

The Theory of Defect Concentration in Crystals*

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The theory of the formation of vacancy and interstitial defects in crystals is re-examined. It is suggested that a Born-von Karman type of lattice provides an adequate model for the calculation of the essential parameters giving the concentration of defects as a function of temperature. It is concluded that the entropy of formation depends only on the lattice frequencies before and after formation of the defect, and no further contribution to the entropy arises even though the enthalpy of formation may appear to remain temperature dependent at constant pressure. Data on vacancy concentration in NaCl and LiF are analyzed roughly in the light of present ideas. The results for NaCl are understandable in a simple way; those for LiF seem to require more complete calculations.

I. INTRODUCTION

THE concentration of lattice defects in a crystal, according to statistical mechanics, is given by¹

$$c = n/N = Ae^{-E/kT}, \quad (1)$$

where n = number of defects; N = total number of atoms; E = energy of formation of a defect; and A = pre-exponential constant. If there are no entropy changes other than the entropy of mixing, then the constant A in (1) is equal to unity. Experimentally, A often differs from unity by orders of magnitude. Two main contributions to the value of A have been considered in the literature.^{2,3} First, the vibrational frequencies around a defect are altered, which contributes to the entropy of formation. Second, the energy of formation depends on the interatomic distance and, hence, on the temperature via the volume expansion. Mott and Gurney² and Frenkel³ assumed that E depends linearly on the temperature as

$$E = E_0 - \alpha T, \quad (2)$$

giving a contribution to A of $e^{\alpha/k}$. However, Haven and van Santen⁴ have pointed out recently that a temperature dependence allotted to the enthalpy of formation requires some entropy of formation because of the thermodynamic connection:

$$(\partial H/\partial T)_P = T(\partial S/\partial T)_P.$$

From this they find a further entropy term to be necessary because of Mott and Gurney's temperature-dependent enthalpy and arrive at a negative contribution to the entropy of formation rather than a positive one as would be derived from (2).

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¹ See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 458.

² N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (University Press, Oxford, 1948), pp. 29-30.

³ J. Frenkel, *Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1946), Chapter I.

⁴ Y. Haven and J. H. van Santen, *Philips Research Repts.* 7, 474 (1952).

Because of this unsatisfactory state of affairs, we decided to reinvestigate this problem by taking account of thermal expansion from the start. We may anticipate the results by stating that we find a common error in previous analyses. Energy terms which depend only on the volume do not contribute to the entropy of formation, and these are the entropy terms which have often been included in the past. According to our analysis, the entropy of formation depends only on the lattice frequencies before and after formation of the defect, and no further contribution to the entropy arises even though the enthalpy of formation may appear to remain temperature dependent at constant pressure.

In Sec. II the detailed thermodynamic arguments are given, and in Sec. III we discuss briefly application to actual experimental data.

II. THERMODYNAMICS OF THE FORMATION OF LATTICE DEFECTS

The discussion will first be carried through for the case of a monatomic substance in which each atom occupies an equivalent position when in the perfect state. Generalization to more complicated substances is easily made. The discussion is limited to the case where hydrostatic pressure is the only stress. The crystal may exist in a perfect state, and this will be assumed to be a lattice of the Born-von Karman type, that is, one in which the thermal oscillations are of sufficiently small amplitude that the potential energy is a quadratic function of the atomic displacements. The energy of the crystal, relative to the state in which the atoms are all at rest at infinite separation, consists of a potential energy of equilibrium ϕ_p plus a dynamic part which, by normal mode analysis, is equal to the kinetic and potential energies of a set of independent simple harmonic oscillators. These oscillators are characterized by their frequencies which, together with ϕ_p (under the condition of hydrostatic pressure), depend on the volume of the crystal and on no other thermodynamic variables.

The internal partition function of the N -atom

perfect crystal is now

$$Z_p = e^{-\phi_p/T} \prod_{\nu_p} e^{-\nu_p/2T} (1 - e^{-\nu_p/T})^{-1}, \quad (1)$$

where ν_p is the frequency of one of the $3N-6$ lattice oscillators, measured in energy units; T is the temperature in energy units; and the product is taken over the entire set of oscillator frequencies.

The Helmholtz free energy, pressure, entropy, and internal energy are given by

$$A_p = -T \ln Z_p = \phi_p + \sum_{\nu_p} \left[\frac{\nu_p}{2} + T \ln(1 - e^{-\nu_p/T}) \right], \quad (2)$$

$$P = - \left(\frac{\partial A_p}{\partial V} \right)_T = - \frac{d\phi_p}{dV} - \sum_{\nu_p} \left[\frac{1}{2} + (e^{\nu_p/T} - 1)^{-1} \right] \frac{d\nu_p}{dV}, \quad (3)$$

$$S_p = - \left(\frac{\partial A_p}{\partial T} \right)_V = \sum_{\nu_p} \left[- \ln(1 - e^{-\nu_p/T}) + \frac{\nu_p}{T} (e^{\nu_p/T} - 1)^{-1} \right], \quad (4)$$

$$U_p = A_p + TS_p = \phi_p + \sum_{\nu_p} \nu_p \left[\frac{1}{2} + (e^{\nu_p/T} - 1)^{-1} \right]. \quad (5)$$

Here the correction to the entropy because of the indistinguishability of the atoms has been omitted, which is permissible because all systems to be considered will have the same number of atoms.

At temperatures appreciably above the characteristic temperature of the crystal, the thermodynamic functions assume the following simplified forms:

$$A_p \cong \phi_p + \sum_{\nu_p} T \ln \frac{\nu_p}{T}. \quad (6)$$

$$P \cong - \frac{d\phi_p}{dV} - \sum_{\nu_p} \frac{T}{\nu_p} \frac{d\nu_p}{dV}. \quad (7)$$

$$S_p \cong \sum_{\nu_p} \left(1 - \ln \frac{\nu_p}{T} \right). \quad (8)$$

$$U_p \cong \phi_p + \sum_{\nu_p} T = \phi_p + 3NT. \quad (9)$$

Consider next a crystal identical with the perfect crystal just treated, except that it possesses one defect, e.g., an atom has been moved from the interior to a site on the surface, or a surface atom has been moved to an interior interstitial position. This imperfect crystal now constitutes a second mechanical system describable by a volume-dependent potential energy of equilibrium ϕ_i and a set of independent simple harmonic lattice oscillators characterized by the volume dependent frequencies ν_i . All of the preceding formulas for thermodynamic quantities now apply to the imperfect lattice simply upon replacement of the subscript p by

the subscript i throughout. The entropy and free energies so calculated do not include the entropy of mixing, which arises because of the different equivalent sites on which the defect may be formed.

At thermal equilibrium the concentration of defects c (atomic fraction) is given by the formula^{1,5}

$$c = e^{-g/T}, \quad (10)$$

where g is the increase of Gibbs free energy of the system, exclusive of the entropy of mixing, attendant upon the formation of one defect at temperature T and pressure P .

Following the preceding discussion, g can be written

$$g = G_i - G_p, \quad (11)$$

where G_i and G_p are the Gibbs free energy of the imperfect and perfect crystals, respectively.

Experimentally one always determines defect concentrations over a restricted range of temperatures, and an equation of the type of (1) is employed to analyze the data in terms of an enthalpy (or energy) of formation and a pre-exponential factor. In most cases a plot of $\ln c$ vs $1/T$ proves to be very nearly linear over the entire experimental range. These circumstances suggest that the most useful form in which to elaborate (10) is the following:

Let T_1 be a temperature near the middle of the experimental range. Development of g in Taylor series about T_1 gives

$$g(T) = g(T_1) + (\partial g / \partial T_1)_P (T - T_1) + \frac{1}{2} (\partial^2 g / \partial T_1^2)_P (T - T_1)^2 + \dots \quad (12)$$

As long as the experimental data can be represented by a straight line in the usual plot, the first two terms of (12) must give an adequate approximation to g . Consequently, we shall discard the quadratic and higher terms. The present model allows one to estimate these terms and confirms the expectation that they are small in cases of interest.

If we employ (11) and the relation $(\partial G / \partial T)_P = -S$, (12) becomes

$$g(T) = g_1 + T_1 s_1 - T s_1 = h_1 - T s_1, \quad (13)$$

where $s = S_i - S_p$ (the entropy of formation of one defect, exclusive of the entropy of mixing), $h = H_i - H_p$, the enthalpy of formation of one defect, and the subscript 1 means that the quantity is to be evaluated at temperature T_1 . Finally, the equilibrium concentration of defects in the temperature range of interest becomes

$$c = \exp\{s_1 - h_1/T\}. \quad (14)$$

The entropy and enthalpy (14) may be written down at once from the preceding formulas. For many cases of interest the lattice frequencies will all be smaller than

⁵ The case of pairs or other complexes of defects requires a simple numerical factor in the exponent of (10). Equation (10) is the basic form, of which Eq. (1) is a common specialization.

T_1 , and good approximations can be found in the early terms of expansions in ν/T . Subsequent developments will be confined to this case. From (8) one finds $s = \sum \ln(\nu_p/\nu_i) + O(\nu^2/T^2)$, so that, to first order,

$$s_1 = \sum \ln(\nu_p/\nu_i), \quad (15)$$

the summation being over all vibrational modes. Equation (15) is essentially the same as a term already employed by Mott and Gurney² to take care of altered vibrational frequencies around a defect. It is now apparent that this vibrational entropy, if properly computed, should not be supplemented by any other entropy terms.⁶ It should be added that thermal expansion and attendant subtle effects, on the basis of which the temperature dependence of the enthalpy of formation was first suggested, are provided for in the present model.

The calculation of h will be simplified here by setting $P=0$, an adequate approximation in most experiments. Then from the relation $H=A+TS+PV$, one finds

$$h = \phi_i - \phi_p + \sum_{\nu_i} \nu_i \left[\frac{1}{2} + (e^{\nu_i/T} - 1)^{-1} \right] - \sum_{\nu_p} \nu_p \left[\frac{1}{2} + (e^{\nu_p/T} - 1)^{-1} \right] \\ = \phi_i - \phi_p + \frac{1}{12T} \sum (\nu_i^2 - \nu_p^2) + O(\nu^2/T^2). \quad (16)$$

Again a good approximation to h_1 will often be obtainable by omitting all terms in ν/T from (16). The ϕ terms should be computed at V_1 , the equilibrium volume at T_1 , rather than at V_0 , the equilibrium volume at $T=0$. This generally involves a slight correction, probably smaller than the inaccuracy in the calculated value of $\phi(V_0)$ itself, which may be estimated as follows:

$$\phi(V) \cong \phi(V_0) + \left(\frac{d\phi}{dV} \right)_{V_0} (V - V_0) + \frac{1}{2} \left(\frac{d^2\phi}{dV^2} \right)_{V_0} (V - V_0)^2. \quad (17)$$

At $T=0$, with neglect of the zero-point vibrational energy, ϕ is just the internal energy of the system. Then $d\phi = -PdV$, $d\phi/dV = -P$, $d^2\phi/dV^2 = -dP/dV = (1/V)B$, where B is the bulk modulus at absolute zero. Setting $P=0$ gives

$$\phi(V_1) \cong \phi(V_0) + \frac{1}{2} BV_0 \left(\frac{V_1 - V_0}{V_0} \right)^2. \quad (18)$$

As examples, for NaCl with $T_1=900^\circ\text{K}$ the second term in (18) equals 3 percent of the first term; for LiF with $T_1=1000^\circ\text{K}$ the second term is 8/10 percent of the first.

⁶ Presumably this conclusion is also valid for the formation of a saddle point configuration during diffusion. Consequently, one of the entropy contributions ΔS_1 , previously considered positive by one of us (G.J.D.) in an earlier analysis of entropies of activation [Phys. Rev. **89**, 185 (1953)], should be zero.

The potentials ϕ can be calculated theoretically by well-known methods.^{7,8} It should be pointed out that in ionic crystals, such as the alkali halides, the condition of electrical neutrality requires that vacancies be created in pairs of opposite sign. At elevated temperatures association of positive and negative vacancies will not be important,⁹ and the concentration of separated pairs of vacancies (number of pairs divided by number of molecules in the crystal) is given by a simple modification of Eq. (10):

$$c = e^{-g/2T}, \quad (19)$$

where g is the Gibbs free energy increase, exclusive of the entropy of mixing, upon formation of a well-separated pair of positive- and negative-ion vacancies. All other formulas are then readily transcribed for this case.

III. COMPARISON WITH EXPERIMENT

Etzel and Maurer¹⁰ have measured the electrical conductivity of NaCl and deduced a concentration of vacancy pairs

$$c = e^{(1.67 - 1.01/T)}$$

in the temperature range 825 to 1000°K. (T in the above is in units of electron volts.) The value 1.01 ev for half the enthalpy of pair formation is in good agreement with Mott and Littleton's¹¹ theoretical value.

To calculate the entropy term, one should make a normal mode analysis of the perfect and imperfect crystals, an especially difficult task for the latter case. An approximate value may be obtained much more simply, however, by using an Einstein model for the lattice, as has already been suggested by Mott and Gurney.² If one assumes, with these writers, that only the nearest neighbors of the vacancy will be affected, and then only in respect to vibrations along a line joining them with the defect, one has a total of 12 altered modes per defect pair. If one assumes that the ratio of the altered to original frequencies is the same for positive and negative vacancies, one obtains from Eq. (15) the entropy change per defect pair of $s_1 = 12 \ln(\nu_p/\nu_i)$. A fit to Etzel and Maurer's data is now obtained if $s_{1/2} = 1.67$, which requires $\nu_p/\nu_i = 1.32$. In the absence of a complete calculation, it may be said that this value seems entirely reasonable. In the simplest possible situation, that of nearest-neighbor interaction only in a cubic lattice, one immediately computes that $\nu_p/\nu_i = \sqrt{2}$, since creation of the vacancy halves the force constant for vibration of the neighbor.

⁷ See reference 2, Chapter II.

⁸ See also the recent review: P. W. M. Jacobs and F. C. Tompkins, Quart. Revs. **6**, 238 (1952).

⁹ A theoretical treatment of association is given by J. R. Reitz and J. A. Gammel, J. Chem. Phys. **19**, 894 (1951).

¹⁰ H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

¹¹ N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

Similar measurements by Haven¹² on LiF gave

$$c = e^{(6.2-1.34/T)}$$

The enthalpy of activation is similar to that for NaCl in the sense that it is increased essentially by the ratio of the cohesive energies (a ratio of 1.32). The entropy term of 6.2, analyzed as for NaCl, requires $\nu_p/\nu_i = 2.8$, a somewhat high value. A resolution of this difficulty would require more detailed calculations. For example, nearest-neighbor interactions could lower this value appreciably. Further, Haven analyzes his data in a somewhat different manner from Etzel and Maurer and the two sets of results are not strictly comparable.

Simple application of the theoretical analysis appears, therefore, to be in reasonable agreement with experiment. There are additional terms, of course, which

¹² Y. Haven, *Rec. trav. chim.* **69**, 1259, 1471 (1950).

contribute to changes of the vibrational frequencies which then should be included in calculating ν_p/ν_i of Eq. (15), such as over-all dilation due to strains around the defects and long-range elastic distortion of the crystal. These effects are being investigated by Huntington^{13,14} both for the formation of defects and the formation of saddle point configuration during diffusion.

At the present state of analysis, from Eq. (15) the strong inference is that the entropy of formation for vacancies is positive while for interstitials it is negative. Extensive calculations will be necessary, however, before dependable theoretical values for this entropy can be found.

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¹³ H. B. Huntington, *Phys. Rev.* **91**, 246 (1953).

¹⁴ H. B. Huntington (to be published).

Temperature Variation of the Magnetic Inelastic Scattering of Slow Neutrons*

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The main features of the temperature variation of the magnetic inelastic scattering of slow neutrons in iron, recently measured by Palevsky and Hughes, are accounted for, by use of a theoretical description of the scattering in terms of the correlation between pairs of spins at different positions and different times. Proofs will be given in a later paper devoted to a general discussion of space-time correlations and of their use in scattering theory.

THE temperature variation of the total scattering cross section of iron for very slow neutrons has been measured by Palevsky and Hughes¹ in the temperature range $100^\circ\text{K} < T < 1300^\circ\text{K}$ and for neutron incident wavelength λ varying from 5 to 13Å. After subtracting the contribution of scattering by the iron nuclei, one obtains a considerable residual cross section σ_{magn} to be attributed to the magnetic interaction of the neutron with the magnetic electrons of iron. Two striking properties of the residual scattering are revealed by the experiment:

(a) For temperatures above as well as below the Curie temperature $T_c = 1043^\circ\text{K}$ of iron, σ_{magn} is proportional to λ , indicating that the scattering is inelastic.

(b) As a function of temperature σ_{magn} , which vanishes at $T=0$ on theoretical grounds, exhibits a maximum at the Curie point, with an abrupt change of slope. Its decrease on the left of the maximum is much faster than on the right. The ratio $\sigma_{\text{magn}}/\sigma_l$ of σ_{magn} to

its largest observed value σ_l is independent of λ and is plotted against T/T_c in Fig. 1 (solid line), with indication of the experimental points. One has $\sigma_l = 3.5$ barns for $\lambda = 8\text{Å}$.

Our object is to interpret briefly these properties, restricting ourselves to temperatures below 1179°K , the α - γ transition point of iron.

The inelastic nature of the magnetic scattering (property *a*) for wavelengths λ larger than the Bragg cutoff is a direct consequence of the strong exchange interaction between the magnetic spins of iron: when the Bragg condition is not satisfied the energy transfer ΔE between neutrons and system of interacting spins is continuously distributed, without singular peak at $\Delta E = 0$. This fact is independent of the presence or absence of long-range order and holds thus for paramagnetic as well as ferromagnetic iron. It was recognized by Van Vleck,² who discussed a few features of the distribution of ΔE in the limit of infinite temperature.

For the magnitude and temperature dependence of

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¹ H. Palevsky and D. J. Hughes, *Phys. Rev.* **92**, 202 (1953).

² J. H. Van Vleck, *Phys. Rev.* **55**, 924 (1939).