

inhomogeneous distortion around the interstitial can be shown to reduce the effective cross section of the interstitial (a similar distortion would increase the cross section of the vacancy). Theoretical estimates of this correction are at present unreliable but are probably not greater than 20 percent.

In principle, the occurrence of pairs is detectable by examining the wavelength dependence of the attenuation. These preliminary experiments are not sufficiently accurate past 9 Å to establish the existence of a wavelength dependence. The fact that no wavelength dependence which would be outside experimental error is observable indicates that only a small fraction of the displaced atoms may be present in the form of pairs. More refined experiments will be necessary to establish this point definitely.

The technique described here is applicable, of course, to other materials. The most important limitation is that the absorption cross section has to be small. It appears that with some refinements the number of displaced atoms may be determined in, say, aluminum

($\sigma_a=0.215$ barn). Experimentation with such a metal calls for low-temperature irradiation and measurement because the defects are known to anneal out well below room temperature. Consequently, the necessary techniques are considerably more involved. Sensitivity may be gained, however, by measuring the total transmitted beam rather than using the spectrometer technique since very little change in lattice parameter is expected. The last cutoff for aluminum appears at $\lambda=2d_{(111)}=4.66$ Å which, because of the nature of the pile neutron spectrum, also offers a substantial increase in intensity. However, this may be compensated for almost completely by the necessity of using a beam of smaller cross section and an external filter because present low-temperature irradiation facilities limit specimen sizes.

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Calculation of the Entropies of Lattice Defects*

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The entropy of lattice defects are here considered in somewhat greater detail than previously. Calculations are out to estimate the intrinsic entropies associated with such lattice defects as interstitialcies and vacancies, and with the activated complexes of vacancy and ring diffusion. The present application is to fcc metals and a very simplified force model representing only the closed-shell, ion-core repulsions of copper has been used. The problem consists in evaluating the change of lattice vibrations with the introduction of each defect. The method is in a first approximation to consider vibrations localized around the defect as separate from elastic vibrations at appreciable distance from the defect. Only in the region far from the defect is the entropy contribution always positive. The surface condition of zero pressure introduces a term which reduces the effect of the "localized" vibrations. In general the intrinsic entropy is less positive for those configurations where there is crowding of the atoms than for those configurations where the atoms have greater free volume.

IN any calculation of the number of defects which may be expected in a crystal at thermal equilibrium at fixed temperature and pressure one proceeds by minimizing the Gibbs free energy of the system. By the general arguments of statistical mechanics one shows that the fraction of the lattice sites which may be associated with a particular lattice defect is given by $\exp(-\Delta G/RT)$, where ΔG is the change in the Gibbs potential of the crystal with the addition of one mole of defects. The wide use of this expression is a natural

consequence of the very great importance of the role of defects in the most of the active fields of present solid state physics, such as optical properties, radiation damage, plastic properties and electrical properties. For those phenomena which depend not simply on the existence of the defects but upon their stepwise motion (diffusion, ionic conductivity, and some aspects of internal friction), the expression¹ for the rate change includes a similar factor, $\exp(-\Delta G^*/RT)$, where ΔG^* is the change in the Gibbs potential with the addition of one mole of defects leaving out of consideration the degree of freedom associated with the direction of motion. Hereafter the asterisk will be omitted here

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¹ Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

and the general features of both situations will be discussed in terms of a simple ΔG .

From the standard thermodynamic relation one shows

$$\Delta G = \Delta H - T\Delta S, \quad (1)$$

where ΔH is the change in enthalpy and ΔS is the change in entropy (exclusive of mixing entropy) resulting from the addition of a mole of defects. Since ΔH and ΔS appear in general quite temperature-independent,² it is customary to speak of a temperature-independent factor $\exp(\Delta S/R)$ and a temperature-dependent factor $\exp(-\Delta H/RT)$, where the nomenclature applies equally to finding the equilibrium number of defects or to the treatment of rate processes involving defects. Accordingly the evaluation of the ΔS in the temperature-independent factor can be approached from another fundamental thermodynamic formula to give

$$\Delta S = -(\partial\Delta G/\partial T)_p. \quad (2)$$

This problem has been treated several times in one form or another in the literature,³ not always from consistent viewpoints. Individual aspects have received particular emphasis in special applications. On some points there has been duplication and confusion. For example the role of the thermal expansion in particular needs some clarification with respect to Eq. (2). One might at first think that ΔG would show a temperature dependence because of the change of volume-dependent atomic forces with the thermal expansion. Some care must be exercised here, however. For theoretical models which set up one term in the Helmholtz free energy, which represents the energy of the crystal at 0°K and is dependent on volume only, the said term can make no contribution to the entropy of the system since

$$\Delta S = -(\partial\Delta A/\partial T)_V, \quad (3)$$

where A is the Helmholtz potential. This point has been recently put forward by Vineyard and Dienes⁴ but it is perhaps well to stress it here also.

The basic approach to this problem should be along the lines of statistical mechanics. The crystal and its defects can be fundamentally treated as a collection of reasonably harmonic oscillators whose vibrational contribution to A is given by

$$A_p = -kT \sum_i \ln\{1 - \exp(-h\nu_i/kT)\}^{-1}, \quad (4)$$

where the ν_i are the frequencies of the crystal. Applying

² For a very complete experimental verification of the temperature independence of ΔS and ΔH in the diffusion of antimony in silver, see Sonder, Slifkin, and Tomizuka, *Phys. Rev.* **93**, 970 (1954).

³ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (University Press, Oxford, 1948); J. Frenkel, *Kinetic Theory of Liquids* (Clarendon Press, Oxford, 1946), Chap. I; G. J. Dienes, *Phys. Rev.* **89**, 185 (1953); Y. Haven and J. H. van Santen, *Phillips Research Repts.* **7**, 474 (1952); Huntington, Shirn, and Wajda, *Phys. Rev.* **91**, 246(A) (1953).

⁴ G. H. Vineyard and G. J. Dienes, *Phys. Rev.* **93**, 265 (1954).

Eq. (3), one obtains

$$\Delta S = -k \sum_i \{ \ln[1 - \exp(-h\nu_i/kT)]^{-1} - (h\nu_i/kT) [\exp(h\nu_i/kT) - 1]^{-1} \}, \quad (5)$$

or for $kT \gg h\nu_i$, which means T well above the Debye temperature,

$$\Delta S = -k \sum_i [\ln(h\nu_i/kT) + \text{terms of order unity}]. \quad (6)$$

If the original frequencies for the lattice are ν_{i0} and the final frequencies with defect are ν_{if} , then the complete change in entropy is

$$\Delta S = k \sum_i \ln(\nu_{i0}/\nu_{if}). \quad (7)$$

The problem of determining the specific entropy of a particular lattice defect (or activated complex) reduces to evaluating the change in the elastic spectrum that results from the introduction of the defect.

One procedure for accomplishing this would be to investigate the perturbations on the actual frequencies of the elastic waves of the crystal that the defect causes. A solution along these lines is being pursued by various investigators⁵ and its successful completion will supply the only completely reliable treatment. The mathematical difficulties are, however, formidable. Our approach has been approximate but affords a program which should give some insight into the physical considerations that are involved. It proceeds from a consideration of localized vibrations as in the Einstein model. In this way one considers three regions: the atoms in the immediate neighborhood of the defect, the region over which the defect sets up an elastic stress field and finally the surface conditions and their influence.

For the immediate neighborhood of the defect an Einstein model is invoked whereby each atom near the defect is considered to vibrate individually as though in the field of its neighbors all held fixed. It is readily apparent that where the defect pushes atoms closer together than the equilibrium distance the frequencies rise and the ΔS is negative. Conversely, where the defect causes local expansion as in the case of a vacancy, one can expect the frequencies to drop and the ΔS to go positive. Again this statistical result finds its ready analog in the thermodynamic relation,

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V > 0. \quad (8)$$

The neglect of coupling between the vibrations inherent in the Einstein model is a serious limitation. Various devices have been used to compensate for its effect for the different defects and will be discussed later. In the region somewhat more removed from the defect, there is a radial strain falling off as r^{-2} . The strain field from this "center of pressure"⁶ is pure shear with no dilatation. Since the strain is practically temperature-

⁵ For example, K. F. Stripp and J. G. Kirkwood, *J. Chem. Phys.* **22**, 1579 (1954).

⁶ A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), fourth edition, Chap. XI.

independent, the stored elastic energy will have a temperature variation determined principally by the temperature variation of the elastic constants of the medium. Because the latter usually decrease with temperature, the contribution to the defect entropy from this region will be positive. This type of argument has been effectively used by Zener⁷ and others in the past, sometimes with the implication that because of it all defect entropies should be positive. It would appear, however, that its validity is limited to those regions where the strains are elastic and the dilatation vanishes. Finally, the boundary conditions at the surface of the specimen have their influence on the defect entropy. In general the condition that the pressure vanishes requires that a constant dilatation be added to the strain pattern of the center of pressure with the sign of the dilatation the same as that of the local pressure, i.e., for an interstitial defect the dilatation is positive, conversely for a vacancy it is negative. The effect of a positive dilatation is to lower the lattice frequencies and again a contraction will raise them. In every case the effect of the surface boundary condition is to compensate in part for the entropy change associated with the immediate region of the defect.

FORCE MODEL AND ATOMIC VIBRATIONS

Application to the consideration of specific defects requires a force model which will give a reasonable characterization of atomic forces with a minimum of mathematical complexity. We have chosen to consider that, in the case of the metals at least, the cohesive forces are primarily volume-dependent and of long-range nature, relatively unaffected by the presence of defects. The repulsive forces are central in nature and arise from the repulsion of the closed ion shells. These vary rapidly with interatomic distance and for many materials make the dominant contribution to the elastic constants. As is quite usual, we shall represent the ion-core interaction by an exponential potential of the Born-Mayer⁸ type,

$$U(r) = A \exp[-\rho(r-r_0)/r_0], \quad (9)$$

where A gives the magnitude of the interaction per ion pair at the equilibrium interatomic distance r_0 and ρ is the dimensionless constant whose magnitude is a measure of the rapidity with which the ion core interaction changes with distance. In this work we have taken ρ to be 13.6, a value which has been shown⁹ to give a reasonable approximation of the elastic behavior of copper. Since we shall be here mainly concerned with ratios of frequencies, it will not be necessary to choose a value for A .

⁷ C. Zener, *J. Appl. Phys.* **22**, 372 (1951); *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), pp. 289–314.

⁸ F. Seitz, *Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. II.

⁹ C. Zener, *Acta Cryst.* **3**, 346 (1950); H. B. Huntington, *Phys. Rev.* **91**, 1092 (1953).

1. Einstein Model

Next, in calculating the elastic frequencies of the atoms near the defect on the basis of the Einstein model, one considers each atom to move in a potential minimum established by its interactions with each of its neighbors, presumed to be held fixed. The increase in energy acquired by the j th atom as it moves from its equilibrium position may be written

$$\Delta V_j = \sum_i \Delta V_{ij}(r_{ij}), \quad (10)$$

where i numbers the neighbors of the j th atom and ΔV_{ij} is the part of ΔV_j which is contributed by the i th atom,

$$\Delta V_i = U'(r)\delta_{i1} + \delta_{i1}^2 U_0''(r)/2 + \delta_{i1}^2 U'(r)/2r, \quad (11)$$

where δ_{i1} and $\delta_{i\perp}$ are the displacements of the j th atom, respectively parallel and perpendicular to the line of centers between i and j . For a collection of particles at stable equilibrium, the potential at the j th particle is

$$\Delta V_j = \frac{1}{2} \sum_i [U'' \cos^2 \theta_i + (U'/r) \sin^2 \theta_i] \delta_j^2, \quad (12)$$

where δ_j is the displacement of the j th atom and θ_i is the angle that the displacement makes with the line of centers between atoms i and j . Our procedure is then to evaluate ΔV_j along the principal axes for each atom in units of $A\delta^2/r_0^2$ and compare the result with the value for the perfect face-centered lattice,

$$\Delta V_1 = \frac{1}{2} \delta^2 [4U'' + 8U'/r]_{r_0} = (2\rho^2 - 4\rho)A(\delta/r_0)^2. \quad (13)$$

This technique has been applied to the following defects: a single interstitial atom, first with the nearest neighbors at their normal lattice positions and later with these neighbors relaxed to new equilibrium position; a single vacancy, both unrelaxed and relaxed; a vacancy at the saddle point for migration, both unrelaxed and relaxed; and a ring mechanism at the saddle point. In a situation of high crowding, ΔV_j is large in the direction of compression because U'' is large and positive. This means increased frequency and lowered entropy. At right angles to the direction of compression, the frequencies are reduced by (U'/r) which is negative but an order of magnitude $1/\rho$ smaller than U'' . For very severe uniaxial compressions it is possible for ΔV at right angles to compression axis to become small and go negative—corresponding to unstable equilibrium. Such a situation did occur for the unrelaxed nearest neighbors of the interstitial, but with relaxation stable equilibrium was restored and the geometric mean of all the frequencies increased. In general the U'/r term played a secondary role.

Because the frequencies vary as the square root of ΔV , the form of Eq. (7) useful for computation was

$$\Delta S = \frac{1}{2} k \sum_j \ln(\Delta V_1 / \Delta V_j). \quad (7a)$$

The corresponding results are tabulated in the first two rows of Table I for unrelaxed and relaxed conditions respectively.

TABLE I. ΔS for various defects. (All values in units of k .)

Defect	Interstitial	Vacancy	Vacancy saddle point	Ring of four
Einstein model	Unrelaxed	—	1.85	-0.65
	Relaxed	-6.4	1.69	+0.87
Coupling correction	0.2	0.09		-1.96
Elastic term	4.9	0.13	0.26	
Surface term	2.1	-0.44	-0.20	
Total	0.8	1.47	0.93	

For the interstitial configuration the frequencies of the interstitial and its six neighbors are analyzed. As a detailed example of the method values for ΔV for the interstitial atom, which is independent of direction, and for the neighbors for radial and tangential motion are shown for both the unrelaxed and relaxed cases in Table II. Because of the negative value of ΔV for the tangential motion of the neighbors, no value can be given for ΔS in the appropriate position in Table I. This example points up the importance of considering the relaxation, and in general it can be said that its effect is considerable, especially when crowding takes place. Here the relaxation consisted of a radial outward motion of the neighbors of about $0.15r_0$, determined as the position of minimum potential energy.

For the vacancy, the twelve nearest neighbors of the vacancy were considered and the effect of the vacancy on their radial and tangential frequencies taken into account. The relaxation consisted of an inward radial displacement of about $0.015r_0$ and reduces the "local" entropy from $1.85k$ to $1.69k$. In considering the saddle point for vacancy diffusion, one is interested in the activated complex which occurs when one of the atoms neighboring the vacancy moves halfway in to fill it. The moving atom passes through the center of a rectangle formed by four atoms at the corners at a distance of $(\sqrt{3}/2)r_0$ before relaxation. Because of the crowding the frequencies of these five atoms are increased, even after a relaxation outward of the corner atoms of about $0.06r_0$. The associated entropy decrease is $-1.10k$. There are, however, fourteen other atoms which are essentially in the environment of a neighbor of a vacancy and they contribute $7/6$ the intrinsic entropy of a vacancy or $1.97k$. For the total entropy of the saddle point (always of course omitting from consideration the degree of freedom associated with the direction of diffusion), an increase of entropy of $0.87k$ results.

In the analysis of ring diffusion,¹⁰ the radial frequencies of four partners in the ring and also their motion perpendicular to the plane of the ring were taken into account, also the motion of the eight atoms directly above and below the ring.

¹⁰ C. Zener, *Acta Cryst.* **3**, 346 (1950).

2. Effect of Coupling

Our procedure has been criticized because we have disregarded the normal modes of the lattice to treat the vibrations of the atoms as uncoupled. To gain some idea of the seriousness of this shortcoming, a normal mode solution was carried out for a seven-particle problem which simulated the configuration of an interstitial atom surrounded by six nearest neighbors. Four force constants were introduced to account for forces of the four following varieties: (a) those between interstitial and neighbors, (b) those between neighbors, (c) those restraining the neighbors from radial motions away from equilibrium position, and (d) those restraining neighbors from tangential displacements. The labor involved was somewhat less than might at first be imagined. All but three of the frequencies were degenerate. The analysis required the solution of one cubic equation. The remaining frequencies were rational functions of the force constants. The product of all 21 frequencies was compared with the analogous product as obtained from the same set of constants using the usual approximation where coupling effects are neglected. Because of the relaxation the distances between neighbors were considerably extended and the coupling forces between them very weak. The principal effect came from the coupling of the motions of the interstitial and individual neighbors. Three sets of triply degenerate frequencies are involved, and their solution depends on a secular determinant of the form

$$\begin{vmatrix} a+c & -a & 0 \\ -a & 2a & -a \\ 0 & -a & a+c \end{vmatrix},$$

where a and c refer to the force constants mentioned earlier in this paragraph. The product of the roots is given by the value of the determinant. For the Einstein model (no coupling) the corresponding product is just the product of the diagonal elements. The ratio of the two is $c/(a+c)$, which is in our case 0.59. The corresponding entropy increase is $-(3k/2)\ln 0.59$, or $+0.81k$.

One must now compare this value with the increase in entropy for a complex of six atoms, stationed at the face centers of a cube to represent the normal lattice and subject to the force constants, b , c , and d . The normal frequencies for this aggregate are easily obtained. A comparison of the frequency product with and without coupling gives an increase of $0.38k$ in entropy. (In effect, coupling adds only nondiagonal

TABLE II. V 's for the interstitial configuration in units of $A\delta^2/r_0^2$.

	V -interstitial	V -neighbor-radial	V -neighbor-tangential
Unrelaxed	7900	5290	-204
Relaxed	1050	1279	339

terms to the potential matrix. It always decreases the frequency product since it increases the frequency spread without changing the sum of the squares of the frequencies.) To the $0.38k$ entropy change must be added the entropy change of the average lattice atom with coupling, to take into account the seventh atom which was formerly the interstitial. It is shown in the Appendix that, on going from the Einstein to the Debye model, the average entropy per degree of freedom increases by $0.078k$. Adding three times this quantity to $0.38k$, one obtains $0.62k$ which is $0.19k$ less than the entropy increase with coupling for the complex with interstitial. It appears that the effect of coupling is small for the intrinsic entropy of an interstitial. In the third line of Table I, $0.2k$ is entered as an estimate of the magnitude of the correction involved.

A similar treatment for a vacancy and its twelve neighbors was not attempted because of the formidable complications associated with the large number of degrees of freedom. However, the two-dimensional analog, namely an hexagonal ring of atoms with and without a central atom, was investigated and the results proved illuminating. The radial and tangential displacements of the hexagon atoms were chosen as coordinates. Symmetry considerations indicate that the normal modes for this system, like that of six similar particles on a string, are characterized by representations of the form $\exp(isn/6)$, where n numbers the particles in rotation and s , running from 1 to 6, numbers the mode. For each value of s there are two modes depending on the phase relation between the radial and tangential motions. Modes with s equal to 1 and 5 are coupled together in two pairs of degenerate frequencies, and similarly for s equal to 2 and 4. The introduction of a central atom adds two more degrees of freedom. The coordinates of this atom represent a quantity with vector symmetry which couples only with the modes with s equal to 1 and 5. The solution of the resulting cubic equation gives three doubly degenerate modes. Evaluation of the frequency products gives for the hexagon with vacancy an entropy increase of $0.46k$ with coupling, and for the filled hexagon (less the entropy change for one normal atom with coupling) $0.37k$, or a net change of $0.09k$ for the vacancy in the hexagon with coupling. It should be pointed out that only one force constant is involved here and that the result is independent of its magnitude. Again the effect of coupling is nearly negligible on the defect entropy. As an indication of its size, $0.09k$ is entered for the vacancy on the third line of Table I.

In their calculation on the effect of vacancies on lattice entropy, Stripp and Kirkwood⁵ give a first order contribution for the isolated vacancy without relaxation of $1.5k$ and a second-order contribution of $0.225k$. For comparison with their value of $1.73k$, the Einstein model with central forces gives

$$\Delta S = -zk/2 \ln(1-3/z) = 1.68k$$

for $z=12$. Adding on the estimated correction of $0.09k$, one obtains $1.77k$ which is certainly fortuitously close. The discrepancy between $1.68k$ and the value of $1.85k$ listed in Table I arises because our model tacitly assumes, in addition to central forces, a volume-dependent, cohesive force to maintain stability.

3. Elastic Energy Contribution

To calculate the contribution to the defect entropy arising from regions somewhat removed from the defect, one can resort to the thermodynamic method of Zener⁷ and apply Eq. (2) using the stored energy for ΔG . This is permissible in this region because elastic theory is valid here and the elastic solution for a center of pressure gives no dilatation. The general form for the displacement from such a center is⁶

$$\xi_i = x_i(A + B/r^3), \quad (14)$$

where the coefficient A gives a uniform dilatation and the B term gives the strain pattern from the center of pressure in an infinite medium. From the displacements one can obtain the strain and the stresses. The resulting expression for the elastic energy density follows:

$$\text{Energy density} = \frac{3}{2}[(3\lambda + 2\mu)A^2 + (2B)^2\mu/r^6], \quad (15)$$

where λ and μ are the Lamé elastic constants. The condition at the surface determines A . For zero pressure at great radius R , one obtains

$$A = 4B\mu/(3\lambda + 2\mu)R^3, \quad (16)$$

which shows that the A term in Eq. (15) is negligible compared with the B term. The total elastic energy outside a sphere of radius r_1 is then approximately

$$\Delta G = 8\pi\mu B^2/r_1^3, \quad (17)$$

and the contribution to ΔS is

$$\Delta S_{\text{elas}} = (-8\pi B^2/r_1^3)(d\mu/dT). \quad (18)$$

This expression has been evaluated for copper, taking for $d\mu/dT = -0.38 \times 10^9$ dynes/cm²-deg as an average between -0.45 and -0.28×10^4 dynes/cm²-deg, respectively the derivatives with respect to temperature of the elastic constants c_{44} and $\frac{1}{2}(c_{11} - c_{12})$ for copper.¹¹ The constant B is determined from our assumed relaxation of defect neighbors and for the interstitial is taken to have the value $0.025d^3$, for the vacancy $-0.0053d^3$, where d is the lattice constant, $3.61A$. The radius r_1 is chosen so that $4\pi r_1^3/3$ is the volume containing the same number of atoms as were considered in the normal mode treatment, seven for the interstitial case and twelve for the vacancy. The resulting value for B^2/r_1^3 was $15.0 \times 10^{-4}d^3$ for the interstitial and $3.9 \times 10^{-5}d^3$ for the vacancy. The values for ΔS_{elas}

¹¹ These experimental values for the variation of the elastic constants of copper with temperature were supplied by Dr. C. S. Smith by private communication.

are given in the fourth row of Table I as $4.9k$ for the interstitialcy and $0.13k$ for the vacancy.

Configurations not possessing spherical symmetry cannot be treated as simply. Because of the importance of the vacancy saddle point in the theory of diffusion we have made an effort to handle this case by introducing a third term in the elastic potential,⁶ so that

$$\chi = \frac{1}{2}Ar^2 - B/r + C(3 \cos^2\theta - 1)/2r^3. \quad (19)$$

The gradient of χ gives the displacement vector but now, in addition to the terms appearing in Eq. (14), there is an additional term in the radial component varying with angle and a nonradial component which arise from the term in the second spherical harmonic. The constants are chosen to give a radial displacement of $-0.015r_0$ for $r = 1.5r_0$, $\theta = 0$ and of $0.06r_0$ for $r = 0.87r_0$, $\theta = \pi/2$. (The direction of the θ axis coincides with the direction of the diffusion jump.) One obtains

$$B = -0.0024r_0^3, \quad 3C = 0.072r_0^5. \quad (20)$$

The contribution to the energy density to be added to Eq. (15) is

$$\frac{1}{2}(3C/r^5)^2(45 \cos^4\theta - 10 \cos^2\theta + 13)\mu. \quad (21)$$

The additional contribution to Eq. (17) is

$$\Delta G(C) = 16.7(3C)^2\mu/r_1^7, \quad (22)$$

where r_1 is the spherical radius needed to enclose 19 atoms, and to Eq. (18) add

$$\Delta S(C) = -16.7(3C)^2/r_1^7(d\mu/dT). \quad (23)$$

The evaluation of Eqs. (18) and (23) for the appropriate choices of B , C , and r_1 gives respectively $0.002k$ and $0.262k$, or a total of $0.26k$ for the entropy change of the vacancy saddle point arising from the stored elastic energy outside r_1 .

4. Surface Effect

As has already been pointed out in the preceding section the elastic solution for a center of pressure contains a term corresponding to a uniform dilatation which is introduced to fit the boundary conditions at the surface of zero pressure. Though this term makes a negligible contribution to the elastic energy of the deformation it makes a considerable contribution to the defect entropy because the elastic constants, and hence the vibration frequencies, are decreasing functions of volume. For the long wave vibrations the change in the frequencies, ν_i , are

$$\Delta\nu_i/\nu_i = \frac{1}{2}(\Delta M_i/M_i + \Delta V/V), \quad (24)$$

where M_i are the appropriate elastic moduli. For copper the effect of pressure on the elastic constants has been measured by Lazarus¹² and found to be linear out to 10^4 bars. At this maximum pressure the fractional changes in the elastic constants were 0.028 for c_{11} ,

0.030 for c_{12} , and 0.01 for c_{44} with a corresponding fractional change of volume of -0.007 . Taking 0.023 as an average fractional change of elastic modulus at 10^4 bars, one obtains

$$\Delta\nu_i/\nu_i = \frac{1}{2}[(0.023/0.007) - 1]\Delta V/V. \quad (24a)$$

With Eqs. (7) and (16) and under the rough assumption that all frequencies are similarly affected by the dilatation $3A$, the entropy change is

$$\Delta S_{\text{surf}} = +3.4(3N)Ak, \quad (25)$$

where N is the total number of atoms in the lattice, $16R_1^3/3d^3$. Evaluation of S_{surf} gives $2.05k$ for the interstitial and $-0.44k$ for the vacancy. For the vacancy saddle point configuration only the B -term affects A (16) and $\Delta S = -0.20k$, where we have assumed surface equilibrium for the saddle-point configuration.¹³

The surface contribution to the entropy could also be calculated¹⁴ directly from the macroscopic relation,

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V = K\beta, \quad (26)$$

where K is the bulk modulus and β is the thermal coefficient of expansion. Evaluated on this basis, the surface terms would be larger by about 70 percent than the values which have been obtained here with the microscopic model, used throughout for consistency.

DISCUSSION

In the last line of Table I are given the totals for ΔS in three important configurations. One must warn against the literal acceptance of these figures at their face value. The calculations in back of the numbers is uncertain (1) because a greatly oversimplified model has been used to represent the atomic forces and (2) because in the calculations themselves some arbitrary approximations were necessarily introduced at such points as the separation of frequencies into "local" and "elastic" modes, the treatment of the effect of coupling, the fitting of the elastic solution, and others. From a critical standpoint the procedure here is not to be considered as a handbook example on the quantitative calculation of defect entropies, but rather as a qualitative display of the way various considerations might enter into a more precise evaluation. From this standpoint several interesting conclusions can be drawn:

(1) The evaluation of defect entropies from a fundamental standpoint devolves into an analysis of the change of the elastic spectrum of the crystal with the introduction of the defect.

(2) Defects which bring about a local crowding of the lattice appear to have a lower specific entropy than

¹³ Because of the short time the diffusing atom spends at the saddle point configuration it is perhaps quite unrealistic to consider any change in "surface term" during the jump.

¹⁴ We are indebted to Dr. J. D. Eshelby for pointing out this alternate procedure.

¹² David Lazarus, Phys. Rev. 76, 553 (1949).

defects which cause expansion. Here the effect of the "local" term is predominant, though it is partially compensated for by the effect of the dilatation introduced to satisfy the condition at the surface. The ΔS_{surf} has always the opposite sign from the "local" term and compensates for about $\frac{1}{4}$ of it.

(3) Though it appears that most of the defects may have positive entropies, the role of the temperature dependence of the elastic constants in causing this effect appears to have been overemphasized in some quarters. Our calculations show that the size of this term as applied only to the elastic region is often rather small. Since it varies as the square of the displacement it becomes most important in situations involving large distortions, as for an interstitialcy.

(4) The errors involved in using an Einstein model for calculating frequency changes appear to be small as indicated by efforts to take coupling into account to the first order.

(5) The comparisons of these estimates with experimental findings on defect entropies, particularly as they come out of diffusion studies, is not altogether satisfactory. For a vacancy mechanism the temperature-independent factor in the diffusion constant should depend exponentially on the entropy of the vacancy saddle-point configuration. In general, experiments show the entropy to be positive but somewhat larger than the $0.9k$ obtained here. Also, the reason for the fairly consistent correlation between the sizes of activation entropy and activation energy, as experimentally observed, is not easily apparent in terms of the present model. This correlation has been displayed in various forms by different investigators, beginning with the well-known Langmuir-Dushman formula and including the semiempirical relation proposed by Dienes¹⁵ and the recent theory of Zener.⁷ The experiments indicate that the largest positive entropies are found for those materials with the largest activation energies. Of the terms in Table I that make up ΔS for the vacancy saddlepoint, the relatively small "elastic" term for the region surrounding the defect should support such a correlation between activation entropy and activation energy. What the effect of the

term depending on the changes in the "local vibrations" should be is not so easy to see. We have stressed the importance of the change in microscopic density for this quantity. Translated loosely into macroscopic thermodynamic terms, the effect of such density changes can be estimated from Eq. (26). The changes in "local vibrations" therefore should apparently depend in part on the relation (26) and in part on the temperature variation of elastic constants. In each contribution the magnitude of the crystal forces and the effect of thermal expansion play their roles so that the aforementioned correlation between activation energy and entropy may be also understandable in terms of this theory (as well as in terms of a theory which considers only the temperature variation of elastic constants).

APPENDIX

The change in entropy per degree of freedom in going from the Einstein to the Debye vibration model can be estimated by assuming for the Debye model that the density of oscillators per frequency range $d\nu$ is given by $K\nu^2$, where K is normalized so that

$$\int_0^{\nu_m} K\nu^2 d\nu = K\nu_m^3/3 = n, \quad (\text{A1})$$

where n is the total number of oscillators. On the other hand, the Einstein spectrum is a delta function centered at some frequency ν_E , so that the sum of the frequencies squared is unchanged,

$$n\nu_E^2 = K \int_0^{\nu_m} \nu^4 d\nu = 3n\nu_m^2/5. \quad (\text{A2})$$

It follows that ν_E/ν_m is 0.77. To find the entropy increase one evaluates the average of the logarithm of the frequency ratio,

$$S = -(kK/n) \int_0^{\nu_m} \ln(\nu/\nu_E) \nu^2 d\nu = 0.078k. \quad (\text{A3})$$

The analogous quantity for a two-dimensional distribution is $0.153k$. In one dimension there is a logarithmic singularity.

¹⁵ G. J. Dienes, J. Appl. Phys. **21**, 1189 (1950).