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On the Calculation of Some Vacancy

Parameters In fcc Materials

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ABSTRACT

The melting point concentration $(n/N)_{mp}$ of monovacancies in fcc metals has been calculated from thermodynamic considerations. A unique result of $(n/N)_{mp} = 5.47 \times 10^{-4}$ for all fcc metals is obtained and compared with the best experimental (extrapolated) results of 1.5×10^{-4} for Pb to 9.0×10^{-4} for Al. The concentration at temperature T (below the melting point) is given by $(n/N)_T = 5.47 \times 10^{-4} \, e^{-E_f(1-T/T_m)/kT}$ where E_f is the energy of formation, k is the Boltzman's constant and T_m is the absolute melting temperature. The Gibbs free energy of vacancy formation at the melting point is found to be $(G)_{T_m} = 7.508 \, kT_m$. A method for calculating the vibrational entropy S_v is shown. S_v/k for Al, Au, Ag, Cu and Pb is calculated to be 2.34, 3.00, 1.84, 1.61 and 2.11 respectively. The formation energy of vacancies can be calculated from the free energy of formation and the vibrational entropy. The formation energies thus calculated for Al, Au, Ag, Cu and Pb are 0.78, 1.20, 0.99, 1.07 and 0.50 electron volts respectively. The ratio of the vacancy volume to the atomic volume at the melting temperature is also calculated. These values are 0.47, 0.46, 0.31, 0.33 and 0.34 for Al, Au, Ag, Cu and Pb respectively.

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I. INTRODUCTION

In recent years the study of point defects in pure metals[1-10], as well as in alloys[11-13], has been a major topic of both experimental and theoretical research in solid state physics and in metallurgy. It has been shown[2-5], at least in fcc metals, monovacancies are predominant at high temperatures. Equilibrium concentration of monovacancies at high temperatures approaching the melting points of Ag, Al, Cu, and Pb has been measured[2-5]. The formation energies of such vacancies (henceforth vacancy will mean monovacancy) has been determined quite accurately for the above mentioned fcc metals. The energy of formation, perhaps, is the easier of the quantities to be determined experimentally. Formation energies obtained from relatively simple quenching experiments compare favorably with the results obtained from the more complicated equilibrium lattice parameter and length change measurements[9]. Moreover the experimentally determined energy of formation E_f and the energy of motion E_m add up to the corresponding activation energy of self diffusion, thereby reassuring the experimental accuracy[9]. Also if the values of the vibrational entropy S_v, which in most of the previous equilibrium measurements had to be assumed were 50% off, the effect on the activating energy of vacancy formation will still be negligible[6,14].

On the other hand the vibrational entropy associated with a vacancy formation can not be determined directly from the equilibrium measurements[2-6]. In the case of quenching experiments, the determination of vibrational entropy S_v requires an extrapolation of

experimental data to $1/T_Q=0$ (where T_Q is the absolute quenching temperature), and such an extrapolation introduces an element of uncertainty in the calculated values of the entropy of formation[13]. Attempts have also been made to theoretically calculate the vibrational entropy of lattice defects by several authors[15-19]. But such theoretical results, as have been pointed out by Huntington et al.[16], is nothing more than an order of magnitude approximation.

Perhaps the most meaningful of the experimentally determined quantities is the mole fraction of vacancies in equilibrium at the thermodynamic melting temperatures of these metals. The melting phenomenon, one of the most studied and yet least understood physical processes[21-23], has (at least intuitively) a strong correlation with point defects. It is seen that many of the physical parameters associated with lattice defects can be empirically related to the absolute melting temperatures. For example the energies of formation[24] and motion[25] of vacancies in fcc metals can be calculated from the melting temperatures. These calculated values agree remarkably well with the best experimental results. Simmons[26] has shown a linear relationship between the melting point concentration of vacancies and the volume change on fusion, and Mehl et al.[27] have semi-empirically calculated the energy of formation of vacancies from the latent heat of melting and the volume change on fusion. Yet another empirical relationship between the free energy of formation and the melting temperatures has been suggested by Gibbs[28]. Ormont[29] has shown that the energy of

formation is approximately one third of the energy required for
sublimation to monatomic gas at the melting point. Although the
purpose of this article is not to postulate a theory of melting,
it is the intention of this author to emphasize these points so that
some further research might be focused on this aspect of vacancy
mechanism of fusion.

Theoretical and experimental information from various investiga-
tions indicates that the concentration of defects at the melting point
of the fcc metals is quite low[9]. In the five above mentioned pure
metals (Au, Ag, Cu, Al and Pb) the melting point concentration is of
the order of 10^{-3} to 10^{-4} mole fractions [1-6]. It can be assumed with
some confidence that in other fcc metals, for which no reliable
experimental data is available, the mole fraction of vacancies at the
melting point also lies in the range of 10^{-3} to 10^{-4}. This is then
the only input information used in this present article. From this
the exact vacancy concentration at the melting point, Gibbs free energy,
entropy of formation, energy of formation and vacancy volume are
calculated for the five fcc metals. Calculated values are compared
with the corresponding experimentally determined values.

II. ESTIMATION OF VACANCY CONCENTRATION

(a) Concentration at the Melting Point

Let us consider one mole of a crystalline solid containing N atoms
and n vacant sites. For the vibrational frequencies of the atoms we
will take an Einstein model of the solid so that each atom in the

perfect crystal is an independent oscillator with a vibrational frequency ν_D. If the coordination number of the crystal is Z then the vibrational frequencies of the Z neighbors to a vacancy are ν_D in two perpendicular directions to the line joining them to the vacant site and some smaller value ν_V along the line. The free energy of the crystal at the melting point containing n vacancies can then be written as

$$F = nE_f - T_m \left[nkZ \ln(\nu_D/\nu_V) + k \ln \left\{ (N+n)! / N! n! \right\} \right] \qquad (1)$$

where E_f is the energy of formation of a vacancy and is independent of temperature, k is the Boltzmann's constant and T_m is the absolute melting temperature.

The last term on the right hand side of Eq.(1) is the configurational entropy of mixing n vacancies and N atoms. This term can be simplified by applying Stirling's approximation as follows

$$k \ln \left\{ (N+n)! / N! n! \right\} = k \left[(N+n)\ln(N+n) - (N+n) - N\ln N - N - n\ln n - n \right] \qquad (2)$$

By collecting terms and rearranging Eq(2), one gets

$$k \ln \left\{ (N+n)! / N! n! \right\} = kN \ln \left[\frac{\left\{ 1+(n/N) \right\}^{(n/N)+1}}{(n/N)^{(n/N)}} \right] \qquad (3)$$

For simplicity let us write

$$k \ln \left\{ (N+n)! / N! n! \right\} = kN \, f(n/N) \qquad (4)$$

where

$$f(n/N) = \ln\left[\frac{\{1+(n/N)\}^{(n/N)+1}}{(n/N)^{(n/N)}} \right] \qquad (5)$$

The mole fraction of vacancies extrapolated to the melting temperature of fcc metals has been reported in literature in the past several years[1-10]. From reliable experiments of quite diverse natures such as calorimetric measurement of stored energy release[1], resistivity measurements in quenched specimen[7-10] and equilibrium length and lattice parameter measurements[2-6], it is seen that at the melting temperature of the fcc metals studied, the vacancy concentration is on the order of 1×10^{-3} to 1×10^{-4}. For other fcc metals which have not yet been studied experimentally, there is no good reason to believe that the melting point concentration of vacancies will be dramatically different from those which have been studied so far. Although it is quite safe to assume that the melting point concentration is within the range as mentioned above, the exact value can not be stated with any great accuracy. Thus in this paper for the melting point concentration of vacancies $(n/N)_{mp}$ we will make the following statement

$$1 \times 10^{-4} \leq (n/N)_{mp} \leq 10 \times 10^{-4} \qquad (6)$$

It will be interesting then to see how the function $f(n/N)$ in Eq.(5) behaves in the range given in Eq.(6). This was done by using an IBM computer. The function $f(n/N)$ was calculated for the values of (n/N) in the range of 0.25×10^{-4} to 100×10^{-4} with step increments of 0.25×10^{-4}. The value of the function $f(n/N)$ within the range of our present interest (i.e. 1×10^{-4} to 10×10^{-4})

was plotted as a function of (n/N) as shown in Fig.1. For clarity not all points are shown in the figure. In Figure 1 is also shown a leastsquare fit of the data by a straight line. Within the range stated in Eq.(6) the fit is quite good. The slope of the straight line was found to be 7.508 and the intercept at (n/N)=0 to be 4.665×10^{-4} (values beyond the third decimal place are not shown). The root mean square deviation in $f(n/N)$ due to the straight line approximation was found to be 7.568×10^{-5}. Thus we could write

$$f(n/N) = 7.508(n/N) + 4.665 \times 10^{-4} \tag{7}$$

The small correction term is not included in Eq.(7) since we will see in the next steps that this term will drop out from our final equation.

Substituting from Eq.(7) in Eq.(1)

$$F = nE_f - T_m \left[nkZ \ln(\nu_D / \nu_V) + 7.508kn + 4.665 \times 10^{-4}kN \right] \tag{8}$$

The term $k\ln(\nu_D / \nu_V)$ in Eq.(8) is the vibrational entropy of formation and can be replaced by the symbol S_V as is done in the past literature[18]. Thus

$$Z \, k \, \ln (\nu_D / \nu_V) = S_V \tag{9}$$

Substituting from Eq.(9) in Eq.(8)

$$F = nE_f - T_m \left[n S_V + 7.508 \, n \, k + 4.665 \times 10^{-4}kN \right] \tag{10}$$

For the condition of equilibrium we minimize Eq.(10) by setting $(\partial F / \partial n)_T = 0$ and by transposing we get

$$E_f = \left(T_m S_V + 7.508 \, k \, T_m \right) \tag{11}$$

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The concentration of vacancies at any temperature T which in our case is the melting temperature is generally written as [9,18]

$$(n/N)_{mp} = e^{S_v/k} \, e^{-E_f/kT_m} \tag{12}$$

By rearranging Eq.(12) we can write

$$(n/N)_{mp} = \exp\left\{ \frac{T_m \, S_v - E_f}{kT_m} \right\} \tag{13}$$

By rearranging Eq. (11) and substituting in Eq.(13)

$$(n/N)_{mp} = e^{-7.508} \tag{14}$$

The result obtained in Eq.(14) is very fascinating and has great implication. It tells us that the vacancy concentration at the melting temperature of the fcc metals is independent of the metal and is given by

$$(n/N)_{mp} = e^{-7.508} = 5.47 \times 10^{-4} \tag{15}$$

The result of Eq.(15) might lead to a new approach to the theory of melting. In Table I, the concentration of vacancies obtained from Eq.(15) is compared with the best experimental results.

(b) <u>Concentration at temperatures below the melting point</u>.

The concentration at any other temperature T can be written as

$$(n/N)_T = e^{S_v/k} \, e^{-E_f/kT} \tag{16}$$

At least one of the unknowns in Eq.(16) can be eliminated by using the formula in Eq.(11). The unknown to be eliminated is the

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vibrational entropy S_v. Since this quantity is more difficult to determine experimentally[2-6] it is advantageous to find an expression for S_v in terms of E_f. It has been pointed out earlier in this paper that E_f is the easier of the vacancy parameters to determine experimentally. Thus combining Eq.(11) and Eq.(16), we can write for vacancy concentration at any temperature T, below the melting point

$$(n/N)_T = 5.47 \times 10^{-4} \exp \left\{ \frac{-E_f(1 - T/T_m)}{kT} \right\} \qquad (17)$$

It has been shown elsewhere[24] that the energy of formation in fcc metals can be correlated with the absolute melting temperatures. In Fig.2 the plot of the ratio of the melting temperature to the atomic volume vs. the energy of formation is shown. The correlation is seen to be fairly good. In the absence of experimental information about the energy of formation, the empirical relation obtained from Figure 2 can be used with some confidence. The relationship obtained from Fig. 2 is

$$E_f = \left(9.2 \times 10^{-3} \ T_m/d^3\right) + 0.4 \qquad (18)$$

where E_f is in eV, T_m is the melting temperature in $^\circ K$ and d is the interatomic distance in Angstrom units. Combining Eq.(17) and Eq.(18), one can then determine the concentration of vacancies at any temperature from the knowledge of the melting temperature and the interatomic distance.

III. CALCULATION OF THE VIBRATIONAL ENTROPY

It was pointed out earlier that it is difficult to determine a quantitative value of the vibrational entropy from experiments.

In most of the previous investigations[2-6] the values of S_v were assumed[9,20]. There has been some attempts in the past to theoretically calculate this quantity[15,17,18,41]. However it is conceded that these theoretical values are only the order of magnitude approximations[14,18]. In this present paper we will try to calculate S_v from the results obtained in sec. II and by further application of some thermodynamic relations. The Gibbs free energy of formation of a vacancy at the melting point can be written as

$$(G)_{T_m} = H - T_m S_v \tag{19}$$

where H and S_v are the enthalpy and entropy of formation of a vacancy respectively and T_m is the absolute melting temperature. At ordinary pressure the enthalpy H is identified with the formation energy E_f. Thus from Eq.(11) and Eq.(19) the Gibbs free energy of formation of a vacancy at the melting point is

$$(G)_{T_m} = 7.508 \ k \ T_m \tag{20}$$

From the well known thermodynamic relation

$$(\delta G / \delta T)_P = -S_v \tag{21}$$

Applying the chain rule we can write

$$(\delta G / \delta T)_P = (\delta G / \delta V)_P \ (\delta V / \delta T)_P \tag{22}$$

where V is the molar volume, P is the pressure and T is the temperature.

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Since the pressure change during melting is negligible we can remove the subscript P in the first partial in Eq. (22). From Eq. (20) we can write for one mole of the solid

$$(dG/ dV) = 7.508 R (dT_m/dV) \qquad (23)$$

where R is the gas constant. Although we have assumed that the pressure change during melting is negligible the melting temperature itself is a function of pressure. By applying chain rule we can write from Eq. (23)

$$(dG/ dV) = 7.508 R \left[(dT/dP) \; dP/dV \right]_{T=T_m} \qquad (24)$$

Substituting from Eq. (24) in Eq. (22) we get

$$(\delta G/\delta T)_P = 7.508 R \left[(dT/dP) \; (dP/dV) \right]_{T=T_m} (dV/dT)_P \qquad (25)$$

But from the well known Clapeyron's equation we have

$$\left(dT/dP \right)_{T=T_m} = (T_m \, \Delta V_f/ \Delta H_f) \qquad (26)$$

where ΔV_f is the volume change on fusion and ΔH_f is the latent heat of fusion at the melting point. We also have

$$1/V (dV/ dT)_P = \alpha \qquad (27)$$

and

$$- 1/V (dV/ dP)_T = \chi \qquad (28)$$

where α and χ are the coefficient of thermal expansion and isothermal

compressibility respectively. Substituting from Equations (26), (27) and (28) in Eq.(25) we get

$$(\delta G/ \delta T)_P = - 7.508 \ T_m \ (\Delta V_f/ \Delta H_f) \ (\alpha / \chi) \qquad (29)$$

Thus the vibrational entropy S_v is obtained by combining Equations (29) and (21) and is given by

$$S_v = 7.508 \ T_m (\Delta V_f/ \Delta H_f \ ) \ (\alpha / \chi) \qquad (30)$$

From the Grüneisen's relationship we have

$$\gamma = (\alpha V \ / \chi \ C_v) \qquad (31)$$

where V and χ are the molar volume and the compressibility respectively at the absolute zero temperature, C_v is the molar specific heat at constant volume and γ is the Grüneisen's constant. Substituting from Eq.(31) in Eq.(30), we can write

$$S_v = 7.508 \ R \ T_m (\gamma \ C_v/ \Delta H_f) \ (\Delta V_f/ V) \qquad (32)$$

The advantage of substitution from Eq.(31) is that the constant γ is fairly temperature insensitive and also if the high temperature values of Cv and V are substituted in Eq.(32) then the expression for the vibrational entropy becomes temperature corrected. Moreover, the volume change on fusion is usually reported in literature as the change in volume on melting divided by the volume of the solid at the melting point. For the melting point value of Cv we can write 3R, where R is the gas constant. By the latter approximation the error

in S_v could not exceed more than 1-2%. Thus we write

$$S_v/R = 22.524 \ R \ T_m \ \gamma \ (\Delta V_f / V_s^{mp}) \ (1/\Delta H_f) \tag{33}$$

where R is the gas constant, T_m is the absolute melting temperature in $^\circ K$, γ is the Grüneisen's constant, ΔV_f is the volume change on fusion, V_s^{mp} is the volume of the solid at the melting point and ΔH_f is the latent heat of fusion at the melting temperature.

Values of S_v calculated from the Eq.(33) are shown in Table II and are compared with other theoretical and experimental values. It can be seen from Table II that the agreement between the experimental value and the calculated value is very good for Al, and the agreement between the assumed values for Ag and Cu is fair but it is quite poor for Au and Pb. However the calculated values are within the range theoretically expected[17,30].

IV. CALCULATION OF THE ENERGY OF FORMATION

Both the vibrational entropy and the formation energy are independent of temperature. The above assumption has been made by all previous investigators and is valid for all practical purposes. Thus we can readily calculate the energy of formation from the results obtained in sections II and III. Noting once again the energy of formation is equal to the enthalpy of formation for small pressures, we can write from Eq.(19)

$$E_f = (G)_{T_m} + T_m \ S_v \tag{34}$$

But the Gibbs free energy of formation is given explicitly in terms

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of the melting temperature in Eq.(20). Thus

$$E_f = (7.508 \ k + S_v) \ T_m \tag{35}$$

Values of S_v can be substituted in Eq.(35) from Eq.(33). Values of E_f thus calculated are shown in Table III and are compared with the best experimental results. The agreement between the experimental and the calculated values is very good for Al, Ag, Cu and Pb. For Au the agreement is not so good. This is because of the fact that the calculated entropy for Au from Eq.(33) is at least 50% higher than the estimated value in the experimental work. Even with such a disagreement for the entropy value, the calculated value of the formation energy is only about 16% higher than the corresponding experimental value (taking into account the systematic error as shown in Table III.).

V.   CALCULATION OF THE VACANCY VOLUME

The vacancy volume is an important parameter in the study of defect properties of solids. Unfortunately very little work has been done in this line. There has been some theoretical work[40-42] for Cu and some experimental values for Au have been cited[1,4,10,39] in the past literature. However it is generally speculated that the vacancy volume in noble metals is roughly 50% of the atomic value. Here we will make an attempt to calculate this quantity from the results of the previous sections by the application of some thermodynamic relations.

From the Maxwell's equations we can write

$$(\delta H/ \delta P)_{S} = V \tag{36}$$

where H is the enthalpy, P is the pressure, S is the entropy and V is the volume. From Eq.(19)

$$H = (G)_{T_m} + T_m S_v \tag{37}$$

But the Gibbs free energy $(G)_{T_m}$ is explicitly derived in Eq.(20). Thus

$$(\delta H/ \delta P)_{S_v} = (7.508\ R + S_v)\ (\ dT/\ dP)_{T=T_m} \tag{38}$$

Substituting from Eq.(26) in Eq.(38) and comparing with Eq.(36) we write

$$V' = (7.508\ R + S_v)\ (\triangle V_f)(T_m/\triangle H_f) \tag{39}$$

where V' is the increase of volume of one mole of the solid due to the equilibrium number of vacancies at the melting point, $\triangle V_f$ is the volume change on fusion, T_m is the absolute melting temperature and $\triangle H_f$ is the latent heat of fusion at the melting point. Dividing both sides of Eq.(39) by the molar volume of the solid V_s^{mp} at the melting temperature

$$V'/V_s^{mp} = (7.508\ R + S_v)(\triangle V_f/V_s^{mp})(T_m/\triangle H_f) \tag{40}$$

The quantity on the left hand side of Eq.(40) is the ratio of the vacancy volume to the atomic volume, and once again $(\triangle V_f/V_s^{mp})$ is the quantity which is readily available in the literature. S_v in Eq.(40) can be replaced by the result obtained in Eq.(33).

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Values of $\left(V'/V_s^{mp}\right)$ calculated from the foregoing treatment are shown in Table IV and compared with the available theoretical or experimental values wherever possible. The only experimental value available is for Au, and the agreement between this value and the calculated value from Eq.(40) is remarkable.

VI. SUMMARY AND DISCUSSION

A) The concentration of vacancies at the melting point of at least five fcc metals (Al, Au, Ag, Cu, and Pb) is found to be 5.47×10^{-4} irrespective of the element. Generalization of this result to include all fcc metals might not be entirely unjustifiable. From Eq.(12) the melting point concentration of vacancies will depend on three quantities viz. S_v, E_f and T_m. Experimental results and theoretical estimations as well as present calculation indicate that values of S_v lie within the range of 1 to 3 entropy units. Present calculation includes wide ranges of formation energy (1.2 eV for Au to 0.50 eV for Pb) and melting temperature (1356°K for Cu to 600°K for Pb).

B) A method for calculating the vibrational entropy is shown in section III. The calculated values of S_v/K are within the expected range. It would seem from this work that for Au the previous investigators[4] have greatly underestimated the vibrational entropy.

C) Except for Au, the experimental values of E_f are in good agreement with the calculated values as shown in Table III. E_f calculated for Au in this work is 1.2 eV compared with 0.94 eV to 0.98 eV reported earlier[1,4,10,35]. The best experimental[43] value

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for the self diffusion activation energy Q is (1.81±0.02) for Au. But for diffusion by the vacancy mechanism $Q=(E_f+E_m)$ where E_m is the energy of motion of a vacancy. Thus from the present work, the upperlimit of E_m is 0.63 eV for Au. **From quenching work of Bradshaw and Pearson[35]** E_m = 0.68 eV for Au, and DeSorbo[1] estimated E_m = (0.6 to 0.7) eV from his calorimetric work. However from Bauerle and Koehler's[10] annealing experiments E_m = 0.82 eV.

D) The best agreement for both S_v/k and E_f between calculated and experimental values was found for Al and the poorest for Au. In Fig. 3, the best quenching[31] and the equilibrium measurement[2] results are compared with the present work. Figure 4 shows such a comparison for Au. In the latter case best quenching[10], calorimetric[1] and equilibrium[4] values are shown along with the present result. For both Au and Al, the equilibrium measurements appear to overestimate the vacancy concentration as compared with the present results as well as quenching and calorimetric measurements.

E) A method is shown for the calculation of the vacancy volume. There are not enough experimental values of this quantity available to test the results. The only experimental value reported[4] is for Au and the agreement is remarkable but this could be purely fortuitous. The ratio of the vacancy volume to the atomic volume calculated in this paper corresponds to the melting point and thus could be somewhat different from the corresponding low temperature value. However it is difficult to say whether the calculated values are lower or higher than the corresponding low temperature values.

This is because at high temperature the atoms vibrate in a relatively weaker force field, thus the relaxation will be smaller and the vacancy volume larger. On the other hand the atomic volume also increases at high temperature due to the average thermal expansion of the lattice. Hence the ratio (vacancy volume to the atomic volume) might not change appreciably.

No attempt has been made in this paper to calculate the mono-vacancy motion energy, primarily because the present approach can not yield this quantity. However a slightly different approach is in sight and this will be presented as a separate article in the near future.

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REFERENCES

1. W.DeSorbo, Phys.Rev.117,444(1960).

2. R.O.Simmons and R.W.Balluffi, Phys.Rev.117,52(1960).

3. R.O.Simmons and R.W.Balluffi, Phys.Rev.119,600(1960).

4. R.O.Simmons and R.W.Balluffi, Phys.Rev.125,862(1962).

5. R.O.Simmons and R.W.Balluffi, Phys.Rev.129,1533(1963).

6. R.Feder and A.S.Nowick, Phil.Mag. 2,379(1958).

7. F.J.Bradshaw and S.Pearson, Phil.Mag.1,812(1956).

8. A.Ascoli, M.Asdente, E.Germagnoli and A.Manora, J.Phys.Chem.Solids, 6,59(1958).

9. A.C.Damask and G.J.Dienes, "Point Defects in Metals," Gordon and Breach,N.Y.(1963).

10. J.E.Bauerle and J.S.Koehler, Phys.Rev.107,1493(1957).

11. M.S.Wechsler, Acta Met. 5,150(1957).

12. K.Mukherjee, Phys.Letters,10,18(1964).

13. K.Mukherjee, D.S.Lieberman and T.A.Read, J.Appl.Phys. (in press).

14. H.B.Huntington, Amer.J.Phys.32,775(1964).

15. G.J.Dienes, Phys.Rev.89,185(1953).

16. C.Zener, J.Appl.Phys.22,372(1951).

17. H.B.Huntington, G.A.Shirn and E.J.Wajda, Phys.Rev.99,1085(1955).

18. H.Brooks, "Impurities and Imperfections,"(Amer.Soc.For Metals, 1958),p.1.

19. G.Schottky, A.Seeger and G.Schmid, Phys.Status Solidi,4,439(1964).

20. R.W.Balluffi, J.S.Kohler and R.O.Simmons, "Recovery and Recrystallization of Metals," (Proc.AIME) Interscience,N.Y. (1962) p.1.

21. J.Frenkel, "Kinetic Theory of Liquids," Dover,N.Y.

22. H.N.V. Temperly, "Changes of State," Cleaver-Hume, London(1956).

23. B.R.T. Frost, "Progress in Metal Physics," Vol.5, p.96, Pergamon Press, London(1952).

24. K.Mukherjee, Phys.Letters, $\underline{8}$, 17(1964).

25. K.Mukherjee, J.Phys.Chem.Solids, $\underline{25}$, 517(1964).

26. R.O.Simmons, J.Phys.Soc.of Japan, $\underline{18}$, II, 172(1963).

27. R.F.Mehl, M.Swanson and G.M.Pound, Acta Met. $\underline{9}$, 256(1961).

28. G.B.Gibbs, Acta Met. $\underline{12}$, 673(1964).

29. B.F.Ormont, Dokl.Akad Nauk S.S.S.R., $\underline{153}$, 115(1963).

30. A.D.LeClaire, Acta Met. $\underline{1}$, 438(1953).

31. W.DeSorbo and D.Turnbull, Acta Met. $\underline{7}$, 83(1959).

32. M.Doyama and J.S.Koehler, Phys.Rev. $\underline{119}$, 939(1960).

33. L.J.Cuddy and E.S.Machlin, Phil.Mag. $\underline{7}$, 745(1960).

34. F.J.Bradshaw and S.Pearson, Phil.Mag. $\underline{2}$, 570(1957).

35. F.J.Bradshaw and S.Pearson, Phil.Mag. $\underline{2}$, 370(1957).

36. S.D.Gertsriken and N.N.Novikow, Fiz.Metal. i Metalloved.Akad.Nauk S.S.S.R., Ural. Filial, $\underline{9}$, 224(1960).

37. Y.Quere, Compt.rend, $\underline{251}$, 367(1960).

38. G.Aroldi, G.L.Bacchella and E.Germagnoli, Phys.Rev.Letters, $\underline{2}$, 145(1959).

39. J.Takamura, Acta Met. $\underline{9}$, 547(1961).

40. L.Tewordt, Phys.Rev. $\underline{109}$, 61(1958).

41. A.Seeger and E.Mann, J.Phys.Chem.Solids, $\underline{12}$, 326(1960).

42. K.H.Bennemann and L.Tewordt, Z.Natur forsch, $\underline{15a}$, 772(1960).

43. S.J.Makin, A.H.Rowe and A.D.LeClaire, Proc.Phys.Soc.(London) $\underline{B70}$, 545(1957).

Table I. Melting point concentration $(n/N)_{mp}$ of vacancies in some

fcc metals.

Metal	$(n/N)_{mp}$ x 10^4 Experimental	Reference	$(n/N)_{mp}$ x 10^4 Calculated (Present Work)
Pb	1.5	6	5.47
Ag	1.7	3	5.47
Cu	1.9	5	5.47
Au	7.2	4	5.47
Al	9.0	2	5.47

Table II. Entropy of formation of vacancies in some fcc metals.

Metal	S_v/k Experimental or assumed (a)	Reference	S_v/k calculated (Present work)
Al	2.4 2.2	2 4	2.34
Au	1.0 1.2±0.3	4 4,10	3.00
Ag	1.5±0.5	3,32,33	1.84
Cu	1.5±0.5(a) 1.5	5 17	1.61
Pb	1.5(a)	6	2.11

Table III.   Formation energy of vacancies in some fcc metals.

Metal	E_f (eV) Experimental	Reference	E_f (eV) Calculated (Present work)
Al	0.75±0.03 0.79±0.03 0.76±0.04	2 31 34	0.78
Au	0.94±0.09 0.98±0.03 0.95±0.10 0.97±0.10	4 10 35 1	1.20
Ag	1.09±0.10 1.10±0.04 1.01±0.03 1.06±0.07	3 32 36 37	0.99
Cu	1.17±0.11 1.0	5 38	1.07
Pb	⩾ 0.53	6	0.50

Table IV. The ratio of the vacancy volume to the atomic volume

in some fcc metals.

Metal	(V'/V) Experimental or Theoretical(t)	Reference	(V'/V_s^{mp}) Calculated (Present Work)
Au	0.45 ± 0.10 0.57 ± 0.05	4,10,39 10,1	0.46
Cu	0.5 ± 0.1(t) 0.53 (t) 0.65 ± 0.15(t)	5,42 40 41	0.33
Ag	....		0.31
Al	....		0.47
Pb	....		0.34

FIGURE CAPTIONS

Fig. 1. Configurational entropy function $f(n/N)$ versus the atomic fraction of vacant lattice sites (n/N) within the range $10^{-4} \leq (n/N) \leq 10^{-3}$. The solid line is the leastsquare fit of the data (not all points are shown).

Fig. 2. Formation energy of monovacancies in fcc metals versus the ratio of the absolute melting temperature and interatomic distance-cube. The values of the interatomic distance d are the room temperature values.

Fig. 3. Atomic fraction of vacant lattice sites (n/N) versus reciprocal absolute temperature in aluminum. The present work (solid line) is compared with Simmons and Balluffi's[2] equilibrium measurement and DeSorbo and Turnbull's[3] quenching results. The slope of the solid line is 0.78eV.

Fig. 4. Atomic fraction of vacant lattice sites (n/N) versus reciprocal absolute temperature in gold. The present work (solid line) is compared with equilibrium data of Simmons and Balluffi[4], quenching data of Bauerle and Koehler[10] and calorimetric results of DeSorbo[1]. Slope of the solid line is 1.2eV.
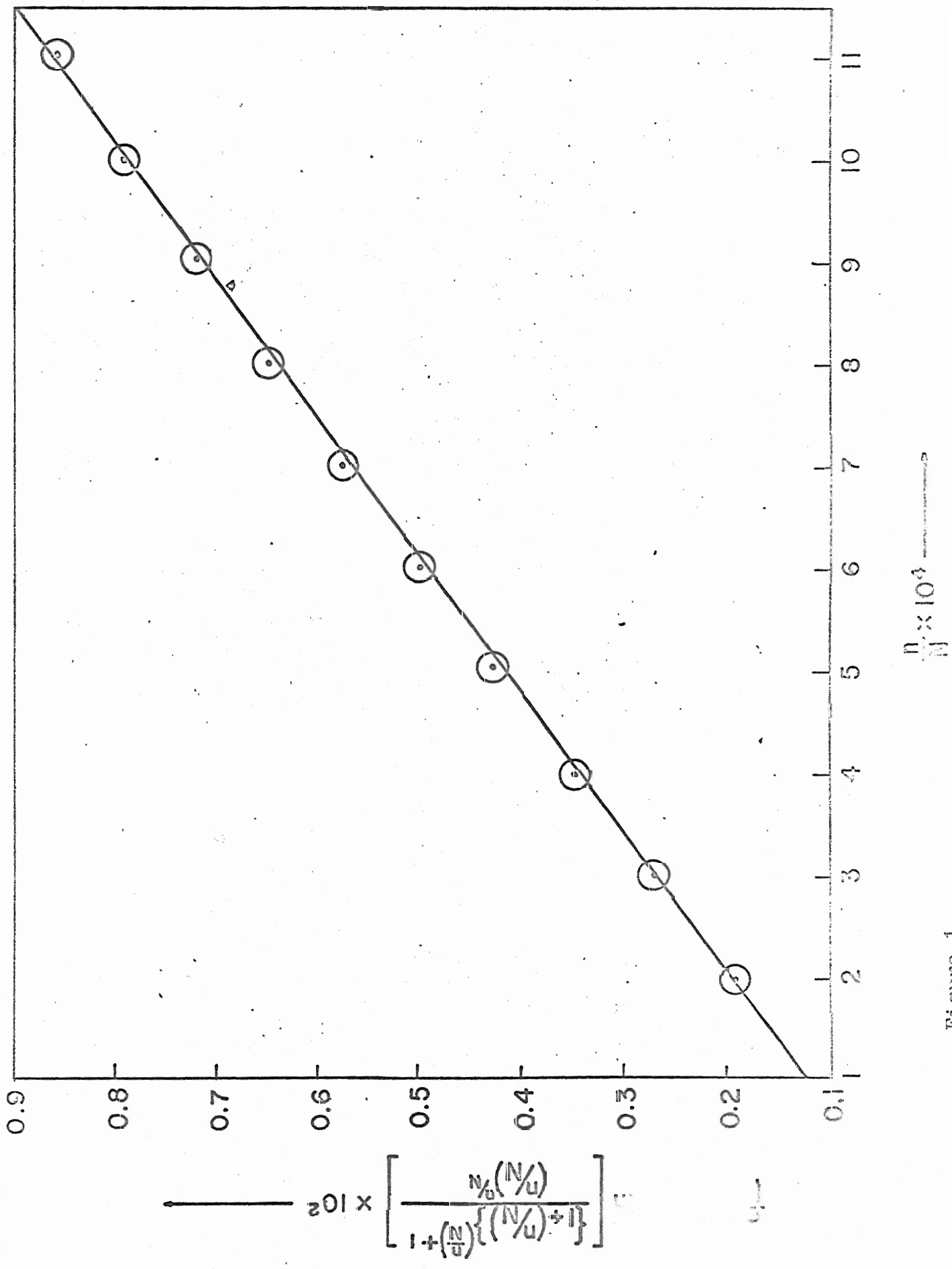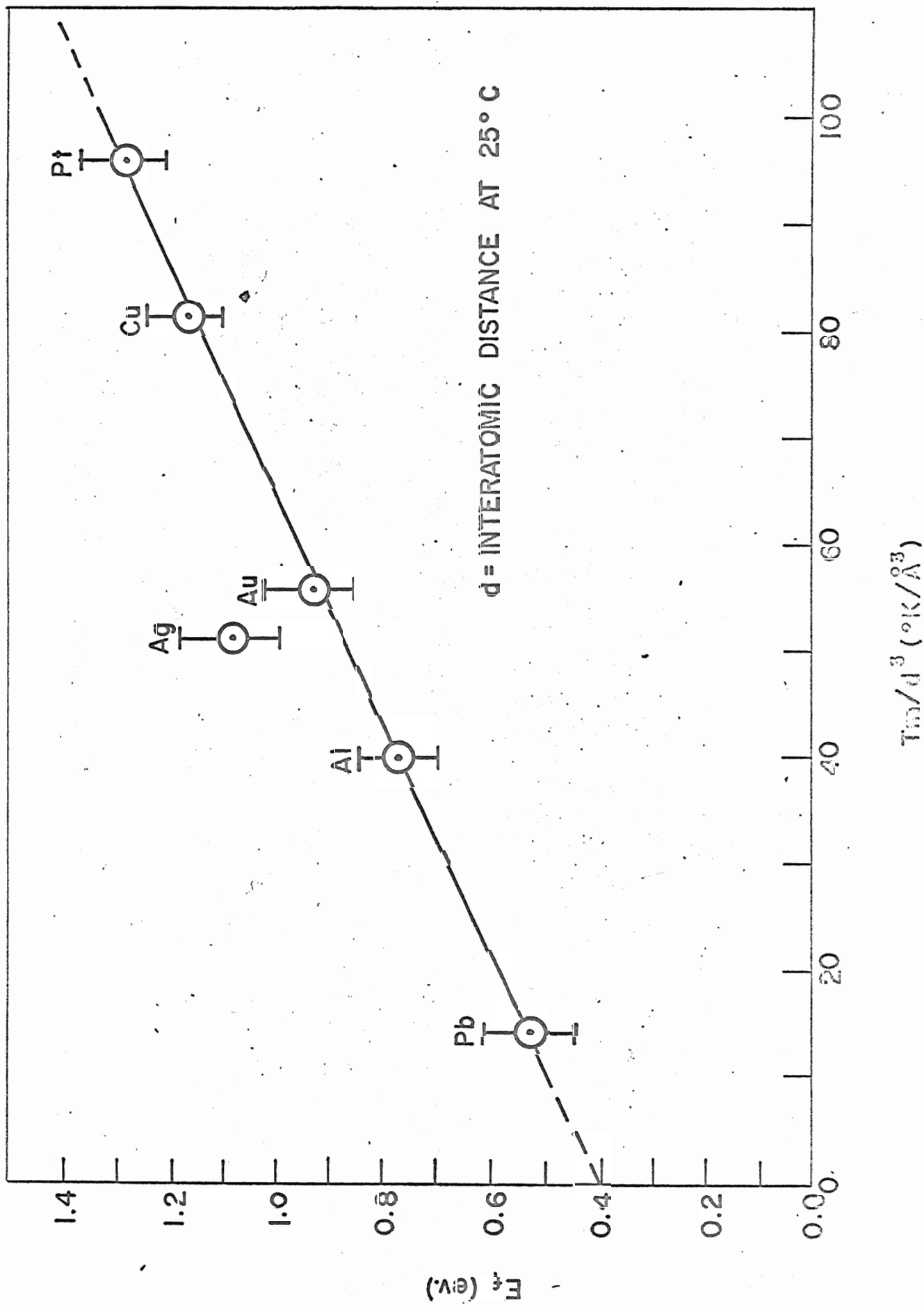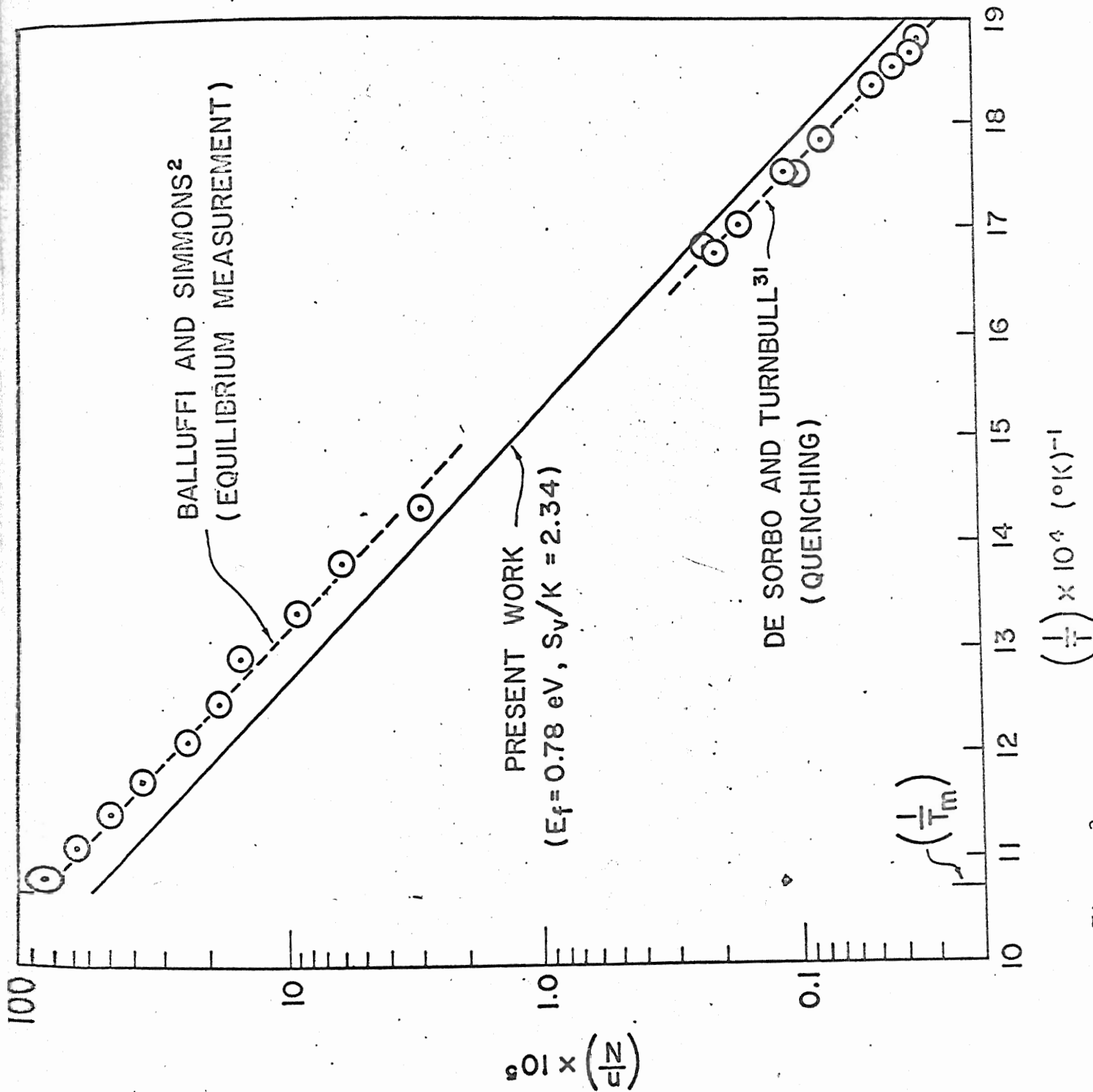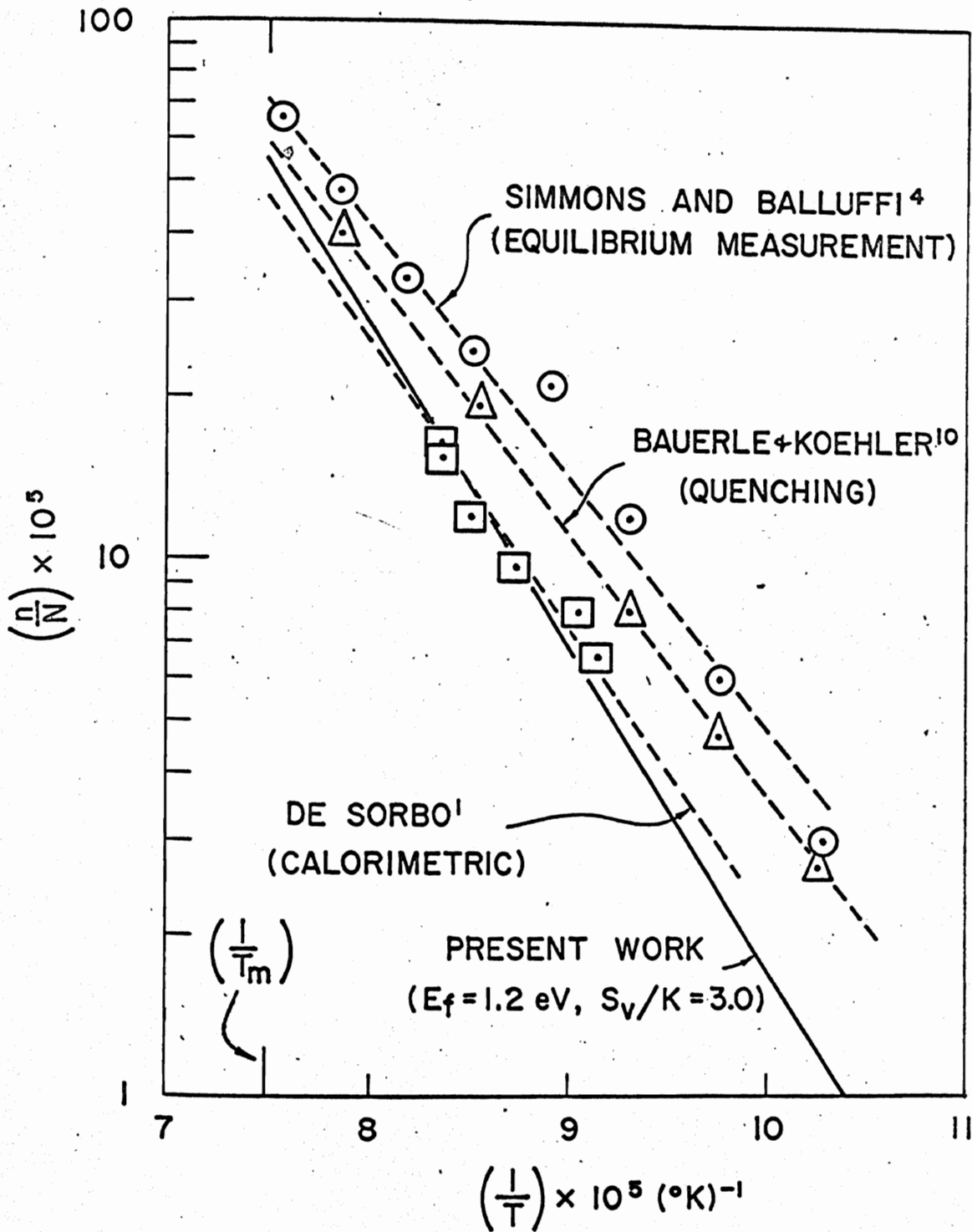
Figure 1.

Figure 2.

Figure 3.

Figure 4.