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Thermodynamic Properties of Solids Containing Defects*

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Using thermodynamics and elasticity theory, a unified treatment of the changes in the properties of solids containing defects is given. The results are expressed in terms of temperature and pressure derivatives of the energy required to form a single defect. The procedure is most useful for defects described by elasticity theory, where it is shown that the required pressure and temperature dependence of the energy is given by the measured pressure and temperature dependence of the elastic constants appearing in the energy expression for zero pressure and temperature. Some results which would otherwise have to be obtained from lengthy and complicated finite-elasticity calculations, as well as other results not obtainable at all from elasticity theory, are given by simple derivatives of the free energy. The results are specialized to a number of particular defects by using various expressions for the defect energies. These calculations are compared with available measurements of the properties of real crystals. For dislocations, reliable expressions for the energy are most soundly based for this case. Unfortunately, there are relatively few measurements for these defects. A number of specific predictions are made, some of which are partially confirmed by the available data. On the other hand, for the discussion of the large volume of measurements available for point defects, there is no generally acceptable model for the defect energy. The extent to which the properties of crystals containing point defects can be correlated on the basis of several models for the defect energy is explored.

I. INTRODUCTION

THE volume change per defect v of a solid containing defects is given by the thermodynamic relation

$$v=\partial g(p,T)/\partial p\,, \tag{1}$$

where g is the change in the Gibbs free energy per defect, and pressure p and temperature T are the independent variables.

As an example of the application of this relationship, we may consider an isotropic crystal containing screw dislocations. The Gibbs free energy per atomic length of dislocation is then given by

$$g=(Gb^2a/4\pi)[\ln(R/r_0)-1]\,, \tag{2}$$

where G is the shear elastic constant, b the Burgers vector, a the atomic spacing, and R and r_0 are the usual outer and inner cutoff radii of the strain field of the dislocation. Because R and r_0 depend on pressure and temperature in the same way, Eq. (2) has the form

$$g=\alpha GV\,, \tag{3}$$

where α is a constant independent of p and T, and V is the volume of the crystal. Applying Eq. (1) to Eq. (3), one obtains immediately

$$v/g=G'/G-1/B\,, \tag{4}$$

where the prime signifies a derivative with respect to pressure, and B is the bulk modulus of the crystal.

This simple result, found here by a single differentiation, has previously been given by Seeger and Haasen,[1–3] who used a result given by Zener,[4] and by Toupin and Rivlin[5] as the result of relatively involved calculations based upon nonlinear elasticity theory. Equation (4) gives the ratio of the volume change to the energy change of a crystal containing screw dislocations in terms of elastic constants and their pressure coefficients, which may be taken, for example, from ultrasonic measurements.

The thermodynamic method of calculation above depends only on the recognition of the fact, demonstrated in a later section, that Eq. (2) with $G=G(p,T)$ is the proper expression for the Gibbs free-energy change in this case. This method is not restricted to calculations of volume changes. It is also not restricted to isotropic, static, or even elastic systems at zero pressure.

Most calculations of the properties of solids containing defects have been made using other methods. These may be classified as (1) atomistic calculations, which take atomic structure into account through the use of interatomic potentials; (2) elasticity calculations; and (3) other miscellaneous procedures, including empirical considerations and various combinations of the first two groups and thermodynamic methods.

The atomistic calculations are numerical in character, and must in general be repeated for each new material. However, they are able in principle to deal with defects producing large distortions (i.e., usually point defects) if the potentials are well enough known. The earliest calculations of properties of crystals containing structural point defects were of an atomistic nature, beginning with the work of Huntington and Seitz[6] on the activation energy of self-diffusion in copper. This has been followed by a large number of similar atomic-type calculations of formation energies of vacancies and interstitials. There is now an extensive literature on this subject, and references can be found in several recent

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[3] A. Seeger and P. Haasen, Phil. Mag. 3, 470 (1958).

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[6] H. B. Huntington and F. Seitz, Phys. Rev. 61, 315 (1942).

review articles.[7,8] Some of these calculations[9–11] also give the volume change associated with the defect. Dienes[12] has used an atomic model in a calculation of the effect of point defects on the second-order elastic constants in bcc and fcc metals.

Possibly the simplest types of calculations are those using the concepts of basic elasticity theory. Eshelby[13] has given a very general treatment of volume and lattice-parameter changes of crystals containing point defects using linear elasticity theory. There are a number of estimates based on linear elasticity theory of the effects of vacancies on the bulk modulus of materials. The earliest of these[14–17] considered only a spherical inclusion in the lattice, and later[18] the effects of relaxation about the inclusion were considered. Nonlinear elasticity theory has been used to calculate the volume changes of crystals containing dislocations, as already mentioned.

The thermodynamic type of calculation is very useful for defects because of its generality and because this approach is indispensible in the calculation of the concentration of thermally generated defects. Starting with a general expression for the Gibbs free energy of a crystal containing defects, thermodynamics has often been used to obtain by simple differentiation expressions for the equilibrium concentration of defects, the entropy, and specific heat of real crystals.[19] However, the rest of the thermodynamic properties are not then found in the same way, nor is any specific model for the pressure and temperature dependence of the formation energy used. On the other hand, Keyes[20] has used thermodynamic relations to relate volume and entropy changes to the Gibbs free-energy changes, and Zener[4] has used thermodynamic relations to derive an expression for volume changes of crystals containing defects.

It is easily seen that all the thermodynamic properties of crystals containing defects can be found once the Gibbs free energy of the imperfect crystals is specified. This fact, however, has not been utilized in any of the defect calculations to the present time. The present work will therefore be concerned with expressing all the thermodynamic properties of crystals containing defects in terms of the Gibbs free energy required to make the defect. The results, given entirely in terms of the pressure and temperature dependence of the formation energy, will be applicable to any type of defect. Various models of defects can then be used to calculate the Gibbs energy appearing in the general expressions.

In order to obtain quantitative results for particular defects, a number of models for various imperfections are introduced and discussed in Sec. III. The results for the energy of formation deduced from these models are used in the general expressions to calculate various physical properties associated with the appropriate defect, and the results are compared to experimental data.

II. THERMODYNAMICS OF IMPERFECT CRYSTALS

For the thermodynamic treatment of imperfect crystals, we must distinguish between two general classes of defects. The first group consists of equilibrium defects for which the concentration of defects is some unique function of the other thermodynamic variables. The second class of defects are those which are fixed in number in the material in nonequilibrium concentrations. This class of defects is encountered in radiation damage, quenching, and plastic deformation experiments. For both classes of defects, the relative concentration of defects is assumed to be small enough so that interactions between defects can be neglected.

The change in the Gibbs free energy resulting from the production of n defects at n specific positions in the lattice is written ng, where the change per defect g is assumed to be independent of the number of defects. If the defects are free to move through the lattice, a further contribution $-TS_c$, where S_c is the entropy of mixing, must be added to ng. The total Gibbs free energy of a solid containing n defects, $\mathcal{G}$, is therefore written

$$\mathcal{G}=\mathcal{G}_p+ng-TS_c\,, \tag{5}$$

where $\mathcal{G}_p$ is the perfect-crystal Gibbs function, from which all the thermodynamic properties of perfect crystals are obtained. If the defects are in thermal equilibrium in the solid, then

$$n=Ne^{-g/kT}\,, \tag{6}$$

where N is the number of atoms in the solid.

Now the thermodynamic definitions of volume V, entropy S, specific heat C, bulk modulus B, and thermal expansion β can be used to express these quantities in terms of g. The changes in these quantities per defect

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[7] A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach, Science Publishers, Inc., New York, 1963).

[8] R. O. Simmons, J. S. Koehler, and R. W. Balluffi, *Radiation Damage in Solids* (International Atomic Energy Agency, Vienna, 1962), Vol. I.

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[13] J. D. Eshelby, J. Appl. Phys. **25**, 255 (1954).

[14] J. K. Mackenzie, Proc. Phys. Soc. (London) **B63**, 2 (1950).

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[16] Z. Hashin, in *Non-Homogeneities in Elasticity and Plasticity*, edited by W. Olszak (Pergamon Press, Inc., New York, 1959).

[17] D. A. G. Bruggerman, Ann. Phys. (N. Y.) **29**, 160 (1937).

[18] L. Melngailis, Phys. Status Solidi **16**, 247 (1966).

[19] R. E. Howard and A. B. Lidiard, in *Reports on Progress in Physics*, edited by A. C. Strickland (The Institute of Physics and the The Physical Society, London, 1964), p. 11.

[20] R. W. Keyes, in *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill Book Co., New York, 1963), p. 71.

are, respectively,

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\begin{aligned}
&v=\Delta V/n=\partial g/\partial p\,,\\
&s=\Delta S/n=\partial g/\partial T+S_c/n\,,\\
&\frac{\Delta C}{n}=\frac{\partial h}{\partial T}+\frac{h}{n}\frac{\partial n}{\partial T},\\
&\frac{\Delta B}{n}=B\left(v+\frac{v}{n}\frac{\partial n}{\partial p}+\frac{\partial^2 g}{\partial p^2}\right)\bigg/\left(V-Bv\frac{\partial n}{\partial p}-Bn\frac{\partial^2 g}{\partial p^2}\right),\\
&\frac{\Delta\beta}{n}=\frac{v\partial n{:}\partial T+\partial^2 g{:}\partial T\partial p}{V+n\Delta V}-\frac{v\beta}{V}.
\end{aligned}
\tag{7}
$$

Here, h, the change in enthalpy for a single defect, is defined by

$$h\equiv g-T(\partial g/\partial T). \tag{8}$$

Since n is either constant or given by Eq. (6) in the two cases of interest here, the configurational entropy does not enter into any of these expressions except for the total entropy change, and all the thermodynamic properties of materials containing defects are given in terms of the isothermal, isobaric work required to form a single defect and its pressure and temperature derivatives. This procedure has previously been used to find the changes in volume, thermal expansion, and specific heat due to point defects in thermal equilibrium, but the temperature and pressure dependence of g has normally been neglected. Quantitative estimates of this approximation have generally not been available. It is just this part of the above relations that is of particular interest here.

For the case of a fixed number of defects (nonthermal equilibrium), the thermodynamic approach has not been used because no expression for the pressure and temperature dependence of the free energy has been available. Although it has been realized that the isobaric, isothermal work done in creating a defect is the strain energy for an elastic system, no relations giving the explicit pressure and temperature dependence of the strain energy have been available. This is essentially a finite-elasticity question, and the final form of the result depends sensitively on the definition of the elastic constants used. We show now that with the proper choice of elastic constants, the higher-order elasticity effects can be entirely included in the pressure- and temperature-dependent elastic constants in a result which has the same form as the infinitesimal elasticity result.

The differential strain energy associated with a displacement of the surface elements **ds** of the material through an amount **δx** under the action of a stress component σ_{ij} can be expressed as an integral of the work δW done over the surface of the element:

$$\delta W=\oint_s(\sigma_{ij}-p\delta_{ij})\delta x_i ds_j. \tag{9}$$

The usual Cartesian tensor notation with summation over repeated indices is used here. The second term in Eq. (9) is $-p\delta V$, where δV is the volume change in going from the initial to the final state. Using the divergence theorem and the equilibrium condition $\partial\sigma_{ij}/\partial x_j=0$, the strain energy per unit volume of the hydrostatically strained initial state $\delta\omega$ is

$$\delta\omega=-p\delta\phi+\sigma_{ij}\delta\epsilon_{ij}. \tag{10}$$

In this relation, ϕ is the dilatation, and the ϵ_{ij} are the infinitesimal strains, measured from the strained initial state, defined by

$$\delta\epsilon_{ij}=\tfrac{1}{2}(\partial\delta x_i/\partial x_j+\partial\delta x_j/\partial x_i). \tag{11}$$

It is important now, in relating σ_{ij} to ϵ_{ke}, to use a particular definition of the elastic constants. The "stress-strain" elastic constants, which are equivalent to the "sound-wave" elastic constants for all pressures,[21] are defined for infinitesimal strains by

$$C_{ijkl}=\sigma_{ij}/\epsilon_{kl}. \tag{12}$$

This relation holds for all pressures. It does not hold, for example, when the Brugger definitions of elastic constants are used.[21]

Using this relation in Eq. (10), the differential strain-energy density is therefore

$$\delta\omega=-p\delta\phi+C_{ijkl}\epsilon_{kl}\delta\epsilon_{ij}. \tag{13}$$

For an isothermal process, this strain-energy density is the change in Helmholtz free energy δF, so if the process is carried out at constant pressure as well, the second term in Eq. (13) is equal to the change in Gibbs energy for the process, $\delta\mathcal{G}$:

$$\delta\mathcal{G}=\delta F+p\delta\phi=C_{ijkl}\epsilon_{kl}\delta\epsilon_{ij}. \tag{14}$$

Although this simple result has the form of the infinitesimal elasticity theory result, the nonlinear effects with pressure and temperature are fully taken into account without the appearance of any explicit temperature and pressure terms. While the answer found above is in some ways as simple as could be, it is nontrivial and makes it a simple matter to determine the proper expression for $g(p,T)$ for a defect described elastically. That is, the temperature and pressure dependence of the Gibbs free energy in an isobaric, isothermal process described by elasticity theory is obtained by using the experimentally measured pressure and temperature elastic constants in place of the corresponding elastic constants in the expression for the strain-energy density obtained at zero temperature and pressure.

The results found in this way for the volume change of a self-stressed medium would otherwise involve fairly involved third-order elasticity theory. The calculation of the bulk modulus change of a self-stressed material by elasticity theory involves fourth-order elasticity theory and fourth-order elastic constants which are not

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[21] D. C. Wallace, Phys. Rev. **162**, 776 (1967).

available. The modulus change computed by the thermodynamic approach correspondingly involves second-order pressure derivatives of elastic constants which are also not generally available. This difficulty can be avoided by using the results of an analysis of pressure-volume relationships made by Anderson.[22] He analyzed a large number of experimental determinations of the pressure-volume relationships of crystals to very high pressures ($\sim 10^5$ bar) and deduced the bulk modulus as a function of pressure by differentiation of the pressure-volume curves. Although the volume dependence of the bulk modulus is not simple, he found that the pressure dependence of B, even to these very high pressures, was a simple linear relationship.

In view of this observed linear pressure dependence of B, it would seem reasonable to suppose that the other elastic constants might be represented in a similar manner. This linear dependence is indeed found for the other constants measured as a function of pressure, although the data available for the shear constants generally extend only to about 10^4 bar.

There has been one measurement of second-order pressure derivatives of elastic constants, made by Chang and Barsch on three cesium halides.[23] They find that these derivatives range between 1 and 5×10^{11} cm^2/dyn for the various constants. The first- and second-order pressure derivatives enter the expression for ΔB in the combination $C'/C+BC''$, so these values for the second-order derivatives would give a contribution comparable to the first, contrary to the assumption made above. However, the Chang and Barsch results are in disagreement with the measurements of p-V relationships by Bridgman,[24] which indicate almost no deviation from linearity in the bulk modulus at pressures up to ten times those used by Chang and Barsch. Furthermore, the small deviations found by Bridgman are in the opposite direction from the Chang and Barsch results. In view of the very linear behavior found from the Bridgman results for the other materials tested, it therefore seems reasonable for the moment to neglect the second-order pressure derivatives in general. It should be noted that if the elastic energy contains a product of elastic constants, as if often the case, the largest contribution to the bulk modulus change is a cross term of the form

$$\frac{B}{C_i}\frac{\partial C_i}{\partial p}\frac{1}{C_j}\frac{\partial C_j}{\partial p}, \quad i\neq j.$$

This term is typically one order of magnitude larger than $\partial C_i/\partial p$, so that values of the second-order pressure derivative as large as 10^{-11} cm^2/dyn still have little effect in the modulus change expression.

The expressions for the entropy, specific heat, and thermal expansion changes, which cannot be calculated at all from elasticity theory, are also expressed in terms of derivatives of elastic constants. The thermal expansion and specific heat changes involve various second-order temperature and pressure derivatives, which are not available. The experimental evidence is, however, again that these second-order changes are small, and they will be neglected in obtaining numerical results.

III. DEFECT MODELS AND COMPARISONS WITH EXPERIMENT

A. Dislocations

1. Models

Only the case of a fixed (nonequilibrium) number of dislocations will be considered, since dislocations cannot exist in thermodynamic equilibrium in crystals.[25–27] The principal effect of the dislocation is to introduce an elastic-strain field into the solid. The magnitudes of these strains are found to be reasonably small, so that they can be adequately treated by elasticity theory.

The strains associated with a linear screw dislocation are pure shear, and the strain energy per atomic length of dislocation in an isotropic medium is given in Eq. (2). For this defect, the number n of defects is taken to be the number of atomic lengths Λ/a in the crystal, where Λ is the total dislocation length. All of the parameters entering Eq. (2) are those of the initial state of the perfect crystal at pressure P and temperature T. The fraction R/r_0 is independent of pressure and temperature, since R and r_0 depend on pressure and temperature in the same way. The total energy depends on the pressure and temperature through the product G and volume. Using this form [Eq. (3)] of g in the general relations, we obtain

$$\begin{aligned}
v&=(1/B)(BG'/G-1)g,\\
s&=-[\beta+(1/G)(\partial G/\partial T)]g,\\
\frac{\Delta B}{n}&=V^{-1}\left(B'-\frac{BG'}{G}+\frac{B^2G''}{G}\right)g\\
\frac{\Delta\beta}{n}&=BV^{-1}\left(B^{-1}\frac{\partial B}{\partial T}-G^{-1}\frac{\partial G}{\partial T}+G^{-1}\frac{\partial^2 G}{\partial p\partial T}\right)g,\\
\frac{\Delta C}{n}&=-\frac{T}{B}\left(\beta+\frac{\partial\beta}{\partial T}+\frac{2\beta}{G}\frac{\partial G}{\partial T}+\frac{\partial^2G/\partial T^2}{G}\right)g.
\end{aligned}\tag{15}$$

Higher-order terms in the number of defects have been neglected.

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[22] O. L. Anderson, J. Phys. Chem. Solids **27**, 547 (1966).

[23] Z. P. Chang and G. R. Barsch, Phys. Rev. Letters **19**, 1381 (1967).

[24] P. W. Bridgman, *Physics of High Pressure* (G. Bell and Sons, London, 1949).

[25] J. Friedel, *Dislocations* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1964).

[26] W. T. Read, Jr., *Dislocations in Crystals* (McGraw-Hill Book Co., New York, 1953).

[27] A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Clarendon Press, Oxford, 1953).

Zener[4] has given a general elasticity expression for the volume change in a self-strained medium, in the form

$$\Delta V=(BG'/G-1)\omega_s/B+(B'-1)\omega_D/B\,, \tag{16}$$

where ω_s and ω_D are the shear and dilatational strain energy of the defect. Since the screw dislocation energy is pure shear energy, this is in agreement with the result found in Eq. (15). Moreover, we find, upon comparing Eqs. (15) and (16), that any defect whose elastic strain energy is expressible in the form of Eq. (3) must be pure shear in nature.

In fact, the strain fields associated with most defects are predominantly shear strains. Besides the screw dislocation, which is composed entirely of shear strains, edge dislocations and point defects treated in a sphere-in-hole model are predominantly shear. Even thermal strains arising from lattice vibrations are mostly shear because $\frac{2}{3}$ of the vibrational modes are shear modes, and the longitudinal modes contain a subtsantial amount of shear components. Arguments have also been given that the activation energy of motion of point defects is also of this form.[28]

The expression in Eq. (15) for the entropy and volume changes are identical to those derived by Keyes[20] for self-diffusion. His calculations were based on a continuum model, and the results were obtained by a thermodynamic procedure. It is apparent by comparison that his calculations were, in fact, based on a *GV* model for the defect diffusion energy.

In order to see the general features of this model, and for use in comparison with experimental results, the quantities given in Eq. (15) are tabulated in Table I for a number of different materials. The values of the parameter involved in the relations have been taken from the recent compilation by Barsch and Chang.[29] For the reasons outlined above, the second-order derivatives of G are neglected in ΔB, ΔC, and $\Delta\beta$. The volume, thermal expansion, and bulk modulus changes have been normalized to the corresponding perfect-crystal property, and the entropy and specific heat to k and $3NkT$, respectively, for the sake of convenience. Ω is the perfect-crystal atomic volume or ionic volume in the case of the ionic crystals.

Because of the predominantly shear nature of most defects, the results in Table I, when divided by the energy of formation g, should serve for an order-of-magnitude estimate for the effects of most defects on the properties of materials. It will be seen later that the results of calculations using various other models for defects are indeed fairly close to the results in Table I. All of the fractional changes are of the order of 1%/at.% of defects per eV of defect energy.

TABLE I. Changes in the properties of a number of solids per unit atomic length of a screw dislocation using isotropic elasticity results.

Material	g (eV)	v/Ω	s/k	$\Delta\beta/n\beta$	$\Delta B/nB$	$\Delta C/3NkT$ ($10^3/°\text{K}^2$)
Al	2.46	1.33	14.4	0.85	−0.23	0.60
Cu	3.35	1.01	12.9	0.44	0.58	0.33
Ag	3.02	1.12	13.5	0.41	0.39	0.42
Au	2.76	0.86	8.3	−0.06	0.00	0.19
Na	0.51	0.48	10.3	1.83	0.43	1.45
K	0.45	0.49	9.4	1.79	0.38	1.35
Fe	5.26	1.23	5.0	−1.41	0.95	−0.07
Si	12.0	4.98	5.7	−4.96	−1.88	−0.04
Ge	11.1	0.25	12.7	−1.82	3.55	−0.19
LiF	7.22	2.58	40.8	−0.24	1.94	1.90
NaF	7.38	2.64	44.8	0.17	1.77	1.95
NaCl	6.36	2.83	50.7	0.47	1.42	3.39
KCl	7.84	2.64	61.5	0.91	2.52	3.64
KBr	3.15	3.10	28.9	1.69	1.58	1.99
KI	6.06	3.28	68.0	2.92	2.14	5.08
RbBr	6.40	2.64	66.0	2.12	2.67	4.40
MgO	22.0	2.32	37.3	1.12	1.39	0.37
CsCl	5.62	1.82	32.2	−1.88	1.90	2.39
CsBr	5.43	1.78	21.2	−2.88	1.78	1.46
CsI	5.34	1.91	36.1	−1.88	1.61	1.43
CuZn	8.61	0.55	22.6	−2.17	0.73	0.33

One objection to the above screw-dislocation model is that it treates the solid as an isotropic medium. The strain-energy density for a screw dislocation in a cubic material is also known for certain types of materials, so that the importance of the assumption of isotropy on the results can be calculated and compared directly in this case. The energy, again pure shear, of a screw dislocation whose Burgers vector is in a $\langle 110\rangle$ direction in a cubic crystal is[26]

$$g=(b^2a/2\pi)[\tfrac{1}{2}C_{44}(C_{11}-C_{12})]^{1/2}\ln(R/r_0)\,, \tag{17}$$

where C_{11}, C_{12}, and C_{44} are the usual cubic second-order elastic constants. Thus, the only effect of anisotropy on the previous results for a screw dislocation is that obtained by replacing the shear constant G and its derivatives appearing in those results by the effective shear constant indicated in Eq. (17) and its derivatives. The thermodynamic quantities corresponding to Eq. (15) are given by the relations

$$\begin{aligned}
v&=(2B)^{-1}[B(C_{44}'/C_{44})+B(C_s'/C_s)-2]g\,,\\
\frac{\Delta S}{n}&=-\left(\beta+(2C_{44})^{-1}\frac{\partial C_{44}}{\partial T}+(2C_s')^{-1}\frac{\partial C_s}{\partial T}\right)g\,,\\
\frac{\Delta B}{n}&=\frac{B}{V_p}\left(\frac{B'}{B}-\frac{C_{44}'}{2C_{44}}-\frac{C_s'}{2C_s}\right)g\,,\\
\frac{\Delta\beta}{n}&=(BV_p)^{-1}\left(\frac{1}{B}\frac{\partial B}{\partial T}-(2C_{44})^{-1}\frac{\partial C_{44}}{\partial T}-(2C_s)^{-1}\frac{\partial C_s}{\partial T}\right)g\,,
\end{aligned} \tag{18}$$

and

$$\frac{\Delta C}{n}=-\frac{T}{B}\left(\beta^2+\frac{\partial\beta}{\partial T}+\frac{2\beta}{(C_{44}C_s)^{1/2}}\frac{\partial(C_{44}C_s)^{1/2}}{\partial T}\right)g\,.$$

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[28] C. Zener, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley, J. H. Holloman, R. Maurer, and F. Seitz (Wiley-Interscience, Inc., New York, 1952), p. 295.

[29] G. R. Barsch and Z. P. Chang, Phys. Status Solidi **19**, 139 (1967).

TABLE II. Changes in the properties of solids per unit atomic length of screw dislocation using anisotropic elasticity results.

Material	g (eV)	v/Ω	s/k	$\Delta\beta/n\beta$	$\Delta B/nB$	$\Delta C/3NkT$ ($10^3/°K^2$)
Al	2.44	1.31	14.5	0.76	−0.28	0.62
Cu	2.86	0.80	12.2	0.40	0.50	0.37
Ag	2.61	0.92	12.2	0.38	0.35	0.40
Au	2.41	0.69	6.9	−0.01	−0.08	0.16
Si	11.7	3.86	5.8	−11.0	−22.8	−0.04
Ge	10.7	0.12	11.8	−1.56	3.34	−0.17
LiF	6.85	3.37	49.8	13.6	−7.49	7.50
NaF	7.32	2.24	40.4	10.1	−6.19	5.24
NaCl	6.25	2.32	44.1	9.38	−5.33	7.65
KCl	6.59	0.73	37.4	7.70	−4.18	4.93
KBr	2.76	1.31	18.7	10.5	−6.90	3.16
KI	5.21	1.40	41.2	12.6	−5.77	9.08
RbBr	5.31	0.77	37.9	10.7	−4.59	7.23
MgO	21.4	2.82	43.2	11.2	−4.88	1.77

The numerical evaluations of Eqs. (18) are given in Table II. Here $C_s=(C_{11}-C_{12})/2$.

The results for the volume and entropy changes from this table are very close to the results given in Table I, except for the potassium and rubidium halides, where the pressure derivatives of C_{44} are negative. In the case of $\Delta\beta$, ΔC, and ΔB, the results in the two tables are almost identical for the metals, but differ significantly for the other materials. The reason for this discrepancy can be seen as follows. The only difference between the isotropic and anisotropic results is that the isotropic elastic constants are replaced in the anisotropic case by the square root of the product of the two cubic constants. The average elastic constants for the isotropic case can be taken to be $G=\frac{1}{2}(C_s+C_{44})$, which differs little from the square-root average. The logarithmic derivative is given by $G'/G=(C_{44}'+C_s')/(C_{44}+C_s)$ in the isotropic case, and by

$$(C_{44}C_s)^{-1/2}\frac{\partial(C_{44}C_s)^{1/2}}{\partial p}=\frac{1}{2}\left(\frac{C_{44}'}{C_{44}}+\frac{C_s'}{C_s}\right) \tag{19}$$

in the cubic case. These two averages also differ little for most materials, except for the potassium and rubidium compounds, where C_{44}' is negative. This is the source of the difference in the volume change results found for these materials in Tables I and II.

The second-order derivative of the elastic constant in Eq. (15) is neglected in the isotropic case, but in the anisotropic case it becomes

$$(C_{44}C_s)^{-1/2}\frac{\partial^2(C_{44}C_s)^{1/2}}{\partial p^2}=\frac{1}{2}\frac{C_{44}'}{C_{44}}\frac{C_s'}{C_s}-\frac{1}{4}\left[\left(\frac{C_{44}'}{C_{44}}\right)^2+\left(\frac{C_s'}{C_s}\right)^2\right]. \tag{20}$$

These terms are zero if the logarithmic derivatives are equal. Since this term is the only important difference between the isotropic and anisotropic results, we see that the determining factor for the deviation of the anisotropic from the isotropic results is the degree of anisotropy in the logarithmic derivatives of the elastic constants. These logarithmic derivatives are very nearly equal for most metals, but differ greatly for ionic crystals in accord with the differences in the results of Tables I and II.

It is also possible to calculate the volume change produced by a screw dislocation in an anisotropic cubic crystal directly, using finite-elasticity theory. The result[30] is the same as that given in Eqs. (18). We again make note of the fact that the result given by lengthy finite-elasticity calculations is obtained here by a very simple differentiation of a result derived using only linear elasticity theory.

The strain-energy density of an edge dislocation in an isotropic medium is

$$g=[(C-G)/C](Gb^2a/4\pi)\ln(R/Y_0), \tag{21}$$

where $C=\frac{1}{3}(3B+4G)$ is the elastic constant appropriate for longitudinal strains. The energy again has the form of an elastic constant times a volume, except that the effective elastic constant G_e is a combination of elastic constants. Therefore, the expressions in Eqs. (15) can be used for edge dislocations simply by replacing G by G_e so that

$$G_e=[(C-G)/C]G,$$

$$\frac{G_e'}{G_e}=\frac{C'-G'}{C-G}-\frac{C'}{C}+\frac{G'}{G},$$

$$\frac{G_e''}{G_e}=2\left(\frac{C'-G'}{C-G}\frac{G'}{G}-\frac{C'-G'}{C-G}\frac{C'}{C}-\frac{C'}{C}\frac{G'}{G}\right)+\frac{C''-G''}{C-G}-\frac{C''}{C}+\frac{G''}{G}, \tag{22}$$

with similar expressions for the temperature derivatives˙ The numerical results obtained in this way are very similar to the isotropic screw dislocation results, so they will not be tablulated.

The energy density of an edge dislocation along the [001] direction whose Burger's vector is in the [110] direction, in a cubic material, is also available and is given by[26]

$$g=\frac{C_{11}-C_s}{(C_LC_{11})^{1/2}}(C_{44}C_s)^{1/2}\frac{b^2a}{2\pi}\ln\frac{R}{Y_0}. \tag{23}$$

The cubic shear and longitudinal elastic constants are C_{44} and C_s, and C_{11} and C_L, respectively, where $C_L=\frac{1}{2}(C_{11}+C_{12}+2C_{44})$. The anisotropic energy in Eq. (23) is again similar to the isotropic result in Eq. (21). Thus, for both edge and screw dislocations, the only difference between the isotropic and anisotropic results is that the isotropic shear and longitudinal elastic constants are usually replaced in the anisotropic case by the square

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[30] K. Swartz and A. V. Granato (to be published).

root of the product of the two cubic shear or longitudinal constants.

The dislocation orientation appropriate for Eq. (23) is the observed dislocation orientation in the NaCl structure, and the results for several of these materials are given in Table III. The only important difference between the isotropic and anisotropic results for the above edge and screw dislocation results is determined by the degree of anisotropy of the logarithmic temperature and pressure derivatives of the elastic constants. Since this anisotropy is small in the case of the metals listed in Table I, it seems reasonable to suppose that the isotropic edge dislocation results would be very similar to the anisotropic elasticity results.

This elastic description of dislocations should be reliable in describing static dislocations, but all effects of the motion of the dislocations have been neglected. This dynamic effect should affect the dislocation contribution to such properties as specific heat, thermal expansion, and entropy. Calculations of this kind have been made in the past,[31] but there are no experimental measurements of these quantities at present.

A small-angle grain boundary can be visualized as being made up of a large number of dislocations, so the properties of dislocations discussed above can easily be extended to grain boundaries. The energy of a general grain boundary can be written[26]

$$E=E_0\theta[(A-\ln\theta)], \qquad (24)$$

where E_0 and A are independent of the angle θ, which measures the orientation difference between the adjoining grains. The constant A is analogous to the $\ln(R/r_0)$ term appearing in the edge and screw dislocation results above, so it would have little or no volume dependence. E_0 is given by

$$E_0=\alpha\tau_0 ba^2 \qquad (25)$$

in units of energy per atomic area of grain boundary. The constant α is a number of order unity, depending on the nature of the grain boundary. The quantity τ_0 is equal to the coefficient of $(b^2/4\pi)\ln(R/r_0)$ in Eqs. (2) or (21) when the dislocations associated with the boundary are screw or edge dislocations, respectively. Therefore, the dislocation results of Table I apply as well to grain boundaries, and the table should be useful in describing the properties of heavily deformed materials.

TABLE. III. Changes in the properties of a number of solids per unit atomic length of edge dislocation using anisotropic elasticity results.

Material	g (eV)	v/Ω	s/k	$\Delta\beta/n\beta$	$\Delta B/nB$	$\Delta C/3NkT$ ($10^3/°K^2$)
LiF	6.01	3.54	45.02	10.23	−6.56	6.02
NaF	6.66	2.70	38.72	9.14	−7.50	4.59
NaCl	5.81	2.70	42.30	8.55	−6.49	6.80
KCl	6.08	1.38	35.43	8.11	−8.11	4.51
KBr	2.61	1.80	17.41	9.61	−9.46	2.78
KI	4.96	1.97	36.77	10.94	−9.49	7.72
RbBr	5.14	1.42	35.44	10.35	−9.54	6.44
MgO	18.30	2.89	35.94	7.80	−4.27	1.35

TABLE IV. Comparison of experimental and calculated results for the ratio of volume change to stored energy in heavily deformed materials (in units of 10^{-4} g/cal).

	Calculated results		
Material	Screw dislocations	Edge dislocation	Experimental results[a]
Cu	7.4	8.3	9.6–13.1
Ni	4.9	5.8	7.5– 7.6

[a] Reference 32.

2. *Experimental Results*

It has been noted that the amount of experimental data related to the dislocation calculations is very limited. In fact, the only measurements directly related to the present calculations are those of stored energy release and volume changes in deformed copper and nickel by Clarebrough, Hargreaves, and West.[32] These results have have already been discussed by Seeger,[2] who used elastic strain-energy densities of dislocations in Zener's[4] formula. The present results are identical to Zener's for the isotropic edge dislocation, and differ little for the anisotropic screw dislocation. In Table IV, measurements of the elastic constants of copper[33] more recent than those used by Seeger have been used, together with the anisotropic screw dislocation results from Table II.

The experimental values are seen to be of the same order of magnitude as the calculated values. However, in the calculated values of the energy and of the volume, the errors due to contributions from the core region and interactions between dislocations should be no more than 10%. The ratio should be expected to be even more accurate, so that the discrepancies cannot be accounted for in terms of dislocations alone. The comparisons show that stored energy or volume measurements can probably be used to count dislocations to within an accuracy of a factor of 2.

It can be seen from Tables II and III that the calculated volume changes associated with dislocations in most of the ionic crystals are 2–4 atomic volumes per atomic dislocation length. Since the local dilatation varies as the inverse of the square of the distance from the center of a dislocation, these values would indicate that there may actually be a hole in the solid centered about the dislocation. There is some experimental evidence for such hollow dislocation cores. Tucker, Laskar, and Thompson[34] measured the effect of the migration of sodium ions along dislocations on the ionic conductivity of LiF and found that the sodium ions moved very easily. They suggested that this might be ac-

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[31] A. V. Granato, Phys. Rev. **111**, 740 (1959).

[32] L. M. Clarebrough, M. E. Hargreaves, and G. W. West, Proc. Roy. Soc. (London) **A232**, 252 (1955).

[33] Y. Hiki and A. V. Granato, Phys. Rev. **144**, 411 (1966).

[34] R. Tucker, A. Laskar, and R. Thompson, J. Phys. Soc. Japan **18**, 120 (1963).

counted for by hollow dislocation cores. The volume changes per atomic length of dislocations in LiF given in Tables II and III are about $3\frac{1}{2}$ atomic volumes, so this conclusion is plausible on the basis of the present work.

We note that the present calculations predict that there would be relatively little pipe diffusion along screw dislocations in such materials as KCl and RbBr. As far as we are aware, however, such an experiment has not been performed on these materials.

Another quantity which may be related to the large volume changes is the thermal conductivity of deformed materials in the 1–30°K temperature range. At these temperatures, the thermal conductivity of insulators is very sensitive to the imperfection content of the material. The thermal resistivity of deformed materials should be largely determined by the scattering of phonons by dislocations. The calculations of this scattering are directly related to the elastic strain fields of the dislocation. However, a comparison of these calculations with experimental results shows[35] that the measured values of the resistivity are two to three orders of magnitude larger than the calculated values. If, on the other hand, the dislocations are hollow, the phonon scattering may be much larger than that previously calculated.

B. Point Defects

1. *Models*

The calculation of the properties of materials containing point defects is limited by the lack of any completely acceptable model for the defect energy. For example, the strains associated with point defects are generally considered to be too large and the defect too small to be treated by continuum elasticity theory. Nevertheless, such elasticity models have proved to be useful for limited purposes. Because of the generality of elasticity calculations, it seems reasonable to suppose that the variation of point-defect properties from material to material might scale with the elastic constants. This was found to be true for the case of vacancy formation energies in a number of metals, as demonstrated by Mukherjee.[36] Furthermore, it is possible that the pressure and temperature dependence of the energy, which is all that is necessary for the present calculations, is given more reliably than the magnitude of the energy. Finally, there are some properties of materials containing defects where an order-of-magnitude estimate is important. For example, various theoretical estimates of the effects of point defects on the elastic constants of copper differ in the sign of the effect and range over two to three orders of magnitude.

Therefore, it seems worthwhile to survey the experimental results and compare them with the available point-defect models. In general, the agreement is found to be not extremely good, but it is better than might have been expected. For example, the magnitude of the effect of point defects on the bulk modulus of LiF is found to be in closer agreement with the thermodynamic calculation given here than with any other theoretical estimate. Also, the method supplies order-of-magnitude estimates for some quantities for which no previous estimates were available.

A useful elastic model for point defects is the "sphere-in-hole" model. The "defect" is constructed by removing a sphere of radius S_2 from the center of a spherical perfect solid, and another sphere of the perfect material, of radius S_1, is inserted into this cavity. The surfaces between the inner sphere and outer shell "weld" together, and the material relaxes so that this interface reaches some equilibrium value of radius R, introducing elastic strains into the medium. The magnitude of the strains introduced is determined by the misfit parameter

$$\gamma \equiv (S_1 - S_2)/S_2. \tag{26}$$

The volume concentration of defects is taken to be

$$\phi = S_2^3/T_2^3, \tag{27}$$

where T_2 is the outer radius of the perfect solid.

A straightforward linear elasticity calculation gives the strain-energy density

$$g/v = (6BG/C)\gamma^2\phi. \tag{28}$$

This energy again has the form G_eV, where the effective elastic constant G_e and its derivatives are given by

$$\begin{aligned} G_e &= BG/C, \\ \frac{G_e'}{G_e} &= \frac{B'}{B} + \frac{G'}{G} - \frac{C'}{C}, \\ \frac{G_e''}{G_e} &= 2\left(\frac{B'}{B}\frac{G'}{G} - \frac{B'}{B}\frac{C'}{C} - \frac{G'}{G}\frac{C'}{C}\right). \end{aligned} \tag{29}$$

The numerical results obtained in this way are tabulated in Table V for the same materials as in Table I. Except for the modulus and thermal expansion changes, which are generally very small in both cases, the results are very similar to those in Table I.

It is possible to describe point defects in a slightly different fashion. A platelet of interstitials or vacancies can be regarded as an edge dislocation loop, for which elasticity expressions of the strain-energy density are available. A single vacancy or interstitial could, therefore, be visualized as a dislocation loop having a diameter of one atomic volume. Although it is doubtful that the energy expression will be reliable at this diameter, it may be reasonable to suppose that the expression should still adequatately describe the temperature and pressure dependence of the energy.

The strain-energy density of an edge dislocation loop of radius R_0 is[26]

$$g = [(C-G)/C]Gb^2R_0[\ln(8R_0/b) - 1]. \tag{30}$$

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[35] M. Moss, J. Appl. Phys. 37, 4168 (1966).

[36] K. Mukherjee, Phil. Mag. 12, 915 (1965).

TABLE V. Changes in the properties of various solids for a point defect as calculated from a sphere-in-hole model. The quantities are expressed per unit energy of formation.

Material	$v/\Omega g$ (eV^{-1})	s/kg (eV^{-1})	$\Delta\beta/n\beta g$ (eV^{-1})	$\Delta B/nBg$ (eV^{-1})	$(\Delta C/ng)/3NkT$ ($10^3/°\mathrm{K}^2$ eV)
Al	0.51	5.19	0.34	−0.09	0.27
Cu	0.36	3.61	−0.01	−0.01	0.10
Ag	0.41	4.18	0.02	0.02	0.14
Au	0.31	3.05	−0.02	0.00	0.07
Na	1.21	15.39	0.30	0.07	4.44
K	1.35	15.96	0.58	0.12	5.25
Fe	0.31	1.50	0.12	−0.08	0.02
Si	0.34	0.68	−0.62	−0.23	−0.00
Ge	0.18	1.33	0.19	−0.38	−0.01
LiF	0.49	5.79	0.01	−0.11	0.27
NaF	0.47	5.98	−0.01	−0.08	0.26
NaCl	0.55	7.66	−0.01	−0.04	0.51
KCl	0.50	7.32	−0.07	−0.19	0.44
KBr	1.23	8.08	−0.14	−0.13	0.62
KI	0.71	9.12	−0.26	−0.19	0.93
RbBr	0.61	8.93	−0.29	−0.36	0.71
MgO	0.14	1.50	−0.01	−0.01	0.01
CsCl	0.48	7.65	0.24	−0.24	0.83
CsBr	0.48	6.93	0.34	−0.21	1.14
CsI	0.50	8.45	0.91	−0.16	0.59
CuZn	0.09	3.74	0.01	−0.00	0.21

This expression has the same combination of elastic constants present in the isotropic edge dislocation energy expression (21). On the basis of this model, the point-defect properties per unit energy are the same as for the edge dislocations in an isotropic material. Furthermore, it seems likely that the dislocation loop energy in an anisotropic medium would also have the same form as the linear edge dislocation energy in that material. In the absence of a formal proof that this is true, we simply assume it to be the case in order to have some estimate of the effect of anisotropy, since there are no anisotropic elasticity solutions available in analytic form for point defects. From the previous discussion of dislocation effects the isotropic elasticity results are not expected to be very reliable for some of the properties in the case of the ionic crystals. On this basis, we might expect the properties of the ionic solids containing point defects to be given by the results in Table III.

2. *Nonequilibrium Numbers of Defects*

Measurements of the stored energy release and volume change after radiation damage are summarized in Table VI.[37–43] Also included in the table are the calculated results from Table V, and in the case of NaCl, the corresponding ratio obtained from Table III. The agreement between experimental and calculated values for the two metals is good. This agreement with results calculated from elasticity theory is somewhat surprising in view of the large strain fields associated with the defects. Using a reasonable value of 5 eV for the formation energy of a Frenkel pair in Eq. (28), for example, we find an effective misfit of about 60% for copper. This is well outside the range of validity of the elasticity theory used above.

TABLE VI. Ratio of stored energy to volume change caused by radiation damage.

Material	Measured value (eV/atom)	Ref.	Calculated value (eV/atom)
Cu	2.8	Blewitt *et al.*[a]	2.7
	3.7	Nilan and Granato[b]	
Al	1.7	Blewitt and Lucas[c]	1.7
	2.6	Isebeck *et al.*[d]	
NaCl	4.9	Kobayashi[e]	2.2 (anisotropic) 1.5 (isotropic)

[a] References 37 and 38.
[b] Reference 39.
[c] Reference 40.
[d] Reference 41.
[e] References 42 and 43.

The result given for NaCl in Table VI is not in as good agreement with the elastic calculation, although the anisotropic result is indeed closer to the experimental result than the isotropic result. It should be noted that the defects created by irradiation of ionic crystals are largely color centers, with highly energetic electronic states associated with them. The fact that the agreement between experimental and calculated results is still poor could be partly due to incomplete bleaching or to some other effect related to the energy states of the color centers.

By using the results of Bauerle and Koehler[44] for the volume change per unit resistivity change observed in quenched gold wires, Simmons and Balluffi[45] calculated the volume change per vacancy to be 0.45 atomic volume. The volume per defect for the sphere-in-hole model, obtained by multiplying the entry in column 2 of Table V by the room-temperature value $g=0.94$ obtained from the data of Simmons and Balluffi,[45] is 0.3 atomic volume. This is smaller than, but of the same order of magnitude as, the measured value. The value for v will be of interest in the discussion of thermal expansion results later.

The effects of point defects on the elastic moduli of materials have been studied in radiation damage experiments. However, there is a large variation in the magnitude of the effects of the defects on the moduli found in the various experiments. Thompson, Blewitt, and Holmes[46] found that the Young's modulus of single crystals of copper was changed by less than 1%/at.% of defects introduced by 20°K neutron irradiation. A decrease of Young's modulus of the order of 1%/at.%

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[37] T. H. Blewitt, R. R. Coltman, and C. E. Klabunde, J. Phys. Soc. Japan **18**, Suppl. III, 288 (1963).

[38] T. H. Blewitt, in *Radiation Damage in Solids*, edited by D. S. Billington (Academic Press Inc., New York, 1962), p. 630.

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[40] T. H. Blewitt and M. W. Lucas, Bull. Am. Phys. Soc. **12**, 302 (1967).

[41] K. Isebeck, F. Rau, W. Schilling, K. Sonnenberg, P. Tischer, and H. Wenzl, Phys. Status Solidi **17**, 259 (1966).

[42] K. Kobayashi, Phys. Rev. **102**, 348 (1956).

[43] K. Kobayashi, Phys. Rev. **107**, 41 (1957).

[44] J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).

[45] R. O. Simmons and R. W. Balluffi, Phys. Rev. **125**, 862 (1962).

[46] D. O. Thompson, T. H. Blewitt, and D. K. Holmes, J. Appl. Phys. **28**, 742 (1957).

of defects was reported by Dieckamp and Sosin[47] for polycrystalline copper foils electron-irradiated at 80°K, and by Muss and Townsend[48] for polycrystalline tungsten irradiated at room temperature with deuterons. However, König, Volkl, and Schilling[49] found a decrease of about 140%/at.% of defects introduced by 30°K α-particle irradiation of polycrystalline copper foils. They also report a corrected value of the Dieckamp and Sosin measurements, which increase that value to a change of 140%/at.% of defects.

The measurements on copper were not of the bulk modulus. The only direct measurement of both the bulk modulus and the volume change on the same specimen is that by Gerlich *et al.*[50] on slow-neutron-irradiated LiF. The ratio of bulk modulus to volume change was found to be -1.8. This is much smaller than the value of -100 found by König *et al.* and Dieckamp and Sosin for Cu, but is not in disagreement with the results of Thompson *et al.*

There is also a wide variation in the theoretical estimates of the effects of point defects on elastic constants. Mackenzie,[14] Eshelby,[15] and Hashin[16] all find the same relation for the change in the bulk modulus due to vacancies, which predicts a decrease of the order of 1%/at.% of vacancies. Dienes[12,51] gave a theoretical estimate of the effect of radiation on the elastic constants of simple metals. For copper he predicted that interstitials would increase and vacancies would decrease the elastic constants by amounts of the order of 10 and 1%/at.% of interstitials and vacancies, respectively. An argument has been given by Zener[52] which suggests that the effect of point defects should be similar to that of phonons. On this basis, one would expect all the elastic constants to decrease with Frenkel defect content, in contrast to the prediction of an increase by Dienes. If the volume change per Frenkel pair is supposed to lie between 1 and 1.5 atomic volumes, then a bulk modulus change of about -4 to -8% per percent Freknel pairs would be expected on this basis. An estimate by Nabarro,[53] using a linear elasticity theory, predicts a change of 3.8 and -2.3% per percent of interstitials and vacancies, respectively. On the other hand, a recent linear elastic calculation by Melngailis[18] yields values of the order of that found by König *et al.* and Dieckamp and Sosin. The thermodynamic result for copper using isotropic elasticity results from Table V and an energy of 5 eV per Frenkel pair is a decrease of only 0.03%/at.% of defects, again in agreement with the results of Thompson *et al.* but in gross disagreement with the result of König *et al.* and Dieckamp and Sosin. On the basis of the present calculations, the modulus change of irradiated copper (as well as Al, Au, and Ag) should be very small and difficult to detect. The corresponding results obtained from Tables V and III for this ratio in LiF in the isotropic and anisotropic cases are -1.0 and -3.3, respectively. Of all the theoretical estimates of this effect, the present calculations are closest to the experimental results in LiF.

There is also an experiment involving equilibrium concentrations of thermally generated defects that can be related to this effect. By measuring the diffusion constant at several different pressures Nachtrieb *et al.*[54] determined the activation volume of self-diffusion in sodium as a function of pressure. This activation volume includes the effects of the migration of the defect, but there is evidence that these contributions are very small in comparison with the effects due to the formation of the defect.[55] The change in the macroscopic bulk modulus due to the presence of vacancies can thus be estimated by using Eq. (7). This calculation indicates that the bulk modulus will be decreased by about 3%/at.% of defects (for the case when the number of defects is fixed). This is opposite in sign from the increase of $+0.14\%$/at.% of vacancies given by Table V and the measured activation energy.[56] However, the sphere-in-hole result is expressed as a small difference in two relatively large terms so that the small magnitude of the calculated result is of more significance than the sign. Another feature of the result is that it serves to illustrate the usefulness of the general thermodynamic relations of Sec. II. The effect of the point defects on the bulk modulus has been deduced without using any elastic measurement or defect model. The accuracy of the estimate is limited only by the accuracy of the diffusion measurements and the difficulty in separating the defect migration and formation contributions.

3. *Equilibrium Numbers of Defects*

Near the melting point of solids, the concentration of defects in equilibrium is large enough to produce measurable changes in some of the properties of the crystal. In the case of metals, these equilibrium defects are lattice vacancies.[57] We shall next compare the results of measured changes in physical properties due to these vacancies in metals with the estimates based on the sphere-in-hole results of Table VI.

The present calculations for the formation entropy of vacancies in metals are not in close agreement with experimental values. The values of s determined from equilibrium measurements of x-ray lattice-parameter and length-change measurements are $1.0k$ for gold,[45] $2.4k$ for aluminum,[58] and $5.8k$ for sodium.[54] The data

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[47] H. Dieckamp and A. Sosin, J. Appl. Phys. **27**, 1416 (1956).

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[52] C. Zener, Acta Cryst. **2**, 163 (1949).

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[55] C. P. Flynn, Phys. Rev. **181**, 682 (1968).

[56] R. Feder and H. P. Charbnau, Phys. Rev. **149**, 464 (1966).

[57] R. O. Simmons, J. Phys. Soc. Japan **18**, Suppl. II, 172 (1963).

[58] R. O. Simmons and R. W. Balluffi, Phys. Rev. **117**, 52 (1960).

Table VII. Comparison of formation energies and equilibrium concentrations of vacancies in metals derived by different authors.

	Length-change–lattice-parameter			Thermal expansion			Specific heat		
Element	Conc. (%)	E_F (eV)	Ref.	Conc. (%)	E_F (eV)	Ref.	Conc. (%)	E_F (eV)	Ref.
Cu	0.02	1.17	a	0.2	0.7	b	0.5	1.05	c
				0.14	0.65	d			
Au	0.07	0.94	e	0.3	0.62	b	0.4	1.0	f
				0.14	0.67	d			
				0.1	0.56	g			
Ag	0.017	1.09	h	0.24	0.65	d	…	…	…
Al	0.09		i	0.22	0.485	d	0.2	1.17	j
	~0.03		k						
Pb	<0.015	…	k	0.09	0.46	d	0.2	0.48	j
Na	0.075	0.42	l	…	…		0.76	0.26	m

[a] R. O. Simmons and R. W. Balluffi, Phys. Rev. **129**, 1533 (1963).
[b] Reference 59.
[c] Reference 62.
[d] Reference 60.
[e] Reference 45.
[f] Reference 63.
[g] Reference 61.
[h] R. O. Simmons and R. W. Balluffi, Phys. Rev. **119**, 600 (1960).
[i] Reference 58.
[j] Reference 64.
[k] R. Feder and A. S. Nowick, Phys. Rev. **109**, 1959 (1958).
[l] Reference 56.
[m] Reference 65.

for other materials were not accurate enough to determine *s*. From Table V and the measured formation energies, we find that the sphere-in-hole model estimates for these entropies are 2.4*k* for gold, 3.9*k* for aluminum, 4.2*k* for copper, 4.6*k* for silver, and 6.5*k* for sodium. The sphere-in-hole model predictions are of the same order of magnitude as the measured results, but the calculated results are consistently higher than the measured values by 1–2 entropy units. However, the calculated results are roughly in the same proportion to each other as the measured results. If the calculated trend from material to material is given more attention than the absolute values, the formation entropies of copper and silver would both be expected to be larger than that for aluminum. This would give a formation entropy of about 2 entropy units higher than the value 1.5*k*, which was assumed in determining *h* in the equilibrium experiments. Therefore, the formation energy would be as much as 0.2 eV larger in these materials than the assignments given previously. The migration energy obtained from this formation energy and the activation energy for self-diffusion would be smaller than previously considered values by the same amount. It is interesting to note that this is just the order of magnitude of the difference between the migration energies determined from equilibrium and the activation energies found in stage-III radiation damage studies.

Although a discrepancy in *s* for aluminum and gold is present and measurements presently available do not support the larger entropy values contemplated here, we are not aware of any experimental result of sufficient accuracy to definitely rule out the calculated values. In fact, Simmons and Balluffi[58] have shown that if the estimates of equilibrium defect concentrations from quenching experiments are plotted along with the concentrations deduced at lower temperatures from equilibrium experiments, the value of the formation entropy obtained for aluminum is 3.6*k*. This would be in close agreement with the prediction of the sphere-in-hole model calculations.

It has usually been assumed in the past that the changes in such properties as the thermal expansion and specific heats of metals containing equilibrium concentrations of point defects are determined almost entirely by the temperature and pressure dependence of the equilibrium concentration of defects. Accordingly, the temperature and pressure dependence of *g* in Eq. (7) has been neglected in interpreting the results of experiments of this nature. This assumption is indeed confirmed by the present calculations. The results of Table V are due to all the effects other than those of the changing defect concentration, so they provide an estimate of the error involved in this approximation.

However, there is a large discrepancy between the equilibrium defect concentrations and energies of formation derived by some authors[59–65] from specific heat and thermal expansion experiments and corresponding results derived from length-change–lattice-parameter measurements. These results are summarized in Table VII. Since the concentration of defects is determined directly from length-change and lattice-parameter measurements,[58] this discrepancy could be interpreted to mean that the above assumption is incorrect.

Another possible reason for this discrepancy, however, lies in the use of incorrect extrapolation procedures. In order to see this, several measurements of the temperature dependence of the thermal expansion of gold, a representative metal, are shown in Fig. 1. In order to

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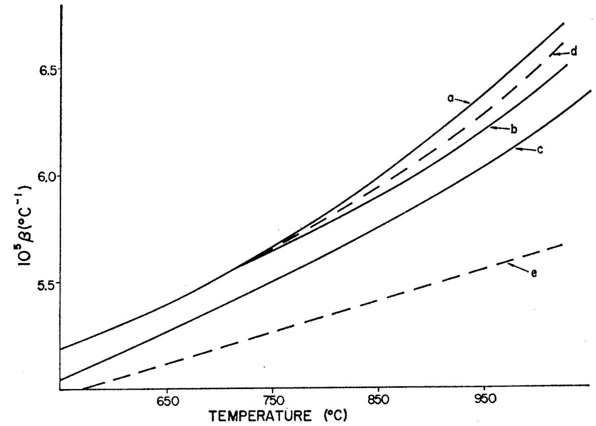

FIG. 1. Thermal expansion of gold. (a) Calculated from $\Delta L/L$ versus given by Simmons and Balluffi (Ref. 45); (b) calculated from $\Delta a/a$ versus T given by Simmons and Balluffi (Ref. 45); (c) measured by Jongenburger (Ref. 59); (d) perfect-crystal curve estimated from the results of Simmons and Balluffi (Ref. 45) and Bauerle and Koehler (Ref. 44) (see text); and (e) linear extrapolation used by Jongenburger (Ref. 59).

obtain the contributions of the equilibrium defects to the thermal expansion, it is necessary to subtract off the perfect-crystal specific heat or thermal expansion. In most of the determinations of this kind, the perfect-crystal contribution has been taken to be a linear extrapolation of the low-temperature measurements where the defect effects are negligible. The dashed line d in Fig. 1 represents the linear extrapolation used by Jongenberger[59] in interpreting his curve c of the figure. However, it has been pointed out by Simmons[57] that the magnitudes of the defect effects obtained in this way have often been too large and the exponential temperature dependences obtained therefore illusory.

We can also show that this extrapolation procedure is incorrect using almost entirely experimental considerations. The fact that the measured value of v is less than 1 in all materials for which it has been measured requires that the volume changes of the perfect crystal should always be less than $3\Delta L/L$ but greater than $3\Delta a/a$. Since the $\Delta L/L$ and $\Delta a/a$ curves are very close together, the thermal expansion of the perfect material can be calculated within a few percent from these curves. This is illustrated in Fig. 2 for the case of gold. Shown in the figure are the measured $\Delta L/L$ and $\Delta a/a$ curves[45] and the calculated perfect-crystal thermal expansion. For this calculation, it was only necessary to assume that the ratio of v to the atomic volume remained fairly close to its room-temperature value of $\frac{1}{2}$. The thermal expansion calculated in this way is shown by the dashed curve in Fig. 1.

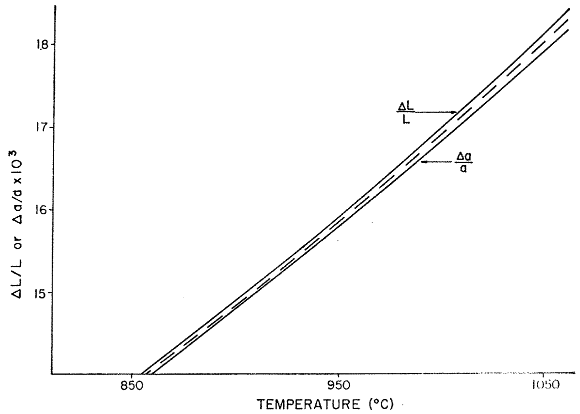

FIG. 2. Length-change and lattice-parameter-change measurements for gold according to Simmons and Balluffi (Ref. 45). The dashed curve is the estimated length change of the perfect crystal (see text).

We see immediately from this calculated perfect-crystal curve that the linear extrapolation of low-temperature data is completely incorrect. The fact that the sudden increase in thermal expansion is much larger than that estimated from usual lattice anharmonicity calculations indicates that the atomic forces are very anharmonic for the magnitudes of atomic displacements encountered near the melting point. Since it is very difficult to calculate this perfect-crystal curve theoretically, it therefore seems that a simple measurement of thermal expansion at high temperature is not sufficient to determine the contributions of equilibrium defects to the crystal properties.

IV. SUMMARY

Using thermodynamics and elasticity theory, a unified treatment of changes in the properties of crystals containing major types of defects is given. Relations for the changes in volume, bulk modulus, entropy, thermal expansion, and specific heat of materials containing defects are expressed in terms of the isobaric, isothermal work required to form the defect and its pressure and temperature dependence. For defects described by elastic strains, it is shown that the required pressure and temperature dependence is given by using the known pressure- and temperature-dependent elastic constants in place of the zero-pressure elastic constants in the linear elasticity results. This greatly increases the usefulness of the general relations. For example, the volume change of an anisotropic crystal containing dislocations is obtained by a simple differentiation of the formula given by the infinitesimal elasticity theory without the necessity of making involved and lengthy finite-elasticity calculations. In addition, all the other thermodynamic properties are also obtained by simple differentiations.

The general results are specialized to a number of particular defects by using models to find expressions for the energy required to form the defect, so that the thermodynamic properties can be calculated. A survey of measurements of properties of imperfect crystals in relation to the present calculations is made. For defects such as dislocations, where the calculations are expected to be most reliable, there are relatively few measurements available, but the agreement with experiment is good. For point defects, where the calculations are expected to be less reliable, there are many measurements, and the agreement with experiment is fair and better than might have been expected. For example, the calculations for the effects of Freknel defects on the bulk modulus of LiF are found to be closer to experimental results than are other available estimates. A number of models for point defects are discussed, but no entirely successful model for all point defects is found. It is found, however, that a simple *GV* form for the energy can be used to estimate the order of magnitude of the changes due to most kinds of defects.

The present calculation of the volume change produced by dislocations predicts that dislocations in certain ionic crystals including LiF may have hollow cores in agreement with the conclusions from measurements of pipe diffusion in LiF. It is predicted that this effect will be absent in certain alkali halides. The calculations suggest that the formation entropies for vacancies in some metals might be larger by 1 to 2 entropy units than has previously been supposed. A discussion of high-temperature thermal expansion and specific heat measurements for metals shows that most previous analyses of these measurements have overestimated the effects due to the thermal equilibrium defects present and underestimated the effects of lattice anharmonicity.

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Magnetoreflection Studies in Arsenic[*][†]

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An infrared magnetoreflection study has been made of the trigonal face of single-crystal arsenic. Oscillations of very large amplitude have been observed with a line shape quite unlike any previously reported. It has been found that the complicated line shape can be understood by assuming that the oscillations are associated with interband transitions between a pair of coupled bands at a point of low symmetry (point Q) in the Brillouin zone. On the basis of this assumption, the data can be interpreted to obtain various band parameters such as the energy gap and the cyclotron effective mass. Some observed nonparabolic effects can also be explained. The magnetoreflection data for the trigonal face are found to be consistent with Lin and Falicov's arsenic energy-band model.

I. INTRODUCTION

RECENT experimental[1–4] and theoretical[5] studies of the semimetal arsenic have greatly advanced our understanding of the band structure of this material. In particular, the band-structure calculation by Lin and Falicov[5] for arsenic using the pseudopotential technique yields a Fermi surface whose shape is in reasonable

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