liquids are essentially heterostructural and heterophase systems. Consequently, a realistic description of thermodynamic properties of glass-forming liquids should be based on the analysis of heterophase fluctuations.

Glasses and liquids as heterophase states were considered in Refs. 1 and 29–31 on the basis of the droplet approach and the mixed-state model. In the droplet approach, nuclei of one phase in the other phase are regarded as isolated droplets that do not interact with one another. In Ref. 1, the free energy of an isolated noncrystalline cluster is described by taking into account the multiplicity of structural states. This allows us to derive kinetic equations (analogous to the Zel'dovich equations) describing the equilibrium size distribution function for clusters as well as the rate of nucleation and growth of nuclei in the noncrystalline solid phase. It has been demonstrated[1] how the possibility of formation of two or more solid amorphous phases from a liquid is taken into consideration. Thus, a kinetic description of the formation of polymorphous glasses has been developed. It turns out, however,[1,29] that the droplet approach is inapplicable for describing the thermodynamics and kinetics of phase transformations of a liquid in a wide temperature range. According to estimates, the width of this temperature interval is proportional to ζ. In this range, the assumption concerning the smallness of the volume fraction of nuclei of a new phase is not justified, and the droplet approach leads to contradictory results. In Ref. 29, the model of mixed state (MSM) is proposed for describing the states of a supercooled liquid, in which the fractions of phases being mixed (liquid and solid) are comparable. In a mixed state, infinitely large percolating solid and liquid clusters coexist. The MSM was used to prove[29,30] that a mixed state can contain only one phase in the entire range of its existence or two phases whose mutual transformations are associated with a first-order phase transition depending on the relation between thermodynamic pa-

rameters. In Ref. 30, a criterion for the existence of the critical point and first-order transitions in the mixed state is obtained. Moreover, it is shown[30] that weak first-order phase transitions (accompanied by small jumps of the order parameter) are quite possible near the percolation threshold of a liquid cluster in glass and a solid cluster in liquid. A detailed analysis of thermodynamics of glasses and glass-forming liquids on the basis of the droplet approach and the MSM has not been carried out yet. This publication aims at filling of this gap. The version of the droplet model used here differs in some details from the approaches described in Refs. 4, 5, and 7; this model will be considered in the next section.

1. DROPLET MODEL

1.1. Basic concepts

Let us consider the thermodynamics of phases 1 and 2 (the first is the high-temperature and the second the low-temperature phase) near the phase-equilibrium curve $T_{12}(P)$ described by the Gibbs condition

$$\mu_1(P,T) = \mu_2(P,T), \qquad (1)$$

where μ_1 and μ_2 are the chemical potentials of phases 1 and 2, respectively. Phase 1 is stable at $T > T_{12}$, while phase 2 is stable at $T < T_{12}$. For definiteness, we shall consider first the thermodynamics of phase 1, taking into account the contribution of heterophase fluctuations, i.e., nuclei of phase 2, in the droplet approach.

The droplet model is based on the following two assumptions.

(A) The interaction between nuclei of phase 2 is insignificant.

This assumption is valid for a small volume fraction of nuclei, when interactions between them (e.g., as a result of collisions or due to exchange interactions) do not play any significant role.

(B) The probability of formation of nuclei of phase 1 in nuclei of phase 2 is negligibly small.

The validity of this assumption can easily be verified. It is admissible when we are dealing with small nuclei of phase 2, but can lead to noticeable errors in the cases when the probability of formation of large nuclei is not small. Weakening or removal of assumption (B) does not involve considerable difficulties.

Let a system contain N atoms (molecules). In the long run, we will be interested in the behavior of the system in the thermodynamic limit ($N \rightarrow \infty$), but the analysis starts from a system containing a finite number of particles.

We denote by N_1 the number of monomers, i.e., the number of atoms of phase 1, and by N_k the number of droplets of phase 2, each of which contains k atoms. Following Frenkel, we treat droplets as molecules. In this case, the total number of molecules is

$$\widetilde{N} = N_1 + \sum_{k \geqslant k_{20}} N_k, \qquad (2)$$

for a constant number of atoms

$$N = N_1 + \sum_{k \geqslant k_{20}} k N_k. \qquad (3)$$

Here k_{20} is the minimum size of a droplet.

The Gibbs free energy (thermodynamic potential) of the system can be written in the form

$$G(P,T) = N_1 \mu_1^0 + \sum_{k \geqslant k_{20}} G_{2k}(P,T) N_k$$

$$+ k_B T \left[N_1 \ln(N_1/\widetilde{N}) + \sum_{k \geqslant k_{20}} N_k \ln(N_k/\widetilde{N}) \right], \qquad (4)$$

where k_B is Boltzmann's constant.

It should be recalled that μ_1^0 is the chemical potential without taking into account the contribution of heterophase fluctuations, and G_{2k} the free energy of a nucleus, which can be presented in the following form for $k \gg 1$:

$$G_k(P,T) = k[\mu_2^0 + p(k)(\mu_s - \mu_2^0)], \qquad (5)$$

where μ_2^0 and μ_s are the chemical potentials of phase 2 in the absence of heterophase fluctuations and of the phase boundary respectively, and $p(k)$ is the fraction of boundary atoms. For spherical droplets with $k \gg 1$, we have

$$p(k) = (36\pi/k)^{1/3}. \qquad (6a)$$

Following Fischer,[10] we can choose the expression for $p(k)$ in a more general form:

$$p(k) = A k^{\sigma - 1}, \qquad (6b)$$

where $0.5 < \sigma < 1$ and A is a geometrical factor. It is convenient to use the expression for $p(k)$ in this form for analyzing the system in the critical region, where $\mu_1 \approx \mu_2 \approx \mu_s$, and σ is one of critical indices.

For small nuclei, when $k < 10^2$ and the radius of a nucleus is equal to two or three atomic spacings, the coefficient $p(k)$ is close to unity, and the division of atoms into surface and bulk atoms is conditional. For this reason, the estimate of the contribution from small nuclei to thermodynamic quantities, which is obtained by using (5), cannot claim high accuracy. However, in the cases when large nuclei start playing a significant role (the behavior of the system in the phase-transition region is just the case), approximation (5) and (6) is quite justified.

Stable equilibrium of the system is attained at the minimum of G, where the following conditions hold:

$$\partial G / \partial N_k = 0; \quad \partial^2 G / \partial N_k^2 > 0. \qquad (7)$$

Using (4) and (7), we can find equilibrium numbers of clusters:

$$N_k = N_1 \exp(-\Delta G_{2k} \beta), \quad \beta \equiv 1/k_B T, \qquad (8)$$

where

$$\Delta G_{2k} = G_{2k}(P,T) - k \mu_1^0(P,T). \qquad (9)$$

Substituting (8) into (2)–(4), we find that for $T \geqslant T_{12}$,

$$G(P,T) = N[\mu_1^0(P,T) - k_B T[1 + R_1(2)]^{-1}[1$$
$$+ R_0(2)] \ln[1 + R_0(2)]], \qquad (10)$$

$$\widetilde{N} = N_1[1 + R_0(2)]; \quad N_1 = N[1 + R_1(2)]^{-1}, \quad (11)$$

where

$$R_m(2) = \sum_{k \geqslant k_{20}} k^m \exp(-\Delta G_{2k}\beta), \quad m = 0, 1, 2, \dots . \quad (12)$$

For brevity, we shall henceforth omit the index ''2'' in the parentheses of R_m when this does not lead to misunderstanding.

It can be seen from (12) that the strong inequality $R_m \gg R_{m-1}$ holds for $k_{20} \gg 1$.

Noting that

$$N_1/N = (1 + R_1)^{-1} = c_1,$$

$$(N - N_1)/N = R_1/(1 + R_1) = c_2, \quad (13)$$

where c_1 and c_2 are the concentrations of atoms belonging to the first and second phase respectively, we can conveniently present expression (10) in the form

$$N^{-1}G(P,T) \equiv \mu(P,T) = \mu_1^0(P,T)$$

$$- c_1 k_B T[1 + R_0(2)]\ln[1 + R_0(2)]. \quad (14)$$

The obtained expression does not depend on N and can be used in the thermodynamic limit $N \to \infty$.

Expressions similar to (8)–(14) are also valid for free energy in the stability region of the low-temperature phase 2 ($T \leqslant T_{12}$) if the contribution from heterophase fluctuations is taken into consideration. For example, the expression for μ can be obtained by the simple substitution of index ''2'' for index ''1'' in (14) and in relations (8), (9), (11), and (12) connected with this expression:

$$\mu(P,T) \approx \mu_2^0(P,T) - k_B T[1 + R_1(1)]^{-1}[1 + R_0(1)]$$

$$\times \ln[1 + R_0(1)]. \quad (15)$$

The sums $R_m(1)$ $(m = 0,1)$ on the right-hand side of (15) differ from those defined by formula (12) in that ΔG_{2k} in them should be replaced by ΔC_{1k} defined by relation (9), where the index ''1'' on the right-hand side is replaced by ''2'', and vice versa.

The second term on the right-hand side of (10), (14), and (15) describes the contribution of heterophase fluctuations. It differs from similar expressions obtained in Refs. 6, 7, 10, and 11 in view of the type of approximations used in its derivation.

In the case of an infinitely small volume fraction of the new phase, when $R_1 \ll 1$, we have

$$\mu(P,T) \approx \mu_1^0(P,T) - k_B T R_0(2) \quad (16)$$

and the formulas derived by us coincide with those in the above-mentioned publications.

1.2. Phase transition

A phase transition in the droplet model is determined on the basis of Eq. (14) from the emergence of a finite probability of formation of an infinitely as large drop, for which

$$\lim_{k \to \infty} \exp(-\Delta G_k \beta) = 1. \quad (17)$$

It can be seen from (5) and (9) that this condition is satisfied just on the phase-equilibrium curve defined by an equality of the form (1) without taking into account heterophase fluctuations:

$$\mu_1^0(P,T) = \mu_2^0(P,T). \quad (18)$$

On the other hand, in order to determine the phase-equilibrium curve, we must equate the total chemical potentials of the phases, taking into account the contribution of heterophase fluctuations. The observed difference is due to the fact that while deriving expressions (14) and (15), we used assumptions (A) and (B) and neglected mutual influence of nuclei as well as heterophase fluctuations in nuclei. It will be proved in the next sections that this drawback of the droplet model can be eliminated by weakening the above assumptions.

1.3. Analyticity of free energy at the phase-transition point

The behavior of free energy at the first-order phase transition point was analyzed by Andreev[32] and by Fisher.[7] It was found that free energy has a noticeable singularity at the transition temperature. It follows from (10) and (13) that, in the version of the droplet model considered above, free energy has no significant singularity at $T = T_{12}$. In order to verify this, it is sufficient to note that both R_1 and R_2 contain the terms $\sim \exp[-k(\mu_1^0 - \mu_2^0)\beta]$ and possess a significant singularity at the phase-transition point (1) for $k \to \infty$, but their ratio has no singularity of this type. A more detailed analysis of equality (14) leads to the following result:

$$\mu(P,T) \approx \begin{cases} \mu_1^0(P,T) - k_B T R_0, & T \to T_{12}(P) + 0, \\ \mu_2^0(P,T), & T \to T_{12}(P) - 0. \end{cases} \quad (19)$$

This expression shows that chemical potential $\mu(P,T)$ is continuous at the transition temperature to within the discrepancy in the definition of transition point noted in the previous section, although its derivatives with respect to P and T obviously have discontinuities. The observed discrepancy can be formally eliminated by the replacement of μ_2^0 by μ_2 (see below). In this case, free energy is continuous at the transition point.

1.4. Metastable states

Expressions (14) and (19) do not describe the free energy of the high-temperature phase in its metastability region, i.e., at $T < T_{12}$. Neither the obtained free energy, nor the equation of state derived from it can be extrapolated from the high-temperature region to this region. This peculiarity of the droplet approach was noted by Fisher.[7] Gunton et al.[33] showed how metastable states of a system can be described on the basis of the droplet model. It should be noted that at $T < T_{12}$, nuclei are characterized by a finite critical size

$$k^* = [\sigma A(\mu_s - \mu_2)/(\mu_1 - \mu_2)]^{1/(1-\sigma)}, \quad (20)$$

such that nuclei are dissolved with a very high probability for $k < k^*$ and grow unlimitedly for $k > k^*$. The system is in the metastable state until a nucleus of a supercritical size appears in it, after which the metastable phase is transformed into a stable phase. It follows hence that only subcritical

nuclei exist in the metastable state and make a contribution to free energy. Consequently, the chemical potential of a metastable phase obeys the following expression:

$$\tilde{\mu}_1(P,T) = \mu_1^0(P,T) - k_B T (1+R_1^*)^{-1}(1+R_0^*)$$
$$\times \ln(1+R_0^*), \quad T \lesssim T_{12}, \qquad (21)$$

where

$$R_m^* = \sum_{k \geqslant k_{20}}^{k^*} k^m \exp(-\Delta G_{2k}\beta), \quad m = 0,1,2,\dots . \qquad (22)$$

The lower boundary of the temperature interval of metastability can easily be established. The difference $\mu_1 - \mu_2$ increases upon cooling, and according to (20), the critical size of the nuclei decreases so that it assumes the minimum possible value at a temperature T_1^* defined by the equality

$$k_{20} = k^*(T). \qquad (23)$$

Upon further cooling, the energy barrier separating the metastable and stable phases disappears, and hence the equation

$$T = T_1^*(P) \qquad (24)$$

defines the spinodal of the high-temperature phase.

Taking (21) into account, we can write the expression for the chemical potential of the high-temperature phase in the form

$$\mu_1(P,T) = \begin{cases} \mu(P,T), & T \geqslant T_{12} \\ \tilde{\mu}_1(P,T), & T \lesssim T_{12}. \end{cases} \qquad (25)$$

Since the size of a critical nucleus of the low-temperature phase becomes finite only at $T < T_{12}$, we can formally use expression (21) in the stability region of phase 1 as well as in its metastability region. For this reason, we shall henceforth use the above definition of the chemical potential of this phase throughout the entire region of its existence without special stipulations.

Expressions similar to (21)–(25) are valid for the chemical potential, critical size of the nucleus of the new phase, and the spinodal of the low-temperature phase in the entire region of its existence, i.e., for $T \lesssim T_2^*$.

1.5. Equations of state

The equations of state of a system, i.e., equations establishing the relation between volume, pressure, and temperature, follow directly from the expressions for the free energy presented in the previous section. Indeed, the expression for volume per atom can be obtained by differentiation of chemical potential with respect to pressure. If we are interested in the equation of state for a phase in its stability region as well as in the metastability region, we must use expression (21) for chemical potential instead of (14). This gives

$$v(P,T) = \frac{\partial \tilde{\mu}_1}{\partial P} = v_1^0 + c_1(v_1^0 - \bar{v}_2)R_1^*[1 + \ln(1+R_0^*)]$$
$$- c_1^2[v_1^0 - \tilde{v}_2]R_2^*(1+R_0^*)\ln(1+R_0^*), \qquad (26)$$

where

$$v_i = \partial \mu_i / \partial P, \quad i = 1,2,s \qquad (27)$$

is the volume per atom in phases 1, 2, and in the boundary layer, respectively,

$$\bar{v}_i = (R_1^*)^{-1} \sum_{k \geqslant k_0}^{k^*} k^2 [v_i + p(k)(v_s - v_i)] \exp(-\Delta G_k \beta),$$
$$(28)$$

$$\tilde{v}_i = (R_2^*)^{-1} \sum_{k \geqslant k_0}^{k^*} k^2 [v_i + p(k)(v_s - v_i)] \exp(-\Delta G_k \beta).$$
$$(29)$$

The first two terms on the right-hand side of (26) describe the mean value of volume per atom, while the last term describes the ''anomalous'' contribution due to pressure dependence of concentration of nuclei. This contribution is noticeable only in the vicinity of the transition point, when the product $c_1^2 R_2$ is not a negligibly small quantity.

The last term on the right-hand side of (26) for $R_0, R_2 \ll 1$ is negligibly small and can be omitted, after which this expression assumes the form

$$v(P,T) = v_1^0(P,T) - c_2[v_1^0(P,T) - \bar{v}_2(P,T)]. \qquad (30)$$

The second term on the right-hand side of (30) describes the contribution of heterophase fluctuations to the volume.

If we disregard the difference in specific volumes in the boundary layer and in the bulk, expression (30) can be simplified:

$$v(P,T) = c_1 v_1^0(P,T) + c_2 v_2^0(P,T). \qquad (31)$$

It should be noted that an expressions of this type is postulated in Ref. 14.

For the thermal expansion coefficient $\alpha = \partial \ln v / \partial T$, we obtain from (31)

$$\alpha = v^{-1}[c_1 \alpha_1^0 + c_2 \alpha_2^0 + (v_1^0 - v_2^0)\partial c_1 / \partial T], \qquad (32)$$

where

$$\alpha_{1,2}^0 = \partial \ln v_{1,2}^0 / \partial T.$$

Expressions similar to (30) and (31) are also valid for the equation of state of the system for $T \lesssim T_2^*$. Comparing these expressions, we can easily find the volume jump during a phase transition, i.e., at $T = T_{12}$:

$$\Delta v(P,T_{12}) = v_1(P,T_{12}) - v_2(P,T_{12}) = (v_1^0 - v_2^0)$$
$$\times [1 - R_1(1) - R_1(2)]. \qquad (33)$$

It can be seen that the inclusion of heterophase fluctuations leads to a decrease in the volume jump occurring during a phase transition.

The specific entropy $s(P,T)$ is the derivative of the chemical potential with respect to T. Using relations (15), (16), (19), (21), and (25), we can obtain expressions for the entropy of stable and metastable states in various approximations. For example, for phase 1 at $T \lesssim T_1^*$, we have

$$s_1(P,T) = -\partial \tilde{\mu}_1(P,T) / \partial T \cong c_1 s_1^0 + c_2 \bar{s}_2 + c_2 \Delta \bar{G} / k_B T$$
$$+ c_1(1+R_0^*)\ln(1+R_0^*), \qquad (34)$$

where $\bar{s}_2$ and $\Delta \bar{G}$ are the values of entropy and free energy of cluster formation defined by expressions of the form (28)

and averaged over the ensemble of clusters. The last terms on the right-hand side describes the contribution of the entropy of mixing.

Expression (34) leads to the following formula for heat capacity:

$$C_{p1} \cong c_1 C_{p1}^0 + c_2 C_{p2}^0 + \Delta \bar{G} \partial c_1 / \partial T. \tag{35}$$

Expressions similar to (31)–(35) were obtained by Frenkel on the basis of the droplet model and were used for analyzing peculiarities in the behavior of thermodynamic quantities near the transition point, which are associated with heterophase fluctuations.[5,6]

1.6. Critical points

The existence of critical points on phase-equilibrium curves (1) and (16) is a question of special importance. At critical points, the difference between the chemical potentials of the phase boundary and phases in equilibrium vanishes. For this reason, the equation for critical points has the form

$$\mu_1(P,T) = \mu_2(P,T) = \mu_s(P,T). \tag{36}$$

It can be easily seen that Eqs. (36) in the general case determine not regions or curves, but points. The properties of the system near the critical point in the droplet model were studied by Fisher[10,12] by using equations of state slightly differing from those presented above. It will be shown below the systems we are interested in (glass-forming liquids) cannot be described in the framework of the droplet approach. The critical points for such systems defined by equations (36) lie outside the range of applicability of the droplet approach (see Sec. 3).

1.7. Modified droplet approach

The version of the droplet model described in previous sections has the obvious drawback that can be eliminated. It can be seen from (19) that the equality of chemical potentials is violated if we take into account the contribution of heterophase fluctuations to the free energy of the high-temperature phase at the transition point ($T = T_{12}$). This discrepancy is associated with assumption (B). It is just the disregard of heterophase fluctuations in droplets of a new phase (including infinitely large drops) that leads to the above-mentioned error.

The obvious way of elimination of the discrepancy in (19) lies in the replacement of the ''unperturbed'' chemical potential $\mu_2^0(P,T)$ in the expression (5) for the free energy of a nucleus by the potential $\mu_2(P,T)$ calculated by taking heterophase fluctuations into consideration. It should be borne in mind, however, that it is expedient to take into account heterophase fluctuations in the free energy of large drops whose size is much larger than the average size of nuclei of the other phase. It should be noted that the phase transition is associated just with the formation of an infinitely large drop for which this requirement is satisfied in all cases.

The average size $\bar{k}$ of a droplet is equal to R_1/R_0. Taking into account what has been said above, we obtain, the following expression for the free energy of formation of large ($k \gg \bar{k}$) drops instead of (5) and (9):

$$G_{2k}(P,T) = k\{\mu_2(P,T) + p(k)[\mu_s(P,T) - \mu_2(P,T)]\}, \tag{37}$$

$$\Delta G_{2k} = G_{2k} - k\mu_1(P,T), \tag{38}$$

where $\mu_1(P,T)$ is the chemical potential of phase 1, taking into account heterophase fluctuations.

The dependence of chemical potentials on the size of nuclei can be written in the form

$$\mu_i = \mu_i(P,T,k) = \begin{cases} \mu_i^0(P,T), & k < \bar{k} \\ \mu_i(P,T), & k > \bar{k} \end{cases}. \tag{39}$$

Using expression (39) in the calculation of sums in (8) and (2)–(4), we find that the phase transition occurs at the temperature T_{12} defined by the equation

$$\mu_1(P,T) = \mu_2(P,T). \tag{40}$$

In this case, instead of (19), we obtain from (15)

$$\mu(P,T) = \mu_1(P,T)|_{T=T_{12}+0} = \mu_2(P,T)|_{T=T_{12}-0}. \tag{41}$$

1.8. Droplet model in the excluded volume approximation

In the version of the droplet model described above, the fraction c_2 of atoms belonging to nuclei of the new phase is taken into account [owing to relation (3)] by fixing the total number of atoms. This approximation remains correct as long as condition (A) is satisfied, i.e., as long as $c_2 \ll 1$. As the value of c_2 increases, the probability of contact and merging of nuclei increases (in proportion to c_2). For $c \cong 0.15$, the percolation threshold for the new phase should be reached, i.e., the overwhelming majority of randomly arranged nuclei are in contact with one another, forming an infinitely large (percolating) cluster.[33,34] However, the formation for such a cluster at $T > T_{12}$ is impossible since it involves an increase in the free energy of the system by an infinitely large value. In the above formulation of the droplet model, nuclei of the new phase whose shape differ significantly from spherical are disregarded (including clusters formed as a result of contact or merging of nuclei of a smaller size) just due to a comparatively large increment of free energy accompanying their formation. On one hand, their contribution to free energy is disregarded in view of a negligibly small formation probability, but on the other hand, the probability of contact between nuclei calculated by using the equilibrium distribution function turns out to be significant. Let us prove this.

The equilibrium concentration of nuclei containing k atoms can be written, in accordance with (8), in the form

$$c_k = N_k/\tilde{N} \cong N_k/N_1 = \exp(-\Delta G_k \beta). \tag{42}$$

Since the free energy of a nucleus of size k formed as a result of contact between two smaller nuclei of size k_1 and $k_2(k_1 + k_2 = k)$ is approximately equal to the sum of free energies of contacting clusters, the concentration $\tilde{c}_k$ of such nuclei is estimated by the formula

$$\tilde{c}_k \cong \exp[-(\Delta G_{k_1} + \Delta G_{k_2} - \Delta G_{12})\beta], \tag{43}$$

Here ΔG_{12} is the free energy of interaction between nuclei. It is proportional to the overlapping of nuclei.

It should be noted that $\Delta G_{k_1}+\Delta G_{k_2}>\Delta G_k$; consequently, if $\Delta G_{12}<0$ or $\Delta G_{12}\ll\Delta G_{k_1}+\Delta G_{k_2}$, the value of $\widetilde{c}_k$ turns out to be smaller than c_k.

Let us estimate the probability of overlapping of a nucleus of size k_1 with any other nucleus of size k if they are formed and grow without any mutual influence. It can easily be verified that the concentration of overlapping nuclei containing k_1 and k_2 atoms and distributed randomly in the volume is approximately equal to

$$w(k_1,k_2)=\{k_1[1+3(k_2/k_1)^{1/3}] \\ +k_2[1+3(k_1/k_2)^{1/3}]\}\exp(-\Delta G_{k_2}\beta). \quad (44)$$

Consequently, the concentration of overlapping nuclei with sizes k_1 and k_2 must have the form

$$c(k_1,k_2)=\{k_1[1+3(k_1/k_2)^{1/3}] \\ +k_2[1+3(k_2/k_1)^{1/3}]\}\exp[-(\Delta G_{k_1}+\Delta G_{k_2})\beta].$$
$$(45)$$

Assuming that k_1 and k_2 are equal to the average size $\bar{k}$ of nuclei, we obtain the following estimate of the concentration of overlapping nuclei:

$$c(\bar{k},\bar{k})\cong 8\bar{k}^2\exp[-(\Delta G_{k_1}+\Delta G_{k_2})\beta]. \quad (46)$$

Comparing formulas (46) and (43), we see that the equilibrium concentration of nuclei obtained by overlapping noninteracting nuclei is much higher than the thermodynamically equilibrium concentration of nuclei having the shape and size of overlapping nuclei. This means that the interaction of nuclei cannot be neglected unless the concentration $c(k_1,k_2)$ is negligibly small.

The result of interaction of clusters can easily be determined. If two nuclei come in contact in the course of the formation and growth, a nuclei of size $k\cong 2\bar{k}$ with a free energy noticeably higher than ΔG_k is formed. For this reason, such nuclei are feeble and dissociate rapidly. In all probability, they first of all split into two smaller nuclei (whose size is approximately equal to $\bar{k}$). As a result, the nuclei coming in contact undergo kinetic ''repulsion.'' This interaction of nuclei should be taken into account while calculating the free energy of the system.

The interaction of nuclei can be taken into account by introducing the formal exclusion of their contact. For this purpose, it is sufficient to require that each nucleus is surrounded by an (at least monatomic) layer of the stable phase. If this condition is observed, estimate (46) becomes invalid since the probability of contact vanishes.

Under this condition, the nuclei is supplemented with an insulating shell, and the total number of atoms in such a nucleus is approximately equal to

$$\widetilde{k}\cong 4\pi(r_k+d)^3/3a^3, \quad (47)$$

where r_k is the radius of the nucleus, d the thickness of the insulating layer, and a the atomic size.

Taking into account (47), we obtain the following expressions instead of (2) and (3):

$$\widetilde{N}=\widetilde{N}_1+\sum_{k\geqslant k_0}N_k, \quad (48)$$

$$N=\widetilde{N}_1+\sum_{k\geqslant k_0}\widetilde{k}(k)N_k, \quad (49)$$

where $\widetilde{N}_1$ is the number of atoms of phase 1 outside the insulating shells.

Using (48) and (49), we obtain the following expression for chemical potential instead of (15):

$$\mu(P,T)=\mu_2^0(P,T)-k_BT\frac{\widetilde{N}_1}{N}(1+R_0)\ln(1+R_0)$$
$$=\mu_2^0(P,T)-k_BT(1+\widetilde{R}_1)^{-1}(1+R_0)\ln(1+R_0),$$
$$(50)$$

where

$$\widetilde{R}_1=\sum_{k\geqslant k_0}\widetilde{k}(k)\exp(-\Delta G_k\beta)=\langle\widetilde{k}\rangle R_0. \quad (51)$$

For example, for $k_0\cong 15$ and $d=1a$, which corresponds to nuclei with $r_k\cong 1.5a$ and the minimum separation between nuclei equal to two characteristic atomic diameters, $\langle\widetilde{k}\rangle\cong 70$. Noting that spheres form a random dense packing for the filling coefficient approximately equal to 0.65, we find that the state with insulated nuclei can exist up to the concentration c_2 of atoms contained in nuclei of the new phase, which is approximately equal to 0.1. This value is slightly lower than the percolation threshold and determines the limits of applicability of the droplet model.

2. THERMODYNAMICS OF GLASSES AND LIQUIDS TAKING INTO ACCOUNT HETEROPHASE FLUCTUATIONS

2.1. Peculiarities of droplet approach in the description of glasses and supercooled liquids

Supercooled liquids and glasses are metastable states which crystallize after a certain time. While describing the thermodynamics of such states, we must omit the crystalline phase. Otherwise, we can describe only the thermodynamics of a normal liquid above T_1^* (see, for example, Sec. 1.4) and the thermodynamics of a crystalline solid, taking into account heterophase fluctuations. The glassy state is metastable and can set in only if crystallization of a supercooled liquid has no time to occur for some reason or another (e.g., due to rapid cooling). Nevertheless, the system can be in this state for such a long time that it is expedient to introduce the free energy of glass confining its calculation only to the contribution of states from a fraction of the total phase space of the system, which is attainable for the phase trajectory over a time much shorter than the characteristic time of crystallization. The free energy and chemical potential of glass that will be used below have just this meaning. Glass is a state of a system with broken ergodicity (see Refs. 2 and 3), whose thermodynamic analysis, taking into account heterophase fluctuations in the form of liquid nuclei, is justified if the equilibrium distribution of these fluctuations sets in over a time much shorter than the time of crystallization. Similarly, the disregard of nuclei of the crystalline phase in the calcu-

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lation of the free energy of a supercooled liquid is justified if their contribution remains much smaller than the contribution of noncrystalline solid nuclei.

Let us apply the droplet model for describing the thermodynamics of a glass and a supercooled liquid taking into account heterophase fluctuations. We denote by μ_1^0 and μ_2^0 the chemical potentials of the liquid and the glass, respectively, without heterophase fluctuations and by μ_s the chemical potential of atoms in the surface layer. We denote by ζ_2 and ζ_s the configurational entropies per atom in the bulk of a solid nucleus (cluster) and in its surface layer, respectively. These quantities were calculated in Ref. 1. It was noted in Introduction that glass can be treated as a monocluster or a polycluster in one of possible SS and is a system with broken ergodicity. We take for the average energy of the glass the quantity averaged over all possible structural states. The configurational entropy of glass is equal to zero in view of violation of ergodicity, and the quantity ζ_2 describes the structure *complexity* (see Refs. 2 and 3). For this reason, the bulk entropies in the glass and in a finite-size cluster in the liquid differ by the quantity ζ_2, and the chemical potentials of atoms in them coincide. We denote by μ_2^e the bulk chemical potential of atoms in a structurally ergodic solid (cluster). Then we can write

$$\mu_2^e(P,T) = \mu_2^0(P,T) - \zeta_2 T. \tag{52}$$

As regards the quantity μ_s, it is smaller than the chemical potential of atoms in the surface layer of crystalline nuclei by approximately $\zeta_s T$, which leads to a noticeable decrease in the free energy of formation of noncrystalline nuclei (see also Refs. 1 and 29). We can now use the theory presented in Sec. 1 for describing the thermodynamics of liquid and glass on the basis of the droplet approach.

2.2. Thermodynamics of glass

Expression (15) describes the chemical potential μ_g of glass on the basis of the droplet model:

$$\mu_g(P,T) = \mu_2^0(P,T) - k_B T \frac{\widetilde{N}_1}{N}(1+R_0)\ln(1+R_0)$$
$$= \mu_2^0(P,T) - k_B T(1+\widetilde{R}_1)^{-1}(1+R_0)$$
$$\times \ln(1+R_0). \tag{53}$$

Among other things, it follows from this equation that, in the case of a positive difference $\mu_s - \mu_2^0$, we have a first-order glass–liquid phase transition at the temperature $T = T_{gl}$, which is determined from the equation

$$\mu_g(P,T) = \mu_1(P,T). \tag{54}$$

Since the chemical potential of glass is higher than that of the crystal, the value of T_{gl} is smaller than the crystallization temperature for the liquid.

2.3. Thermodynamics of liquid

In the droplet model, the thermodynamics of liquids is described by an expression of the type (53), the only difference being that it contains μ_2^e defined by expression (52) instead of μ_2^0. This gives

$$\mu_1(P,T) = \mu_1^0(P,T) - k_B T \frac{\widetilde{N}_1}{N}(1+R_0^e)\ln(1+R_0^e)$$
$$= \mu_2^0(P,T) - k_B T(1+\widetilde{R}_1^e)^{-1}(1+R_0)$$
$$\times \ln(1+R_0^e), \tag{55}$$

where

$$R_m^e = \sum_{k \geqslant k_{20}} k^m \exp(-\Delta G_{2k}^e \beta), \quad m = 0,1,2,... \tag{56}$$

and [see Eq. (9)]

$$\Delta G_{2k}^e = G_{2k}^e(P,T) - k\mu_1(P,T). \tag{57}$$

Taking into account (56) and (57) for small values of the fraction x of atoms belonging to solid clusters (which is just the condition of applicability of the droplet model), we can write expression (55) in the form

$$\mu_1(P,T) = \mu_1^0(P,T) - k_B T \langle k \rangle^{-1} x(1-\widetilde{x}), \tag{58}$$

where

$$x = R_1^e(2) = \langle k \rangle \exp\{-k_0[\mu_2^e - \mu_1 + p(k_0)(\mu_s - \mu_2^e)]\}$$
$$\cong k_0 \exp\{-k_0[\mu_2^e - \mu_1 + p(k_0)(\mu_s - \mu_2^e)]\},$$
$$\widetilde{x} \equiv x\langle \widetilde{k} \rangle / \langle k \rangle. \tag{59}$$

It follows from (55) that, at the temperature $T = T_e$ determined from the equation

$$\mu_1(P,T) = \mu_2^e(P,T) = \mu_g(P,T) - \zeta_2 T, \tag{60}$$

the first-order liquid–solid phase transition takes place.

A comparison of (54) and (60) shows that the formation of an infinitely large drop and conversion of glass into liquid must take place at the temperature T_{gl} which does not coincide with the temperature T_e of formation of an infinitely large solid cluster in the liquid. The reason behind such a difference in temperatures of transition can easily be established. In the expression for free energy, clusters are ergodic; moreover, this expression takes into account the contribution from clusters of all possible configurations. This means that, at $T < T_e$, the liquid is metastable to structurally ergodic clusters. On the other hand, expression (54) implies that the glass at $T > T_{gl}$ is metastable relative to liquid. The difference $T_e - T_{gl}$ is proportional to ζ_2.

The observed difficulty in the description of the thermodynamics of glasses and liquids indicates that the droplet model is inapplicable for describing phase transitions with broken ergodicity, which are accompanied by a loss of configuration entropy and the formation of structures with a nonzero complexity. In Refs. 29 and 30, a description of thermodynamics of a liquid on the basis of the mixed state model is proposed for the temperature interval in which the droplet model is inapplicable. Mixed state is the term applied to the state of the system in which coagulation of solid nuclei into large clusters is not ruled out and in which infinitely large, mutually percolating liquid and solid clusters can coexist. Structural rearrangements in a solid cluster restoring its ergodicity mainly occur due to displacements of phase boundaries. This process can be too long as compared to a reason-

able time of experiment. In this case, measurements reveal not actual (manifested over infinitely long intervals of time), but apparent violation of ergodicity. A detailed analysis of this process is essential for describing relaxation properties in the liquid, but is beyond the scope of this paper.

3. THERMODYNAMICS OF MIXED STATE

3.1. Free energy in the model of mixed state

In Ref. 29, the existence of mixed state in clusterized liquids is established, and the expression for free energy of such a state is derived. The derivation of the expression is carried out by using the assumption that the fractions of nuclei of both phases are comparable, and the sizes of nuclei of both phases are bounded from below by certain values k_{01} and k_{02}. Moreover, we assume that the presence of isolated liquid nuclei in glass does not lead to restoration of its ergodicity.

Assuming for simplicity that

$$k_{01} = k_{02} = k_0, \tag{61}$$

and that large nuclei (with $k \gg k_0$) can be treated as complex molecules combining small ''molecules'' (with $k = k_0$) of both types, we can obtain the following expression for the free energy of mixed state in the mean-field approximation:

$$G_{\text{mix}}(P,T) = N\mu_{\text{mix}}(P,T),$$

$$\mu_{\text{mix}} = \mu_1(1-x) + [\mu_2^e + r(x)\zeta_2 T]x + p(k_0)x(1-x)(\mu_s$$
$$- \mu_2^e - r(x)\zeta_2 T) + k_B T k_0^{-1}[x \ln x + (1-x)$$
$$\times \ln(1-x)]. \tag{62}$$

Here x is the fraction of atoms of the solid phase. It will be shown below that x plays the role of order parameter. The function $r(x)$ describes the loss of ergodicity of a percolating solid cluster. It tends to zero as the percolation threshold for such a cluster is reached from above and is close to unity when the infinitely large (percolating) liquid cluster disappears. The analytic expression for x is unknown although its physical nature is simple: the skeleton of an infinitely large percolating cluster acquires regions in which atoms are ''frozen'' and virtually do not change their configuration. In the bulk of a solid, virtually all atomic configurations are frozen, and hence $r(x) = 1$ in this case. It can be seen that the emergence of a term proportional to $r(x)$ in (62) is due to ergodicity breaking in the process of formation of a noncrystalline solid.

The first term on the right-hand side of (62) describes the contribution of the liquid fraction, the second the contribution of the solid fraction, the third the contribution of phase boundaries, the last term being proportional to the entropy of mixing of phases.

An expression for free energy similar to (62) was also used in Refs. 36 and 37.

The equilibrium values of x and free energy in the mixed state can be determined from the conditions of minima of expression (62) as a function of x, i.e., from the equation

$$\frac{\partial\mu_{\text{mix}}}{\partial x} = \mu_2^e - \mu_1^0 + p(k_0)(1-2x)(\mu_s - \mu_2^e)$$

$$+ \left\{ [1 - p(k_0) + 2p(k_0)x]r(x) + [\{1 - p(k_0)\}x \right.$$

$$+ p(k_0)x^2] \frac{\partial r(x)}{\partial x} \right\} \zeta_2 T + k_B T k_0^{-1} \ln \frac{x}{1-x} = 0$$
$$\tag{63}$$

for

$$\partial^2\mu_{\text{mix}}/\partial x^2 > 0. \tag{64}$$

For further analysis, we introduce some additional assumptions concerning the function $r(x)$. We shall assume that this function is negligibly small up to values of the order parameter slightly higher than $x = 1/2$. Moreover, we assume that $r(x)$ differs from unity insignificantly near the percolation threshold of a liquid cluster in the solid fraction. The use of these assumptions does not lead to any qualitative changes in the results of analysis, but simplifies it considerably.

Let us first consider the thermodynamics of the mixed state for small values of x in the vicinity of T_e, when the violation of ergodicity is not observed or is insignificant. For $x \ll 1$, relations (62) and (63) for $r(x) \equiv 0$ lead to

$$\mu_{\text{mix}}(P,T) = \mu_1^0(P,T) - k_B T k_0^{-1}x(1-x), \tag{65}$$

$$x \cong \exp\{-k_0[\mu_2^e - \mu_1 + p(k_0)(\mu_s - \mu_2^e)]\beta\}. \tag{66}$$

An analysis shows that Eq. (63) has only one real-valued root satisfying condition (64) (i.e., defining the minimum of μ_{mix}) for

$$p(k_0)\Delta\mu_s \equiv p(k_0)(\mu_s - \mu_2^e) < 2k_B T_e k_0^{-1}. \tag{67}$$

In this case, the fraction x increases continuously upon cooling, and no phase transitions are observed in the mixed state, in particular, no first- and second-order phase transition occur at $T = T_e$. It should be recalled (see the previous section) that a phase transition takes place in the droplet model irrespective of condition (67) at $T = T_e$ if $\Delta\mu_s \geq 0$.

Under the condition

$$p(k_0)\Delta\mu_s > 2k_B T_e k_0^{-1} \tag{68}$$

Eq. (63) at $T = T_e$ has three real solutions two of which satisfy condition (64), i.e., define the minima of μ_{mix}. The third real solution determines the maximum value of μ_{mix}. This equilibrium state of the system is unstable.

For

$$p(k_0)\Delta\mu_s = 2k_B T_e k_0^{-1} \tag{69}$$

the derivative $\partial x/\partial T$ together with the second derivatives of μ_{mix} with respect to P and T are infinitely large for $T = T_e$, i.e., a second-order phase transition occurs in the mixed state.

It can be seen that x plays the role of the order parameter. Expression (66) defines its temperature dependence for small values of x. Let us write expressions for $x(T)$ that are valid over a wider range of x.

When condition (67) is satisfied, expressions (62) and (63) lead to the following approximate expression for $x(T)$ obtained by expanding x in the vicinity of $x = 1/2$:

$$x = \frac{1}{2} + \frac{3\,\delta}{3 + 4\,\delta^2}, \tag{70}$$

where

$$\delta = \frac{h_e(T_e - T)}{T_e[4k_0^{-1}k_B T - 2p(k_0)\Delta\mu_s]}, \tag{71}$$

$$h_e = \partial(\mu_2^e - \mu_1^0)/\partial T|_{T=T_e}. \tag{72}$$

When condition (68) is satisfied, two stable equilibrium states of the system exist in the temperature interval $[T_-, T_+]$, where

$$T_\pm \cong \frac{h_e \pm p(k_0)F\Delta\mu_s}{\Delta s_e + \ln[(1 \pm F)/(1 \mp F)]},$$

$$F = [1 - 2k_B T_e/k_0 p(k_0)\Delta\mu_s]^{1/2}, \quad \Delta s_e = h_e/T_e. \tag{73}$$

Here we do not write out the cumbersome analytic expressions for the order parameter in stable equilibrium states. As regards the temperature dependence of the order parameter for an unstable equilibrium state in the vicinity of the temperature T_e (for $T_+ > T > T_-$), it can be approximately described by formulas (71) and (72).

It can be easily established that the state with the parameter $x < 1/2$ is stable for $T > T_r$, while the state for which $x > 1/2$ is stable for $T < T_e$. At $T = T_e$, a first-order phase transition takes place.

When a second-order phase transition occurs [condition (69)], the following expression holds for the order parameter:

$$x = \frac{1}{2}\left(1 + \sqrt{3(T_e - T)/T_e}\right) \quad \text{for } T < T_e \tag{74a}$$

$$x = \frac{1}{2}\left(1 - \sqrt{3(T - T_e)/T_e}\right) \quad \text{for } T > T_e. \tag{74b}$$

The above expressions for the chemical potential of the system in a mixed state clarify (but do not exhaust, see below) the question concerning the existence of phase transitions at $T = T_e$. It can be seen that a first- or second-order transition can indeed exist at this temperature. At the same time (see Sec. 4), transitions associated with transformations of glass and liquid with isolated nuclei of the new phase (isolated droplets) into a mixed state can take place in addition to the phase transitions described above.

Let us now consider the thermodynamics of a mixed state with a small volume fraction of the liquid phase, i.e., $y \equiv 1 - x \ll 1$. For this purpose, we put $r(x) = 1$ in (62) in accordance with the above assumption. Calculations similar to those made while deriving expressions (65) and (66) readily give

$$\mu_{\text{mix}}(P, T) = \mu_2^0(P, T) - k_B T k_0^{-1} y(1 - y), \tag{75}$$

$$y \cong \exp\{-k_0[\mu_1^0 - \mu_2^0 + p(k_0)(\mu_s - \mu_1^0)]\}. \tag{76}$$

3.2. Specific volume and entropy of mixed state

Using the expressions for chemical potential and equilibrium value of the order parameter derived in the previous section, we can obtain the equation of state and the expression for entropy for a system in the mixed state. The case

described by relation (67), when no first-order phase transition exists, is most interesting. In the same approximation as that used while deriving (31), we obtain the following equation of state:

$$v \cong (1 - x)v_1 + x v_2. \tag{77}$$

Here v_1 and v_2 are specific volumes per atom in the liquid and solid components, respectively.

It can be seen that this expression coincides in form with expression (31) obtained on the basis of the droplet model.

The entropy satisfies the following expression:

$$s = (1 - x)s_1 + x s_2 + k_B k_0^{-1}[x \ln x + (1 - x)\ln(1 - x)], \tag{78}$$

where s_1 and s_2 are the entropies per atom in the liquid and solid components, respectively. The last term describes the entropy of mixing.

It can be seen from the above expressions that specific volume and entropy in the mixed state are weighted average quantities (if we take into account the contribution of the entropy of mixing in the case of specific entropy).

If we measure $v_1(T)$ and $s_1(T)$ under a fixed pressure at temperatures so high that the value of x (66) is negligibly small and extrapolate the obtained dependences to the region of low temperatures, measure the values of $v_2(T)$ and $s_2(T)$ for glass at a temperature slightly lower than the glass-transition point T_g, and extrapolate the obtained dependences to the temperature range above T_g, the substitution of these quantities into (77) and (78) makes it possible to find the order parameter $x(T)$ empirically.

3.3. Compressibility, heat capacity, and thermal expansion coefficient of mixed state

Let us write the expressions for the compressibility κ, heat capacity C_p, and the thermal expansion coefficient α being measured, which can be expressed in terms of the derivatives of $v(P,T)$ and $s(P,T)$ with respect to P and T. Let us consider the case of an ergodic mixed state [$r(x) = 0$]. It follows from (77) and (78) that

$$\kappa = \frac{x v_1 \kappa_1 + (1 - x)v_2 \kappa_2}{x v_2 + (1 - x)v_1}$$

$$+ \frac{x(1 - x)(v_1 - v_2)^2}{[x v_2 + (1 - x)v_1][4k_0^{-1}T - 2p(k_0)\Delta\mu_s]} \cong x\kappa_1$$

$$+ (1 - x)\kappa_2$$

$$+ \frac{x(1 - x)(v_1 - v_2)^2}{[x v_2 + (1 - x)v_1][4k_0^{-1}T - 2p(k_0)\Delta\mu_s]}, \tag{79}$$

$$C_p = (1 - x)C_{p1} + x C_{p2}$$

$$+ \frac{x(1 - x)\{k_0(s_2 - s_1) + k_B \ln[x/(1 - x)]\}^2}{k_0[1 - 2k_0 p(k_0)x(1 - x)\Delta\mu_s/T]}, \tag{80}$$

$$\alpha = \frac{x v_1 \alpha_1 + (1 - x)v_2 \alpha_2}{x v_2 + (1 - x)v_1}$$

$$+ \frac{x(1-x)(v_1-v_2)\{k_0(s_2-s_1)+k_B \ln[x/(1-x)]\}}{k_0[1-2k_0 p(k_0)x(1-x)\Delta\mu_s/T]}.$$

$$(81)$$

Here $\kappa_i = \partial \ln v_i/\partial P$, $i=1,2$.

The above expressions together with (70) and (74) show that κ, C_p and α are monotonic functions of T when conditions (67) are satisfied, but become infinitely large and undergo discontinuities at $T=T_e$, when equality (69) holds.

For $r(x)\neq 0$, the expressions for κ, C_p, and α become more cumbersome and for this reason are not given here.

3.4. Fluctuations of order parameter

It would be interesting to describe the fluctuations of the order parameter $x(T)$ in the mixed state. Noting that the fluctuations of the free energy of an aggregate of k atoms are k_BT, i.e.,

$$\langle [G(k)-\bar{G}(k)]^2 \rangle \equiv \langle \delta G(k)^2 \rangle = k_B T, \qquad (82)$$

where

$$\bar{G}(k) = k\mu(P,T), \qquad (83)$$

from (82) and from the equality

$$2\langle \delta G(k)^2 \rangle = k\langle (x-\bar{x})^2 \rangle \partial^2 \mu/\partial x^2 \qquad (84)$$

we obtain

$$k\langle (x-\bar{x})^2 \rangle = 2k_B T/(\partial^2 \mu/\partial x^2). \qquad (85)$$

This expression shows that the fluctuations of the order parameter have maximum intensity in the temperature range in which the second derivative $\partial^2 \mu/\partial x^2$ of chemical potential is small. Let us write the explicit expression for $\langle (x-\bar{x})^2 \rangle$ under the condition (67), assuming that the nonergodocity parameter is zero ($r(x)=0$):

$$k\langle (x-\bar{x})^2 \rangle = \frac{2k_B T\bar{x}(1-\bar{x})}{k_0^{-1}k_B T - 2p(k_0)\Delta\mu_s\bar{x}(1-\bar{x})}. \qquad (86)$$

It follows hence that the value of $k\langle (x-\bar{x})^2 \rangle$ becomes infinitely large when condition (69) is satisfied, and T tends to T_e.

4. PHASE TRANSITION INVOLVING THE FORMATION OF A MIXED STATE

In the previous two sections, we derived expressions for the free energy of a system in various SS. The droplet model describes glass (liquid) in the presence of nuclei of the liquid (solid) phase in the form of isolated droplets in it. In the mixed state, the droplets of the two phases can merge into one and get mixed, forming finite as well as infinitely large clusters. In Refs. 29 and 30, the MSM was used for describing the mixed state. It was proven that weak first-order phase transitions near the percolation threshold for the liquid phase in glass and solid state in liquid have a high probability. In spite of the fact that the order parameter (the probability that an atom belongs to a percolating cluster) as well as the scaling laws typical of second-order phase transitions are connected with the formation of a percolating cluster, a direct

relation between the percolation problem and the problem on thermodynamic phase transitions has not yet been analyzed completely (see Ref. 38).

Here we present the results of a more consistent analysis (than that in Ref. 30) of phase transitions associated with the formation of mixed states. Comparing expressions for free energy of the system in different SS, we can find the stability regions for the mixed state as well as for glass and liquid (taking heterophase fluctuations into consideration).

Let us first compare the chemical potentials for the liquid and for the mixed state. For this purpose, we use approximate expressions (58), (59) and (65), (66) which are valid for a small fraction of solid clusters. In order to distinguish between the mixed and the droplet states, we mark the order parameter x by indices m and d so that x_d is defined by expression (59) and x_m by expression (66).

Equating the chemical potentials

$$\mu_1(P,T) = \mu_{\text{mix}}(P,T) \qquad (87)$$

and solving the obtained equation for T, we obtain the transition temperature $T_{t1}(P)$. Below this temperature, the mixed state is stable, while the droplet state of the liquid is metastable or unstable. The liquid is stable at $T>T_{t1}$. At $T=T_{t1}$, we have a first-order phase transition in the general case. This transition is associated with a change in the topological structure of solid clusters in the liquid: isolated small nuclei are combined into large clusters and form a percolating cluster for $x=x_c\cong 0.15$. According to estimates, $x_m\cong x_c$ at $T=T_{t1}$. In this case, $x_d\cong 0.1$, so that the statement formulated in Ref. 1 and concerning the existence of weak first-order phase transitions near the percolation thresholds in the mixed state can be regarded as substantiated.

Let us obtain a rough estimate of T_{t1} that is valid for $p(k_0)\Delta\mu_s < 2k_B T/k_0$:

$$T_{t1} \cong T_e + \left[\frac{2k_B T_e/k_0 - p(k_0)\Delta\mu_s}{\Delta s_e} \right]. \qquad (88)$$

It can be seen that in this case $T_{t1}>T_e$. For $\Delta\mu_s=0$, the transition temperature T_{t1} is close to T_e.

Equating μ_g (58) and μ_{mix} (75), i.e.,

$$\mu_g(P,T) = \mu_{\text{mix}}(P,T), \qquad (89)$$

we can find the temperature T_{t2} of transition of glass to the mixed state. For negligibly small values of $\Delta\mu_s$, the temperature T_{t2} is close to T_{gl} and is shifted in the region of lower temperatures upon a decrease in $\Delta\mu_s<0$. For this case, the following estimate is valid:

$$T_{t2} \lesssim T_{gl}. \qquad (90)$$

At $T=T_{t2}$, a weak first-order phase transition associated with a transformation of glass to the mixed state also takes place. In the mixed state, a percolating liquid cluster is formed.

Thus, the mixed state is a special phase of a glass-forming liquid in which infinitely large (mutually percolating) liquid and noncrystalline solid clusters coexist. The temperature interval $[T_{t2},T_{t1}]$ in which the mixed state exists is determined by the configurational entropy and is quite broad when the chemical potential of atoms in the surface layer of
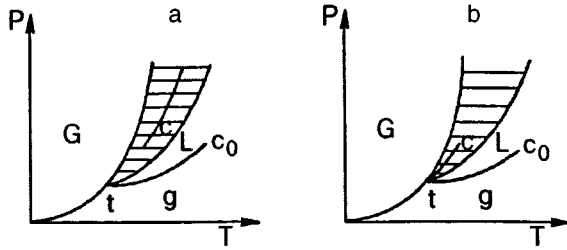
FIG. 1. Schematic phase diagrams of amorphous phases: G stands for glass, L for liquid, and g for gas; the region of existence of the mixed state is hatched; c_0 is the critical point of the gas–liquid system, c the critical point of the system liquid–noncrystalline solid, and t the triple point. The cases with $\partial\Delta\mu_s/\partial P>0$ (a) and $\partial\Delta\mu_s/\partial P<0$ (b) are depicted.

solid nuclei is smaller than $2k_B T_e/k_0$. For example, T_{t1} can be higher than the crystallization temperature for the liquid. In this case, a transition to the mixed state occurs in the normal (not supercooled) liquid.

Besides, when condition (68) is satisfied, two phases exist in the mixed state: the high-temperature phase with a small fraction of solid phase ($x<1/2$) and the low-temperature phase in which the fraction of the solid phase exceeds 1/2. The phase transition occurring at $T=T_e$ is accompanied by a jumpwise change in the fraction of the solid phase.

5. PHASE DIAGRAMS AND TEMPERATURE DEPENDENCE OF ORDER PARAMETER

The stability regions for (liquid and solid) droplet states as well as the stability region of the mixed state were determined above. In the case when condition (68) is satisfied in the range of the mixed state, the $T=T_e(P,T)$ curve is the boundary separating the stability regions of high- and low-temperature phases on the (P,T) plane. Figure 1 shows schematically the phase diagrams constructed on the basis of these results. It should be recalled that the stability region for the crystalline solid phase is not shown in the figure.

The temperature dependences of order parameter at constant pressure are shown in Fig. 2. Small jumps of the order parameter can be seen near the percolation thresholds for liquid and solid clusters. It follows from (87) and (89) that the jump in the order parameter is approximately equal to the square of its value, i.e., amounts to ~ 0.02.
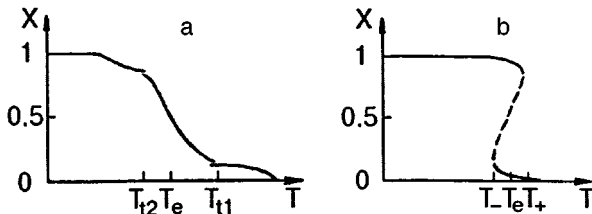

FIG. 2. Schematic representation of temperature dependences of the order parameter for $p(k_0)\Delta\mu_s<2T_e k_0^{-1}$ (a) and $p(k_0)\Delta\mu_s>2T_e k_0^{-1}$ (b).

6. DISCUSSION

In this section, the results of the description of thermodynamics of droplet and mixed states obtained above are compared with the previous results obtained by using other approaches mentioned in Introduction. The ideas concerning the nature and structure of glass-forming liquids and glasses used here are in qualitative agreement with those formulated by various authors during many decades. As regards the structural details of different approaches, the discrepancies are much more numerous. By comparing the basic results, we can better determine the advantages and drawbacks of different models and approaches.

6.1. Adam–Gibbs–DiMarzio approach

It was mentioned in Introduction that the decrease in the configurational entropy of a supercooled liquid in this approach is associated with the formation of clusters possessing the specific configurational entropy (per molecule) that decreases with temperature and can be presented in the form

$$\zeta=\Delta C_p(T-T_c)/T_g, \qquad (91)$$

where T_c is the temperature at which the entropies of the liquid and of the crystal are equal, viz., the *Kautzmann* temperature.

In our analysis, the decrease in configurational entropy is described by the ergodicity breaking parameter $r(x)$ whose temperature dependence in the vicinity of T_g can apparently be represented in linearized form (91). However, in this case, the constant T_c is deprived of a physical meaning. A similar opinion on the Kautzmann temperature was also formulated by other authors (see, for example, Ref. 20).

6.2. Two-state model

If we interpret two structural states of molecules in the TSM as pertaining to the solid and liquid fractions, this model is qualitatively similar to the mixed state model. It was noted above that the TSM postulates a formula of the form (31) and (77) that describes the specific volume in the droplet model as well as in the mixed state model to a high degree of accuracy. As regards the order parameter x, its temperature dependence in TSM is described by the following expression:

$$x(T)=\frac{\exp[-h(1-T/T_e)\beta]}{1+\exp[-h(1-T/T_e)\beta]}. \qquad (92)$$

Here $T_e=h/s$, and h and s are the differences in enthalpy and entropy in the two states, which can be obtained from the fitting of experimental data.

Expression (92) can be obtained by minimization in x of the chemical potential of a substance in which molecules can be in two states:

$$\mu(P,T)=(1-x)\mu_1+x\mu_2+k_BT[x \ln x+(1-x)\ln(1-x)]. \qquad (93)$$

A comparison of (93) and (62) shows that these expressions coincide for $\Delta\mu_s=0$, $k_0=1$, and $r(x)=0$.

The TSM makes sense when each molecule is statistically independent and can be in two different structural

states. This assumption is justified only in the case when intermolecular interactions can be replaced by a certain mean field to a high degree of accuracy. Obviously, the assumption is wrong if a supercooled liquid contains the liquid and solid fractions in comparable amounts. In this case, it is impossible to introduce a unified mean field. At the same time, the TSM can be used successfully for interpreting and numerical fitting of experimental data (see above). This means that an expression of the type (92) correctly approximates the behavior of the order parameter for an appropriate choice of fitting parameters. Expression (70) obtained on the basis of the MSM must also possess this property. In order to compare expressions (70) and (92), we write the latter in the form of an expansion in deviations of temperature from T_e. This gives

$$x = \frac{1}{2} + \frac{3\,\delta}{3 + 4\,\delta^2}, \tag{94}$$

$$\delta = h(T - T_e)/4k_B T T_e. \tag{95}$$

Observing that relation (71) can be represented in the form

$$\delta \cong \frac{h_e(T - T_e)}{4k_B T T_e(k_0^{-1} - p(k_0)\Delta\mu_s/2k_B T_e)} \equiv \frac{\widetilde{h}_e(T - T_e)}{4k_B T T_e}, \tag{96}$$

we see that expressions (71) and (92) differ insignificantly in form over a wide temperature interval if $p(k_0)\Delta\mu_s < 2k_B T_e k_0^{-1}$ and $h = h_e$. It follows from (96) that, with increasing $\Delta\mu_s$, the value of $\widetilde{h}_e$ increases and becomes infinitely large at the critical point for $p(k_0)\Delta\mu_s = 2k_B T_e k_0^{-1}$. It can be seen that, if condition (67) is satisfied, the TSM gives an expression for x close in form to that obtained on the basis of the MSM. If this condition is not satisfied, the TSM leads to qualitatively different results since phase transitions at $T = T_e$ are impossible in this model.

For $k_0 \approx 10$–15, the entropy of mixing is smaller than that appearing in the TSM in which it is normally assumed that $k_0 = 1$. Consequently, the contribution to free energy from the term proportional to entropy of mixing in the TSM is exaggerated.

It should be noted that cooperative phenomena (e.g., α-relaxation and the formation of a Fischer cluster in a supercooled liquid) cannot be explained consistently in the TSM. Indeed, the driving force of formation of a Fischer cluster depends on the contribution of phase boundaries to the free energy of the system, but this contribution in the TSM is assumed to be zero.

6.3. Model of free volume

The thermodynamics of glasses and supercooled liquids is described in Refs. 22 and 23 on the basis of the model of free volume. In this approach, solid and liquid-like atomic cells (Voronoi polyhedra) are introduced. The volume v_0 of a solid cell is close to that in a crystal. Liquid-like cells contain an excess (free) volume $v_{fi} = v_i - v_0$. Here v_i is the volume of a Voronoi polyhedron of the ith atom. It is assumes that the free energy of an atom (including vibrational entropy) depends only on v_{fi}. In addition, the cooperative

(communal) entropy S_c to which atomic configurations of liquid clusters contribute is determined. Liquid clusters consist of coupled liquid-like cells whose number in a cluster is equal to or larger than $v_0/\overline{v}_f$, where $\overline{v}_f$ is the average free volume per liquid-like cell. (In our notation, $v_0/\overline{v}_f = k_0$.) The basic property of S_c is that it depends on the fraction y of atoms belonging to liquid clusters and increases rapidly with the formation and growth of a percolating cluster near the percolation threshold.

The chemical potential of the system (see formula (41) in Ref. 22) can be written in the form

$$\mu = y\mu_1 + (1-y)\mu_2 - TS_c + k_B T[y\ \ln\ y + (1-y)$$
$$\times \ln(1-y)]. \tag{97}$$

Here we used the notation adopted in this paper. The chemical potentials μ_1 and μ_2, which are functions of volume and temperature, were obtained in the framework of the chosen model.[22]

The most significant results of the theory developed here can be formulated as follows:

(1) a phase transition takes place at the percolation threshold of a liquid cluster;

(2) it is a first-order phase transition generated by a rapid increase in S_c behind the percolation threshold.

It should be noted that the chemical potential (97) is close in form to those used for describing the droplet and mixed states [see formula (62)]. Indeed, if we put in (62) $r(y)\zeta_2(1-y) \equiv S_c(y), k_0 = 1$ and neglect the contribution of phase boundaries, expressions (62) and (97) coincide. It can be seen that the contribution of entropy of mixing in (97) is exaggerated, and the interfaces between the liquid and solid phases are disregarded. Nevertheless, the thermodynamics of the system in the TSM is qualitatively similar to that described by Cohen and Grest.[22]

6.4. Theory of self-forming frustration-limited domains

A thermodynamic theory of supercooled liquids based on the assumption that the system possesses an ''excluded'' critical point was proposed by Kivelson *et al.*[21] It is assumed that the behavior of a supercooled liquid in a wide temperature interval, including the region of existence of the liquid and extending to the region above the crystallization temperature, is close to critical. The reason behind short-range ordering is associated with intermolecular forces, but the short-range order generated by them is such that it is incompatible with the long-range ordering and with the formation of an extended solid structure. If, for example, intermolecular forces lead to the formation of noncrystalline icosahedral clusters, the merging of these clusters into a single structure is ruled out due to an increase in mechanical stresses with the size of a solid nucleus. In the absence of such accumulating stresses, we should expect the existence of a critical point, associated with long-range ordering of domains. Frustrations rule out the possibility of emergence of such a point but the behavior of the system remains close to critical. The assumption concerning the presence of

frustration-limited domains (solid nuclei) in supercooled liquids was also used by Malomuzh [39,40] who described relaxation phenomena in glass-forming liquids.

Under the assumption that the critical point should exist in the absence of frustrations at a certain temperature T^*, Kivelson et al. [21] proposed the scaling law for the size R_d of frustration-limited domains: $R_d \sim \varepsilon^\nu$, $\nu > 1$ for $\varepsilon = (T - T^*)/T^*$. They also proposed a qualitative phase diagram of the system on the (T, K) plane, where K is the so-called frustration parameter that has not received a reasonable definition yet.

In actual practice, the thermodynamics of a liquid containing frustration-limited domains is studied insufficiently. The main qualitative assumption in the proposed model is that the thermodynamics of a supercooled liquid is determined by locally ordered clusters, and there exists a certain characteristic transition temperature T^* below which cooperative processes are manifested.

The description of thermodynamics of a glass-forming liquid proposed in this paper resembles qualitatively the model of frustration-limited domains in that we also have a characteristic temperature T_{t1} similar to T^*, below which the system is in the mixed state. The thermodynamics of the mixed state is determined by the properties of solid and liquid clusters, and hence dynamic processes must be cooperative. As regards the critical behavior of the system in the vicinity of T_{t1} and the scaling relations associated with this temperature, they indeed are observed in the mixed state near the percolation thresholds for liquid and solid clusters since the percolation itself is associated with a phase transition.[38] The order parameters in this case is the probability that an atom belongs to an infinitely large cluster. As regards thermodynamic phase transitions, we should expect in all probability a weak first-order phase transition at $T = T_{t1}$ (see Sec. 4).

CONCLUSIONS

An analysis of the contribution of heterophase fluctuations to the free energy of liquids and glasses leads to the conclusion that, along with the droplet states (in which heterophase fluctuations are in the form of isolated drops), a mixed state in which infinitely large liquid and noncrystalline solid clusters coexist also takes place. Transitions from droplet states to a mixed state are phase transitions in the sense that two order parameters in the mixed state differ from zero along with $x(T)$, i.e., the probabilities that atoms belong to infinitely large liquid and solid clusters. On the other hand, only one of these order parameters in the droplet state differs from zero. Universal scaling laws should be expected to hold for quantities depending on the topology of an infinitely large cluster near the percolation threshold. Since the free energy of the system in the models used here does not depend explicitly on the above order parameters, no direct relation between percolation and phase transitions is observed. At the same time, it was proved that droplet states become thermodynamically disadvantageous when the volume fraction of droplets is close to the percolation threshold in the continual approximation. On the other hand, the free energy calculated in the MSM for small volume fractions of heterophase fluctuations becomes higher than the free energy of the droplet state. This leads to the conclusion that in the general case we should expect a weak first-order phase transition near the percolation threshold.

It is important to note that the volume fractions of heterophase fluctuations in the droplet state are comparatively large ($\sim 0.05 - 0.1$) in rather wide temperature intervals, which makes them accessible for direct experimental observations.

A comparison of the expressions derived for equations of state, compressibilities, thermal expansion coefficients, and heat capacity with experimental data will make it possible to establish the relation between thermodynamic and structural characteristics of glass-forming liquids and glasses.

*E-mail: bakai@kipt.kharkov.ua

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Nonstationary effects in NbSe$_3$ intercalated with hydrogen

Kh. B. Chashka, V. A. Bichko, M. A. Obolenskii, Raid Hasan, and V. I. Beletskii

Kharkov State University, 310077 Kharkov, Ukraine*

Temperature dependences of resistivity and current-voltage characteristics of NbSe$_3$ single crystals intercalated with hydrogen are investigated in the temperature range 90–300 K in the normal state and in a state with a charge density wave near the first phase transition at 145 K. A state with nonlinear conductivity at $T > 145$ K, IVC with a negative differential resistance, and low-frequency voltage oscillations in the state with the CDW are discovered. The results are interpreted on the basis of concepts of redistribution of intercalated hydrogen under the action of temperature diffusion and electric field during the propagation of a charge density wave. © *1998 American Institute of Physics.* [S1063-777X(98)00701-4]

The transition to a state with a charge density wave (CDW) which is typical of many compounds with an anisotropic electron spectrum is manifested most clearly in quasi-one-dimensional compounds.[1] For example, niobium triselenide NbSe$_3$ exhibits two transitions accompanied by the formation of CDW at 145 and 59 K. The charge carrier density in the CDW state in a given direction (x) can be represented in the form

$$\rho(x) = \rho_0[1 + \alpha \cos(Qx + \varphi)], \qquad (1)$$

where ρ_0 is the uniform electron density, $\alpha\rho_0$ the amplitude of charge modulation, $\mathbf{Q} = 2\mathbf{k}_F$ the modulation wave vector, and $\mathbf{k}_F$ the Fermi wave vector. The phase φ characterizes the position of the CDW relative to the ionic lattice.

Additional information on the transition and structure of the state with a CDW was obtained from the experiments with NbSe$_3$ single crystals under the action of external factors (mechanical deformation,[2] axial loading,[3] and hydrostatic pressure[4]) as well as under intrusion of impurities.[1]

It was shown in Refs. 3 and 4 that the Fermi surface (FS) is distorted under the action of axial or hydrostatic pressure. This in turn leads to a decrease in the area of the FS regions coinciding upon a parallel translation by the vector $\mathbf{Q} = 2\mathbf{k}_F$, and hence to an increase in the number of noncondensed charge carriers in the CDW state, resulting in partial suppression of the CDW. The doping of quasi-one-dimensional structures (NbSe$_3$ and TaS$_3$) with transition metals[1] also leads to partial suppression of the state with CDW and, in addition, to a shift of temperature corresponding to the onset of the CDW transition. It is well known, however,[1] that it is difficult to obtain a uniform distribution of impurities in the sample as a result of doping. Also, the number of elements that can be used for doping crystals based on chalcogenates of transition metals is not very large.

Intercalation by light impurities (e.g., hydrogen) considerably extends the potentialities of the experiments. A considerable advantage of this method lies in the possibility of varying the hydrogen concentration in the same sample. In view of its small atomic radius, hydrogen virtually does not distort the matrix lattice. At the same time, being a charged impurity, it must change the occupancy of the conduction band of the matrix.[5]

In our earlier publication,[6] we proved that the temperature of the first CDW transition (at 145 K) depends on the amount of intercalated hydrogen weakly and nonmonotonically. The CDW state is partially suppressed in this case, which is manifested in a decrease in the amplitude of resistive anomaly at $T < 145$ K. For a certain hydrogen concentration, NbSe$_3$ exhibits a metal-semiconductor transition.

We shall describe below the results of analysis of nonstationary effects associated with the passage of current through NbSe$_3$ single crystals intercalated with hydrogen in the CDW state.

EXPERIMENTAL TECHNIQUE

All measurements were made on NbSe$_3$ single crystals obtained from the chemical gas-transport reaction. Single crystals were saturated with hydrogen from the gaseous phase under a pressure of 10 bar, after which a fraction of hydrogen was removed consecutively by periodic annealing under a pressure $P \approx 10^{-9}$ bar. The temperature of heating during annealing did not exceed 200 °C; the results of mass spectrometry indicate that evolution of hydrogen under such conditions occurs without a loss in the stoichiometric composition of the compound NbSe$_3$. This technique made it possible to obtain all the results on virtually the same initial sample of NbSe$_3$ and to attribute all the changes in elecrophysical parameters observed in experiments only to the change in hydrogen concentration in the sample and to the state of hydrogen in the lattice.

Temperature dependences $R(T)$ of electrical resistance were measured by the four-probe method in direct current in the temperature range 90–300 K.

The differential resistance, threshold fields E_{th} of CDW disruption and corresponding transport currents I_{th} were determined from the current–voltage characteristics (IVC). The experimental setup allowed us to record directly the $U(I)$ dependence by using the $x-y$ graphic recorder and to determine the nonlinear contribution to IVC with the help of a compensating bridge circuit. We recorded $(U_x - U_f)$ as a function of I, where U_x is the voltage across the sample determined by the slope of the IVC in the state with a linear (ohmic) conductivity and U_f the current value of the voltage
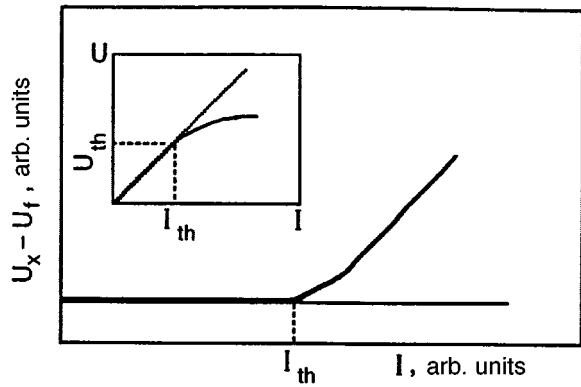
FIG. 1. Typical IVC of a sample in the CDW state, recorded according to the bridge circuit. The inset shows the same IVC recorded by using a conventional method.

across the sample. Such a method of IVC recording has made it possible to increase by three orders of magnitude the resolution in detecting the emergence of a nonlinear segment. The threshold field E_{th} was determined from bridge IVC as $(I_{th}R_x)/L$, where R_x is the ohmic resistance of the sample on the linear segment of the IVC, L the separation between potential contacts, and I_{th} the current determined from the IVC obtained by using the bridge circuit (Fig. 1), and corresponding to the emergence of a disbalance voltage of 1×10^{-7} V. The sweep time for direct current could be varied during the IVC recording from 1 to 10^2 s.

RESULTS OF MEASUREMENTS

Figure 2 shows typical $R(T)$ curves recorded for NbSe$_3$ single crystals saturated with hydrogen during consecutive annealing in vacuum. Annealing and thermal cycling of the
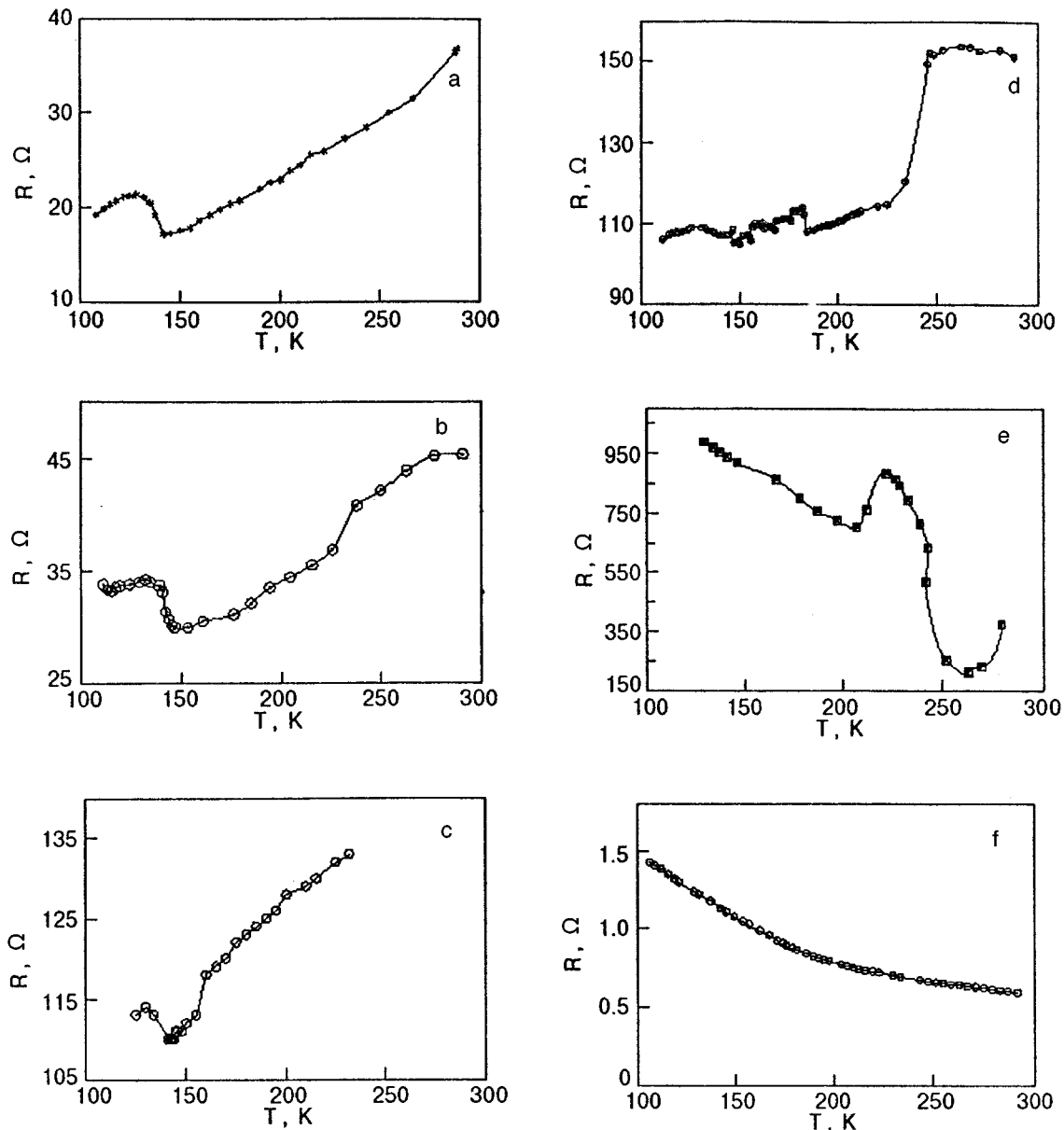

FIG. 2. Temperature dependences of the resistance of a NbSe$_3$ single crystal saturated with hydrogen at $P = 10$ bar(a), after the first annealing (b), immediately after the second annealing (c), and after 48 (d), 96 (e) and 144 h (f).
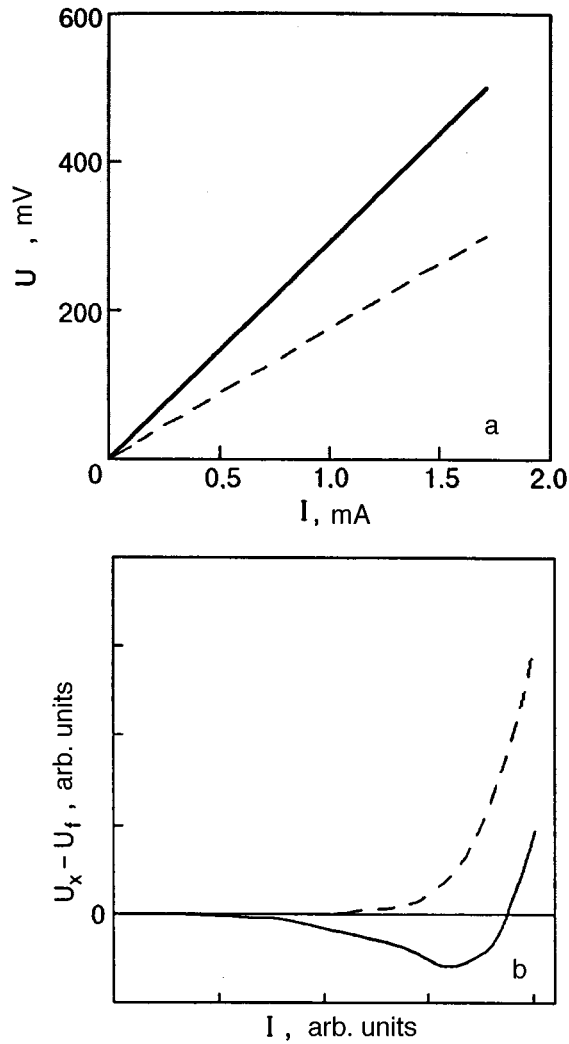
FIG. 3. IVC of a NbSe$_3$ sample recorded by a conventional method at $T_1 = 292$ K (solid curve) and $T_2 = 150$ K (dashed curve) immediately after saturation (a) and by the bridge method at $T < 145$ K for a sample with hydrogen (solid curve) and without it (dashed curve) (b); $(U_x - U_f)$ is the nonlinear contribution to IVC.

samples in the course of measurements led to a change in the form of the $R(T)$ dependence and to an increase in the value of R in general.

Figure 3 shows examples of IVC recorded for a NbSe$_3$ sample immediately after its saturation with hydrogen. The IVC obtained conventionally in the temperature range $T > T_{CDW}$ (Fig. 3a) can be described by Ohm's law, while the IVC obtained in the region of $T < T_{CDW}$ by the bridge method (Fig. 3b) deviate from the linear dependence to the side corresponding to an increase in the differential resistance of the sample, which was not observed for pure samples. With increasing transport current, this deviation was compensated by the contribution of CDW to conductivity.

After the first annealing, when the sample was in a state corresponding to the $R(T)$ dependence depicted in Fig. 2b, the IVC whose typical shape is shown in Fig. 4 were recorded. It should be noted that the IVC has such a shape in the temperature range 100 K $< T < 300$ K. For small currents,
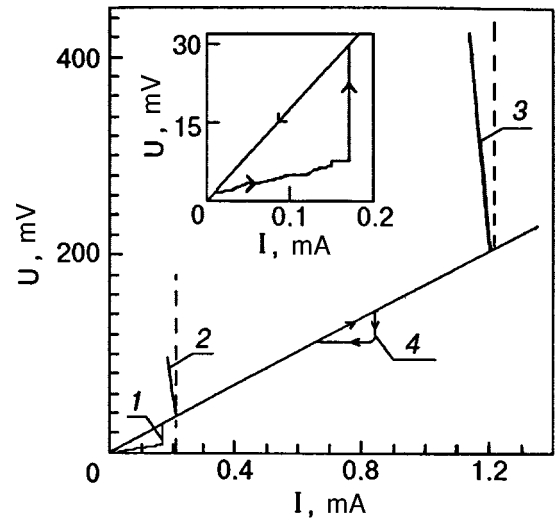

FIG. 4. Typical IVC for NbSe$_3$ samples recorded after the first annealing in the temperature range 100 K $< T < 300$ K. The inset shows the IVC hysteresis on segment 1 on a magnified scale.

the region of high nonlinear conductivity σ_1 is observed. With increasing current, the voltage (1) increases step wise, which is followed by the region of conductivity σ_2 described by Ohm's law (in this case, $\sigma_1 \approx 7\sigma_2$). In this state, two voltage jumps (2 and 3) are usually observed. These jumps emerged for the same values of the field which did not depend on temperature and amounted to $E_1 = 55$ V/m and $E_2 = 200$ V/m. The maximum values of the field on the IVC segments 2 and 3 were $65 \pm 10\%$ V/m and $370 \pm 10\%$ V/m, respectively. The regions of jumps 2 and 3 are segments with a negative differential electrical resistance (NDER). This is manifested most clearly in region 3 in which an increase in voltage is accompanied by a decrease in current. The variation of the sweep rate allowed us to estimate the time during which the sample is in the state with a NDER ($T_{NDER} \simeq 0.4$ s). After each jump, the sample returned to the state with the ohmic conductivity σ_2.

It can be seen from Fig. 4 that, in the case of reverse variation of current, the IVC is described by Ohm's law with the conductivity σ_2, and a stepwise decrease 4 of voltage opposite to 1 takes place only once.

When the sample is in the state corresponding to the $R(T)$ dependence depicted in Fig. 2c voltage oscillations were observed on the IVC recorded by the bridge method in the temperature range 112 K $< T < 121$ K in the fields $E > E_{th}$. An example of recorded IVC with oscillations is shown in Fig. 5a. The oscillation frequency does not depend of the sweep rate or transport current and amounts to ~ 0.3 Hz. The oscillation amplitude ΔU (Fig. 5b) depends linearly on the transport current. As the sweep rate for the transport current increases in the region of maxima and minima of voltages, the oscillatory curve displays a fine structure depending on the transport current (Fig. 6). For small currents, the structure has the form of instabilities that acquire the shape typical of relaxation processes with increasing current.
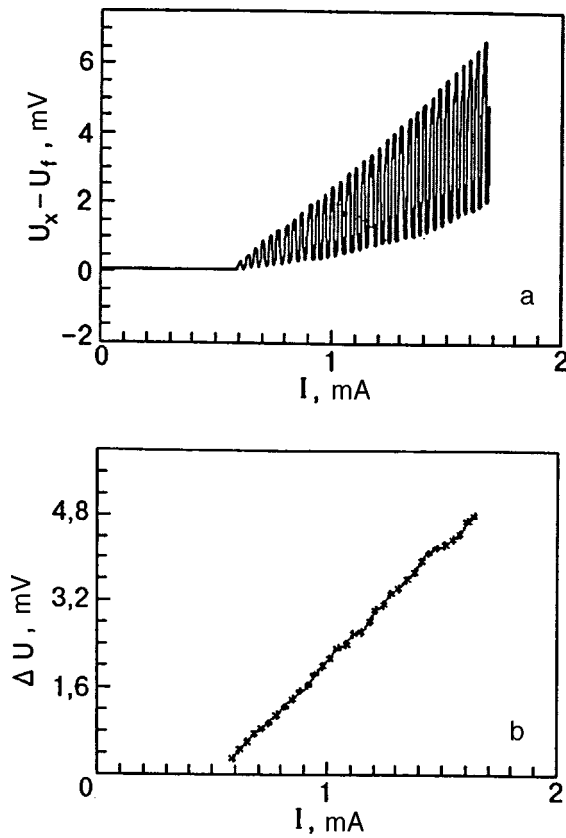
FIG. 5. Voltage oscillations on IVC of NbSe$_3$ samples after the second annealing, obtained at $T = 121$ K (a) and the oscillation amplitude as a function of transport current (b).

DISCUSSION OF RESULTS

Experimental results show that intercalation of hydrogen in the NbSe$_3$ lattice leads to significant changes in the temperature and field dependences of electrical conductivity in the normal as well as in the CDW state. In ordinary metals, hydrogen atoms are interstitial impurities possessing a high
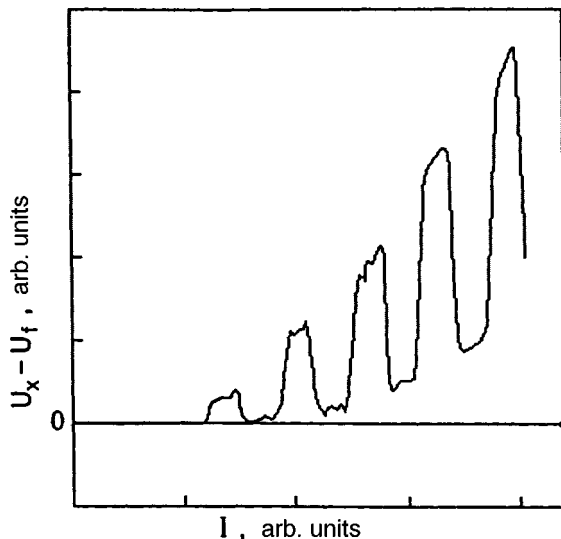

FIG. 6. An example of IVC recording corresponding to Fig. 5 for an increased sweep rate of transport current.

mobility even at low temperatures.[5] This is even truer true of low-dimensional conductors based on chalcogenides of transition metals in which hydrogen atoms are partially located in the Van der Waals gap. In the presence of a mobile impurity, the processes of heat and charge transfer can create in metals atomic flows and gradients of concentrations of mobile impurities associated with them.

In the presence of an electric field, the force $F = e^*E$ is generated, where e^* characterizes the electric charge acted upon only by the same forces as those acting on hydrogen atoms intercalated in the metal in the presence of the external field alone. Under the action of this force, hydrogen concentration is redistributed and increases near the cathode. Along with the flow induced by the electric field, a diffusion flow associated with the concentration gradient is formed. In this case, the total flux of hydrogen can be written in the form

$$J = -nD \ \mathbf{grad} \ c + ncMF, \tag{2}$$

where c is the hydrogen concentration, i.e., the ratio of the number of hydrogen atoms to the number of matrix atoms, n the number of lattice atoms per unit volume, D the diffusion coefficient, and M the mobility of intercalated hydrogen atoms.[5] On segment 1 of IVC (see the inset to Fig. 4), the second term in relation (2) obviously prevails at first as a result of the high mobility, small gradient, and high (on the average) concentration of hydrogen in the sample. As the electric field increases, the concentration gradient increases as a result of transport, the average concentration of hydrogen in most part of the volume decreases, and the first term in (2) becomes predominant.

It can be seen from Fig. 2 that hydrogen redistribution in the sample leads to the $R(T)$ dependence typical of semiconductors. Hence we can assume that the same processes occurring during the recording of IVC are responsible for the formation of a region with the semiconducting behavior of the resistance and a high resistivity near the cathode. These processes corresponds to segments 2 and 3 on the IVC on which the resistance increases sharply (see Fig. 4). In this state, the second term in relation (2) decreases abruptly, and the total hydrogen flux is determined by the first term, i.e., the semiconducting layer is resolved by diffusion, and hydrogen is redistributed over the volume of the sample.

The characteristic time required for damping of diffusion processes is defined by the formula

$$\tau_{\text{dif}} = l^2/D, \tag{3}$$

where l is the distance over which diffusion takes place.[5]

Assuming that the time during which the voltage across the sample attains the value at which the jump takes place and the interlayer with a high resistivity is formed is equal to τ_{dr}, while the time of switching to the initial state is τ_{dif}, we can estimate the characteristic values of $D \approx 2.5 \times 10^{-2}$ cm^2/s. This value is several orders of magnitude higher than the values of diffusion coefficient for three-dimensional metals,[5] indicating exceptionally high diffusive mobility of hydrogen in NbSe$_3$. Such a process of formation of semiconducting regions must apparently be observed for large currents also, but it could not be detected in view of superheating (Joule) effects.

As the hydrogen concentration decreases, but the sample is still in the metallic state with the temperature dependence of resistance depicted in Fig. 2c, periodic oscillations of voltage are generated in the temperature range below T_{CDW} corresponding to the first transition. At the present time, experimental results do not allow us to indicate unambiguously the reason behind the generation of such oscillations, but we can assume that the propagation of a CDW in the corresponding state with CDW in fields $E > E_{th}$ affects the hydrogen subsystem. It should be noted that in states with the resistive anomaly associated with CDW (see Figs. 2a and 2b) as well as upon a subsequent transition of the sample to the semiconducting state (see Figs. 2d, 2e, and 2f), voltage oscillations are not generated. The reason behind such a behavior is still unclear.

It was proved in Ref. 7 that CDW in low-dimensional systems intercalated with hydrogen can lead to the formation of a superstructure of hydrogen clusters. Under the action of electric and magnetic fields, this structure may move. The CDW transition in quasi-one-dimensional $NbSe_3$ is manifested most clearly, and the formation of a quasiperiodic structure of hydrogen clusters is quite probable. Taking into account what has been said above about the observed IVC, we can assume that the sample can be divided into alternating metal–semiconductor regions. Unfortunately, we are not in a position to determine the size of these regions so far. The displacement of such regions under the action of CDW must be characterized by a large effective mass and a low mobility, which can lead to a low-frequency generation in contrast to the high-frequency generation observed during the propagation of CDW alone in $NbSe_3$. This effect is probably similar to the motion of a domain in the Gunn diode[8] taking into account the fact that the velocity of the domain in the diode is determined by the drift velocity of electrons, which amounts to 10^7 cm/s. This determines the high frequency of oscillations, and the velocity of the cluster super-structure in our case will be determined by the diffusion rate of hydrogen, which is several orders of magnitude lower. The linear increase in the oscillation amplitude with the current (an analog of Ohm's law) remains unclear. It should be noted that temporary low-frequency oscillations of voltage were observed by us earlier[9] while studying superconducting bridges made of $NbSe_2$ as well as by other authors who studied narrow long superconducting films in the resistive state.[10] It should be noted that the resistive state of superconductors and the state with a CDW propagating near threshold fields of disruption have many peculiarities in common (see, for example, Ref. 1).

*E-mail: mikhail.a.obolenskii@univer.kharkov.ua

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Point-contact spectroscopy of organic conductors $[(C_2H_5)_4N]_{0.5}[Ni(dmit)_2]$ and $(BEDT\text{-}TTF)_2I_3$

G. V. Kamarchuk, A. V. Khotkevich, and V. M. Bagatskii

B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of the Ukraine, 310164 Kharkov, Ukraine*

A. V. Kravchenko

Kharkov State University, 310077 Kharkov, Ukraine

Point-contact spectra of organic conductors $[(C_2H_5)_4N]_{0.5}[Ni(dmit)_2]$ and $(BEDT\text{-}TTF)_2I_3$ have been measured. The plots of point-contact functions of the electron–phonon interaction in these compounds have been constructed, and mean and root-mean-square values of frequency have been obtained. The relation between the intensity of the electron-vibrational interaction and conducting properties of the materials under investigation have been obtained. A correlation is observed between the intensity of these processes and the superconducting transition temperature. The criterion for the synthesis of new organic superconductors is discussed. © *1998 American Institute of Physics.* [S1063-777X(98)00801-9]

Persistent interest in the study of organic conductors observed in recent years is stimulated by a number of factors among which the search for new superconducting materials plays an important role. In such investigations, main attention is paid to an analysis of the properties of familiar organic superconductors aimed at determining the pairing mechanisms and obtaining the criteria for the synthesis of new organic superconductors with predictable properties. One of the key problems of utmost importance for explaining superconductivity in organic compounds is associated with the role of intramolecular vibrations (IMV) which are not observed in ordinary metals. Yamaji[1] proposed a superconductivity mechanism for organic metals involving an IMV donor. Subsequently, various methods were used[2–4] to obtain data indicating the possibility of operation of such a mechanism in BEDT–TTF salts. For example, a strong interaction between conduction electrons and IMV of an organic conductor was observed.[3,4] These results lead to the conclusion that the IMV contribution to the formation of the superconducting phase of such compounds can be significant. The variation of the intensity of such processes upon a transition from one compound to another and their correlation with the superconducting properties of the materials remain unclear. It is logical to assume that if the IMV contribution to the formation of the electron–phonon interaction (EPI) in organic conductors is significant, the intensity of the electron-vibrational interaction (EVI) can correlate with the superconducting parameters of the material (in particular, the superconducting transition temperature T_c). In other words, materials with a higher T_c must display a higher intensity of interaction between conduction electrons and the IMV of the organic conductor, and vice versa. For this reason, it would be interesting to compare the results of measurements of EPI spectra with the values of T_c in different organic compounds. In order to simplify the problem, it is expedient to use first organic compounds with close compositions and structures, such as, for example, compounds belonging to families based on $[BEDT\text{–}TTF]^{n^+}$ and $[M(dmit)_2]^{n^-}$ (M stands for metal and dmit$=C_3S_5$). Since the superconducting transition temperatures for such compounds are known as a rule, it is sufficient to study the EPI spectra of the objects under investigation. It should also be noted that the EPI data for organic compounds from the $M(dmit)_2$ family are scarce or not available at all, and hence the measurement of EPI spectra for such materials forms an independent problem which is interesting as such.

We chose as objects of investigation the compound $(BEDT\text{–}TTF)_2I_3$ and one of organic conductors $[(C_2H_5)_4N]_{0.5}[Ni(dmit)_2]$. Let us first consider the results obtained for the compound from the family $M(dmit)_2$. The crystals of $[(C_2H_5)_4N]_{0.5}[Ni(dmit)_2]$ were grown during electrochemical synthesis under galvanostatic conditions. The synthesis was carried out in the mixed solvent CH_3COCH_3–CH_3CN (1:1) from the initial salts $[(C_2H_5)N]ClO_4$ and $[(C_2H_5)_4N]_2[Ni(C_2S_5)_2]$. The crystals of $[(C_2H_5)_4N]_{0.5}[Ni(dmit)_2]$ had the form of dark plates with an average area 1×2 mm and a thickness of the order of 0.1 mm. They have the structure of layered materials similar to that of BEDT–TTF salts (see, for example, Ref. 5). Anions $[Ni(dmit)_2]$ are packed in the crystal ''plane to plane,'' which is typical of all quasi-two-dimensional organic metals, and form stacks. The system of stacks forms highly conducting anion layers alternating with layers of cations $[(C_2H_5)_4N]_{0.5}$. Thus, as in the case of $(BEDT\text{–}TTF)_2I_3$, the highest conductivity is also observed in layers formed from the set of dimer units of a composition close to BEDT–TTF. At low temperatures, the compound $[(C_2H_5)_4N]_{0.5}[Ni(dmit)_2]$ is characterized by a metal-type conductivity, while its nearest analog $[(C_2H_3)_4N][Ni(dmit)_2]_2$ goes over to the superconducting state under pressure.[6]

We studied heterojunctions Cu–$[(C_2H_5)_4N]_{0.5}[Ni(dmit)_2]$ and Cu–$(BEDT\text{–}TTF)_2I_3$ at $T=4.2$ K. Crystal of organic metals were mounted in a special device for creating point
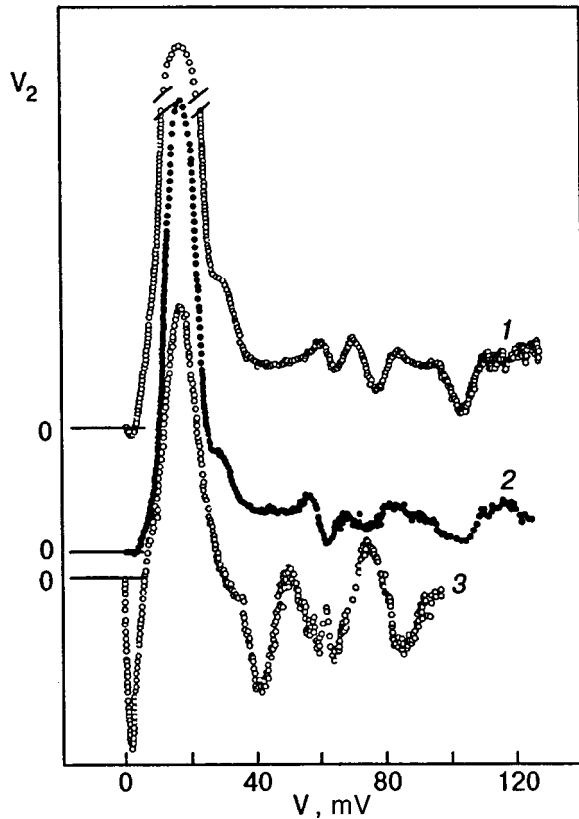
FIG. 1. Point-contact spectra for Cu–[(C$_2$H$_5$)$_4$N]$_{0.5}$[Ni(dmit)$_2$] heterojunctions for R_0, Ω: 45 (curve *1*), 66 (curve *2*), and 150 (curve *3*).

contacts and were brought in contact with a copper electrode in liquid helium. Heterojunctions were created by using the displacement technique[7] and were formed in the region of contact between the edges of an organic crystal and the copper electrode (see the inset to Fig. 1 in Ref. 4). Such a geometry of arrangement of electrodes made it possible to obtain and study mainly the junctions whose axis was oriented along anionic planes in the case of [(C$_2$H$_5$)$_4$N]$_{0.5}$[Ni(dmit)$_2$] and along cation planes in the case of (BEDT–TTF)$_2$I$_3$, i.e., in the direction corresponding to the highest conducting properties of the organic crystal. It was proved in Ref. 8, 9 that, for contacts with the axis in the plane of organic molecules, the main contribution to point-contact spectra comes from processes associated with the current flowing along layers formed by organic molecules (the contribution from the transverse component has the minimum value in this case). For this reason, peculiarities associated with the scattering of charge carriers in a highly conducting plane of organic molecules are manifested with the highest probability and have the maximum intensity. Accordingly, the effect of EVI on the point-contact spectrum is the strongest in this case. Consequently, in order to analyze the manifestations of the IMV contribution to the point-contact spectrum and its correlation with the conducting properties of organic metals, it is sufficient to study the characteristics of junctions oriented along conducting layers.

We measured the current–voltage characteristics (IVC) of points contacts and their second derivatives (point-contact spectra) at 4.2 K. The point-contact spectra of Cu–[(C$_2$H$_5$)$_4$N]$_{0.5}$[Ni(dmit)$_2$] junctions contain the superposition of contributions from copper and the organic metal. The contribution from copper has the form of a high-intensity low-energy peak at 17–18 meV due to the interaction of conduction electrons with transverse acoustic phonons. According to the form of the obtained point-contact spectra, we are dealing, as in Ref. 3, with asymmetric junctions. As a matter of fact, the point-contact spectrum of heterojunctions of metals is the sum of partial contributions of the spectra of each conductor. In the case of a symmetric heterojunction, the volume of phonon generation in each electrode is the same, which leads to the equality of the contributions of contacting metals of electrodes with close electronic parameters to $(d^2V/dI^2)(V)$. A change in the size of the region of constriction formed by one of the electrodes leads to a change in the corresponding contribution to the point-contact spectrum. In heterojunctions of metals with different Fermi velocities, the intensities of singularities in the point-contact spectra are redistributed in accordance with the relation $g_{pc}(\omega) \propto g_{pc}^{(1)}(\omega) + (v_F^{(1)}/v_F^{(2)})g_{pc}^{(2)}(\omega)_{pc}[g_{pc}(\omega)$ is the point-contact EPI function, and 1 and 2 are the numbers labelling the metals in contact]. The second derivatives of IVC for a symmetric point contact display a suppression of the intensities of the peaks responsible for EPI processes in the material with a higher Fermi velocity and, accordingly, an increase in the intensity of the peaks in the point-contact spectrum, which are due to the metal with a lower Fermi velocity. For Cu–[(C$_2$H$_5$)$_4$N]$_{0.5}$[Ni(dmit)$_2$] junctions, such an effect should result in suppression of EPI singularities in copper and enhancement of peaks from the organic metal against the background of the former effect. However, the experimentally observed spectra are characterized by a higher intensity of copper peaks. It was proved in Ref. 3 that the most probable reason behind this effect can be the lack of symmetry of the contact, namely, the fact that the contact region is mainly formed due to copper and not due to the organic conductor. Such a situation is quite realistic in the case under investigation also since we used the materials similar to those used in Ref. 3 and created point contacts by the methods similar to those in Refs. 3, 4.

Singularities of the second derivatives of IVC of the contacts under investigation for an energy above 32 meV (the boundary energy for the EPI spectrum of copper) correspond to the interaction of charge carriers with the vibrational modes of the organic conductor. The most clearly pronounced singularities are peaks corresponding to the energies 56–58, 70, 84, and 96 meV. Singularities at higher frequencies could not be observed since the material heating effects in the constriction region at voltages $V > 100$ mV led to the loss of stability of the junctions, a change in their resistance, or complete breakdown.

The shape of singularities of point-contact spectra for Cu–[(C$_2$H$_5$)$_4$N]$_{0.5}$[Ni(dmit)$_2$] junctions depends on the condition of electron passage through the point contact much more strongly than in the case of junctions between traditional conductors. As a matter of fact, the organic conductor [(C$_2$H$_5$)$_4$N]$_{0.5}$[Ni(dmit)$_2$] as well as (BEDT–TTF)$_2$I$_3$ is close in electronic parameters to semimetals.[6,11] A typical feature of such materials is the existence of point-contact spectra

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with opposite singularities, namely, along with ordinary ("direct") dependences, inverse spectra, i.e., the second derivatives of IVC of contacts with the opposite sign, can be observed in some cases.[4,12] Inverse spectra are typical in the case of small inelastic mean free paths for electrons, as a result of which electron states can be localized in the region of constriction.[13] The EPI disturbs the localization of electrons and leads to an increase in the conductivity of the contact (accordingly, a decrease in its resistance), which is registered as a minimum on the second derivatives of IVC (in contrast to the peak in the case when the contact resistance increases). The accumulation of phonons in the constriction region upon an increase in voltage can also lead to a decrease in the mean free path in the contact region. In this case, the mode of the passage of electrons through the contact changes from the ballistic to diffusion mode for which weak localization effects play a significant role. This must naturally affect the behavior of singularities in the point-contact spectrum. As a result, point-contact spectra of an intermediate type appear (with inverse singularities at high voltages). Curve *3* in Fig. 1 can serve as an example of a characteristic. It contains a number of minima which correspond to peaks at energies 56–58, 70, and 84 meV on curves *1* and *2* and are their mirror image relative to the abscissa axis. The small variation of the position of singularities on the curves can easily be explained. Curves of the type *3* are characterized by the background function which obviously differs from the background function in the case of a "direct" spectrum. The summation of the spectral function and the background function in the (opposite) cases under consideration will probably lead to different displacements of peaks on the EPI spectra, which can lead to a certain mismatching in the position of EPI peaks on different types of spectrum.

It was noted above that the experimental setup for Cu–(BEDT–TTF)$_2$I$_3$ junctions was similar to that used for the conductor [(C$_2$H$_5$)$_4$N]$_{0.5}$[Ni(dmit)$_2$]. We obtained the second derivatives of IVC corresponding to the orientation of the contact axis along high-conductivity planes of organic molecules. The behavior of such spectra was analyzed in detail in Ref. 4; hence we shall confine ourselves here to an analysis of point-contact EPI functions reconstructed from the measured second derivatives of IVC of the junctions. We selected for calculations five most intense (according to preliminary estimates) point-contact spectra of heterojunctions of organic conductors under investigation. Typical dependences or normalized point-contact EPI functions for each material are shown in Fig. 2. The values of mean $\langle\omega\rangle$ and root-mean-square $\langle\omega^2\rangle^{1/2}$ frequencies of vibrations are 13.54, 17.803 and 15.86, 15.414 for the first and second curve respectively. The plots of the functions g_{pc} make it possible to estimate the contribution of the EVI to the point-contact spectrum. It can be seen from the figure that the intensity of high-frequency peaks corresponding to the interaction of electrons with IMV on curve *1* is much higher than the intensity of similar singularities on curve *2*. This speaks in favor of a considerably larger contribution of the EVI to the point-contact spectrum for (BEDT–TTF)$_2$I$_3$ than in the case of [(C$_2$H$_5$)$_4$N]$_{0.5}$[Ni(dmit)$_2$].
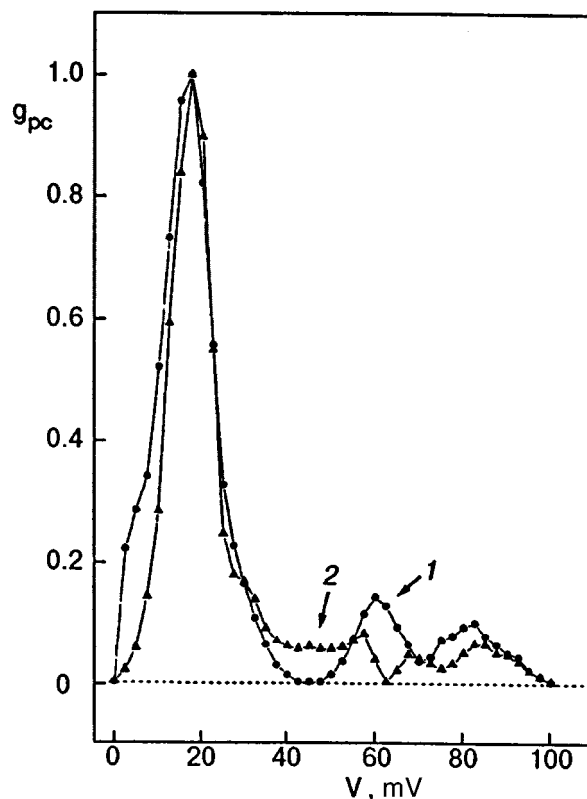
Our results also correlate with the results of optical

FIG. 2. Point-contact functions of electron–phonon interaction for heterojunctions Cu–(BEDT–TTF)$_2$I$_3$ (dark circles, curve *1*) and Cu–[(C$_2$H$_5$)$_4$N]$_{0.5}$[Ni(dmit)$_2$] (dark triangles, curve *2*).

investigations[14] in which it was noted that the intensity of the peak at 1300 cm^{-1} in optical reflection spectra for M(dmit)$_2$ salts is much lower than the intensity of corresponding singularities in the salts (BEDT–TTF) with a charge transfer. This might indicate a lower EVI level in such materials. If we take into account the assumption that IMV make a certain contribution to the formation of the superconducting phase of such materials, it is not surprising that (BEDT–TTF) salts are superconducting, while most of M(dmit)$_2$ compounds are normal metals, and only some of these go over to the superconducting state under pressure.[6] Thus, a correlation is observed between the EVI intensity and the superconducting transition temperature of the organic compounds under investigation.

Taking into account what has been said above, it is logical to assume, in view of the correlation between the intensity of the point-contact spectra and the value of T_c, that the EVI level can serve as a criterion for the synthesis of new organic conductors. This is especially important for families of organic conductors for which superconducting properties are expected, but the values of T_c for whose known representatives are difficult to measure. Consequently, by measuring the EPI spectra for materials with a close composition and observing their variation in a series of analogous materials, we can predict the prospects of the synthesis of new organic conductors belonging to this series. Since the search for new superconductors among organic materials is often carried out for analogs of a certain specific family, and the synthesis of each new compounds takes quite a long time,

the proposed criterion can help to reduce considerably the range of the search and hence to save the required time of investigations.

*E-mail: kamarchuk@ilt.kharkov.ua

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EPR studies of N, H, and D atoms trapped in the matrix of solid molecular nitrogen

Yu. A. Dmitriev and R. A. Zhitnikov

A. Ioffe Physicotechnical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia*

The behavior of nitrogen, hydrogen, and deuterium atoms trapped from the gaseous phase and matrix-isolated in solid molecular hydrogen are studied by the EPR method. It is established that all these atoms are localized in the substitutional position of the matrix crystal lattice. The linewidths in the EPR spectrum of nitrogen are found to be one fourth of the linewidths recorded by most authors. It is shown that a version of theoretical calculation gives a linewidth matching with the experimental value. It is proposed that two different types of matrix surroundings are possible for a nitrogen atom trapped in the substitutional position, one of which corresponding to the undistorted crystal lattice of N_2. The EPR line broadening under the action of zero-point atomic vibrations is observed for hydrogen and deuterium atoms. The magnitude and temperature dependence of the spin-lattice relaxation time for N, H, and D atoms in the solid N_2 matrix are obtained experimentally. © *1998 American Institute of Physics.*
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INTRODUCTION

Nitrogen atoms in the matrix of solid molecular N_2 were one of the first objects of matrix isolation studied by the EPR method.[1] This system proved to be most promising for obtaining high concentrations of atomic matter.[2] Atomic nitrogen and its compounds in matrices of solidified gases are also objects of persistent interest of researchers working in the fields of astrophysics and chemical physics. A still larger number of publications are devoted to matrix-isolated hydrogen atoms in view of the following three circumstances: (1) simplicity of the electron shell of the atoms, and hence the possibility of a more exact calculation of the variation of EPR spectral parameters due to interaction with the matrix surroundings, which makes it possible to verify theoretical approaches; (2) the small mass of atoms ensuring manifestations of essentially quantum effects such as quantum diffusion, subbarrier chemical reactions, zero-point vibrations, and ortho–para conversion in the matrix; and (3) the abundance of hydrogen which is the most wide-spread element in the Universe and hence is an exceptionally interesting object of investigation for scientists studying chemical reaction in the interplanetary space.

Using the experimental setup described in our earlier publication,[3] we obtained nitrogen atoms trapped from the gaseous phase in solid N_2 by deposition of products of a gas discharge in nitrogen on a cold surface ($T = 1.3$–4.2 K). The results proved to be quite unexpected: the EPR linewidth for nitrogen atoms in the N_2 matrix was equal to $\Delta H = 0.49(3)$ G irrespective of the temperature, which amounts to one fourth of the linewidths reported by most of other authors. For example, Cole *et al.*[1] obtained nitrogen atoms in the N_2 matrix by deposition of the products of a high-frequency gas discharge on a surface at $T = 4.2$ K as in our experiments. The linewidth in the obtained EPR spectra was ~ 2.5 G. The hyperfine structure (HFS) constant A, its matrix shift $\Delta A = A - A_f$, the g-factor, and the linewidths

are given in Table I. Cole *et al.*[1] did not assess the atomic concentration, and hence their results cannot be used to find out whether this broadening is associated with the dipole–dipole interaction of electron spins of trapped atoms or is caused by other factors. However, Jen *et al.*[4] recorded the same linewidth (2.3 G) for N atoms in N_2, obtained by deposition from the gaseous phase. These authors noted that in view of the small concentration of atoms, the line broadening cannot be due to the dipole–dipole interaction between electron spins of nitrogen atoms. As regards other spectral parameters, the HFS constants reported in these two publications coincide to within experimental error, while the g-factors differ significantly. A quite different method of obtaining stabilized nitrogen atoms in the N_2 matrix was used by Wall *et al.*[5] A sample of solid molecular nitrogen was exposed to the γ-radiation from a Co-60 source. The spectral parameters, including the linewidth (~ 2 G) coincide with those obtained in experiments with deposition (see Table I). It is significant that solid nitrogen itself was prepared in Ref. 5 by freezing the liquid phase, which should result, according to the authors, in the growth of a denser and more homogeneous sample than in experiments on deposition from the gaseous phase. Special attention was paid to the determination of concentration of atoms in the matrix. For N in N_2, samples with different concentrations of atoms varying from 0.001 to 0.07% were obtained. It was noted that the linewidth remained unchanged. This means that the measured value of 2 G is determined not by the dipole–dipole interaction of electron spins of trapped atoms. In Ref. 2, the sample was prepared by condensation in superfluid helium of the He–N_2 gaseous mixture passed through a discharge. In these experiments, a superconducting magnet creating a strongly nonuniform field was used. For this reason, apparatus effects led to an additional broadening of the EPR line for N atoms trapped in N_2 microscopic crystals. Hiraoka *et al.*[6] obtained trapped nitrogen atoms in EPR experiments by exposing a

TABLE I. Spectral parameters for nitrogen atoms in molecular nitrogen matrix obtained by different methods.

A, MHz	$A - A_f$, MHz	g	ΔH, G	Method of obtaining	Reference
11.5–13.7	1.1–3.3	1.0005(2)	$\cong 2.5$	deposition	1
12.08(12)	1.63(12)	2.00200(8)	2.3	deposition	4
11.5(5)	1.1(5)	2.0	$\cong 2$	radiation	5
11.83(16)	1.38(16)	2.00155(5)	0.4–0.6	chemical	7
11.85(6)	1.40(6)	2.00201(12)	0.49(3)	deposition	our results

Remark. Numbers in parentheses indicate errors in last digits.

polycrystalline N_2 sample to x-rays at a temperature of 4.2 K. The sample contained a mixture of molecular N_2 and H_2 (5.0 mol. % of H_2 impurity in N_2). The parameters of EPR spectra for N and H atoms in the solid nitrogen matrix are not presented, but is can be seen from the reported spectra that the linewidth for N in N_2 is approximately equal to 2.5 G. The only publication in which the linewidth for N in N_2 are close to our results is the paper by Lindsey.[7] It follows from the data reported in this article that the linewidths are equal to 0.4–0.6 G in the temperature range 7.7–28.5 K. Lindsey[7] used a quite different method for obtaining trapped atoms. Atomic nitrogen was formed as a result of co-condensation of Cs atoms and molecular oxygen with an excess of N_2.

Thus, the accumulated data on EPR linewidths for N in N_2 are contradictory. According to the results obtained by most authors, the EPR linewidth in the absence of the con-centration dipole–dipole broadening varies from 2 to 2.5 G irrespective of the method of growing the matrix (from the gaseous or liquid phase) and the method of creating atomic centers of N in it (irradiation or deposition from a gas dis-charge). In Ref. 7 (chemical method of creation of atomic centers) and in our experiments (deposition method), the linewidths were in the range 0.4–0.6 G. Such a strong dis-crepancy deserves attention and calls for an explanation.

In order to determine the EPR linewidth of atoms trapped in the N_2 matrix more precisely, it would be inter-esting to obtain the spectra of H atoms in the same matrix and under the same condition and to compare them with the results obtained for N atoms.

1. NITROGEN ATOMS IN N_2 MATRIX

The region of localization of a nitrogen atom in the ma-trix can be determined by comparing the experimental and theoretical values of the matrix shift of the HFS constant. Our observation of narrow EPR lines has made it possible to measure the HFS constant and the relative matrix shift of the HFS constant for trapped atoms to a high degree of accuracy: $A = 11.85(6)$ MHz, $\Delta A/A_f = 13.4(6)\%$, where $A_f = 10.45$ MHz is the HFS constant for a free nitrogen atom. The g-factor was found to be equal to 2.00201(12). Adrian[8] derived the following formula for the matrix shift of the HFS constant for a nitrogen atom:

$$\Delta A_N = -m \frac{2e^2}{R^6} \left(\frac{1}{E_N} + \frac{1}{E_N + E_M} \right)$$

$$\times \frac{E_M \alpha_M}{E_N + E_M} \langle s|z|p_z \rangle^2 A_{N^{14}2s}, \qquad (1)$$

where $A_{N^{14}2s}$ is the HFS constant for a $2s$ electron in a free ^{14}N atom, $\langle s|z|p_z \rangle^2 = 0.607 a_0^2$ is the square of the matrix element of the operator z calculated for a transition between the $2s$ and $2p$ states of the nitrogen atom,[9] $E_N = -0.402(e^2/a_0)$ is the energy of excitation of a $2s$ elec-tron to the $2p$ energy level, E_M the ionization energy for a matrix atom with the negative sign, α_M the polarizability of a matrix atom, R the distance to the nearest matrix particles, m the number of such particles, and a_0 the Bohr radius.

It follows from formula (1) that the matrix shift of the HFS constant for a trapped nitrogen atom is always positive, i.e., the effect of the matrix leads to an increase in the HFS constant. This effect is the stronger, the higher the polariz-ability of the matrix atoms (molecules) and the smaller the distance to the nearest neighbors. Thus, substituting the ex-perimental value of $\Delta A = 1.40$ MHz into this formula, we can determine the distance to the nearest molecules of the matrix, and hence determine the region of localization of the trapped atom. For the nitrogen matrix, we have $\alpha_{N_2} = 11.74 a_0^3$ and $E_{N_2} = -0.57(e^2/a_0)$. This gives $R = 7.48 a_0$. An undistorted crystal lattice of solid nitrogen at helium temperatures is a face-centered cubic (fcc) lattice with a lattice constant of $10.7 a_0$[10] and the distance to the centers of mass of the nearest neighbors $R_{0sub} = 7.54 a_0$ (sub-stitutional position of the atom). Accordingly, $R_{0oct} = 5.33 a_0$ for an octahedral position of the atom. Thus, the observed EPR spectra are due to nitrogen atoms trapped in the substi-tutional positions in the crystal lattice of molecular N_2. The data contained in Table I lead to the conclusion that in ex-periments of other authors the atoms are also in substitu-tional positions since the matrix shift of the HFS constant for an atom in an octahedral interstitial position would be ap-proximately eight times larger, i.e., ~ 11 MHz. This means that the strong broadening of the EPR lines of N atoms in N_2 in these experiments cannot be explained by the localization of atoms at other positions in the crystal lattice. In all prob-ability, the broadening of EPR lines for N atoms is primarily due to hyperfine interaction of spins of unpaired electrons of the atoms in the $^4S_{3/2}$ state with the nuclear magnetic mo-ments of matrix molecules. Let us assess this broadening.

Natural nitrogen mainly contains the isotope ^{14}N(99.63%) with a nuclear spin equal to unity. The concen-tration of the isotope ^{15}N (0.37%, with a nuclear spin of 1/2) introduces a negligibly small contribution to line broadening.

Molecular nitrogen consisting of centrally symmetric molecules has two modifications: the orthomodification (with the total nuclear spin of a molecule $I=0,2$ and with an even angular momentum $J=0,2,4,...$) and the paramodification ($I=1$, $J=1,3,5,...$). The rotational energy of a molecule is $E_J = B_e J(J+1)$, where B_e is a constant equal to 2.875 K for a $^{14}N_2$ molecule. Consequently, molecules in gaseous nitrogen at room temperature are distributed over the values of I in accordance with a statistical weight: $I=0$ for 1/9 of all molecules, $I=1$ for 1/3 of molecules and $I=2$ for 5/9 of molecules. In the formed nitrogen crystal, this distribution is preserved. The symmetry group of the crystal lattice at helium temperatures is $Pa3$. The unit cell contains four molecules whose centers of gravity lie at the sites of the fcc lattice, and the axes are directed along the spatial diagonals of the cube (the so-called orientationally ordered phase)[10] with librational vibrations of molecules.

Let us estimate the anisotropic, i.e., dipole–dipole component of EPR line broadening for nitrogen atoms due to hyperfine interaction with atomic nuclei surrounding N_2 molecules. These lines are close in shape to Gaussian curves, which is confirmed by the assumption concerning their broadening due to the interaction with nuclear magnetic moments of the matrix.[11] Thus, the theoretical value of the linewidth can be obtained by calculating $(\Delta H_{theor})_{dip} = \sqrt{4(M_2)_{dip}}$, where $(M_2)_{dip}$ is the second moment of the line for the dipole–dipole interaction. The second moment for a powdered sample with cubic symmetry in the case of broadening due to interaction with the nuclear magnetic moments located at the sites of a regular lattice is given by[12]

$$(M_2)_{dip} = \frac{4}{15} g_n \beta_n I(I+1) \sum_j \left(\frac{1}{r_j}\right)^6. \quad (2)$$

Here β_n is the nuclear magneton, g_n the g-factor of the nucleus, I its spin, and r_j the separation between the trapped atom and the jth atomic nucleus of the lattice molecule. The summation is carried out over all nuclei. We apply this formula in the case when lattice sites contain two-nucleus symmetric molecules 1/3 of which has the total nuclear spin equal to unity, and 5/9 of these molecules have a spin equal to two. The right-hand side of formula (2) splits into two terms:

$$M_2 = \frac{4}{15} \cdot \frac{1}{3} g_n \beta_n \cdot 1(1+1) \sum_j \left(\frac{1}{r_j}\right)^6 + \frac{4}{15} \cdot \frac{5}{9} g_n \beta_n$$
$$\times 2(2+1) \sum_j \left(\frac{1}{r_j}\right)^6.$$

In both terms, summation is carried out over all molecules. Let us now consider the quantity r_j. The separation between the nuclei in a nitrogen molecule is $\delta = 2.1a_0$. The nuclei of a molecule are indistinguishable, which means that each nucleus occupies one of the two positions with a probability of 1/2. After averaging over nuclear coordinate wave functions of the Hamiltonian of the dipole–dipole interaction between the electron spin and nuclear spins [in the derivation of formula (2)], we obtain the following expression for the quantity $(1/r_j)^6$:

$$\left(\frac{1}{r_j}\right)^6 = \left(\frac{1}{r_{0j}}\right)^6 \left[\left(\frac{1}{1+x^2-2x\cos\gamma}\right)^3 + \left(\frac{1}{1+x^2+2x\cos\gamma}\right)^3\right],$$

where r_{0j} is the separation between the trapped atom and the center of gravity of the matrix molecule, $x=(\delta/2)/r_{0j}$, and γ is the angle formed by the line connecting the equilibrium position of the trapped atom and the center of gravity of a neighboring molecule with the axis of the molecule. The quantity in the brackets assumes the maximum value when these directions coincide. The ratio of this value to the value equal to two (which corresponds to $x=0$, i.e., to the disregard of the size of a molecule) is equal to 1.41 for molecules from the first coordination sphere, 1.19 for the second sphere, 1.13 for the third, and so on. Let is calculate the second moment and the linewidth taking into account the directions of molecular axes. Summation is carried out within the first four coordination spheres, while, for molecules lying at larger distances, summation is replaced by integration (the concentration of molecules in solid nitrogen is $2.77 \times 10^{22} cm^{-3}$). As a result, we obtain the following expression for the linewidth due to dipole–dipole interaction:

$$(\Delta H_{theor})_{dip} = 0.25 G. \quad (3)$$

Let us now estimate the contribution of the isotropic hyperfine interaction to the linewidth. For this purpose, we use the formula obtained initially for calculating the contact interaction of F-centers with the nuclei of adjacent atoms in the KCl crystal lattice[13] and later applied successfully for a number of new systems, e.g., for calculating the width of the EPR line for H in H_2[14,15]:

$$(M_2)_{is} = \frac{64}{27} \pi^2 \sum_j \mu_j^2 \frac{I_j+1}{I_j} |\Psi(j)|^2 \cdot 34.13, \quad (4)$$

where $(M_2)_{is}$ is the second moment of the isotropic interaction curve in gauss, μ_j the magnetic moment of the jth nucleus of a neighboring nitrogen molecule (in nuclear magnetons), I_j the spin of the jth nucleus, $|\Psi(j)|^2$ the density of an unpaired electron at the jth nucleus in atomic units, and Ψ the electron wave function.

In order to calculate $|\Psi(j)|^2$, we must orthogonalize the electron wave function of the nitrogen atom to the electron wave function of the matrix molecule. This leads to the emergence of electron wave functions of the molecule with the same spin component as for unpaired electrons of the atom in the wave function of the trapped impurity atoms. Since the density of $2p$-electrons of the N_2 molecule at its nuclei is zero, while, in calculating $(M_2)_{is}$ we must take into account only the impurity of intrinsic $2s$-electrons of the molecule in the wave function of the atom. The wave functions of $2s$-electrons in the molecule and in the atom are close in this case. This impurity of a $2s$-electron of the molecule is proportional to the overlap integral $\langle \Psi_{2s}(N_2)|\Psi_{2p}(N)\rangle$. It is well known[15] that electron orbitals can be orthogonalized by the method of successive approximations:

$$|\Psi_{n+1}(i)\rangle = K_n(i)\left[|\Psi_n(i)\rangle - \sum_{j\neq i} c_{ij} S_n^{ij} |\Psi_n(j)\rangle\right], \quad (5)$$

where $K_n(i)$ is the normalization constant, c_{ij} are indeterminate coefficients, and $S_n^{ij} = \langle \Psi_n(i) | \Psi_n(j) \rangle$. The coefficients c_{ij} must satisfy the condition $c_{ij} + c_{ji} = 1$. Such a method of orthogonalization is a Gram–Schmidt transformation in the case when one of the coefficients c_{ij} or c_{ji} is assumed to be zero. For $c_{ij} = c_{ji} = 1/2$, we are dealing with the Löwdin transformation. In calculations of a contact hyperfine interaction, a certain orthogonalization method (Schmidt or Löwdin transformation) is often used without mentioning the reason behind the specific choice. However, the values of energy of contact interaction calculated on the basis of these two methods can differ significantly. This circumstance was emphasized in Ref. 15, in which the linewidths for hydrogen atoms trapped in para-H_2 were calculated. Li and Voth[15] stressed that in actual practice the coefficients c_{ij} defined by the condition of minimum of the electron energy for the system under investigation cannot be chosen arbitrarily. The calculations made by these authors proved[15] that these coefficients for H in H_2 are close to 1/2, and the theoretical widths are close to experimental values. On the contrary, Schmidt transformation led to linewidths differing considerably from experimental results. In our estimates of the isotropic component of the linewidth $(\Delta H)_{is} = \sqrt{4(M_2)_{is}}$ by formula (4), we used the Löwdin transformation procedure and the Ruthan–Hartree–Fock electron wave functions of the nitrogen atom,[16] which led to the following value:

$$(\Delta H_{\text{theor}})_{is} = 0.56 \text{ G}. \tag{6}$$

Since line broadening can be governed by two different mechanisms (dipole–dipole and contact hyperfine interactions), the shape of the line is a convolution of two Gaussian functions, and the linewidth can be defined as $\Delta H_{\text{theor}} = \sqrt{(\Delta H_{\text{theor}})_{\text{dip}}^2 + (\Delta H_{\text{theor}})_{\text{is}}^2}$. Substituting the quantities (3) and (6) into this formula, we obtain

$$\Delta H_{\text{theor}} = 0.61 \text{ G}, \tag{7}$$

which is comparable to the width of narrow lines recorded in our experiments $[\Delta H_{\text{exp}} = 0.49(3) \text{ G}]$ and by Lindsey[7] (0.4–0.6 G) and is much smaller than the results obtained by other authors (2–2.5 G).

Thus, the data on the linewidths for N in N_2 can be divided into two ranges: 2–2.5 G and 0.4–0.6 G. It is reasonable to assume that this is due to the existence of two different equilibrium surroundings for a nitrogen impurity atom trapped in the substitutional position in the crystal lattice of solid N_2. According to the above theoretical estimates, one of such equilibrium surroundings is apparently the structure of undistorted crystal lattice of solid nitrogen. Another possible version of the matrix surroundings of an impurity atom is also a substitutional position, but neighboring nitrogen molecules are, for example, turned so that their axes are directed towards the center of a matrix cell with the trapped atom that can be regarded as a vacancy in view of its small size. In this case, the increase in the energy of intermolecular interaction between particles of the first and next coordination spheres is compensated by a slight (by $0.3–0.35a_0$) displacement of the centers of gravity of nearest neighbors towards the impurity atom. In this case, calculations give for the EPR linewidth of N in N_2 $\Delta H_{\text{theor}} = 2.0–2.5 \text{ G}$. As regards the matrix shift of the HFS

constant, it must increase, in accordance with formula (1), from 1.38–1.40 MHz (see Table I) for a undistorted lattice to approximately 1.8 MHz. It can also be seen from the table that the most accurate result for ΔA of broad lines indeed leads to a value larger than that measured by us or in Ref. 7. The reasons behind and conditions for the realization of a certain equilibrium surroundings cannot be indicated at this stage. The second type of surroundings is apparently observed when stresses facilitating the rearrangement of the local surroundings of an impurity atom are created in the matrix.

2. HYDROGEN AND DEUTERIUM ATOMS IN N_2 MATRIX

Hydrogen and deuterium atoms form another object for which, in analogy with N atoms in N_2, we can expect both narrow and broad EPR lines in the matrix of solid molecular nitrogen. In Ref. 17, the EPR spectrum of H atoms in N_2 was obtained for the first time. The parameters of this spectrum at the substrate temperature 1.6 K were as follows: $A = 1415.1(3)$ MHz, $\Delta A/A_f = -0.38(2)\%$, $g = 2.00207(12)$. It was found that the linewidth for a sample obtained by deposition on the surface at a temperature $T_d = 1.6$ K is 4 G. In the case when the substrate temperature was 4.2 K, the linewidth was 1.2 G. In both cases, the width of the recorded lines did not change upon a further decrease or increase in the sample temperature. A considerable broadening observed at $T_d = 1.6$ K can be explained by the growth of the sample with a large number of defects at this temperature. However, a comparison of our present results for N in N_2 $[\Delta H_{\text{exp}} = 0.49(3) \text{ G}]$ with our earlier results[17] shows that even the lines with $\Delta H = 1.2$ G are much broader than should be expected for hydrogen atoms in the substitutional position in the undistorted crystal lattice of solid molecular nitrogen. Indeed, the theoretical estimates of $(\Delta H_{\text{theor}})_{\text{dip}}$ and $(\Delta H_{\text{theor}})_{\text{is}}$ obtained according to the above procedure for a nitrogen atom lead to the following value for an H atom:

$$\Delta H_{\text{theor}} = 0.57 \text{ G}. \tag{8}$$

In the present research, we obtained the EPR spectra for hydrogen and deuterium atoms trapped in the matrix of solid N_2 from a gas discharge in the $N_2:D_2:H_2$ mixture. The conditions of sample growth were close to those under which we recorded the EPR spectrum for nitrogen atoms (see Sec. 1). The parameters of the spectra for H and D atoms at the substrate temperature 1.5 K were as follows. For hydrogen atoms: $A_H = 1415.24(26)$ MHz, $g_H = 2.00209(12)$, $(\Delta H)_H = 0.83(5)$ G $(\Delta A/A_f)_H = -0.364(19)\%$. For deuterium atoms: $A_D = 217.299(53)$ MHz $g_D = 2.00207(12)$, $(\Delta H)_D = 0.81(5)$G, $(\Delta A/A_f)_D = -0.439(25)\%$. Thus, the linewidth was found to be close to the theoretical value and smaller than in Ref. 17. A probable explanation of the fact that much broader lines (4 G) were obtained in Ref. 17 at 1.6 K lies in a higher concentration of molecular hydrogen in the N_2 matrix and a higher rate of deposition of the sample.

An analysis of the results [relations (7) and (8)] leads to the conclusion that the calculated value of the linewidth for nitrogen is slightly higher than the experimental result, while for hydrogen the theoretical value is smaller than experimental. It should be noted that, in contrast to atomic nitrogen, H

atoms, which are a light impurity in the crystal lattice, perform intense vibrations about their equilibrium positions. If the inequalities

$$\hbar\omega \gg kT; \quad \hbar\omega \gg hf, \tag{9}$$

hold in this case, i.e., the resonant frequency f of the EPR transition is much smaller that the frequency ω of zero-point vibrations of a trapped atom, and the temperature T of the sample is small enough to assume that only the zero-point vibrational level is populated, the Hamiltonian of interaction of the electron spin of the atom with the nuclear magnetic moments of a matrix molecule should be averaged over the positions of the atom in a matrix cell described by its coordinate wave function. Since the energies of the dipole- and contact hyperfine interactions increase with decreasing distance between H and a neighboring molecule of the matrix, the EPR linewidth for vibrating hydrogen atoms must be larger than the value for a stationary atom. Indeed, it was established in Ref. 18 that, as a result of zero-point vibrations, the EPR linewidth for hydrogen atoms trapped in a substitutional position in the xenon matrix increases by 80%. In this case, for the sample temperature $T = 4.2$ K and EPR spectrometer of the 3-cm range, we have $kT = 0.36$ meV, $hf = 0.038$ meV, and $\hbar\omega = 10$ meV, i.e., inequalities (9) hold. Obviously, the frequency ω of zero-point vibrations for a more compact denser matrix cell of solid N_2 is still higher than for xenon, and hence relations (9) hold.

It was noted above that our method of calculation of the linewidth for a stationary atom gives a slightly exaggerated value of ΔH_{theor} (this follows from a comparison of the theoretical, 0.61 G, and experimental, 0.49 G, linewidths for atomic nitrogen). This means that the linewidth for a stationary hydrogen atom estimated in the same way would be approximately equal to 0.46 G. The effect of zero-point vibrations on the linewidth calculated by formulas (2) and (4) can be found by the averaging of the square of the overlap integral $\langle \Psi_{2s}(N_2)|\Psi_{1s}(H)\rangle^2$ of a trapped atom, determining the energy of contact interaction with the nuclei of neighboring nitrogen molecules, and of the function $1/r^3$, determining the coordinate dependence of the energy of dipole–dipole hyperfine interaction, over the coordinate wave function. While obtaining numerical estimates, we used for a hydrogen atom the model of harmonic oscillator in a spherically symmetric potential well. In this case, its coordinate wave function can be written in the form

$$\Phi(r) = \left(\frac{\lambda}{\pi}\right)^{3/4} \exp\left(-\frac{\lambda r^2}{2}\right), \tag{10}$$

where $\lambda = \ln 2/(r_{0.5})^2$ and $r_{0.5}$ is the amplitude of zero-point vibrations of the atoms, determined by the distance between the equilibrium position and a position in which the probability of finding the atom is equal to half the probability of its being in the equilibrium position. Assuming that $\overline{\Delta H_{theor}} = \Delta H_{exp}$, we obtain the following estimate for the amplitude of zero-point vibrations of a hydrogen atom: $r_{0.5} \approx 0.8a_0$. This is a reasonable value matching with that given by Baldini[19] for hydrogen atoms in a substitutional position in the crystal lattice of solid argon: $r_{0.5} \approx 1.0a_0$.

It should be noted that the amplitude of zero-point vibrations of hydrogen atoms is smaller than for deuterium atoms

in view of the smaller mass of the former atoms, and hence the linewidth for H must be slightly larger than for D atoms. According to calculations in which we assume that $\overline{\Delta H_{theor}} = \Delta H_{exp} = 0.83$ G for hydrogen atoms and take into account the fact that $r_{0.5}$ is proportional to $m^{-1/4}$, we can expect that $\overline{\Delta H_{theor}} = 0.76$ G for deuterium. In other words, the difference between this value and that for hydrogen is slightly smaller than 10%, and the isotopic effect in linewidths is therefore within the experimental error.

For a xenon matrix, it was found experimentally that the difference in the linewidths for hydrogen and deuterium atoms in a substitutional position in the cryocrystal is of the order of 10%.[18]

In the analysis of linewidth, we assume that H and D atoms are localized in the substitutional position in the crystal lattice. Let us prove that this is indeed true. As in the case of nitrogen atoms considered in Sec. 1, we shall proceed from the measured value of the matrix shift of the HFS constant. The theoretical values of the quantities $(\Delta A/A_f)_H$ were calculated for some matrices by Adrian.[20] Among these matrices, solid argon is the closest to N_2 as regards its parameters (lattice constant and polarizability of matrix particles). Adrian[20] obtained the following values for the relative matrix shift of the HFS constant of hydrogen atoms in argon: -0.72% for a substitutional position of the atom and 0.80% for an octahedral interstitial position. A still larger positive shift must be observed for a tetrahedral position. The experimental value was found to be $-0.469(8)\%$.[21] The extraordinarily small value of the linewidth [0.055(15) G] indicates strong regularity of the crystal surroundings. A comparison of experimental and theoretical values of the relative matrix shift of the HFS constant leads to the conclusion that hydrogen atoms are stabilized in the substitutional positions in the solid Ar crystal lattice. In view of the closeness of the parameters for solid Ar and N_2, hydrogen atoms must have a positive shift of the HFS constant in octahedral position in N_2 and a negative shift in substitutional positions. If the EPR spectra recorded by us are due to H atoms in substitutional positions in the N_2 matrix, the ratio of the matrix shifts in the two matrices (N_2 and Ar) under investigation calculated in accordance with the theory[20], i.e., $w_{exp} = (-0.364/-0.469) = 0.78$, must correlate with the quantity $w = (\alpha^{N_2}/\alpha^{Ar}) \times (R_0^{Ar}/R_0^{N_2})^6$, in which the first parentheses contain the ratio of polarizabilities of matrix particles and the second the ratio of the distances to nearest neighbors for the substitutional positions in these matrices, raised to the sixth power. This means that the Van der Waals interaction of an H atom with matrix particles makes a decisive contribution to the matrix shift of hydrogen atoms in substitutional positions. Substituting the values $\alpha^{Ar} = 11.08a_0^3$, $\alpha^{N_2} = 11.74a_0^3$, $R_0^{Ar} = 7.10a_0$, $R_0^{N_2} = 7.54a_0$ into the above expression for w, we obtain $w_{theor} = 0.74$, which is very close to the experimental value w_{exp}. We took the value $7.54a_0$ as the typical distance to nearest neighbors in the nitrogen matrix, neglecting a small eccentricity of the electron shell of a nitrogen molecule.[10] Thus, the EPR spectra recorded by us are due to hydrogen and deuterium atoms trapped in the substitutional position by the crystal lattice of solid molecular nitrogen.
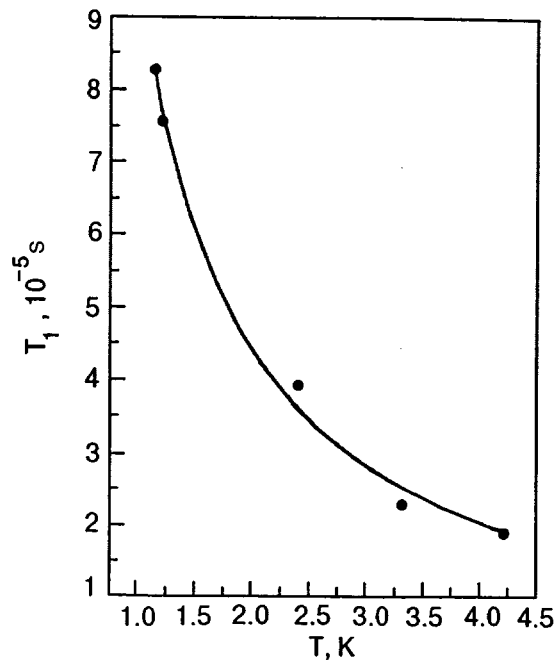
FIG. 1. Temperature dependence of the spin–lattice relaxation time for nitrogen atoms in the N_2 matrix.

3. SPIN–LATTICE RELAXATION

We measured the spin–lattice relaxation time T_1 for N, H, and D atoms in the matrix of solid molecular nitrogen by the method of saturation. Figure 1 shows the change in the time T_1 with the sample temperature. The experimental dependence (dots) is successfully approximated by the power function $T_1 = 0.0001T^{-1.12}$s (solid curve). The closeness of the exponent to -1 suggests the one-phonon mechanism of spin–lattice relaxation. A similar power dependence close to $T_1 \propto T^{-1}$ was obtained for H and D atoms in solid nitrogen. The relaxation times for these atoms coincide ($T_1^{H} = T_1^{D}$) and are approximately an order of magnitude larger than the spin-lattice relaxation time for nitrogen atoms: $T_1^{H} \approx 10T_1^{N}$. Such a strong difference between the values of T_1 for hydrogen and nitrogen atoms can be explained by the dependence of this quantity on the spin of a paramagnetic particle.[22] The value of T_1 is inversely proportional to the square of the energy of magnetic interaction of a paramagnetic particle with the surroundings, i.e., to the square of the particle spin. Consequently, the following relation must be satisfied for the ratio of spin–lattice relaxation times for hydrogen and nitrogen atoms in the same sample: $T_1^{H}/T_1^{N} = [(3/2)/(1/2)]^2 = 9$, which is in accord with the results of experiments.

CONCLUSION

Thus, we obtained nitrogen, hydrogen, and deuterium atoms trapped in solid molecular nitrogen by deposition from the gaseous phase and studied them by the EPR method. It was found that all these atoms are localized in substitutional positions in the matrix crystal lattice. The linewidths in the recorded EPR spectra were found to be approximately one fourth of the values obtained in most of known experiments. It turned out that there exists a version of theoretical calculations giving a linewidth matching with the experimental

value. In all probability, two different types of equilibrium surroundings are possible for a nitrogen atom trapped in a substitutional position, one of which corresponding to an undistorted N_2 crystal lattice, and the other to a position in which the axes of nearest neighboring molecules are directed towards the trapped atom, and the centers of gravity of molecules are displaced by $0.3 - 0.35a_0$ to the center of the matrix cell.

For hydrogen and deuterium atoms, we considered the EPR line broadening under the action of zero-point vibrations of atoms in the N_2 matrix and obtained experimental results on the magnitude and temperature dependence of the spin–lattice relaxation time for N, H, and D atoms in this matrix.

*E-mail: dmitriev@mares.ioffe.rssi.ru

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The types of acoustic excitations in two-condensate relativistic superfluid systems

S. I. Vilchinsky

Taras Shevchenko University, 252022 Kiev, Ukraine*

P. I. Fomin

N. Bogoliubov Institute of Theoretical Physics, National Academy of Sciences of the Ukraine, 252143 Kiev, Ukraine**

The equations describing the propagation of acoustic waves in relativistic superfluid two-condensate systems are derived and solved. It is shown that the presence of an additional acoustic mode and two types of waves of fourth sound is a peculiarity of the system under investigation. © *1998 American Institute of Physics.* [S1063-777X(98)00201-1]

In this paper, we consider the propagation of acoustic excitations in a relativistic quantum system in a local equilibrium state below the critical point in the case when one normal and two superfluid component (two types of condensates) coexist with their own densities $\rho_n(x), \rho_l(x)$, and $\rho_r(x)$ of a certain generalized charge and with their own velocity field $u^\nu(x), v_l^\nu(x)$, and $v_r^\nu(x)$. Each condensate is characterized by its own gas of excitations with the density $\rho_{nl}(x)$ and $\rho_{nr}(x)$ and its own conserved current j_l^ν and j_r^ν. The velocities of both gases of excitations are assumed to be identical since they are leveled out by viscosity. Nonrelativistic systems of such type were analyzed in Refs. 1–6. The phenomenological relativistic theory of superfluidity for systems with two types of condensates was considered in Ref. 7, while the propagation of acoustic excitations in a nonrelativistic two-condensate system was discussed in Refs. 2, 4 and 6.

We write equations of hydrodynamics describing the system under investigation.[7] This system includes

(a) the continuity equations

$$\partial_\nu j_l^\nu = 0, \quad \partial_\nu j_r^\nu = 0, \tag{1}$$

where

$$j_l^\nu = \rho_{nl} u^\nu + \rho_l v_l^\nu, j_r^\nu = \rho_{nr} u^\nu + \rho_r v_r^\nu,$$

$$\rho_{nl} + \rho_{nr} = \rho_n.$$

It follows from Eqs. (1) that the densities ρ_n, ρ_l, and ρ_r are defined as Lorentz-invariant, and velocity vectors in components have the form ($c = 1$)

$$w^\nu = (1/\sqrt{1 - \mathbf{w}^2}, \quad \mathbf{w}/\sqrt{1 - \mathbf{w}^2}), \quad w^\nu w_\nu = 1,$$

where w^ν stands for u^ν, v_l^ν, and v_r^ν;

(b) continuity equation for entropy

$$\partial_\nu S^\nu = 0, \tag{2}$$

where $S^\nu = S_n u^\nu$;

(c) equations for superfluid motions

$$(\mu_l / \gamma_l) v_l^\nu \partial_\nu v_l^\lambda = \Delta_l^{\lambda\nu} \partial_\nu (\mu_l / \gamma_l),$$

$$(\mu_r / \gamma_r) v_r^\nu \partial_\nu v_r^\lambda = \Delta_r^{\lambda\nu} \partial_\nu (\mu_r / \gamma_r), \tag{3}$$

where

$$\Delta_r^{\lambda\nu} = g^{\lambda\nu} - v_r^\lambda v_r^\nu, \quad v_{r\nu} \Delta_r^{\lambda\nu} = 0, \quad v_{l\nu} \Delta_l^{\lambda\nu} = 0;$$

$$\Delta_l^{\lambda\nu} = g^{\lambda\nu} - v_l^\lambda v_l^\nu, \quad v_{l\nu} \Delta_l^{\lambda\nu} = 0;$$

$g^{\lambda\mu}$ is the metric tensor, μ_l and μ_r are chemical potentials defined by the following thermodynamic identity:

$$dP = S_n dT + \rho_r d(\mu_r \gamma_r^{-1}) + \rho_{nr} d\mu_r + \rho_{nl} d\mu_l$$
$$+ \rho_l d(\mu_l \gamma_l^{-1}), \tag{4}$$

where P is the pressure, T the temperature, and the Lorentz factors γ_l and γ_r are defined as follows:

$$\gamma_l = v_l^\nu u_\nu = 1/\sqrt{1 - (\mathbf{v}_l - \mathbf{u})_E^2},$$

$$\gamma_r = v_r^\nu u_\nu = 1/\sqrt{1 - (\mathbf{v}_r - \mathbf{u})_E^2},$$

where the subscript E denotes the Einstein difference in velocities; and

(d) the equation of energy–momentum conservation

$$\partial_\nu T^{\lambda\nu} = 0, \tag{5}$$

where the energy–momentum tensor has the form

$$T^{\lambda\nu} = (TS_n + \mu_l \rho_{nl} + \mu_r \rho_{nr}) u^\lambda u^\nu + \gamma_l^{-1} \mu_l \rho_l v_l^\lambda v_l^\nu$$
$$+ \gamma_r^{-1} \mu_r \rho_r v_r^\lambda v_r^\nu - P g^{\lambda\nu}.$$

Here we choose the energy–momentum tensor in additive form. In this case, we disregard the mixed term containing the product of superfluid velocities of both condensates of the type

$$w_{rl}(v_l^\nu v_r^\lambda + v_r^\nu v_l^\lambda),$$

describing the effect of reciprocal drag by superfluid motions predicted by Andreev and Bashkin.[2] A comparison of the results obtained in Refs. 4 and 6, in which the propagation of sounds in nonrelativistic two-condensate superfluid systems were considered without taking the drag effect into account, with the results obtained by Andreev and Bashkin[2] who included this effect shows, however, that the inclusion of mixed terms does not change the number and nature of acoustic modes in the system under investigation and only changes insignificantly the velocity of sounds. We can naturally expect that the situation in the relativistic case will be

similar, but for simplicity we shall disregard the contribution of the mixed term to the velocity of sounds since calculations in this case are much more cumbersome.

Let us find the solutions of the system of equations (1)–(5) describing acoustic processes. The sounds will be described in an explicitly covariant form. We shall mark by the subscripts ''0'' and ''1'' the equilibrium values of quantities (assuming that they are independent of coordinates and time) and small deviations from equilibrium values, respectively. In the equilibrium state, as well as in an analysis of a similar problem in the nonrelativistic theory of superfluidity, we can assume that the superfluid and normal components move with the same velocity: $u_0^\nu = v_{l0}^\nu, u_0^\nu = v_{r0}^\nu$.

It should be noted that, since

$$u_\nu u^\nu = 1; \quad v_{l\nu}v_l^\nu = 1, \quad v_{r\nu}v_r^\nu = 1, \quad u_{0\nu}u_0^\nu = 1.$$

The quantities u_1^ν, v_{r1}^ν, and v_{l1}^ν in the linear approximation are orthogonal to u_0^ν:

$$u_{0\nu}u_1^\nu = v_{r1}^\nu u_{0\nu} = v_{l1}^\nu u_{0\nu} = 0. \tag{6}$$

Using the orthogonality relations (6), we obtain the following relations accurate to within second-order terms: $\gamma_l \cong 1, \gamma_r \cong 1$.

After linearization of Eqs. (1)–(5) and cancelling out the derivatives of u_1^ν, v_{r1}^ν, and v_{l1}^ν, we obtain a system of three equations describing the propagation of sounds in the two-condensate relativistic system under investigation:

$$\partial_u^2 \varepsilon_1 + \theta P_1 = 0;$$

$$\partial_u^2 \sigma_1 + \beta \theta P_1 + \alpha_l \theta \mu_{l1} + \alpha_{r1} \theta \mu_{r1} = 0;$$

$$\delta \partial_u^2 \rho_1 + v \partial_u^2 \sigma_1 + (\rho_{l0}/\mu_{l0})\theta \mu_{l1} + (\rho_{r0}/\mu_{r0})\theta \mu_{r1} = 0. \tag{7}$$

Here

$$\sigma \equiv S/\rho, \quad \theta \equiv \Delta^{\lambda\mu}\partial_\lambda \partial_\mu, \quad \partial_u \equiv u_0^\nu \partial_\nu,$$

$$\beta \equiv \frac{\delta_0(\rho_{l0} + \rho_{r0})}{\rho_0 \omega_{n0}}, \quad \omega_{n0} \equiv (TS_n + \mu_l \rho_{nl} + \mu_r \rho_{nr})_0,$$

$$\alpha_l \equiv -(\rho_{l0}\sigma_0/\mu_{l0}\rho_0)\frac{\omega_{n0} + \mu_{l0}(\rho_{l0} + \rho_{r0})}{\omega_{n0}},$$

$$\delta \equiv 1 - (\rho_{n0}/\rho_0),$$

$$\alpha_r \equiv -(\rho_{r0}\sigma_0/\mu_{r0}\rho_0)\frac{\omega_{n0} + \mu_{r0}(\rho_{l0} + \rho_{r0})}{\omega_{n0}},$$

$$\nu \equiv -\rho_{n0}/\sigma_0,$$

and ε is the invariant energy density defined by the equality $\varepsilon = u_0^\nu u_0^\mu T_{\nu\mu}$

Analyzing the solution of system (7) in the form of plane waves (all thermodynamic quantities vary according to the law $\exp(ik^\nu x_\nu)$, and k^ν is the four-dimensional wave vector)

and choosing P, μ_l, and μ_r as independent variables, from the compatibility condition of Eqs. (7) we obtain the dispersion equation in the wave vector κ, which defines the square of the velocity of sound:

$$\kappa^6 \{[\sigma(\partial\rho/\partial P) + \nu(\partial\sigma/\partial P)][(\partial\varepsilon/\partial\mu_l)(\partial\sigma/\partial\mu_r)$$
$$- (\partial\varepsilon/\partial\mu_r)(\partial\sigma/\partial\mu_l)] + [\sigma(\partial\rho/\partial\mu_l)$$
$$+ \nu(\partial\sigma/\partial\mu_l)][(\partial\varepsilon/\partial P)(\partial\sigma/\partial\mu_r) - (\partial\varepsilon/\partial\mu_r)$$
$$\times(\partial\sigma/\partial P)] + [\sigma(\partial\rho/\partial\mu_r) + \nu(\partial\sigma/\partial\mu_r)][(\partial\varepsilon/\partial P)$$
$$\times(\partial\sigma/\partial\mu_l) - (\partial\varepsilon/\partial\mu_l)(\partial\sigma/\partial P)]\}$$
$$+ \kappa^4 \{[\sigma(\partial\rho/\partial P) + \nu(\partial\sigma/\partial P)][\alpha_r(\partial\varepsilon/\partial\mu_l)$$
$$- \alpha_l(\partial\varepsilon/\partial\mu_r)] + (\rho_{l0}/\mu_{l0})[(\partial\varepsilon/\partial P)(\partial\sigma/\partial\mu_r)$$
$$- (\partial\varepsilon/\partial\mu_r)(\partial\sigma/\partial P)] + [\sigma(\partial\rho/\partial\mu_l)$$
$$+ (\nu(\partial\sigma/\partial\mu_l)][\alpha_r(\partial\varepsilon/\partial P) - \beta(\partial\varepsilon/\partial\mu_r)]$$
$$+ (\rho_{r0}/\mu_{r0})[(\partial\varepsilon/\partial P)(\partial\sigma/\partial\mu_r) - (\partial\varepsilon/\partial\mu_r)$$
$$\times(\partial\sigma/\partial P)] + [\sigma(\partial\rho/\partial\mu_r) + \nu(\partial\sigma/\partial\mu_r)]$$
$$\times[\alpha_l(\partial\varepsilon/\partial P) - \beta(\partial\varepsilon/\partial\mu_l)]\} + \kappa^2 \{\alpha_r[\sigma(\partial\rho/\partial\mu_l)$$
$$+ \nu(\partial\sigma/\partial\mu_l)] + \alpha_l[\sigma(\partial\rho/\partial\mu_r) + \nu(\partial\sigma/\partial\mu_r)]$$
$$+ (\rho_{r0}/\mu_{r0})[\alpha_l(\partial\varepsilon/\partial P) + (\partial\sigma/\partial\mu_l) + (\partial\varepsilon/\partial\mu_l)$$
$$\times(\partial\sigma/\partial P) - \beta(\partial\varepsilon/\partial\mu_l)] + (\rho_{l0}/\mu_{l0})[\alpha_r(\partial\varepsilon/\partial P)$$
$$+ (\partial\sigma/\partial\mu_r) + (\partial\varepsilon/\partial\mu_r)(\partial\sigma/\partial P) - \beta(\partial\varepsilon/\partial\mu_r)]\}$$
$$+ \alpha_l(\rho_{r0}/\mu_{r0}) + \alpha_r(\rho_{l0}/\mu_{l0}) = 0. \tag{8}$$

In an analysis of a similar problem in the nonrelativistic theory of superfluidity, we assume that the quantities containing the thermal expansion coefficient $\beta = \rho^{-1}(\partial\rho/\partial T)$ are small as compared to those which do not contain β in view of the smallness of this coefficient. Moreover, since $\mu \to \mu_{nrel} + c^2$ in the nonrelativistic limit, we will henceforth assume for the sake of simplicity, following Ref. 8, that

$$\rho^{-1}(\partial\rho/\partial T) \ll 1, \quad T/\mu_l \ll 1, \quad T/\mu_r \ll 1. \tag{9}$$

It was shown in Ref. 8 that the following relations hold under these conditions:

$$[1 - (\partial P/\partial\varepsilon)(2\sigma/\partial\mu_l)] \ll 1, \quad [1 - (\partial P/\partial\varepsilon)(\partial\sigma/\partial\mu_r)] \ll 1. \tag{10}$$

In addition, (9) and (10) lead to the inequality

$$[1 + T\sigma/(\mu_l + \mu_r)]^{-1}\left[\frac{T}{\mu_l\rho_l + \mu_r\rho_r}\right](\partial P/\partial\varepsilon)(\partial P/\partial T) \ll 1. \tag{11}$$

Taking into account relations (9)–(11), and after long transformations we can reduce Eq. (8) to the form

$$\kappa^6 - \kappa^4 \left\{ \frac{(\partial T/\partial\sigma)\sigma^2(\rho_{l0}+\rho_{r0})(\omega_{n0}+\omega_{l0}+\omega_{r0})+(\partial P/\partial\varepsilon)(\mu_{l0}\rho_{l0}+\mu_{r0}\rho_{r0})}{\mu_{l0}\rho_{l0}+\mu_{r0}\rho_{r0}} \right.$$
$$\left. + \frac{\rho_{l0}\rho_{r0}[\mu_l\rho_l(\partial\mu_l/\partial\rho_r)+\mu_r\rho_r(\partial\mu_r/\partial\rho_l)]}{\sigma^2(\rho-\rho_{n0})+\rho_{l0}\rho_{r0}[(\partial\mu_l/\partial\rho_l)+(\partial\mu_r/\partial\rho_r)]} \right\} + \kappa^2 \left\{ \frac{(\partial T/\partial\sigma)\sigma^2(\rho_{l0}+\rho_{r0})(\omega_{n0}+\omega_{l0}+\omega_{r0})(\partial P/\partial\varepsilon)}{\mu_{l0}\rho_{l0}+\mu_{r0}\rho_{r0}} \right.$$
$$+ \frac{(\partial T/\partial\sigma)\sigma^2(\rho_{l0}+\rho_{r0})(\omega_{n0}+\omega_{l0}+\omega_{r0})[\mu_l\rho_l(\partial\mu_l/\partial\rho_r)+\mu_r\rho_r(\partial\mu_r/\partial\rho_l)]}{(\mu_{l0}\rho_{r0}^{-1}+\mu_{r0}\rho_{l0}^{-1})\{\sigma^2(\rho-\rho_{n0})+\rho_{l0}\rho_{r0}[(\partial\mu_l/\partial\rho_l)+(\partial\mu_r/\partial\rho_r)]\}}$$
$$\left. + \frac{\rho_{l0}\rho_{r0}[\mu_l\rho_l(\partial\mu_l/\partial\rho_r)+\mu_r\rho_r(\partial\mu_r/\partial\rho_l)](\partial P/\partial\varepsilon)}{\sigma^2(\rho-\rho_{n0})+\rho_{l0}\rho_{r0}[(\partial\mu_l/\partial\rho_l)+(\partial\mu_r/\partial\rho_r)]} \right\}$$
$$- \frac{(\partial T/\partial\sigma)\sigma^2(\rho_{l0}+\rho_{r0})(\omega_{n0}+\omega_{l0}+\omega_{r0})[\mu_l\rho_l(\partial\mu_l/\partial\rho_r)+\mu_r\rho_r(\partial\mu_r/\partial\rho_l)]}{(\partial\varepsilon/\partial P)(\mu_{l0}\rho_{r0}^{-1}+\mu_{r0}\rho_{l0}^{-1})\sigma^2(\rho-\rho_{n0})+\rho_{l0}\rho_{r0}[(\partial\mu_l/\partial\rho_l)+(\partial\mu_r/\partial\rho_r)]} = 0. \tag{12}$$

The first root of this equation, i.e.,

$$\kappa_1^2 = (\partial P/\partial\varepsilon) \tag{13}$$

determines the velocity of first sound whose waves are oscillations of density and pressure in the absence of temperature oscillations. The obtained expression coincides with the expression for the velocity of first sound in relativistic one-velocity systems.[8] The second root

$$\kappa_2^2 = \frac{(\partial T/\partial\sigma)\sigma^2(\rho_{l0}+\rho_{r0})(\omega_{n0}+\omega_{l0}+\omega_{r0})}{\mu_{l0}\rho_{l0}=\mu_{r0}\rho_{r0}} \tag{14}$$

determines the square of the velocity of propagation of second sound waves that are oscillations of temperature and entropy in the absence of pressure oscillations. In the case when one of the densities of the condensates vanishes, the obtained expression coincides with the relevant expression for the squared velocity of second sound in a one-condensate relativistic system.[8]

The third root

$$\kappa_3^2 = \frac{\rho_{l0}\rho_{r0}[\mu_l\rho_l(\partial\mu_l/\partial\rho_r)+\mu_r\rho_r(\partial\mu_r/\partial\rho_l)]}{\sigma^2(\rho-\rho_{n0})+\rho_{l0}\rho_{r0}[\partial\mu_l/\partial\rho_l)+(\partial\mu_r/\partial\rho_r)]} \tag{15}$$

defines the squared velocity of one more (third) acoustic mode whose propagation is a specific property of two-condensate systems. In the case when one of superfluid densities vanishes, the velocity of sound in (15) also vanishes. The waves of this sound are oscillations of densities and chemical potentials.

The acoustic waves considered above are of the same type as in the nonrelativistic theory of superfluidity. In the nonrelativistic limit $(c\to\infty, \mu\to\mu_{nrel}+c^2)$, the expressions obtained for velocities are transformed into the expressions for velocities of acoustic modes obtained by Khalatnikov[6] during the solution of a similar nonrelativistic problem without drag effect.

Let us now consider the propagation of fourth sound waves in a two-condensate system. By definition,[9] fourth sound corresponds to oscillations emerging in the system when the normal component is retarded. In our analysis of fourth sound, we assume that the following relations hold in view of the retardation of the normal component:

$$u^\nu(x) = u_0^\nu(x), \quad u_1^\nu(x) = 0.$$

We shall linearize equations under the simplifying conditions

$$u_0^\nu = v_{l0}^\nu, \quad u_0^\nu = v_{r0}^\nu, \quad \gamma_l = \gamma_r = 1.$$

The linearized system of equations in this case has the form

$$\partial_u\rho_l + \rho_{l0}\partial_\nu v_{l1}^\nu + \rho_{r0}\partial_\nu v_{r1}^\nu = 0,$$

$$\sigma_0\partial_u\rho_1 + \rho_0\partial_u\sigma_1 = 0,$$

$$\mu_0 v_{l0}^\nu\partial_\nu v_{l1}^\lambda = \Delta_l^{h\nu}\partial_\nu\mu_{l1}, \quad \mu_{r0}v_{r0}^\nu\partial_\nu v_{r1}^\lambda = \Delta_r^{\lambda\nu}\partial_\nu\mu_{r1},$$

$$\partial_u\varepsilon_1 + \mu_{l0}\rho_{l0}\partial_\nu v_{l1}^\nu + \mu_{r0}\rho_{r0}\partial_\nu v_{r1}^\nu = 0,$$

$$\mu_{l0}\rho_{l0}\partial_u v_{l1}^\nu + \mu_{r0}\rho_{r0}\partial_u v_{r1}^\nu - \Delta^{\lambda\nu}\partial_\lambda P_1 = 0. \tag{16}$$

Cancelling out the derivatives of velocities and assuming that the second equation from (16) implies that only two thermodynamic variables are independent in the case under investigation, we obtain a system of two equations. The solvability condition of the system leads to a biquadratic dispersion equation that can be used for deriving the following expressions for the velocities of fourth sound:

$$\kappa_{4l}^2 = \frac{\rho_{l0}(1+\rho_0\sigma_0\xi_l)}{\mu_0\rho_0[(\partial\rho/\partial P)-\xi_l(\partial\rho_l/\partial T)]},$$

$$\kappa_{4r}^2 = \frac{\rho_{r0}(1+\rho_0\sigma_0\xi_r)}{\mu_0\rho_0[(\partial\rho/\partial P)-\xi_r(\partial\rho_r/\partial T)]}, \tag{17}$$

where

$$\xi_l = \frac{\sigma_0(\partial\rho_l/\partial P)+\rho_0(\partial\sigma/\partial P)}{\sigma_0(\partial\rho_l/\partial T)+\rho_0(\partial\sigma/\partial T)},$$

$$\xi_r = \frac{\sigma_0(\partial\rho_r/\partial P)+\rho_0(\partial\sigma/\partial P)}{\sigma_0(\partial\rho_r/\partial T)+\rho_0(\partial\sigma/\partial T)}.$$

The existence of two types of fourth sound waves is a typical property of two-condensate systems. In the case when one of the densities vanishes, the corresponding acoustic mode vanishes also, and the obtained equation is transformed into the expression for the velocity of fourth sound in a one-condensate system.[10] Fourth sound waves are oscillations of temperature, entropy, and corresponding density in the case when the normal component is retarded, which is in accord

with the type of oscillations in a similar wave in the nonrelativistic theory.[4,5] In addition, in the nonrelativistic limit this result is transformed into the expressions for the velocities of fourth sound derived by Mineev.[4]

*E-mail: sivil@popper1.isf.kiev.ua
**E-mail: pfomin@gluk.apc.org

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Acoustic emission accompanying the superconducting transition in HTS ceramics TlBaCuO

I. V. Ostrovskii and I. N. Salivonov

Taras Shevchenko University, 252033 Kiev, Ukraine
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A peak of acoustic emission (AE) is observed experimentally at the superconducting transition temperature in samples of the superconducting ceramics $Tl_2Ba_2CuO_{6+x}$. AE signals have been recorded by a piezoelectric transducer with the resonant frequency 1 MHz in the temperature range 80–300 K. Relaxation anomalies are attributed to a change in the charge state of linear defects and variations of the parameters of the cuprate layer in the samples. © *1998 American Institute of Physics.* [S1063-777X(98)01001-9]

Phase transition (PT) in high-T_c (HTS) materials remain the objects of interest for experimenters. The results of investigation of electric, magnetic, elastic, and other properties of HTS materials are discussed in the literature.[1–4] However, a comprehensive theory describing the nature and peculiarities of the superconducting transition in HTS materials has not yet been developed.

Acoustic emission studies of loading of Y- and Bi-based superconducting ceramics are described in Refs. 5 and 6. The authors of these publications obtained interesting results indicating the efficiency of acoustic emission (AE) in studying physical and mechanical properties of HTS materials. It was shown that AE methods can be used for detecting structural transformations in Bi-based ceramics.[6]

In spite of a large number of experimental studies of HTS materials, thermally activated acoustic emission has been investigated insufficiently. The same also applies to emission accompanying a cyclic variation of temperature in the range including the phase transition. Such experiments not only provide new information on HTS materials, but are also interesting from the point of view of fundamental physical studies.

It should be noted that the results obtained in earlier attempts to measure AE during superconducting PT in HTS materials did not permit an unambiguous interpretation of physical processes associated with the PT in ceramics;[7] moreover, the experimental technique often did not meet the requirements on reliability of experimental results (e.g., adhesiveless contact between a porous sample and an AE transducer and a high rate of temperature variation).[8]

In this paper, we report on the results of experimental studies of the intensity of thermally stimulated acoustic emission as a function of temperature in the vicinity of the superconducting transition in $Tl_2Ba_2CuO_{6+x}$ ceramics. The existence of acoustic emission in Y-based HTS materials during the superconducting transition was established earlier.[9]

EXPERIMENTAL TECHNIQUE

During preparation of experiments, special attention was paid to the selection of glue for fixing a piezoelectric transducer to an HTS ceramic sample. We first investigated various types of glue (epoxy adhesives and glues based on organic solvents) with various solidification times. Test experiments allowed us to select a glue that does not make any contribution to AE signals in the temperature range under investigation.

The AE intensity was measured in the temperature range 80–300 K. Acoustic emission signals were detected by a piezoelectric transducer with a resonant frequency of 1 MHz. The experimental setup operated in the frequency range 0.2–2.0 MHz. The temperature variation rate was the same for the upward and downward motion along the temperature scale and was equal to 0.1 or 0.5 K/min for different series of experiments. The acoustic contact between the sample and the piezoelectric transducer was ensured by a specially selected glue. The transducer made of a piezoelectric ceramic of the lead zirconate-titanate (PZT) type detected acoustic signals of AE and transformed then into electric signals which were subsequently amplified by a special preamplifier and detected by an acoustic emission device AF-15. The temperature was controlled by a semiconducting pickup and measured by a special instrument. The measuring chamber supplied with a temperature-stabilization system was placed in nitrogen vapor. Temperature variation was carried out by varying the gaseous nitrogen flux.

DISCUSSION OF EXPERIMENTAL RESULTS

The results of acoustic emission experiments are presented in Fig. 1, where the AE intensity N is given in relative units. The absolute value of the intensity varied from 70 to 700 pulse/s. The curves were plotted on the basis of experimental results averaged over five thermal cycles. It can be seen that the maximum AE intensities recorded during heating (curve *1*) and cooling (curve *2*) differ by approximately an order of magnitude.
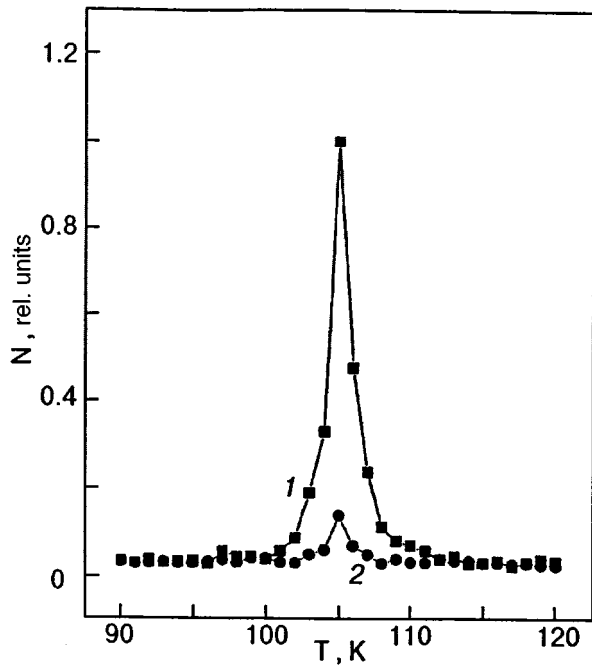
FIG. 1. Temperature dependence of AE intensity N upon heating (curve *1*) and cooling (curve *2*) at a rate of 0.1 K/min.

FIG. 2. Temperature dependences of relative resistance $R/R(293$ K$)$ of the sample and the rate of its variation dR/dT.

In order to verify the coincidence of the temperature T_a corresponding to AE peaks with the superconducting transition temperature T_c, the electrical resistance of the sample was measured by the four-probe method. It was found that the temperature region in which the sample resistance varies sharply coincides with the region of increase in the AE intensity. The temperature corresponding to the peak on the intensity curve $N(T)$ virtually coincides with the maximum rate dR/dT of variation of the sample resistance (Fig. 2).

The obtained results can be explained from the point of view of the charge state of defects in HTS ceramics. The HTS samples used in our experiments had grained structure, and hence contained groups of various dislocations, concentrated mainly at the surface of micrograins. A change in the sample temperature gave rise to elastic stresses causing changes in the state of dislocations. Group dislocation effects in crystals and ceramics are usually accompanied by the emission of acoustic pulses.[10]

The mechanism of the emergence of AE during PT can be described as follows. Dislocations in HTS ceramics as well as in any other material are electrically charged, but their electric field is screened at a temperature $T < T_c$. In the initial state ($T > T_c$), various types of elastic fields including long-range fields of dislocations, dislocation groups, and micrograin boundaries exist in the sample. As a result, a certain initial field of stresses in formed in the sample. At temperatures above T_c, mechanical stresses have two components: purely elastic stress and that associated with ponderomotive forces induced by the electric fields of dislocations and polarization charges. Temperature variations change the type and magnitude of internal elastic and electric fields. The screening of electric fields of dislocations and their groups as a result of cooling below T_c decreases internal forces of interaction, giving rise to pulses of mechanical stress. As temp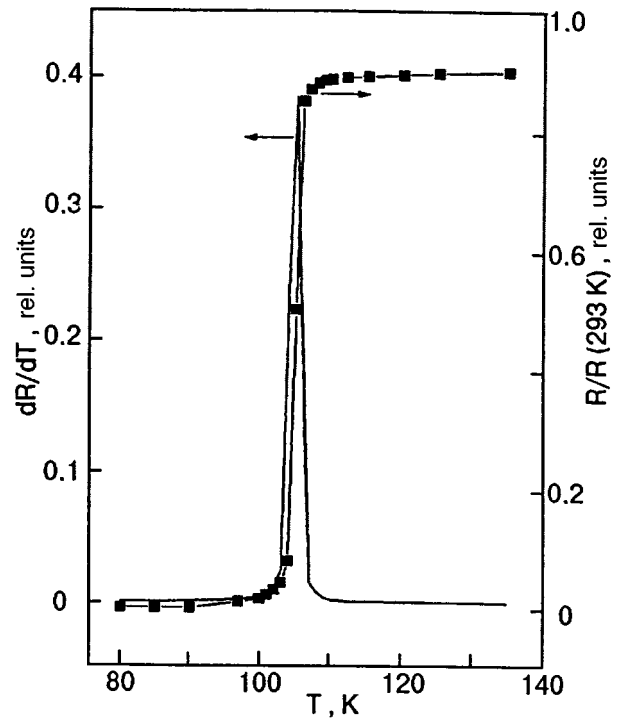erature increases above T_c, the electrostatic interaction again comes into play, and internal elastic stresses again change jumpwise. Thus, at $T = T_c$, mechanical stresses in the bulk of the sample must change, which was detected by us from the change in the AE intensity.

Undoubtedly, AE contains a contribution associated with temperature changes in mechanical stresses in micrograins of the sample due to purely geometrical changes in its size, i.e., thermal deformations. This contribution, however, is not large. For example, the maximum value of the AE intensity in our experiments was ~ 700 pulse/s, while the AE intensity of barium titanate ceramics,[11] which was attributed to purely mechanical effects, did not exceed 140 pulse/s. In our experiments, such a background signal amounted to 20–30 pulse/s.

In general, different heights of AE intensity peaks recorded during heating and cooling can be attributed to relaxation processes, leading to temperature annealing of internal stresses upon heating to room temperature. The AE signal in the PT region recorded during cooling cannot have a high intensity since it is due to a change in internal stresses from low (relaxed) values to still smaller stresses in the superconducting state. The maximum intensity of the signal recorded by us was 70 pulse/s. In the case of heating, the sample near T_c goes over to a state with relatively higher internal (unrelaxed) stresses, which can be detected from a change in the AE intensity. We recorded its maximum value ~ 700 pulse/s.

Strictly speaking, relaxation processes must affect the form of the $N(T)$ dependence if the rate of temperature variation is higher than or comparable with the rate of relaxation processes in the ceramic material.
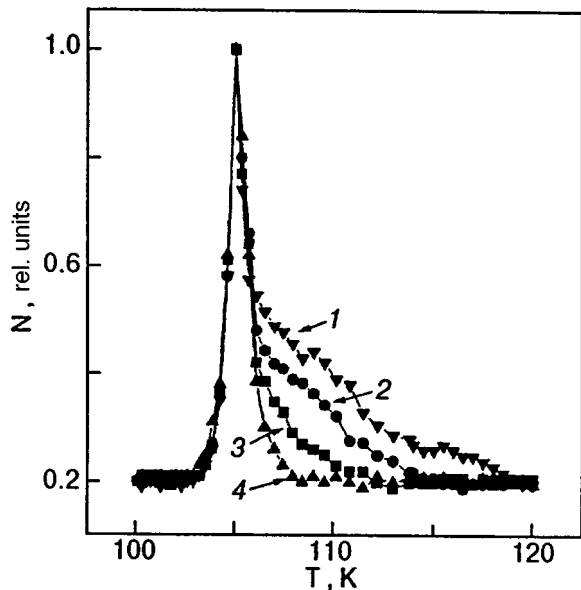
FIG. 3. Temperature dependence of the AE intensity for different rates of sample heating, K/min: 0.2 (curve *1*), 0.3 (curve *2*), 0.4 (curve *3*), and 0.5 (curve *4*).

In order to determine the effect of temperature variation rate on acoustic emission, we measured the AE intensity at temperature variation rates of 0.5, 0.4, 0.3, and 0.2 K/min. The results are presented in Fig. 3. It can be seen that in a certain temperature range the emission intensity is elevated for all curves except curve *4*, indicating a transient process. In our opinion, this confirms the above assumptions concerning the reason behind the difference in the heights of AE intensity peaks recorded during heating and cooling.

Recent x-ray studies[12] proved that oxygen atoms in cuprate planes are displaced as well as barium atoms relative to these planes during the superconducting transition in HTC ceramics. Such structural changes can make a significant contribution to acoustic emission. Moreover, it was found[12] that the amplitudes of thermal vibrations of atoms can change significantly (by 20%) in the vicinity of the superconducting transition temperature. These processes are not instantaneous, but occur with a certain time constant.

The absence of "blurring" of the $N(T)$ dependence at a sample heating rate of 0.2 and 0.1 K/min (Figs. 1 and 3) indicates that the rate of relaxation processes is higher than the temperature variation rate. Since the temperature variation rate was virtually constant in the course of experiments, we could calculate the time of attenuation of relaxation processes, which amounted to (25 ± 2) min.

CONCLUSION

We can draw the conclusion that the superconducting PT in the samples of HTS ceramics $Tl_2Ba_2CuO_{6+x}$ is accompanied by acoustic emission. Sources of emission can be associated with a change in the stressed state in internal microscopic regions or in individual grains of the ceramic sample as well as with a change in the parameters of the structure in the region of cuprate layer. In all probability, changes in internal microscopic stresses are also connected with a change in the electric state of structural defects and their congestions.

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SHORT NOTES

Resistive studies of creep controlled by plastic deformation of a vortex lattice

M. A. Obolenskii, A. V. Bondarenko, V. A. Shklovskii, R. V. Vovk, and A. A. Prodan

*Kharkov State University, 310077, Kharkov, Ukraine**

Current–voltage characteristics (IVC) are measured for YBaCuO single crystals in a magnetic field applied at 45° to twinning planes. The current- and field dependences of the pinning potential are derived from the IVC curves. The obtained dependences indicate that the flux creep in the range of relatively strong magnetic fields is controlled by the plastic deformation of the vortex lattice. © *1998 American Institute of Physics.* [S1063-777X(98)01101-3]

Magnetic studies of YBaCuO single crystals in the temperature range $80\ \mathrm{K} < T < 85\ \mathrm{K}$ proved that the magnetic flux dynamics in weak and strong magnetic fields differ significantly.[1] At $T = 85\ \mathrm{K}$ in weak fields $H \leqslant 3\ \mathrm{kOe}$, the effective pinning potential increases with the magnetic field in proportion to $B^{6/5}$ (B is the magnetic induction), which is in qualitative agreement with the theory of collective pinning.[2] However, in strong fields $H \geqslant 5\ \mathrm{kOe}$, the pinning potential decreases with increasing magnetic field. Such a behavior was interpreted by Blatter *et al.*[2] as the creep controlled by plastic deformation of the vortex lattice (VL).

The current dependence of pinning potential in the case of creep controlled by diffusion of dislocations is given by[3]

$$U_{\mathrm{pl}}(J) = U_{\mathrm{pl}}^0(B)[1 - (J/J\mathrm{pl})^\mu], \qquad (1)$$

where $\mu = 1/2$ and J_{pl} is the critical depinning current corresponding to plastic flow. Under the assumption that the current dependence of pinning potential is determined by relation (1), the pinning potential decreases with increasing magnetic field in proportion to $B^{-0.7}$,[1] which is in qualitative agreement with the field dependence of pinning potential in the case of plastic deformation of the vortex lattice[4]

$$U_{\mathrm{pl}}^0(B) \approx \varepsilon \varepsilon_0 a_0 \sim B^{-1/2}. \qquad (2)$$

Here $\varepsilon = m/M$ is the anisotropy parameter, $\varepsilon_0 = \Phi_0/(4\pi\lambda)$ the energy of a vortex filament, $a_0 \approx (\Phi_0/B)^{1/2}$ the separation between vortices, Φ_0 the magnetic flux quantum, and λ the magnetic field penetration depth.

It should be noted that it is difficult methodologically to single out the current- and field dependences of pinning potential from an analysis of experimental data since both the induced current density and the magnetic induction in the sample change in the course of measurements. In addition, resistive measurements make it possible to estimate the critical depinning current[5] by using the Bardeen–Stephen model, which is important for obtaining quantitative estimates of pinning parameters. The number of resistive experiments on YBaCuO single crystals for high densities of transport currents is scarce,[5,6] and the results of measurements have not been analyzed from the point of view of plastic deformation of the VL.

In this communication, the dynamics of magnetic flux in YBaCuO single crystals with pinning at point defects is analyzed. The results of measurements of IVC of a bridge containing a system of unidirectional twins are presented for the vector **J** oriented parallel to the ab-plane and almost parallel to the planes of twin boundaries (TB) (the angle between the vector **J** and the TB plane was 7°). Measurements were made at $T = 85.1\ \mathrm{K}$, i.e., below the melting point of the vortex lattice. The magnetic field vector was oriented at an angle $\theta = 45°$ to the axis **c** of the crystal. Such a choice was dictated by the fact that a fraction of vortex filaments are trapped by the TB plane when the disorientation angle θ between the vector **B** and TB planes is smaller than a certain critical value θ^*, which can affect significantly the magnetic flux dynamics. For angles $\theta > \theta^*$, twins do not deform a vortex filament,[2] and hence the pinning at TB is equivalent to the pinning at point defects. It can easily be proved on the basis of the model developed by Blatter *et al.*[7] that the critical angle in anisotropic case is defined by the relation $\theta^* = \varepsilon^{-1} \tan(2\Delta U/U)^{1/2}$, where U is the linear tension of a vortex filament in the bulk of the superconductor, and ΔU the difference in the energies of a vortex in the bulk of the superconductor and a vortex localized at a twin boundary. The ratio $\Delta U/U$ for YBaCuO single crystals is approximately equal to 10^{-2},[8,9] and, assuming that $\varepsilon = 1/6$, we obtain $\theta^* \approx 50°$. Thermal fluctuations and interaction between vortices reduce the value of θ^*. An analysis of the angular dependences of pinning parameters shows that the value of θ^* in the magnetic field range under investigation is 15–20°.[6] Thus, in the experimental geometry in question, pinning takes place at point defects.

The superconducting transition temperature T_c of the sample was 92 K for the transition width $\Delta T_c = 0.3\ \mathrm{K}$ in zero magnetic field. The width of the bridge was 0.2 mm and the thickness was 20 μm. In order to improve heat removal, the sample was glued to a bulk copper substrate by the epoxy glue BF-2. Measurements made in the normal state proved that the deviation of the sample temperature from the equilibrium value did not exceed 10^{-2} K for a maximum power of 70 μW liberated in the sample during measurements. The IVC curves were recorded in direct current.

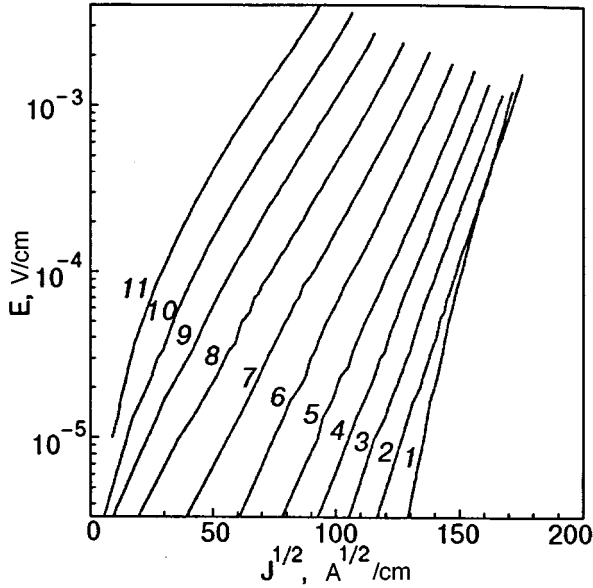Figure 1 shows IVC in the log E vs. $J^{-1/2}$ coordinates. It

FIG. 1. Current–voltage characteristics for a YBaCuO single crystal, measured at $T = 85.1$ K for various values of the field H, kOe: 4.7, 5.3, 6.5, 7.5, 8.6, 9.7, 10.8, 12.0, 13.2, 14.3, and 15.4 (curves *1–11*, respectively).

can be seen that the $E(J)$ dependence in the field interval 5.3 kOe $\leq H \leq 13.2$ kOe is correctly described by relation (1) for $\mu = 1/2$. An increase (to $H > 14$ kOe) or a decrease (to $H < 5$ kOe) of the magnetic field leads to a negative curvature of the $E(J)$ curve, indicating a decrease in the exponent μ. The field dependence of μ is represented by curve *1* in Fig. 2.

The exponent $\mu = 1/2$ obtained in the field range 5.3 kOe $\leq H \leq 13.2$ kOe can signify a creep controlled by the diffusion of dislocations in the VL. In order to determine the pinning potential $U_{pl}^0(B)$ from the experimental dependences $E(J)$, we must know the critical current J_{pl}. The value of J_{pl} can be assessed by using the Bardeen–Stephen model. Indeed, experimental studies of IVC for YBaCuO single crys-

tals for the field orientation $\mathbf{H}\|\mathbf{c}$ proved[5] that the differential resistance $\rho_d(J) = dE(J)/dJ$ for transport currents exceeding the critical depinning current does not depend on current and is successfully described by the Bardeen–Stephen model:[10]

$$\rho_d = \rho_{BS} = \rho_N B / H_{c2}. \tag{3}$$

Consequently, the value of the critical current J_{pl} can be estimated by extrapolating the ratio $\rho_d(J)/\rho_{BS}$ to unity.

The resistivity ρ_N at 85 K, which is determined by the extrapolation of the linear segment of the $\rho(T)$ curve, was 6×10^{-5} $\Omega \cdot$ cm. The second critical field H_{c2} can be assessed assuming that $dH_{c2}^{\|}/dT = -1.8$ T/K for $\mathbf{H}\|\mathbf{c}$, while the dependences on the angle and temperature is determined by the relation $H_{c2}(\theta, T) = (dH_{c2}^{\|}/dT)(T - T_c)/\varepsilon(\theta)$, where $\varepsilon(\theta) = (\varepsilon^2 \cos^2\theta + \sin^2\theta)^{1/2}$ and $\varepsilon = 1/6$. The value of H_{c2} obtained in this way for $T = 85.1$ K and $\theta = 45°$ is ≈ 180 kOe. By way of an example, the inset to Fig. 2 shows the current dependence $\rho_d(J)/\rho_{BS}$ obtained from the measurements in the magnetic field $H = 10.8$ kOe. It can be seen that in the range of currents under investigation, the ratio $\rho_d(J)/\rho_{BS}$ is smaller than unity, while the current dependence is almost linear in semilogarithmic coordinates.

In view of what has been said above, we determined the value of J_{pl} by a linear extrapolation of the ratio $\rho_d(J)/\rho_{BS}$ to unity (see inset to Fig. 2). Substituting the values of J_{pl} obtained in this way into formula (1) and interpolating the experimental curves by this equation, we have obtained the field dependence of pinning potential presented by curve *2* in Fig. 2. It can be seen that the pinning potential U_{pl}^0 in magnetic fields $H \geq 5.3$ kOe decreases with increasing magnetic field, and the dependence $U_{pl}^0(B)$ cannot be described by the power dependence $U_{pl}^0 \sim B^\nu$ with a constant exponent ν. It can be seen from the figure that the exponent ν decreases gradually from -0.55 for $H \approx 6$ kOe to -1.1 for $H \geq 11$ kOe. The value of $\nu \approx -0.55$ is close to the theoretical value -0.5. Possible reasons behind the increase in the absolute value of ν near the melting temperature of the vortex lattice were discussed in Ref. 1.

According to formula (2), the value of U_{pl}^0 in a magnetic field $H = 5.3$ kOe for $\lambda(T = 85 \text{ K}) \approx 3000–4000$ Å varies from 1100 to 1900 K. Thus, the experimental value of $U_{pl}^0(H = 5.3 \text{ kOe}) \approx 1600$ K is in good agreement with theoretical estimates.

The sign reversal of the exponent μ observed in a magnetic field $H = 4.7$ K might indicate a transition to creep controlled by elastic deformation. This is confirmed by the decrease in the pinning potential with magnetic field, which is predicted by the theory of collective pinning.[2]

Let us consider briefly the difference between our results and the results obtained in Ref. 1. In Ref. 1, the exponent μ was always negative, although it was assumed in the processing of experimental results that the current dependence of pinning potential is described by formula (1) with $\mu = 1/2$. However, we obtained the value of $\mu = 1/2$ in a wide field interval (5.3 kOe $\leq H \leq 13.2$ kOe). It was mentioned above that this difference in exponents μ can be associated with the
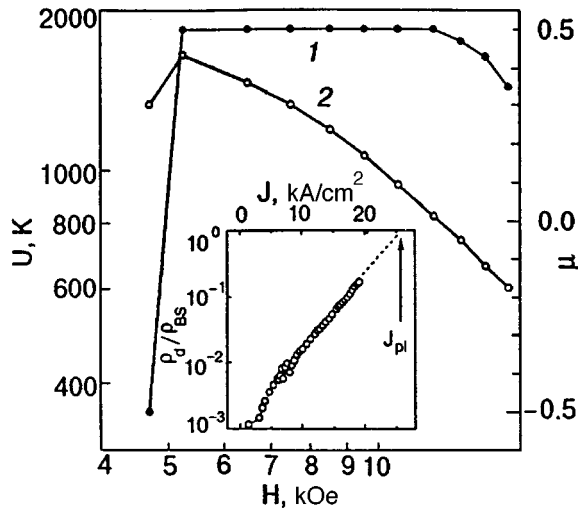

FIG. 2. Field dependences of the exponent μ (curve *1*) and pinning potential (curve *2*). The inset shows the current dependence of pinning potential normalized to the resistance to viscous flux flow in the Bardeen–Stephen model.

difficulties in the separation of the current- and field dependence of pinning potential. It should also be noted that the authors of Ref. 1 did not mention the presence or absence of twin boundaries. If crystals contained twins, enhanced pinning on TB planed could affect the magnetic flux dynamics significantly in our experimental geometry ($\mathbf{H}\|\mathbf{c}\|$TB). For example, twice as large values of pinning potential obtained in Ref. 1 can be just due to the presence of twins.

Summarizing the experimental results described above, we can draw the following conclusions. The current dependence of pinning potential is in good agreement with the model of diffusion of dislocations in the vortex lattice, and the value of pinning potential corresponds to the energy of plastic deformation of the vortex lattice. The field dependence of pinning potential matches to theoretical predictions for the creep controlled by inelastic deformation of the vortex lattice away from the melting point of the vortex lattice. As we approach the melting point, the pinning potential decreases upon an increase of the field at a rate higher than predicted by the theory.

*E-mail: mikhail.a.obolenskii@univer.kharkov.ua

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LETTERS TO THE EDITOR

Two-gap superfluidity in the theory of a Fermi liquid

A. I. Akhiezer, A. A. Isaev, S. V. Peletminsky, and A. A. Yatsenko

National Science Center ''Kharkov Physicotechnical Institute'', 310108 Kharkov, Ukraine

The possibility of a phase transition from the one-gap superfluid state with the singlet or triplet pairing of fermions to the two-gap superfluid state corresponding to the superposition of states with the singlet and triplet pairing in a Fermi liquid is considered. The thermodynamic stability of new two-gap solutions is analyzed. © *1998 American Institute of Physics.* [S1063-777X(98)01201-8]

As a rule, superfluid states in a Fermi liquid (FL) are considered as emerging as a result of a phase transition from the normal state. Such states are characterized by a single order parameter, which is singlet (scalar) if the spin S of a Cooper pair is equal to zero and triplet (vector) is the spin of a pair $S=1$. However, phase transition that might also take place in the superfluid FL can lead to the emergence of new superfluid states. Thus, we are speaking of phase transitions from one superfluid state to another. A new superfluid state can be characterized by not one but several order parameters. In this communication, we consider the case when the states of a Cooper pair emerge in a superfluid Fermi liquid in the form of a superposition of states with the singlet and triplet pairing. For these states, the spin of the pair is equal either to zero, or to unity with a certain probability.

Our analysis is based on the theory of a superfluid FL developed in Ref. 1. For a superfluid FL with the singlet–triplet (ST) pairing of fermions, the matrix order parameter has the form

$$\Delta_{12} = [\Delta_0(\mathbf{p}_1)(\sigma_2)_{\sigma_1,\sigma_2} + \Delta(\mathbf{p}_1)(\sigma\sigma_2)_{\sigma_1,\sigma_2}]\delta_{\mathbf{p}_1,-\mathbf{p}_2}, \tag{1}$$

where σ_i are Pauli matrices, $1 \equiv \mathbf{p}_1, \sigma_1$. The quantities Δ_0 and Δ_i in (1) define the singlet and triplet components of the order parameter Δ, respectively. Henceforth, we shall assume that the structure of Δ_0 and Δ_i is such that $\Delta_0(\mathbf{p}) = \Delta_0(p)$ and $\Delta_i(\mathbf{p}) = R_{ik}p_k^0\Delta(p)$, where R_{ik} is a certain rotation matrix ($R\widetilde{R} = 1, R_{ik}^* = R_{ik}$). Omitting intermediate calculations, we write the final equation for determining the temperature dependence of the order parameters $\Delta_0 = \Delta_0(p = p_F)$ and $\Delta = \Delta(p = p_F)$:

$$d(x,T)d[xd(x,T),T] \equiv D(x,T) = 1, \tag{2}$$

where

$$d(x,T) = \frac{4g_s g_t \lambda(x,T) - g_s - g_t}{g_t - g_s},$$

$$\lambda(x,T) = \int_{-\theta}^{\theta} \frac{d\xi}{E} + \tanh\frac{E}{2T}, \quad E = \sqrt{\xi^2 + x^2}.$$

Here g_s and g_t are the singlet and triplet dimensionless coupling constants and θ the cutoff parameter. The order parameters $\Delta_0(T)$ and $\Delta(T)$ in this case can be determined from the relations $\Delta_0(1/2)x[1 + d(x,T)]$, $\Delta = (1/2)x[1 - d(x,T)]$. One-gap solutions can be obtained from (2) as solutions of the equations $d(x,T) = 1$ (singlet) and $d(x,T) = -1$ (triplet), and the corresponding critical temperatures T_s and T_t can be found from the equations $d(0,T_s) = 1$ and $d(0,T_t) = -1$. For definiteness, we assume that $g_s > g_t$. An analysis of the behavior of the function $D(x,T)$ shows that no one-gap solutions exist at temperatures $T > T_s$, only one singlet solution exists for $T_t < T < T_s$, while for $T_{st} < T < T_t$ the system is characterized by two one-gap (singlet and triplet) solutions. Finally, at $T < T_{st}$ we have two new ST solutions in addition to the known solutions. In order to determine the critical temperature T_{st} at which ST solutions emerge for the first time, we have two equations:

$$d(x,T) = -1, \quad xd_x'(x,T) = 2. \tag{3}$$

The first of these equations indicates that ST solutions are continuously branched from the one-gap triplet solution, while the second equation is the condition that the derivative $D_x'(x,T)$ vanishes at the branching point. The calculation of the second derivative $D_{xx}''(x,T)$ at the critical point (x_{st}, T_{st}) gives $D_{xx}''(x_{st}, T_{st}) = 0$, i.e., the mechanism of branching of ST solutions is the formation of inflection on the curve $z = D(x, T_{st})$ for $x = x_{st}$. The temperature behavior of ST branches of solutions of the equation $D(x,T) = 1$ near the critical temperature T_{st} is determined by the formulas

$$x_{\pm}(T) = x_{st} \pm \sqrt{\beta(T_{st} - T)/A},$$

where

$$\beta = 2d_{xT}'' - d_T'(d_x' + x_{st}d_{xx}''),$$

$$A = \frac{1}{3}d_{xxx}''' - (d_x')^3 - \frac{3}{2}d_x'd_{xx}'' - \frac{1}{2}x(d_{xx}'')^2;$$

in this case, it is necessary that $\beta/A > 0$. We shall give the results of numerical determination of the critical temperatures T_{st}, T_s, and T_t for a model case with $g_s = 0.25$ and $g_t = 0.2$ for $\theta = 0.01\varepsilon_F : T_{st} = 2.84 \times 10^{-3}\varepsilon_F, T_s = 4.46 \times 10^{-3}\varepsilon_F$, and $T_t = 3.33 \times 10^{-3}\varepsilon_F$. At the temperature $T = 2 \times 10^{-3}\varepsilon_F$, for ST solutions we have $\Delta_0 = \pm 2.58 \times 10^{-3}\varepsilon_F$ and $\Delta = 4.05 \times 10^{-3}\varepsilon_F$. It should also

be noted that the above analysis remains valid in the case when the coupling constants satisfy the inequality $g_t > g_s$, the only difference being that the ST solution now branches from the singlet one-gap solution.

An analysis of thermodynamic stability shows that the expansion of the thermodynamic potential Ω of the triplet and ST solution $[\Omega(x_+(T)) = \Omega(x_-(T))]$ has the form

$$\Omega_\lambda - \Omega(x_{st}, T_{st}) = \kappa(T_{st} - T) + \gamma_\lambda(T_{st} - T)^2$$

$[\lambda = (t, st)]$, where the coefficient κ does not depend on the type of solution, and the coefficients γ_λ can be expressed in terms of the derivatives of the function $d(x, T)$ with respect to x and T. If $\gamma_t > \gamma_{st}$, the ST state is thermodynamically advantageous, while for $\gamma_t < \gamma_{st}$ the triplet state is more advantageous. However, in both cases the ST solutions are less stable than the singlet solution $x_s(T)$. Thus, ST states emerge in the form of branching from the thermodynamically less stable triplet branch and corresponds to a certain metastable state in the superfluid FL. This state can probably be stabilized by application of an external magnetic field as, for example, in the case of the superfluid A-phase of ^{3}He.

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CHRONICLES

On the 90th birth anniversary of Lev Davidovich Landau (1908–1968)

A. I. Akhiezer

National Science Center ''Kharkov Physicotechnical Institute'', 310108 Kharkov, Ukraine

The 90th birth anniversary of Lev Davidovich Landau, one of the most outstanding physicists of the XX century, falls on January 22, 1998.

L. D. Landau made immense contributions to quite different fields of theoretical physics. He was not only a great scientist possessing a rare universalism, but also a unique Teacher with a capital T. He founded a world-famous school of theoretical physicists who also contributed significantly to the development of physical science through their works. Landau was an outstanding teacher who read brilliant lectures not only on theoretical physics, but also on general and elementary physics. The ethical image of Landau is also enviable, and he is remembered for his refusal to compromise on basic matters, kindness and goodwill, as well as the moral support he extended to budding scientists in their hour of need.

Landau led a magnificent and yet tragic life. He became a legend in his lifetime, and rightly so, since he attained exceptional success in his scientific activity and also came face to face with death on two occasions. The first time was in 1938 when he was arrested by the NKVD agents as an ''enemy of the people'', and the second time it was a bizarre car accident in 1962.

He was saved on the first occasion by Petr Leonidovich Kapitza. This was a heroic feat, as Kapitza did not flinch and wrote a letter directly to Stalin the very next day after Landau's arrest. In his letter, Kapitza gave Landau an excellent testimonial and pleaded, ''... in view of his exceptional talent, to give appropriate instructions to consider his case with extreme care... I also feel'', wrote Kapitza, ''that we must take into consideration his temper which can be called nothing but outrageous. He is a tease and a bully, loves to find faults in others and having found them, especially in pompous old men like our academicians, starts mocking them disrespectfully. This has earned him many foes... But in spite of all the drawbacks in his disposition, I find it very hard to believe that Landau could do something dishonorable.''

Landau was spared from a savage reprisal. Owing to the stupendous efforts of Kapitza, Landau was set free. However, the charges against him were not withdrawn, and he was released under Kapitza's guarantee. The courage and fortitude of this great man and scientist deserve all praise. It was indeed a heroic deed during such hard days. In all other organizations, a general staff meeting would be called on the day following the arrest of an ''enemy of the people'', where the Director, striking his chest with his fists, would thank Yezhov's agents for helping unmask a ''fierce enemy of the people who had concealed himself unostentatiously in our team''. However, Kapitza did not call any such meeting, did not engage himself in any breast-beating or confession of the sins he had never committed, but threw himself with rare fortitude to save an absolutely innocent person and conquered. The scientific community owes him a debt of gratitude for this.

Landau's rehabilitation came only in 1990, many years after his death. Thus starting from April 28, 1939, the day he was released, right until his death on April 1, 1968, he remained accused and ''adequately exposed as a participant of the anti-Soviet group''.

The collected works of Landau contain only one paper by Landau on electromagnetic showers published during 1938, the year of his arrest. In 1939 also, there was only one work on the de Haas-van Alphen effect which had actually been written much earlier. However, a large number of papers started appearing from 1940 onwards. This is due not only to the fact that Landau had been freed, but also because he was on very good terms with Petr Leonidovich Kapitza, who was sympathetic towards Landau. So closely related were the interests and works of these two magnificent scientists that the Institute of Physical Problems was called the Kapitza-Landau Institute abroad.

The second tragedy struck on January 7, 1962 when Landau, driven by some ''evil force'', decided to go by car to Dubna in spite of a road made highly slippery with ice. His savior angel Kapitza was not around to dissuade him from undertaking the journey. The car in which Landau was travelling collided with a truck, and Landau received fatal injuries which were not compatible with life according to the medicine luminaries of Moscow. However, Landau's life was saved, thanks to the heroic efforts of the doctors, nurses, and the united efforts of physicists from all over the world who acquired the necessary medicaments and sent them by air to Moscow. The battle to save Landau's life was launched in the true sense of the word and was won only formally, since only the body of Landau could be saved while his intellect was lost. It was awful to watch Landau without his brilliant intellect. The only redeeming point was that Landau did not feel nor realize the magnitude of the tragedy. If someone approached him with a scientific question, Landau would usually ward him off saying, ''let us discuss it tomorrow.'' His memory preserved only his knowledge of foreign languages which he had mastered perfectly.

Lev Davidovich Landau was born on January 22, 1908 in Baku. His father was a petroleum engineer, and his mother was a doctor. Landau's mathematical talent was revealed in early childhood. He remarked later that he could not remember when he had learnt differentiation and integration. At the age of 14, Landau joined the Baku University from where he moved to the physics department of the Leningrad University from where he graduated in 1927.

This was a period of tumultuous growth of the new physical theory called quantum mechanics. The scientific career of Landau was thus related closely with all stages of growth of this important physical theory. Landau had to work a lot to keep pace with the new science. He even suffered from nervous exhaustion at one stage, lost his sleep, but managed to withstand the strain.

Landau's friends G. A. Gamow and M. P. Bronshtein went on to become renowned physicists. Gamow created the theory of alpha decay of nuclei, predicted the existence of relict radiation left by the Big Bang marking the formation of our Universe. He was one of the first to explain the genetic code associated with the structure of genes. Bronshtein was the first to quantize the gravitational field.

In 1929, Landau was sent abroad by the Peoples' Commissariat on Education, and spent one and a half years working in Denmark, England and Switzerland. The most important of his visits was in Copenhagen where theoretical physicists from all over Europe gathered at the Theoretical Physics Institute of the great Niels Bohr and discussed the fundamental problems of contemporary theoretical physics at the famous seminars conducted by Bohr. The scientific atmosphere, augmented by the charming personality of Bohr, had a decisive influence on the formation of Landau's outlook on physics, and he always considered himself to be a pupil of Niels Bohr. Later, he visited Copenhagen on two occasions in 1933 and 1934.

On his return to Leningrad in 1931, Landau worked at the Leningrad Physicotechnical Institute from which he moved to Kharkov in 1932, to work at a new research center, the Ukrainian Physicotechnical Institute (UPTI).

This institute was founded in 1928 following the decision of the Ukrainian government at the initiative of Academician Abram Fedorovich Ioffe, a leading organizer of Soviet physics. As the foremost task, Ioffe pointed towards the need to ''decentralize physics'', i.e., to create a network of physics institutes all over the country instead of confining them to just Leningrad and Moscow. As the first step, he emphasized the need to create a powerful physics institute in Kharkov, an important industrial center of the country and the capital of the Ukraine. (The capital of the Ukraine was shifted to Kiev in 1934 under orders from Stalin.)

The core of the staff at UPTI was formed by physicists migrating from the Leningrad Physicotechnical Institute (LPTI). The group of scientists leaving for Kharkov were seen off at the railway station with fanfare since their departure was seen as an important patriotic step.

A famous architect of Leningrad designed the building for the new institute according to the project of its future director Ivan Vasil'evich Obreimov. The UPTI building turned out to be an excellent structure.

Many talented scientists including I. V. Obreimov, A. I. Leipunskii, L. V. Shubnikov, K. D. Sinel'nikov, A. K. Val'ter, V. S. Gorskii, G. D. Latyshev, A. F. Prikhot'ko, O. N. Trapeznikova, and L. V. Rozenkevich migrated from Leningrad to UPTI.

L. D. Landau was invited to work at UPTI by I. V. Obreimov, the Director of the Institute. Many years later, Ivan Vasil'evich told the author that Landau was underestimated at UPTI, and Obreimov, who knew how talented Landau was, offered him the post of head of the theoretical physics division and gave him full freedom in preparing young theoretical physicists and in the choice of the scientific topics. In effect, Obreimov created the first division of theoretical physics of this kind in any physics institute of the country. It can be stated that the formation of this division and the migration of Landau to UPTI was facilitated by the complex relation between Ioffe, the director of LPTI, and Landau who was an outspoken person and did not hesitate to criticize some specific works of Ioffe on thin-film insulators. According to Landau, these works were fallacious.

Landau's task was quite obvious from the very beginning: it included organizing the theoretical department, discovering talented youth and supervising them, theoretical physics studies and teaching in Kharkov educational institutions, writing of books and reviews on theoretical and general physics, and creative contacts with the experimenters at UPTI.

After Landau's arrival in Kharkov, UPTI became one of the best centers of theoretical physics in the world. The ''Journal of Soviet Physics'', which began to be published at the Institute, acquired worldwide fame.

An International Conference on Theoretical Physics was held in Kharkov in the summer of 1934. The conference was attended by Niels Bohr and many leading theoretical physicists both from the Soviet Union and abroad. These included V. A. Fock, I. E. Tamm, Ya. I. Frenkel', E. Williams, R. Peierls, I. Waller, and others. One could see Bohr and Landau walking in the courtyard of UPTI and engrossed in a lively discussion of physical problems.

During this period, leading physicists like P. Dirac, V. A. Fock, R. Peierls, V. Weisskopf, H. Placzek and G. A. Gamow visited UPTI and worked there, frequently for long periods.

Let us now turn to the scientific and organizational work of Landau in establishing the theoretical physics department. The main idea was that a young scientist, who wanted to devote his life to theoretical physics and to work under the guidance of Landau for this purpose, had to pass the so-called theoretical minimum examination conducted personally by Landau and covering the main branches of theoretical physics.

The theoretical minimum included classical mechanics, fundamentals of statistical physics and thermodynamics, continuum mechanics, special theory of relativity and classical electrodynamics, electrodynamics of continuous media, general theory of relativity and gravitation, nonrelativistic quantum mechanics, relativistic quantum mechanics, quantum statistics and kinetics. In addition, it was essential to possess adequate knowledge of mathematical analysis, dif-

ferential equations and the theory of functions of complex variables. The programs of theoretical minimum were worked out meticulously by Landau himself with a view to avoid any overcrowding with superfluous details complicating the task of the examinees. Only the most important topics were selected. The same yardstick was used for mathematics. Landau did not ask for the proofs of various subtle theorems. All that was required was a quick evaluation of integrals, the solution of the basic differential equations, and the application of the theory of functions of a complex variable.

In all, eight examinations had to be taken in various branches of physics, in addition to one in mathematics. A budding scientist after passing the theoretical minimum was taken into Landau's group and could even address him familiarly as 'thou'. Landau assigned a scientific topic to those passing the theoretical minimum. This assignment had to be completed independently without Landau's help, and would eventually form the material for a Ph.D. thesis.

A. S. Kompaneyets and E. M. Lifshitz were the first to have passed theoretical minimum in Kharkov and to become pupils of Landau. The author was the third, and I. Ya. Pomeranchuk the fourth. Laslo Tisza was the fifth to pass the examination. A total of 43 persons passed these tests between 1934 and 1961.

A Faculty of Physics and Mechanics was opened in the Mechanical Engineering and Machine Building Institute in Kharkov, on the lines of the Physics and Engineering Faculty at the Leningrad Polytechnical Institute. The department of physics at this faculty was headed by I. V. Obreimov. Landau headed the chair of theoretical physics at this department. In 1935 he became the head of the department of experimental physics at the Kharkov University. Landau involved the staff of the theoretical physics department headed by him at UPTI in teaching activity. Teaching was an essential part of staff activity and was carried out in rotation, i.e., each member taught different courses in different years. Thus, theoretical physics and general physics were mastered in the best possible way by the young scientists.

Landau attached a lot of importance to the teaching activity, and his teaching methods and programs can truly be called revolutionary. Let us cite a few examples. Before Landau, theoretical mechanics was taught independently of theoretical physics, and in the most archaic manner at that, even without the use of vector algebra. But mechanics, after all, is the very basis of theoretical physics. Hence Landau combined the subject of theoretical mechanics with theoretical physics and made it the first subject that was taught in the general course on theoretical physics. The presentation of theoretical mechanics was based on the variational principle and the introduction of Lagrangian functions. This established a connection with the subsequent sections of theoretical physics and a common approach for understanding theoretical physics as a single entity. Much attention was paid to explain the properties of the space-time symmetry and to force interactions. A book containing problems in mechanics was published, and exercises from this book were solved by the students. Unfortunately, no subsequent editions of the book were published.

The second important reform concerned the presentation of the fundamentals of electricity and magnetism. According to Landau, Einstein's special theory of relativity had to be taught before electrodynamics, and a large number of problems had to be solved before the field theory and Maxwell's electrodynamics could be touched. We shall not go into details of the manner in which other sections of theoretical physics were taught, although many important and interesting steps were taken, especially in the description of quantum mechanics. Let us dwell a little on the teaching of general physics.

Landau himself started teaching general physics to the first-year students at the physics faculty. The subject covered mechanics and molecular physics. A large number of pitfalls still plague these topics. These include the introduction of the concepts of mass and force, the definition of inertial reference systems, Newton's laws, the concept of temperature, irreversibility of thermal phenomena, and the introduction of the concept of entropy. All these concepts were presented in a simple, clear and logical manner by Landau who never used excessive mathematics and avoided the description of experimental details which could only obscure the clear physical picture. The main experiments were demonstrated at the lectures. In Kharkov, this was done by a special assistant. Later, when Landau taught this course at the Moscow State University, the demonstration of the experiments was done by P. L. Kapitza. Thus the course on general physics in Moscow was taught jointly by Landau and Kapitza.

Landau's lectures on general physics at the Kharkov University were so magnificent that they were attended not only by the staff of the theoretical physics department, but also by leading scientists like L. V. Shubnikov, V. S. Gorskii, and L. V. Rozenkevich.

Landau was a great patriot and considered it very important to raise the level of teaching physics in the country. He wanted to enlist in this task the support of higher authorities and requested an audience with N. I. Bukharin, who was a member of the Politbureau of the Central Committee of All-Union Communist Party (Bolsheviks). Bukharin received Landau who was fascinated by the former and even published an article ''Bourgeoisie and Contemporary Physics'' in **Izvestiya** of November 23, 1935. The very title of the paper shows that Landau was devoted to the ideas of socialism, highly valued the scientific contribution of Marx and, like Einstein, held Lenin in great esteem. It is not for nothing that in Copenhagen, Landau was considered at least ''pink'' if not ''red''. He went to Copenhagen on three occasions and returned to his motherland each time. It should be pertinent to mention here that N. I. Bukharin evinced a keen interest in the achievements of physical science when he received Landau, and listened to Gamow's lecture on nuclear power in Leningrad. He even offered Gamow the facility of all electric power stations of Leningrad for one night for experiments on releasing nuclear energy. N. I. Bukharin, the real initiator of thermonuclear research in the USSR, was later executed as an ''enemy of the people''.

Reforms in the teaching of physics hurt the interests of many representatives and professors of the old thought to whom Kapitza referred as ''pompous old academicians'' in his letter to Stalin. Animosity and resentment against Landau

were rising and looking for an opportune moment to surface. Such an opportunity arose after the murder of S. M. Kirov, the Secretary of the Leningrad Regional Party Committee, when Stalin's reign of terror began.

Landau was dismissed from the university in March 1937. The reasons for his dismissal were not mentioned in the order, but it turned out later that Landau was removed due to his propaganda of idealism. Evidently, he was made a victim of slander and denunciation.

As a mark of protest, Shubnikov and other members of the theoretical physics department working at the university tendered their resignation. This was treated as a strike, and the entire group was summoned to Kiev by the minister of higher education V. P. Zatonskii. Discussions with Zatonskii clearly revealed the contents of denunciations against Landau. At the end of the meeting, the minister advised the ''strikers'' to return to their place and continue working. However, Landau returned to his work.

Meanwhile, the atmosphere at the UPTI also started becoming unfavorable for Landau. The leadership of the Institute started giving preference to second-rate works over Landau's outstanding works, and even started dubbing the former as works significant for the defense of the country.

Landau decided to go to Moscow and work with P. L. Kapitza for whom the USSR government had built a new, first-rate institute. In the spring of 1937, Landau finally moved to Moscow and became the head of theoretical division at the Institute of Physical Problems. He remained at this post for the rest of his life. The multifaceted genius of Landau was revealed to the fullest extent at this Institute which became like home for him.

Moving to Moscow was the wisest step taken by Landau, for it saved his life. Stalin's terror had begun and was spreading. Revelling in denunciations and slander, demons unleashed their bloody atrocities, mocking, torturing and killing absolutely innocent people.

At night people feared the arrival of ''ravens'' (special cars for arrested people). Finally they came to the UPTI courtyard also and took away remarkable people and excellent scientists like Shubnikov, Gorskii and Rozenkevich for slaughter. Had Landau remained in Kharkov, he would have inevitably met the same fate as Shubnikov and other friends and would have been executed. The wave of terror engulfed Landau in Moscow only after a year, and he remained alive only owing to Kapitza's intervention.

Among the experimenters at UPTI, Landau was closest to Lev Vasil'evich Shubnikov, one of the most famous and prominent physicists of our time, one who made remarkable discoveries. For example, he discovered that magnetic field cannot penetrate a superconductor, and that the resistance variation of bismuth in a magnetic field is oscillatory in nature. Landau kept himself abreast of all the works of Shubnikov. They discussed scientific problems jointly, and their continued interaction enriched both. After moving to Moscow, Landau interacted with P. L. Kapitza more than any other experimenter. There is no doubt that the brilliant discovery of superfluidity of helium II by Kapitza led to the emergence of an equally brilliant work by Landau on the theory of superfluidity of quantum liquids.

Landau's activity in Moscow was an ''analytical continuation'' of Landau's work in Kharkov, if one may say so. His ideas and plans were the same, but their magnitude and scope grew enormously. It was the same theoretical minimum, the same seminar, the same favorite work, the same task of writing books and papers, and the same connection with experimenters, but all this activity now involved new people not only from Moscow, but from all over the Soviet Union. New brilliant students appeared as well as new remarkable results of Landau's multifaceted genius.

Landau's seminar was transformed into a weekly gathering of physicists in Moscow, which was attended by scientists from Leningrad, Kharkov, Kiev, Tbilisi, and other cities. It was not a simple matter to speak at Landau's seminar since Landau treated the material to be discussed very critically. However, it was always a great honor for a scientist to present the results of his work at the seminar, and Landau's approval was the ultimate praise one could hope for. A situation arose in which Landau became the highest authority for theoretical physicists, and his opinion was the last word not only for young specialists, but for prominent scientists also.

What did Landau achieve? His legacy is enormous and covers literally all branches of theoretical physics.

In quantum mechanics, Landau introduced the density matrix in 1927 independently of von Neuman. This work shows the depth to which the 19-year old youth had grasped the ideas of quantum mechanics.

In 1931, Landau completed a fundamental work together with R. Peierls, analyzing the uncertainty principle in the relativistic region and setting new constraints on the measurement of various dynamic variables.

Landau evinced a very keen interest in the problems of quantum electrodynamics. As early as 1934, he studied the formation of electron-positron pairs during collisions of heavy charged particles. His works on determining the asymptotic forms of the so-called quantum electrodynamic Green's functions appeared in the fifties in coauthorship with A. A. Abrikosov and I. M. Khalatnikov. As a result of these investigations, Landau and Pomeranchuk arrived at the paradoxical conclusion that the real physical charge of the electron must be equal to zero owing to polarization of vacuum (so-called ''nullification of charge'' or ''moscow zero''). The solution of the problem appeared much later following the emergence of non-Abelian gauge field theories, viz., the theory of strong interactions and the theory of electroweak interactions, combining the theories of weak and electromagnetic interactions. Unlike Abelian quantum electrodynamics, these theories also contain the antiscreening effect in addition to the charge screening effect. In the unified theory, antiscreening exceeds screening, which is characteristic only of the Abelian field theory. Hence charge nullification does not occur in real physics. One can only lament over the fact that unification of interaction came much too late for Landau and Pomeranchuk, both of whom having passed away by that time.

Studies of quantum electrodynamics were carried out in full swing in Landau's school in Moscow, Leningrad and Kharkov. However, Landau's interests were not confined to

just these studies. The range and depth of his scientific interests were truly enormous. In our age it is hard, nay, impossible, to find a scientist with such a broad range or, in the language of physics, spectrum of interests. His universalism was truly unique as it was characterized by a rare insight into the essence of physical phenomena.

Landau predicted the existence of neutron stars (pulsars).

Landau created the theory of second-order phase transformations.

He constructed the theory of the intermediate state in superconductors. The Landau-Ginzburg equation has an enormous significance in the theory of superconductivity.

Landau's diamagnetism is quite famous.

Landau constructed the theory of superfluidity and the theory of Fermi liquids.

In the physics of elementary particles, Landau's contribution comes in the form of the two-component neutrino theory and the introduction of the concept of combined parity (independently of Lee and Yang).

Landau proposed a general approach for studying the peculiarities of Feynman diagrams.

Landau made significant contribution to the development of several branches of physics, like plasma physics and the physics of magnetism. But before discussing these subjects, it must be remarked that Landau always found the ''appropriate mathematics'' each time for each work. He had an excellent knowledge of mathematical analysis, but was essentially a pragmatist and did not indulge in profound mathematical theories. He even scoffed such an approach and mentioned that he knew mathematics because he had solved all the problems from the book ''The Ten Sages''. Of course, such a 'philosophy' had to be revised strongly at times. For example, his knowledge of group theory was evidently inadequate, and this became apparent when he created his theory of second-order phase transformations. Luckily for him, N. G. Chebotarev, who was a leading specialist in the subject of algebra, was visiting the Kharkov Mathematical Institute next to UPTI at that time. Landau and Chebotarev played tennis together, and this interaction helped Landau understand the theory of groups which was essential for constructing the theory of phase transformations.

Many mathematical papers by Landau were simply marvelous. For example, he obtained Mellin's transformation and Poisson's sum rules on his own, without knowing about their existence for a long time. Mellin's transformation was necessary for him to solve kinetic equations in the theory of electromagnetic showers constructed by him.

Landau arrived at Poisson's sum rule while constructing the general theory of the de Haas–van Alphen effect. It is significant each new ''conjecture'' was always pertinent to the theory being developed by him.

At the dawn of his career, Landau completed his classical work on the kinetic equation for the Coulomb interaction of particles. In this work, he established the form of the collisions integral in the Coulomb interaction. At the beginning, this work was treated as purely academic research. But as more and more scientists started studying the properties of plasma, plasma physics became one of the most important branches of science, especially in view of the possibility of creation of plasma thermonuclear devices. It was here that scientists recalled Landau's work on the kinetic equations in the Coulomb interaction of particles, and the collision integral came to be known as Landau's collision integral. Without this integral, one cannot solve the relaxation problem in plasma, the problem on the electrical conductivity of plasma, or the problem on plasma heating.

Let us now consider another plasma problem. Collisions of particles are rare in plasma, hence the starting mathematical equation for describing the properties of such a plasma is the kinetic equation that does not take into consideration the collisions between particles, but does include the self-consistent field of particles. This equation was first obtained by A. A. Vlasov and is called Vlasov's equation.

Analyzing the quantum equation of plasma without the collision integral, Landau came to the remarkable conclusion that plasma oscillations will attenuate in spite of the absence ofcollisions. He discovered attenuation of waves which is now called Landau damping.

Magnetism was an old fascination of Landau. During his deputation abroad, he determined the energy spectrum of an electron in a magnetic field (Landau levels) and used it in the problem on the magnetic properties of a free electron gas. He discovered that, in spite of the prevailing opinion, a gas acquires a diamagnetic moment in the quantum theory, which partially neutralizes the so-called Pauli's spin paramagnetic moment. In this connection, an argument arose between Landau and Pauli, and was won by the former.

The most important work by Landau in the field of magnetism concerned the movement of magnetic moment in a ferromagnetic. Together with E. M. Lifshitz, he constructed the equation of motion for the moment. This equation is used widely for studying various processes in magnetically ordered media. It is also especially important for studying oscillatory phenomena in such media.

Landau had an excellent perception of physics associated with magnetism. We can mention, for example, the simplicity and elegance with which he explained the macroscopic nature of Bloch spin waves and how clearly everything fell into place after this.

It should also be mentioned that Landau is the author of the first mathematical theory of the domain structure of ferromagnets.

It is impossible to cover in this brief review the entire scientific legacy of Landau. Speaking of Landau and recalling his famous scientific discoveries, we must compare them with rare and precious stones, which compose a sort of crown over Landau' head. However, there are ''many more smaller diamonds and gems'', as the saying goes from the opera ''Sadko'', ''not counting diamonds in stone caves''. They were also scattered in his encyclopedic course on theoretical physics, in problems contained in this course, in the original derivations by Landau of many laws and relations.

The creation of this course was the task of a lifetime and a matter of pride for Landau. In conformity with Landau's wishes, the course was written in coauthorship with his closest pupil Evgenii Milhailovich Lifshitz. This course is really an epic in the true sense of the word, and theoretical physics has been taught for many decades with the help of these

books all over the world. It can be stated with confidence that students will be using these textbooks not only in the 20th century, but in 21st as well!

Six volumes of the course were published during Landau's lifetime. These include mechanics, statistical physics, field theory, electrodynamics of continuous media, hydrodynamics and the theory of elasticity, and nonrelativistic quantum mechanics. Relativistic quantum mechanics and physical kinetics were published after Landau's death. (These books were written in coauthorship with B. B. Berestetskii and L. P. Pitaevskii.) Landau's course is incredible, for it is hard to imagine how one person could have possessed such a colossal amount of material. These volumes are not only splendid textbooks, but can be compared with Rayleigh's famous ''Papers''. If one starts investigating any specific question pertaining to macrophysics, one must first see what Rayleigh and Landau thought and wrote about it. This is especially true for fluid dynamics and macroscopic electrodynamics.

Landau was fully cognizant of the achievements in modern experimental physics, and this is equally true for the nuclear physics, solid state physics, and the physics of elementary particles. He always listened keenly to the experimenters describing their results. However, as was mentioned above, he was very close to two great masters in experimental physics Lev Vasil'evich Shubnikov and Petr Leonidovich Kapitza. Their experiments inspired Landau, and discussions with Landau helped Shubnikov and Kapitza.

Landau earned worldwide fame after moving to Moscow. He was elected a Member of the USSR Academy of Sciences in 1946. Later he won many orders, including the Order of Lenin twice, and the title of Hero of Socialist Labor. These awards were given not only for purely scientific achievements, but also for his contribution in fulfilling practical assignments of the State. He won three State Awards, and the Lenin Prize in 1962. There was no dearth of honors bestowed on him by other countries also. As early as in 1951, he was elected a member of the Danish Academy of Sciences, and in 1956 he was elected to the Dutch Academy of Science. In 1959, he became a member of the British Physical Society, and an Overseas Member of the Royal Society in 1960. In the same year, he was elected to the National Science Academy, USA, and to the American Academy of Arts and Sciences. Landau won the F. London award (USA) and the Max Planck medal (FRG) in 1960. Finally, he won the Nobel Prize in Physics in 1962 ''for pioneering research in the theory of condensed state of matter, especially liquid helium.''

Muscovites took pride not only in that the city housed the Kremlin, the Tret'yakov Gallery, and the Arts Theater, but also in the fact that Academician Lev Landau lived and worked in Moscow.

Six years after the tragic accident, Landau passed away on April 1, 1968. Scientists as well as people from different walks of life all over the world mourned the death of a genius, the passing away of a great scientist and teacher who left an indelible mark in the history of science and civilization.

Translated by R. S. Wadhwa

International Conferences held to commemorate the 80th birth anniversary of I. M. Lifshitz (1917–1982)

A. M. Kosevich, L. A. Pastur, and V. G. Peschansky

B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of the Ukraine, 310164 Kharkov, Ukraine

The 80th birth anniversary of Il'ya Mikhailovich Lifshitz, a leading scientist who made an enormous contribution to the development of physical science and founded a large school of theoretical physics, fell on January 13, 1997.

International conferences were held in many countries to commemorate the jubilee of Prof. I. M. Lifshitz.

A conference on statistical physics dedicated to the memory of I. M. Lifshitz was held in the Rutgers University, New Jersey, USA on December 15 and 16, 1996. The memorial part of the conference was organized by J. Lebowitz, a Professor at this University and Editor-in-Chief of the **Journal of Statistical Physics**, who is well known for his work in various branches of mathematical and theoretical physics of the condensed state. Professor Lebowitz is an old admirer of the scientific works of Il'ya Mikhailovich. It was he who organized in 1986 a special issue of the **Journal of Statistical Physics** to commemorate the 70th birth anniversary of I. M. Lifshitz (unfortunately, none of the journals published in the Soviet Union could bring out such a special issue).

The USA event was held as a regular conference on statistical physics, which has been organized with notable enviable success by Prof. Lebowitz twice every year for many years now. A. G. Grosberg and Ya. G. Sinai also actively participated in the organization of the conference. This conference was undoubtedly one of the best in the series both as regards the scientific level and the number of participants who represented a wide geographical affiliation: USA, Russia, Ukraine, England, Germany, France, Poland, Switzerland, Brazil, and Mexico. The largest number of participants came from the USA, but at least one third of them were representatives from the former Soviet Union. Hence although English was naturally the working language of the conference, the language behind the scenes was mainly Russian. A running joke among the non-Russian-speaking participants was requesting permission from the audience to speak in English.

The scientific program of the conference, in keeping with the established tradition, consisted of 20-minute talks and five-minute reports (about 80 in all were presented at the conference) connected directly or indirectly with the scientific activity of Il'ya Mikhailovich. Hence it is not surprising that the range of the topics covered at the conference was very broad, and even touched such fine aspects as the biochemical evolution, which was the subject of the lecture delivered by the Nobel laureate P. W. Anderson.

A memorial session to I. M. Lifshitz was held on the first evening of the conference under the chairmanship of Ya. G. Sinai. Zoya Ivanovna, widow of I. M. Lifshitz, took part in the meeting. The meeting aroused considerable interest among the participants, many of whom know Il'ya Mikhailovich only through his work and were never acquainted personally with him. The colleagues and friends of Il'ya Mikhailovich participating in the conference spoke warmly about his remarkable human qualities.

The conference was divided into 12 sessions spread over three days, starting at 9 A.M. and running till late evening.

The following 20-minute reports were presented at the conference:

M. Grinfeld (Educational Testing Service, Princeton, USA): ''I. M. Lifshitz' Results in Continuum Theory of Phase Transformation in Solids'';

I. Erukhimovich (Moscow State University, Russia): ''Sol–Gel Transitions in Weak Gels as a Genuine Phase Transition Due to Spontaneous Breaking of Monomers' Identity'';

O. Penrose (Heriot-Watt University): ''On the Lifshitz–Slyosov Theory of Coarsening in Alloys'';

M. Marder (University of Texas, USA): ''Statistical Mechanics of Cracks'';

A. Bertozzi (Duke University, USA): ''Singularities in Long Wave Unstable Interface Equations'';

L. Pastur (Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine): ''Localization of Surface Waves: An Exactly Soluble Model'' and ''Some Remarks About the Work of A. Slutskin'';

I. M. Khalatnikov (Tel-Aviv University, Israel and L. D. Landau Institute for Theoretical Physics, Moscow, Russia): ''Chaos in Cosmology'';

A. Abrikosov (Argonne National Laboratory, USA): ''Lifshitz Resonant Tunneling as the Mechanism of c-Axis Transport in High-Temperature Superconductors'';

L. Gorkov (Florida State University, USA and L. D. Landau Institute for Theoretical Physics, Moscow, Russia): ''Lifshitz-Kosevich Oscillations in Superconductors at Fields Well Below H_{c2}'';

A. F. Andreev (P. L. Kapitza Institute for Physical Problems, Moscow, Russia): ''Bose-Condensation and Superconductivity in Mesoscopic Systems: Spontaneous Violations of Homogeneity of Time'';

H. Saleur (University of Southern California, USA): ''Exact Correlations and Transport Properties in Quantum Impurity Problems'';

R. Shankar (Yale University, USA): ''Renormalization Group for Fermions: An Introduction'':

E. Brezin (ENS): ''Random Matrices: From $2D$ Quantum Gravity to Disordered Systems'';

J. L. Birman (CUNY, USA): ''Random Matrix Theory of Impurity-Band Tails: An Old Problem Revisited'';

S. Nechaev (L. D. Landau Institute for Theoretical Physics, Moscow, Russia): ''Random Matrix Approach for Words Enumeration in the Braid Groups'';

A. A. Chernov (Universities Space Research Association, USA): ''Growth Induced Imperfections in Protein Crystals'';

A. Khokhlov (Moscow State University, Russia): ''Statistical Mechanics of Ion-Containing Polymers'';

S. Obukhov (University of Florida, USA): ''Long-range Forces in a Polymer Melt: Polymer-Magnet Analogy'';

G. Zaslavsky (NYU, USA): ''Renormalization Approach to the Kinetic Description of Chaotic Dynamics'';

Ya. Sinai (Princeton University, USA): ''On the Distribution of Maximum of Fractal Brownian Motion'';

P. W. Anderson (Princeton University, USA): ''Some Thoughts on the Evolution of Independent Entities'';

C. Tang (NEC, USA): ''Why Do Proteins Look Like Proteins?'';

E. Shakhovich (Harvard University, USA): ''Statistical Mechanics of Protein Folding, Design and Evolution'';

D. Thirumalai (University of Maryland, USA): ''Cellular Protein Folding: How Nature Beats Topological Frustration'';

M. Hecht (Princeton University, USA): ''Combinatorial Methods for Protein Design: Novel Proteins by the Dozen'';

K. Dill (University of California, San Francisco, USA): ''Partition Functions of Bimolecules and Other Compact Polymers'';

A. Grosberg (MIT, USA): ''Thermodynamics Versus Kinetics in Protein Folding'';

M. Frank-Kamenetskii (Boston University): ''Specificity and Affinity of Bimolecular Interactions'';

M. Kardar (MIT, USA): ''Conformations of Charged Heteropolymers'';

V. Pande (UC Berkeley, USA): ''Freezing Transitions of Compact Polyampholytes'';

D. Torney (Los Alamos National Laboratory, USA): ''Spectral Analysis of Biological Sequences'';

E. Siggia (Cornell University, USA): ''Physics from Jelly Fish'';

S. Fraden (Brandeis University, USA): ''Modelling Cellular Guts With Colloidal Soups'';

M. Cieplak (Polish Academy of Sciences, Poland): ''Cell Dynamics of Model Proteins'';

A. Stasiak (Lausanne, Switzerland): ''Ideal Geometric Forms of Knots and Equilibrium Trajectories of Knotted Polymers'';

MEMORIAL SESSION TO I. M. LIFSHITZ

Ya. Sinai, Chair, ''The Life and Scientific Work of Ilya Lifshitz''

A. Grosberg, I. M. Khalatnikov, L. A. Pastur, A. A. Abrikosov, L. P. Gorkov, A. F. Andreev, A. A. Chernov, J. Birman, J. Lebowitz, and Mrs. Zoya Lifshitz.

INFORMAL SESSION

C. Doering, Co-chair, ''What Can Mathematics and Physics Contribute to Biology at the Present Time?''

C. Peskin (Courant Institute, NYU, USA): ''Random Walks on Microtubules'';

A. Libshaber (Rockefeller University, USA): ''DNA and Recognition'';

A. Parsegian (NIH, USA): ''Harnessing the Hubris: a Wishlist of Useful Things Physicists Can Do in Biology.''

An international conference dedicated to the 80th birth anniversary of Academician I. M. Lifshitz was held at the Kharkov University from 21st to 23rd January, 1997. After the welcoming address by V. V. Ul'yanov, Chairman of the Organizing Committee, A. M. Kosevich, L. A. Pastur, V. G. Peschansky, V. V. Slezov, and A. A. Slutskin reminisced about their dearest teacher Il'ya Mikhailovich. This was followed by scientific papers. The organizing committee members (N. T. Gladkikh, A. M. Ermolaev, V. V. Ul'yanov) did not do any pruning of the papers submitted by the contributors and allowed all those desiring to honor the memory of the outstanding scientist I. M. Lifshitz who had worked for many years at the Kharkov Physicotechnical Institute and Kharkov University. Il'ya Mikhailovich founded the department of Theoretical Physics at the Kharkov State University and was its chairman until he moved to Moscow. As a result, about 200 papers were presented at the conference. About a third of them were read as ten-minute reports while the remaining ones were presented at poster sessions.

The topics of the papers presented at the conference were quite diverse, and included the theory of the condensed state, low-dimensional systems and superconductivity, including high-temperature superconductivity, solid state spectroscopy, magnetic properties of the condensed media, mass transport in real crystals, relaxation phenomena in solids, plasticity and strength, localization effects, photo-induced effects in light-sensitive layers, surface phenomena and phase transitions in thin films, low-temperature materials science, etc.

The conference turned out to be quite fruitful and facilitated a closer cooperation between researchers working in fields bordering on theoretical and experimental physics. It is hard to name all the interesting papers presented at the conference. We shall mention only those relating mainly to the low-temperature physics and theoretical physics:

M. Ya. Azbel (Harvard University, Cambridge, USA, and Tel Aviv University, Israel): ''Transport in $2D$ Systems'';

M. I. Kaganov (Belmont, USA): ''Local Geometry of the Fermi Surface and High-Frequency Properties of Metals'';

A. M. Kosevich, E. S. Syrkin, and A. V. Tutov (Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine): ''Surface Shear Waves in FCC Crystals'';

M. M. Bogdan, I. V. Gerasimchuk, and A. S. Kovalev (Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine): ''Dynamics and Stability of Localized Modes in Nonlinear Media with Point Defects'';

V. G. Peschansky (Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine) and D. I. Stepanenko (Kharkov State University, Ukraine): ''Nonlinear Magnetohydrodynamic Waves in Compensated Metals'';

T. N. Antsygina, L. A. Pastur, and V. A. Slyusarev (Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine): ''On the Self-consistent Localization Theory'';

I. V. Krasovskii (Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine) and V. I. Peresada (Kharkov State University, Ukraine): ''Spectral Density of a Periodic Jacobi Matrix'';

V. Ya. Maleev (Institute of Radioengineering and Electronics, Kharkov, Ukraine): ''Physics of Structural Transformations in the system DNA-Water'';

V. V. Slezov (Physicotechnical Institute, Kharkov, Ukraine) and O. A. Osmaev (Kharkov State University, Ukraine): ''Impurity Segregation in Grain Boundaries of Polycrystals'';

A. M. Ermolaev, N. V. Gleizer, and N. V. Ul'yanov (Kharkov State University, Ukraine): ''Quantum Spin Excitations in Normal Metals with Resonance Electron States in a Magnetic Field'';

V. V. Ul'yanov, O. V. Zaslavskii, and Yu. V. Vasilevskaya (Kharkov State University, Ukraine): ''Quantum Spin Systems: New Methods and Exactly Solvable Potential Models'';

G. Gonsalez de la Cruz and Yu. G. Gurevich (Center for Research and Advanced Educational Techniques, Mexico), and O. I. Lyubimov (Kharkov State University): ''Transient Thermoelectric Phenomena in Semiconductors'';

Kh. B. Chashka, M. A. Obolenskii, V. A. Bychko, R. A. Hasan, V. I. Beletskii (Kharkov State University), A. V. Basteev and A. N. Prognimak (Institute for Machine-Building Problems, Kharkov): ''Electrophysical Properties of Quasi-One-Dimensional Metal-Hydrogen System'';

S. A. Gredeskul, M. Zusman, Y. Avishai (Ben Gurion University, Israel) and M. Ya. Azbel': ''Electron Localization in Two-Dimensional System with Point Scatterers in a Magnetic Field'';

O. Galbova and G. Ivanovsky (Skopje, Macedonia), O. V. Kirichenko and V. G. Peschansky (Institute for Low Temperature Physics and Engineering, Kharkov): ''Acoustic Transparency of Layered Conductors'';

E. V. Bezuglyi, N. G. Burma, A. L. Gaiduk, I. G. Kolobov, and V. D. Fil' (Institute for Low Temperature Physics and Engineering, Kharkov) and van Kempen (Univ. of Nijmegen, Netherlands): ''Electron Relaxation Rate in Al'';

A. S. Bakai (Physicotechnical Institute, Kharkov), V. Z. Bengus, and E. D.Tabachnikova (Institute for Low Temperature Physics and Engineering, Kharkov): ''Microscopic Mechanism of the Effect of Topological and Chemical Order in Metal Glasses on Resistance to Plastic Shear'';

V. D. Natsik and S. N. Smirnov (Institute for Low Temperature Physics and Engineering, Kharkov): ''Electron States and Elastic Waves in a Crystal with a Disclination'';

V. V. Pustovalov (Institute for Low Temperature Physics and Engineering, Kharkov): ''Effect of Superconducting Transition on Low-Temperature Jumplike Deformation of Metals and Alloys'';

V. V. Eremenko, V. A. Sirenko, and V. V. Bruk (Institute for Low Temperature Physics and Engineering, Kharkov): ''Magnetostriction in Superconductors'';

E. E. Semenenko and V. I. Tutov (Physicotechnical Institute, Kharkov) ''Superconductivity of Beryllium Films Deposited on a Hot Substrate'';

E. Ya. Rudavskii, I. A. Usherov-Marshak, V. K. Chagovets, and G. A. Sheshin (Institute for Low Temperature Physics and Engineering, Kharkov): ''Kinetics of Nucleation and Stratification of ^{3}He–^{4}He Superfluid Solutions. Formation of the Metastable Phase'';

I. N. Adamenko, A. V. Zhukov, and K. E. Nemchenko (Kharkov State University): ''Thermal Conductivity of Solids and Quantum Liquids Associated With the Flow and Diffusion of Thermal Excitations'';

D. V. Abraimov, A. B. Verkin, A. Yu. Kolesnichenko, A. V. Khotkevich, and V. V.Khotkevich (Institute for Low Temperature Physics and Engineering, Kharkov): ''Point-Contact Spectroscopy of Electron–Phonon Interaction in Zirconium'';

E. N. Khats'ko, A. S. Chernyi, and A. I. Kaplienko (Institute for Low Temperature Physics and Engineering, Kharkov) and V. P. D'yakonov (Physicotechnical Institute, Donetsk): ''Low-Temperature Magnetic Properties of $KDy(WO_4)_2$'';

L. T. Tsymbal and A. N. Cherkasov (Physicotechnical Institute, Donetsk): ''Suppression of Deformation and Induction Interactions of Electron and Ionic Subsystems in Compensated Metals'';

A. G. Belov, G. M. Gorbulin, I. Ya. Fugol', and E. M. Yurtaeva (Institute for Low Temperature Physics and Engineering, Kharkov): ''Spectroscopic Evidence of Electron Localization in Neon Cryocrystals.''

The Russian Academy of Sciences and the Moscow State University where Il'ya Mikhailovich taught during the last 18 years of his life organized an international conference on ''Problems in the Theory of Condensed State'' in Moscow on June 1–4, 1997. This conference attracted not only numerous pupils of Il'ya Mikhailovich, but also scientists who have actively continued the trends of theoretical physics initiated by him. These include the electron theory of metals with an arbitrary form of the electron energy spectrum, theory of disordered media, and the peculiar approach adopted by I. M. Lifshitz towards the polymer physics. The Organizing Committee headed by Yu. M. Kagan and A. R. Khokhlov invited several leading scientists from USA, England, Germany, Italy, France, Japan and Israel to participate in the Conference. Research centers from Russia and Ukraine were also amply represented. English and Russian were working languages of the conference. In his introductory remarks, Yu. M. Kagan described the remarkable achievements of I. M. Lifshitz in the theory of condensed state, touched upon the most important results obtained by him in the solid state theory and polymer physics.

M. V. Sadovnichii, the Rector of the Moscow State University, emphasized the role of Il'ya Mikhailovich as an outstanding professor who made a tremendous contribution in

preparing the scientific personnel at the Physics Faculty and helped in building the reputation and image of the Moscow University. He mentioned the brilliant knowledge of the mathematical apparatus which Prof. Lifshitz used successfully in solving various physical problems. Thanks to I. M. Lifshitz, an active cooperation grew between physicists well-versed in the modern mathematical apparatus, and mathematicians interested in physical problems. A brilliant example of such cooperation and interaction were the papers presented by the mathematicians S. P. Novikov and Ya. G. Sinai. Lifshitz' ideas in studying the topological structure of the electron energy spectrum of metals were realized in Novikov's paper in the form of elegant and rigorous mathematical theorems.

A. F. Andreev, Vice-President of the Russian Academy of Sciences, referred to the role played by Il'ya Mikhailovich in the development of research activity at the Institute of Physical Problems, in which he succeeded L. D. Landau in 1968 as the Head of the Theoretical Physics Division at the invitation of P. L. Kapitza.

The scientific level of the conference was very high and probably matched the level of the remarkable First International Conference on Solid State Theory organized by Prof. Lifshitz in 1963. The following list of the oral papers presented at the conference devoted to I. M. Lifshitz should provide an idea about the participants and the wide range of the problems discussed there:

B. I. Halperin (Harvard University, USA): ''Quantum Hall Effect: The State of the Art'';

A. I. Larkin (L. D. Landau Institute for Theoretical Physics, Moscow, Russia): ''Divergence of Classical Trajectories and Quantum Chaos'';

P. Fulde (Max-Planck Institut für Physik Komplexer Systeme, Dresden, Germany): ''Crystallization of Electrons'';

A. A. Slutskin (Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine): '' 'Frozen' Electron Phase and Electron Glass in Narrow-Band Conductors'';

V. G. Peschansky (Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine): ''On Galvanomagnetic Phenomena in Layered Conductors'';

M. I. Tribelsky (University of Tokyo, Japan): ''Symmetry and Direct Transition 'Rest State-Turbulence' in Dissipative Systems'';

V. Ya. Demikhovskii and D. I. Kamenev (Nizhny Novgorod State University, Russia): ''Quantum Chaos in Degenerate Hamiltonian System'';

A. V. Dmitriev and A. B. Evlyukhin (Moscow State University, Russia): ''High Electric Field Transport and Breakdown in a Semiconductor with an Impurity Band'';

S. V. Novikov and A. Ya. Maltsev (Landau Institute for Theoretical Physics, Moscow, Russia): ''Ideas of I. M. Lifshitz and Topological Phenomena in Normal Metals'';

C. Castellani, C. Di Castro, and M. Grilli (Universita di Roma ''La Sapienza,'' Italy): ''Non-Fermi Liquid Behavior and d-Wave Superconductivity near the Charge-Density-Wave Quantum Critical Point'';

M. Springford (N. H. Wills Physics Laboratory, University of Bristol, USA) and A. Wasserman (Oregon State University, Corvallis, Oregon, USA): ''Quantum Oscillations in Interacting Systems'';

V. P. Mineev and M. G. Vavilov (Landau Institute for Theoretical Physics, Moscow, Russia): ''De Haas-van Alphen Effect in Superconductors'';

A. M. Dykhne (TRINITI) and I. M. Kaganova (Institute for High Pressure Physics, Troitsk, Russia): ''Absorption of Electromagnetic Waves by a Conductor with Small-Scale Inhomogeneities'';

J. L. Birman (City College of Cuny, N.Y., USA): ''Random Matrix Theory: Impurity Band Tails and Mean-Field Approximations'';

Ya. G. Sinai: ''Stationary Distributions for Burgers Equation with Random Forcing'';

A. A. Chernov: ''Formation and Perfection of Protein Crystals'';

S. A. Gredeskul, M. Zusman, Y. Avishai (Ben-Gurion University of the Negev, Beer Sheva, Israel), and M. Ya. Azbel' (Tel Aviv University, Israel): ''Spectral Properties and Localization of an Electron in a $2D$ System with Point Scatterers in a Magnetic Field'';

M. V. Feigel'man and M. A. Skvortsov (Landau Institute for Theoretical Physics, Moscow, Russia): ''Statistics of Electron Levels in the Vortex and Low-Temperature Dissipation'';

A. M. Kosevich (Institute for Low Temperature Physics and Engineering, Kharkov, Ukraine): ''Geometry of the Fermi Surface and Localized Electron States at the Free Surface of a Metal'';

A. F. Andreev (P. L. Kapitza Institute for Physical Problems, Moscow, Russia): ''Bose-Condensation and Superconductivity in Mesoscopic Systems'';

L. P. Pitaevskii (P. L. Kapitza Institute for Physical Problems, Moscow, Russia, and Department of Physics, Technion, Haifa, Israel): ''Phenomenological Theory of Mode Collapse-Revival in Confined Bose Gas'';

L. V. Keldysh (P. N. Lebedev Physics Institute, Moscow, Russia): ''The Nonlinear Optical Response of Excitons in Semiconductors''

V. V. Slesov (Kharkov Institute of Physics and Technlology, Ukraine): ''Kinetics of the First Kind Phase Transitions in Solid Solutions'';

I. P. Ipatova and V. A. Shchukin (A. F. Ioffe Physicotechnical Institute, St. Petersburg, Russia): ''Compositon Domains in Films of Semiconductor Alloys'';

V. B. Shikin and Yu. V. Shikina (Institute of Solid State Physics and Institute of Microelectronics Technology, Chernogolovka, Russia): ''Role of Initial Conditions in the Development of Spinodal Decomposition'';

I. M. Suslov (P. L. Kapitza Institute for Physical Problems, Moscow, Russia): ''Density of States of a Disordered System Near the Mobility Edge in $(4-\varepsilon)$ Dimensions'';

A. Grosberg (MIT, USA): ''Statistical Mechanics of Disordered Polymers and the Protein Folding Problem'';

A. J. Libshaber (Rockefeller University, New York, USA): ''DNA and Information: An Experiment on Kinetics of Search and Error Detection'';

K. Yoshikawa (Nagoya University, Japan): ''Hierarchy in Coil-Globule Transition of DNA Chains'';

T. M. Birstein, L. I. Klushin, and A. A. Mercurieva (Institute of Macromolecular Compounds, St. Petersburg, Russia): ''Regular and Singular Phase Diagrams for Polymeric Brushes with Liquid-Crystalline Ordering'';

I. Ya. Erukhimovich (Moscow State University, Russia): ''Sol-Gel Transition in Weak Gels as Spontaneous Breaking of the Monomer Identity: The Infinite Cluster Structure, Phase Diagrams and Scattering'';

E. Raphael (Laboratorie de Physique de la Matiere Condense U. R. A. C. N. R. S., College de France, Paris, Cedex): ''Adhesion of Elastomers'';

S. I. Kuchanov (M. V. Keldysh Institute of Applied Mathematics, Moscow, Russia) and S.V. Panyukov (P. N. Lebedev Physics Institute, Moscow, Russia): ''The Lifshitz Entropy in Statistical Physics of Heteropolymers'';

M. Rubinstein and A. V. Dobrynin (University of North Carolina, Chapel Hill, USA) and S. P. Obukhov (University of Florida, Gainesville, USA): ''Cascade of Transitions of Polyelectrolytes in Poor Solvents'';

A. N. Semenov (University of Leeds, UK): ''Polymer Interfaces and Adsorbed Layers: the Effect of Chain Ends'';

S. Lustig (Du Pont Central Research Experimental Station, Wilmington, Denmark): ''Solvent Transport in Polymers'';

A. R. Khokhlov (Moscow State University, Russia) and P. G. Khalatur (Tver' State University, Tver', Russia): ''Protein-like Copolymers: Computer Simulation.''

Another 72 reports were presented in two poster sessions. In addition to the sessions devoted to scientific works, a memorial session was held, in which M. I. Kaganov, A. F. Andreev, L. P. Pitaevskii, Ya. G. Sinai, and A. G. Grosberg reminisced about Il'ya Mikhailovich Lifshitz, an outstanding scientist, a talented teacher, and a charming person. At all three conferences commemorating the jubilee of I. M. Lifshitz, it was noted regretfully that a remarkable scientist and a gifted person, who earned the affection of all those who had the fortune to come in contact with him, had left us too early.

Correlation of the properties of high-T_c superconductor La$_{2-x}$Sr$_x$CuO$_4$ and anharmonicity of atomic potentials

V. G. Chudinov, A. G. Chirkov, and R. R. Nurgayanov

Physicotechnical Institute, Ural Branch of the Russian Academy of Sciences, 426001 Izhevsk, Russia*

The molecular dynamics method is applied to the La$_{2-x}$Sr$_x$CuO$_4$ system to prove that canonicity conditions are violated in the case of a large contribution of anharmonism. This can lead to the formation of ''hot'' regions ~ 0.5 nm in the vicinity of Sr impurity atoms with an average kinetic energy two or three orders of magnitude higher than in the matrix even at low temperatures. The matrix is ''effectively'' cooled and can basically carry superconducting current due to percolation for any electron pairing mechanism. The velocity distribution is described by not one but at least two Maxwell functions. The fcc lattice of Ni near the phase-transition point also acquires ''hot'' spots which are not, however, localized in space, but migrate (with a lifetime $\sim 10^{-12}$ s) and have a much smaller difference in kinetic energies (by a factor of 1.5–2.0). At low temperatures, canonicity conditions are always satisfied. © *1998 American Institute of Physics.* [S1063-777X(98)00301-6]

1. Sievers and Takeno[1] proved in 1988 that localized low- or high-frequency oscillations can be excited in homogeneous lattices in the case of a large contribution of anharmonism (depending on its sign). Burlakov *et al.*[2] discovered that these oscillations are genetically connected with envelope solitons, and no complete thermalization is observed. In the framework of local anharmonism, it was established[3] that either local ''cold'' or local ''hot'' regions can be formed near defects. It was assumed that anharmonic oscillators (system) were in equilibrium with the phonon field (reservoir). The hypothesis on microscopic ''hot'' spots was also put forth in attempts made to explain ''cold'' thermonuclear reaction.[4] Localization of kinetic energy was discovered in Ref. 5 by using the molecular dynamics method in the strongly anharmonic anisotropic system La$_{2-x}$Sr$_x$CuO$_4$ in the vicinity of Sr impurity atoms. However, the influence of this phenomenon on the physical nature of high-temperature superconductivity is not completely clear. The quasi-harmonic approximation[3] with a small contribution of anharmonism, which is normally used, might turn out to be inapplicable in this case.

2. In this research, we analyze the effect of the noncanonicity of the system on its dynamic properties. We shall estimate the extent of noncanonicity by the deviation from the ideal Maxwell velocity distribution for a given average kinetic energy of atoms.

Special attention was paid to the attainment of equilibrium by the system, which set in over 10–20 periods of oscillations with the relaxation time τ_r. To within the accuracy of our computer experiment, equilibrium is reached over a time $\sim 5 \times 10^{-11}$ s, i.e., $\sim 10 \tau_r$. For τ_r we take the time after which the state of the system becomes independent of the initial conditions. The effect of the crystallite geo-

metrical parameters was also verified and was eliminated to within the experimental error.

It follows from fundamental principles that the basic laws of thermodynamics can be observed only in canonical systems.[6,7] Normally, systems that are not closed are regarded as noncanonical.[8,9] It has been proved, however, that only a very small number of systems satisfy the canonicity conditions rigorously. An example of such a system is an ideal gas in which atoms interact according to the laws for perfectly rigid spheres[7] or a gas with the potential energy of repulsion $\sim A/r^n (n > 4)$.[10] In condensed media, the problem boils down to an analysis of a gas of quasiparticles (phonons), but the phonon gas can be regarded as ideal only in the harmonic approximation. If we take anharmonism into consideration, the system is in general not canonical, and the emergence of soliton-like excitations becomes possible. Such excitations have solutions only in special cases, which lead to results that are not typical of static thermodynamics, i.e., local energy and concentration distributions, heat transfer, and so on.

Simulation was carried out by the molecular dynamics method according to the program specially oriented to HTS materials with interatomic interaction potential calculated in Ref. 11 for the compound La$_{2-x}$Sr$_x$CuO$_4$. The crystallite consisted of ~ 2000 atoms (in two stationary La(Sr)–O layers and a layer of mobile CuO$_2$ atoms). We used cyclic boundary conditions along the directions a and b and attained relaxation times $\sim 10^{-10}$ s by using $\sim 10^6$ iterations. The same but randomly directed velocities were imparted to all atoms at the initial moment, and then the system was brought to equilibrium.

3. By way of an example, Fig. 1 shows equilibrium velocity distributions for oxygen atoms in the La$_{2-x}$Sr$_x$CuO$_4$ system for various values of x (compounds with $x = 0$ and
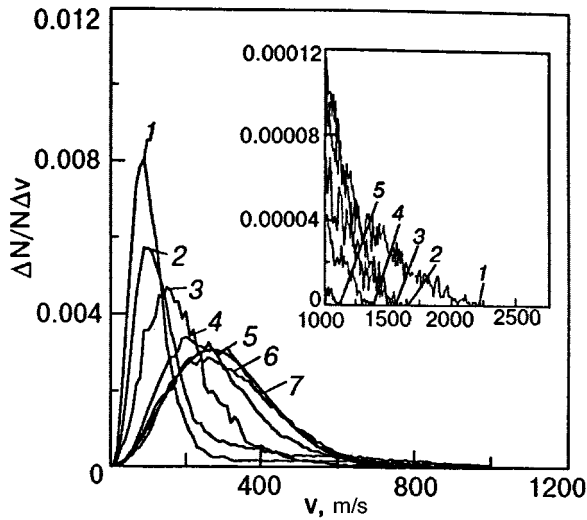
FIG. 1. Velocity distribution in $La_{2-x}Sr_xCuO_4$ for average kinetic energy 70 K for various Sr concentrations x: 0.17 (curve *1*), 0.25 (curve *2*), 0.12 (curve *3*), 0.08 (curve *4*), 0.03 (curve *5*), and 0 (curve *6*); curve *7* corresponds to Maxwell's distribution at $T = 70$ K.

FIG. 2. Velocity distribution near the melting point of nickel at $T = 930$ K: experimental distribution (curve *1*) and theoretical curve (*2*). The best description is obtained at $T_1 = 910$ K with the weight contribution 0.97 and $T_2 = 1610$ K with the weight contribution 0.03.

$x > 0.17$ are model compounds). The maximum deviations from the Maxwell distribution are observed for $x = 0.17$. It should be noted that the dependence of the superconducting transition temperature on the Sr concentration is parabolic with the peak at $x = 0.17$, and the system is superconducting in the concentration range $x = 0.05 - 0.25$.

The experimental curve was fitted by four Maxwell distribution functions with $T_1 = 9$ K, $T_2 = 11$ K, $T_3 = 400$ K, and $T_4 = 900$ K with the weight contributions of 0.75, 0.1, 0.1, and 0.05 respectively. Virtually all highenergy distributions are created by oxygen atoms of the CuO_2 layer, which are localized near Sr impurity atoms. Their average energy is approximately 100 times higher than the average energy of matrix atoms. A much weaker effect is observed in extreme model cases for $x = 0$ and 2, when the contribution of anharmonism in the system is significant, but systems are homogeneous. The velocity distribution differs from the Maxwell distribution less strongly: $T_1 = 50$ K, $T_2 = 110$ K, and the weight contributions are 0.55 and 0.45, while $T_1 = 40$ K, $T_2 = 120$ K, and the weight contributions are 0.5 and 0.5, respectively. For other concentrations, the situation is intermediate. It should be noted that no local oscillations are observed for $x = 0$, while for $x = 2$ they have the form of migrating excitations of the soliton type. Spatial localization of kinetic energy is of the same type, but only at each specific instant of time. In linear systems, such a situation is well known from theoretical publications as well as from computer experiments.[12]

In addition, we made test calculations for γ-Ni at $T = 300$ K (solid state, small contribution of anharmonism) and in the premelting region $T \geqslant 1300$ K (strong anharmonism). In the former case, no difference between the theoretical and calculated dependences of velocity distribution was observed to within experimental error even for a time $\sim 10^{-12}$ s. However, detailed analysis shows that in the latter case at least two distributions are required (with $T_1 = 910$ K and $T_2 = 1610$ K with the weight factors 0.97 and
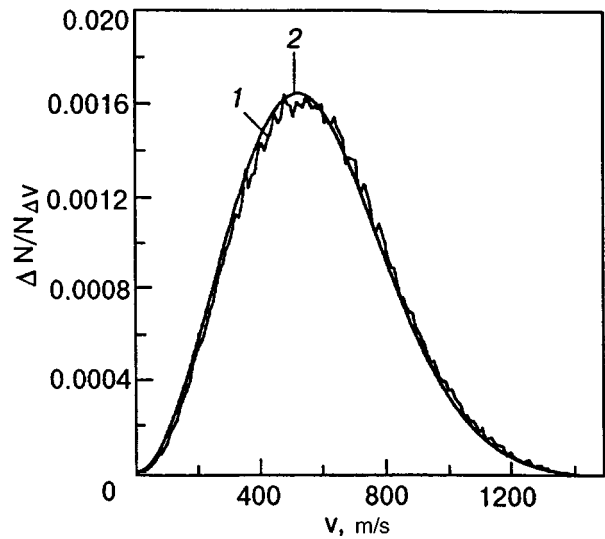
0.03, respectively) (Fig. 2). Naturally, the difference is much smaller than for $La_{2-x}Sr_xCuO_4$, but is still significant. In the theory of liquid and amorphous states, the hypothesis concerning the inhomogeneity of these media was put forth long ago.[13] For example, "hot" spots can be responsible for these effects. A similar situation was observed by us in the amorphous alloy $Ni_{80}Zr_{20}$.[14]

It is quite possible that the violation of canonical conditions can lead to the emergence of "hot" spots at which a thermonuclear reaction can be realized (the temperature of the body $\sim 10^3$ K, while at "hot" spots it can be $\sim 10^5$ K, and the probability of such a reaction is high at $\sim 10^7$ K). This hypothesis was discussed in detail by Tsarev.[15] At any rate correlations are observed, for example, for the systems Pd–D and $YBa_2Cu_3O_7$–D with a strong anharmonism.

4. Thus, it is shown for the systems $La_{2-x}SrCuO_4$ and Ni that static and dynamic inhomogeneities in which the velocity distributions can be described by a set of Maxwell functions at various temperatures can emerge in condensed media with a strong anharmonism due to violation of canonical conditions. The superconducting transition temperature correlates with the extent of deviation from canonicity.

*E-mail: chud@fti.udmurtia.su

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