Anharmonicity in Diffusion *, **

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It is emphasized that anharmonic effects are important in determining the parameters describing diffusion processes at elevated temperatures in crystals. The relevance of anharmonicity to the reaction rate and the dynamical theories of diffusion, and to models of defect formation and migration, is discussed. A comparison is made between the theoretical results and some collected experimental data pertaiining mainly to ionic crystals.

1. Introduction

The material discussed in this paper concerns the effect of anharmonicity on the energies, entropies and volumes for formation and for motion of defects in crystals. We shall distinguish between quasi-harmonic effects and explicit anharmonic effects. The former have been studied by several workers [1–3], but errors and misunderstandings present in the early literature persist today. Unfortunately, in many cases, these alter the entire character of the interpretation which can be placed on the experimental results. Explicit anharmonicities are scarcely understood for perfect crystals [4] and have not yet been incorporated into any discussion of thermal defect structure. Although we shall not present any comprehensive discussion of explicit anharmonic effects in this paper, we show for the case of ionic crystals how important these effects can be.

It is a reasonably good approximation to take the normal modes as harmonic vibrations. However, unlike the case of a lattice made from perfect springs, it is necesary to assume that the phonon frequencies are functions of the state of the crystal. Thus, the vibrational free energy of a vibrational mode of frequency ω may be written with fair accuracy as

$$F_\omega = k\,T \log\left(\frac{\hbar\,\omega}{k\,T}\right) \tag{1}$$

(in the high-temperature approximation) just as for a perfectly harmonic oscillator. The difference is that the frequencies, ω, of vibrations in the anharmonic crystal depend on the molar volume, V, and on the temperature, T. The quasi-harmonic approximation attributes all frequency shifts to changes in the crystal volume so that the frequencies are explicitly dependent on the molar volume V alone and are temperature dependent only through thermal expansion. Residual frequency shifts with temperature at constant volume are then regarded as explicit anharmonic shifts.

We obtain the free energy of an entire crystal containing N atoms by summing over all $3\,N$ vibrational modes and adding the non-vibrational potential energy:

$$F = \mathcal{V} + k\,T \sum_{\alpha=1}^{3N} \log\left(\frac{\hbar\,\omega_\alpha}{k\,T}\right). \tag{2}$$

In the quasi-harmonic model $\mathcal{V}(V)$ and $\omega_\alpha(V)$ are explicit functions of the volume V alone. Accordingly, the entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -k \sum_\alpha \left\{\log\left(\frac{\hbar\,\omega_\alpha(V)}{k\,T}\right) - 1\right\}. \tag{3}$$

The Gibbs function is obtained when we acknowledge that the potential energy contains one term $\mathcal{V}_0(V)$, associated with the crystal, and a second term $p\,V$ which is the potential energy of an enclosing constant pressure bath. Then

$$G = \mathcal{V}_0(V) + k\,T \sum_\alpha \log\left(\frac{\hbar\,\omega_\alpha(V)}{k\,T}\right) + p\,V \tag{4}$$

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[1] N. M. MOTT and R. W. GURNEY, Electronic Processes in Ionic Crystals, Oxford University Press, Oxford 1940.

[2] G. H. VINEYARD and G. J. DIENES, Phys. Rev. **93**, 265 [1954].

[3] J. B. HUNTINGTON, G. A. SHIRN, and E. S. WAJDA, Phys. Rev. **99**, 1085 [1955].

[4] For several reviews see "Phonons" (ed. R. W. H. STEVENSON), Oliver and Boyd, London 1966, and G. LEIBFRIED and W. LUDWIG, Solid State Physics, Vol. **12** (eds. F. SEITZ and D. TURNBULL), Academic Press, New York 1961.

in which the explicit volume dependence of the quasi-harmonic approximation are indicated. Figure 1 shows a sketch of the typical variation of F with T and V; the heavy line marks the locus of points with $(\partial F/\partial V)_T = 0$ at which the crystal finds equilibrium at zero pressure.

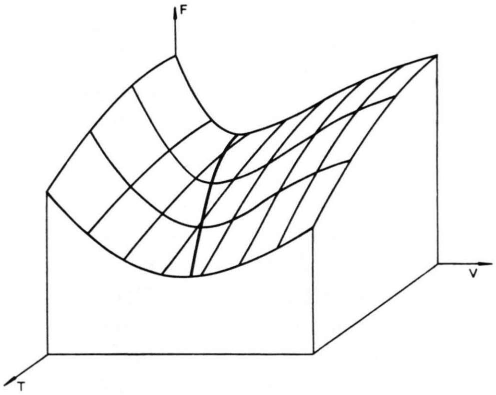

Fig. 1. The typical variation of free energy F with volume V and temperature T. A heavy line marks the locus of points with $(\partial F/\partial V)_T = p = 0$ at which the crystal finds equilibrium at zero pressure for various temperatures.

The quasi-harmonic theory is often useful in defect calculations because it permits neat results to be derived within a well-specified framework.

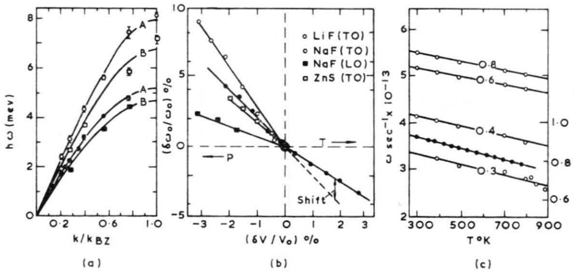

Fig. 2. The variation of normal mode frequencies with temperature and pressure; (a) The dispersion curves of Ne at two densities (A is about 4 per cent more dense than B); explicit temperature induced shifts are relatively small (after LEAKE et al.[15]). (b) The optic mode frequencies vary as shown with temperature and with pressure but the shift is apparently *not* dependent on the volume alone for LiF (data from MITRA et al.[16]). (c) Temperature changes cause similar fractional shifts of phonon frequencies in Al at various displacements from Γ towards X (the numerical labels give k/k_{BZ}) according to LARSSON et al.[7]. The elastic constants also suffer a comparable change according to SUTTON[8].

The general character of the frequency shifts observed in real crystals, including the degree to which the quasi-harmonic approach is valid, may be assessed from the data collected in Fig. 2. The phonon dispersion curves for Ne at two volumes differing by 4% show[5] a frequency shift $\sim 10\%$ in both the longitudinal and transverse branches (see Fig. 2 a). However, LEAKE et al.[5] find that the shift between 4 °K and 25 °K *at constant volume* is relatively small ($\lesssim 2\%$), in accord with the quasi-harmonic postulate. The situation is less satisfactory for the optic modes of ionic crystals. Figure 2 b shows how some optical mode frequency vary with volume for dilatations induced by temperature change and by pressure change[6]. The explicit anharmonicity made evident by the differing pressure and temperature induced rates of change for LiF has found a further confirmation in studies of the dielectric constant as a function of state[7, 7a]. Finally, in Fig. 2 c is shown the temperature variation of modes at various displacements from Γ (zone center) towards X ([100] zone face) in Al[8]. The various normal modes are seen to vary with temperature in much the same way[9] as $\sqrt{C_{11}}$, also shown in Fig. 2 c.

In summary, then, we can find a reasonable approximation to the free energy and the Gibbs function of many crystals by means of Eqs. (2) and (4) with $\mathcal{V}$ and ω explicitly dependent on the volume. This approximation is likely to be much less satisfactory, however, when the optic modes of ionic crystals play an important part.

2. Defect Formation

Say that the Gibbs functions before and after a defect forms in a system maintained at constant temperature and pressure are G and G'. Then from the quantity

$$g = G' - G \tag{5}$$

we can obtain the energy, the entropy and the volume of formation. Since $(\partial G/\partial T)_p = -S$, $(\partial G/\partial p)_T = V$ and the internal energy is

$$U = G + S\,T - p\,V$$

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[5] J. A. LEAKE, W. B. DANIELS, J. SKALYO, B. C. FRAZER, and G. SHIRANE, Phys. Rev. **181**, 1251 [1969].

[6] S. S. MITRA, C. POSTMUS, and J. R. FERRARO, Phys. Rev. Letters **18**, 455 [1967].

[7] R. P. LOWNDES and D. H. MARTIN, Proc. Roy. Soc. London A **316**, 351 [1970].

[7a] R. P. LOWNDES, Phys. Rev. B **1**, 2754 [1970].

[8] K. E. LARSSON, S. HOLMRYD, and U. DAHLBORG, in: Inelastic Scattering of Neutrons in Solids and Liquids, I.A.E.A., Vienna 1961.

[9] P. M. SUTTON, Phys. Rev. **31**, 516 [1953].

it follows that the formation entropy is

$$s = S' - S = -\left(\frac{\partial g}{\partial T}\right)_p, \qquad (6)$$

the volume change on formation is

$$v = V' - V = \left(\frac{\partial g}{\partial p}\right)_T, \qquad (7)$$

and the energy is

$$\varepsilon = U' - U = g + s\,T - p\,v\,. \qquad (8)$$

Here, primed quantities identify properties of the imperfect crystal.

From Eq. (4) we can write down the g-function in the quasi-harmonic approximation and hence obtain s, v and ε. The result is

$$g = \mathcal{V}_0(V') - \mathcal{V}_0(V) + k\,T\sum_{\alpha=1}^{3N}\log\frac{\omega_\alpha'(V')}{\omega_\alpha(V)} + p(V'-V), \qquad (9)$$

with

$$s = -k\sum_{\alpha=1}^{3N}\log\frac{\omega_\alpha'(V')}{\omega_\alpha(V)}, \qquad (10)$$

$$v = V' - V \qquad (11)$$

and

$$\varepsilon = \mathcal{V}_0'(V') - \mathcal{V}_0(V)\,. \qquad (12)$$

Note that these quantities contain components evaluated for two different crystal volumes – that of the imperfect crystal, namely V', and the value V for the perfect crystal. However, g is a function of state which can be expressed in terms of any two thermodynamic variables. Since negligible work is done in a reversible compression of the crystal through v we can equally calculate g as the free energy change on formation *at constant volume*, namely,

$$\begin{aligned} g(V,T) &= F(V,T) - F(V,T) \qquad (13)\\ &= \mathcal{V}_0'(V) - \mathcal{V}_0(V) + k\,T\sum_{\alpha=1}^{3N}\log\frac{\omega_\alpha'(V)}{\omega_\alpha(V)}\,. \end{aligned}$$

Equations (9) and (13) are obviously related by the equilibrium condition $(\partial G/\partial V)_T = 0$.

Some possible variations of g with V and T are sketched in Fig. 3; these sketches are compatible with the Grüneisen approximation. The solid line in each case indicates the $V-T$ curve of the crystal for $p=0$ and the broken extrapolation from high temperature has a slope which gives the formation entropy when projected onto the plane $V=\text{const}$, and an intercept on the plane $T=0$ which gives the formation energy, ε. It is often assumed that ε can be calculated as a change in potential energy at 0 °K but both Fig. 3 and Eq. (12) indicate that this may lead to errors. These errors are evidently most marked in those cases, such as that shown in Fig. 3 b, in which both ε and s are strongly volume dependent. The tangent to $g(V,T)$ which yields the high-temperature values of ε and s is obviously sensitive to explicit anharmonicities which cause additional curvatures of the surface $g(V,T)$ at elevated temperatures.

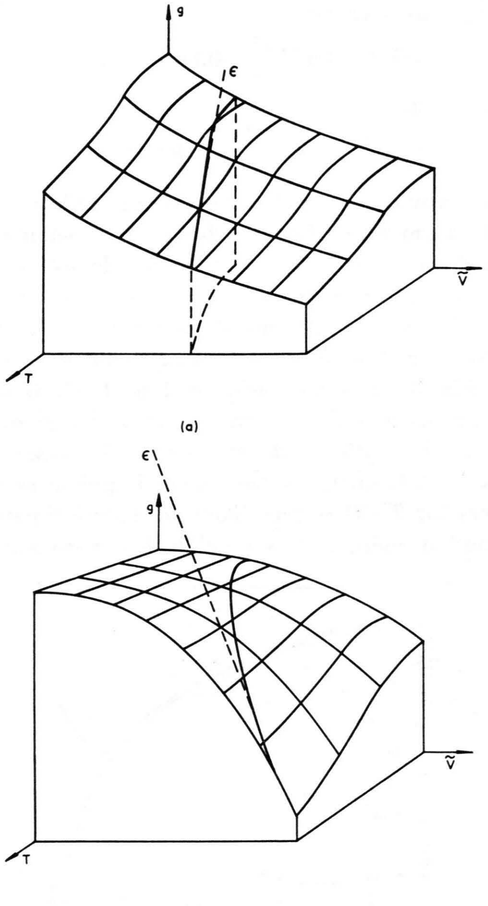

Fig. 3. Two possible forms of $g(V\,T)$. (a) shows ε and s relatively temperature independent whereas they are strongly temperature dependent in (b). Both cases are compatible with quasi-harmonic theory which simply has the phonon frequencies and the non-vibrational energy constant throughout a section of the surface at any constant volume.

An example occurs in the theory of vacancy formation in 1 : 1 salts, which is often treated by the Mott-Littleton method applied to the parameters for a crystal at 0 °K[10]. We can see the main points

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[10] See L. J. Barr and A. B. Lidiard, in: A Treatise on Physical Chemistry, Vol. **10** [1969], for a recent review of the Mott-Littleton method.

from the Jost model. The vacancy formation energy on the Jost model is just the cohesive energy per molecule minus the dielectric relaxation energy

$$E_{\mathrm{r}} = \frac{e^2}{2R}\left(1 - \frac{1}{\epsilon}\right), \qquad (14)$$

with R the atomic cell radius and ϵ the dielectric constant. Actually, the cohesive energy E_{c} is about 90% of the Madelung energy. In terms of the spacing r_0 of ions we have

$$g \sim 0.9 \times 0.874 \frac{e^2}{r_0} - 0.805 \frac{e^2}{r_0}\left(1 - \frac{1}{\epsilon}\right).$$

Thus, the term

$$g(T) \sim \frac{e^2}{2R\epsilon} \quad (p = 0), \qquad (15)$$

alone provides a good order-of-magnitude estimate of the formation g-function for $p = 0$. It should also provide a realistic order-of-magnitude estimate of the temperature dependence of g at zero pressure since the cancelling terms of the form $C\,e^2/R$ have a weaker variation. The relationship between this case and Fig. 3 b is made clear by Fig. 4 which shows the variation with temperature of ϵ^{-1} and of $\omega_0{}^2$ (ω_0 is the optic mode frequency) in some 1 : 1 salts [11–15]. Clearly, the Born model applied to parameters for $T = 0$ is very likely to underestimate the formation energy. It is notable that many calculations using this method for charged defects have yielded formation energies which are much too small [10].

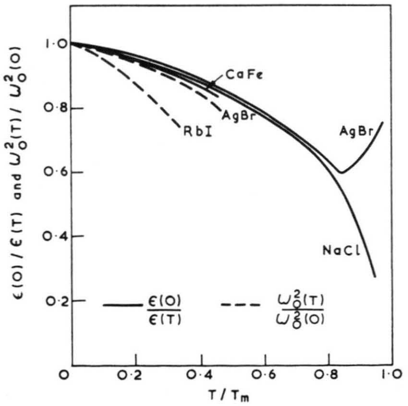

Fig. 4. The variation with temperature of the inverse dielectric constant (at ~ 10^{10} cps) according to RAO and SMAKULA [11, 12] (NaCl, CaF_2), EVERETT et al. [13] (AgBr) and LOWNDES and MARTIN [7, 14] (NaCl, AgBr). The optic mode frequency is still more strongly temperature dependent according both to the Szigetti relation and to the data of JONES et al. [15] for AgBr and RbI (broken lines).

There remain further difficulties with the quasi-harmonic approach for optic modes, as mentioned above. These do not spoil Eq. (15), which provides a very reasonable estimate of the formation entropy:

$$s \sim -\frac{\varepsilon}{\epsilon}\left(\frac{\partial \epsilon}{\partial T}\right)_p \sim 5\,k - 10\,k\,,$$

for the values

$$\varepsilon \sim 2 \text{ eV} \quad \text{and} \quad \epsilon^{-1}(\partial\epsilon/\partial T)_{\mathrm{p}} \sim -3 \times 10^{-4}\ {}^\circ\mathrm{K}^{-1}$$

which are appropriate for Schottky pairs in 1 : 1 salts. However, the presence of explicit anharmonicities does reduce further the practical utility of the Mott-Littleton method employing parameters appropriate to the crystal at 0 °K.

3. Migration Processes

Theoretical models have been still less successful in describing migration processes than formation processes [10]; much of the difficulty may again be associated with an inadequate treatment of the phonon frequency shifts. Using the reaction rate model the jump rate may be obtained as

$$w = \nu_{\mathrm{D}} \cdot \exp\{-\hat{g}/k\,T\} \qquad (16)$$

in which

$$\hat{g} = \mathcal{V}_{\mathrm{S}}(V_{\mathrm{S}}) - \mathcal{V}_0(V_0) + k\,T \sum_{\alpha=1}^{3N} \log \frac{\omega_\alpha{}'(V_{\mathrm{S}})}{\omega_\alpha(V_0)} + p(V_{\mathrm{S}} - V_0), \qquad (17)$$

with subscripts S and 0 marking saddle-point properties and properties of the normal state in which the migrating atom ocupies its initial lattice site [16]. A constant volume constraint does not modify the jump rate w, and g can therefore be written, following Eq. (13), as a function of state

$$\hat{g}(\tilde{V}\,T) = -k\,T \log(W/\nu_{\mathrm{D}}) \qquad (18)$$

$$= \mathcal{V}_{\mathrm{S}}(\tilde{V}) - \mathcal{V}_0(\tilde{V}) + k\,T \sum_{\alpha=1}^{3N} \log \frac{\omega_\alpha{}'(\tilde{V})}{\omega_\alpha(\tilde{V})}.$$

In Eqs. (17) and (18) the $\omega_\alpha{}'$ correspond to vibrations in a plane along the potential ridge separating the initial and final potential wells; $\omega_1{}' = 2\,\pi\,\nu_{\mathrm{D}}$ is

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[11] K. V. RAO and A. SMAKULA, J. Appl. Phys. **36**, 3953 [1965].

[12] K. V. RAO and A. SMAKULA, J. Appl. Phys. **37**, 319 [1966].

[13] G. EVERETT, A. W. LAWSON, and G. E. SMITH, Phys. Rev. **123**, 1589 [1961].

[14] R. P. LOWNDES and D. H. MARTIN, Proc. Roy. Soc. London A **308**, 473 [1969].

[15] G. O. JONES, D. H. MARTIN, P. A. MAWER, and C. H. PERRY, Proc. Roy. Soc. London A **261**, 10 [1961].

[16] G. H. VINEYARD, J. Physic. Chem. Solids **3**, 121 [1957].

an arbitrary, constant frequency which we set equal to the Debye frequency. $\mathcal{V}_S$ and $\mathcal{V}_0$ are respectively the non-vibrational potential energies in the saddle-point configuration and in the ground state, for the crystal volumes indicated.

The motion entropy, $\hat{s}$, volume, $\hat{v}$, and energy, $\hat{\varepsilon}$, are obtained from $\hat{g}$ by standard thermodynamic prescriptions which yield results analogous to Eqs. (10) and (11) and (12). In practice the volume dependence has largely been ignored and the energies, entropies, etc. calculated directly from the potentials $\mathcal{V}$ and the frequency shifts $\omega' - \omega$ obtained from models apropriate to crystals at 0 °K. The energies so deduced have tended to be too small and, in the only published case[13], the entropy has the wrong sign and is much too small in magnitude. There has been no "successful" calculation of any motion volume.

The observed motion entropies are unexpectedly large (up to $\sim 5\,k$) and in metals are related fairly well to the motion energy by the ZENER[17] relation $\hat{s} \sim -\hat{\varepsilon}(\mu^{-1}\,\partial\mu/\partial T)$ with μ some shear modulus of the host crystal. In this paper we shall not present the results of detailed calculations, which at present appear impracticable, but shall instead show how the empirical data can be explained by means of two assumption. These are as follows.

(a) We shall assume first that only small frequency shifts take place when a migrating atom moves to the saddle-point position at constant volume, so that the second term in Eq. (18) is small and the function $\hat{g}$ depends mainly on $\tilde{V}$ rather than on T, as shown in Fig. 5.

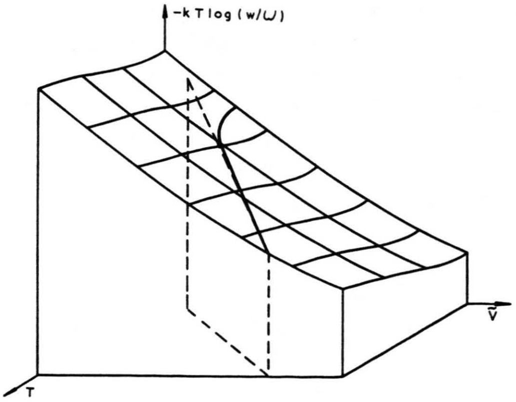

Fig. 5. A model surface for $g(V, T)$ showing only small entropy changes associated with the displacement of an atom to the saddlepoint at constant volume.

(b) Second, we assume that the potential as a function of position, as the representative point passes through the barrier in configuration space, maintains approximately the same functional form as the crystal dilates and simply changes in the amplitude of the potential variation. For example, Fig. 6 indicates by arrows paths through a barrier at various dilatations. We assume that the potential varies in a similar way along each path but that the size of the variation depends on V.

It should be noted that both assumptions concern the form of the surface $\mathcal{V}(\boldsymbol{s})$ which describes the potential of a crystal as a function of position, $\boldsymbol{s}$, in (mass weighted) configurations space. Little is known about the true form of this surface far from the locus of equilibrium points. The present assumptions allow us to systematize diffusion data in terms of the form of the surface close to the equilibrium position.

The nature of the model energy surface ensures that the barrier height may be written

$$\hat{g} = \tfrac{1}{2}\,\omega^2\,s_0{}^2, \tag{19}$$

with ω a frequency describing the mean vibrations along the jump direction and s_0 a critical (mass weighted) distance along this path. In monatomic crystals the vibrational spectrum can be described reasonably well by the Debye approximation, which allows ω to be written in terms of elastic constants. It can be shown[18] using the dynamical theory of diffusion[19] that longitudinal modes are three times more efficient in causing jumps than longitudinal modes, but the contribution of shear modes, while thus reduced, is still dominant. An appropriate form of g follows for monatomic crystals as

$$\hat{g} = c\,\Omega\,\delta^2 \tag{20}$$

with c an elastic constant given by[18]

$$\frac{15}{2\,c} = \frac{3}{c_{11}} + \frac{2}{c_{11} - c_{12}} + \frac{1}{c_{44}} \tag{21}$$

and Ω the atomic volume. δ describes the shape of the energy surface along the jump path; this parameter turns out to be remarkably constant among different materials having the same crystal structure. Table 1 shows how Eqs. (20) and (21) with

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[17] C. ZENER, in: Imperfections in Nearly Perfect Crystals, ed. W. SHOCKLEY, John Wiley & Sons, New York 1952.

[18] C. P. FLYNN, Phys. Rev. **171**, 682 [1968].

[19] See e. g. N. B. SLATER, The Theory of Unimolecular Reactions, Cornell 1959.

Table 1. Vacancy motion energies in fcc crystals obtained from Eqs. (20) and (21) with $\delta^2 = 0.104$. The elastic constants are values appropriate to a temperature of 0 °K (data taken from FLYNN [18]).

	Elastic consts. (10^{12} dyne cm^{-2})			Motion energy (eV)	
	c_{11}	$\frac{1}{2}(c_{11} - c_{12})$	c_{44}	theory	exp.
Cu	1.762	0.256	0.818	0.84	0.88 [a]
Ag	1.315	0.171.	0.511	0.83	0.82 [a]
Au	2.016	0.159	0.454	0.82	0.83 [a]
Ni	2.612	0.552	1.317	1.42	~1.3 [b]
Al	1.143	0.262	0.316	0.83	~0.65 [a]
Pb	0.555	0.050	0.194	0.48	0.56 [a]
Ar	0.0439	0.0128	0.0164	0.089	0.08 [c]

[a] Obtained from Q and the equilibrium vacancy concentration.
[b] From annealing studies.
[c] Value quoted is $Q/2$.

$\delta^2 = 0.104$ reproduce the known motion energies of monatomic solids from elastic constants for $T = 0$ °K. There is evidently a notable similarity among the energy surfaces along the jump paths for crystals having a common structure [18]. This may originate partly in the predominance of pairwise repulsive forces in the saddle point configuration [18].

A further success of the model is that it reproduces the Zener relation for the motion entropy since the quantity $\hat{g}$ in Eqs. (20) and (21) is indeed proportional to an elastic constant which is heavily weighted by shear contributions just as in Zener's original discussion. Actually, the elastic constant is multiplied by the atomic volume so the model reproduce "GV" results of KEYES [20], which have recently been re-examined by HOLDER [21].

Turning now to the case of diatomic crystals we find a quantity of data which supports our assumed energy surface. It is difficult to obtain sufficiently accurate jump rates by extracting the defect concentrations from observed diffusion coefficients but our discussion finds an immediate application to the *relative* rates of two processes activated by the same phonons in a single type of crystal. Say that particular phonons with frequency $\omega(p, T)$ vary with temperature and pressure in a way which is typical of those phonons which strongly influence the jump rate for each of two jump processes, A and B, which take place in the crystal. Then from our model assumptions we may write

$$\hat{g}_A = \tfrac{1}{2}\,\omega^2\,q_A{}^2; \qquad \hat{g}_B = \tfrac{1}{2}\,\omega^2\,q_B{}^2, \tag{22}$$

with q_A and q_B parameters which describe the size of the fluctuation needed to cause the representative point to pass over the saddlepoint in the two processes. Then, the ratio of the jump rates is

$$w_A/w_B = \exp\{-\omega^2(q_A{}^2 - q_B{}^2)/k\,T\}\,, \tag{23}$$

in which we take equal pre-exponential factors for the two processes in accordance with our assumption that the same set of phonons is responsible for both migration rates. We shall also presume that q_A and q_B are sensibly independent of the crystal volume and are, therefore, in the quasi-harmonic approximation, independent of temperature also.

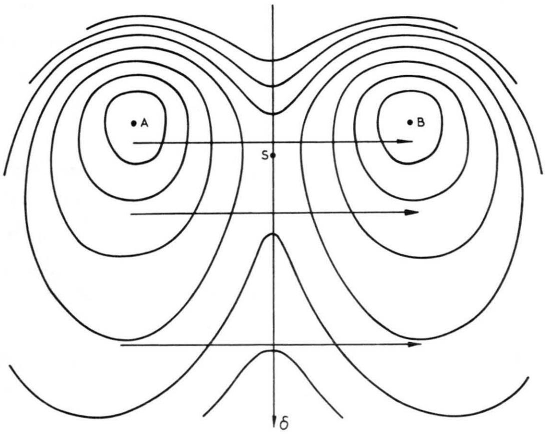

Fig. 6. Showing schematically how the barrier impeding migratory transitions changes in height as a crystal expands.

An important point is now immediately apparent. The two jump rates can be equal only if $q_A = q_B$ in which case they are always equal, or if $\omega^2 = 0$, which is obviously not admissible. It follows that *the jump rates of two processes activated by the same phonons in a single crystal should never cross.* As we show below the experimental facts are in accordance with this rule. It is usually the case that phonon frequencies decrease with increasing volume and therefore $\omega^2(T)$ extrapolates to zero at temperatures above the melting point (cf. Fig. 4). Thus, the jump rates of processes activated by the same phonons should extrapolate towards equality at some temperature $T > T_m$.

It is often possible to ignore the effects of correlation as being negligibly small. When this approximation is permissible there is an abundance

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[20] R. W. KEYES, in: Solids Under Pressure, eds. PAUL and WARSCHAUER, McGraw-Hill, New York 1963.

[21] J. HOLDER, Thesis, University of Illinois 1968.

of cases in which two jump rates may be compared directly without concern over the elimination of the defect concentrations. For example, the independent components of the diffusion tensor in non-cubic crystals are activated by a common defect concentration and their relative magnitudes reflect differences among jump rates only (neglecting correlation factors). Similarly, the intrinsic diffusion coefficients of cations and anions in ionic crystals supporting Schottky disorder have *relative* magnitudes which are substantially independent of the defect concentration. The same is true of the relative mixing rates contributed to the cation sublattice of silver halides by cation vacancies and interstitials.

A variety of examples are collected in Fig. 7, which shows $\log(D_A/D_B)$ as a function of T_m/T, with T_m the melting temperature, for several cases of each mechanism mentioned above[22]. Not only do the jump rates not cross [i. e. $\log(D_A/D_B)$ never equals unity], the ratio also tends to unity at temperatures in excess of T_m, just as expected from Eq. (23).

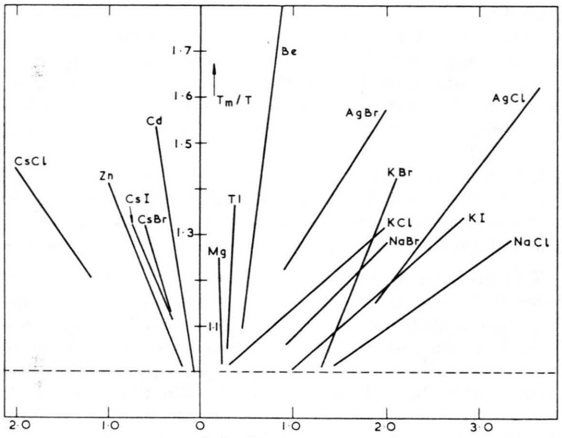

Fig. 7. The ratio D_A/D_B of diffusion coefficients for two intrinsic processes in a single crystal for various cases[22] which include: (a) diffusion parallel and perpendicular to the *c* axis in hexagonal metals; (b) anion and cation diffusion in alkali halides; (c) cation vacancy and interstitial diffusion in silver halides.

It is particularly interesting to note that the temperature dependence of w_A/w_B in the salts is so strong that the jump rates approach equality at temperatures very little greater than T_m, whereas for metals the intercept is at much higher temperatures. The behaviour of the metals is consistent, at least in order of magnitude, with the fractional temperature dependence of the elastic constants and the theory given above for elemental crystals; that for the salts is not consistent with the elastic constants, and it is worth recalling that the GV model proves generally unsatisfactory for salts[20]. A further, related point is that Born model calculations of migration energies appear to have more success for neutral interstitials[23] than for charged vacancies[24].

It seems most likely that this characteristic behaviour has its origin in the major role of optical modes in promoting diffusion on the sublattices of ionic crystals. The optic modes cause opposite displacements of the two sub-lattices and are therefore unusually efficient in moving the ions towards a saddlepoint. More important still is the fact that the polarization surrounding a charged defect must move with the defect as it migrates between sites. Thus, a vacancy jump path through configuration space must have major components along optical mode axes in order that the screening infra-red polarization shall accompany the excess charge of the defect as it moves through the crystal. It therefore seems reasonable that the optic mode frequency, ω_0, should be taken for ω in the model Eqs. (19), (22) and (23). The optical mode frequencies of salts are, of course, known to be strongly temperature dependent (see e. g. Figs. 2 and 4), as also is the related static dielectric constant. While precisely quantitative data are wanting it does appear from Figs. 4 and 7 that the temperature dependence of ω_0^2 is indeed at least qualitatively compatible with the observed temperature dependence of the relative diffusion coefficients, as suggested by Eq. (23) with $\omega = \omega_0$.

When $q_A \cong q_B$ the approximations involved are obviously not reliable because slight differences between the activation processes may then become important. This is well illustrated by the case of Cd. When the diffusion rates shown in Fig. 7 are corrected for correlation[22] the resulting jump rates for the two independent jump processes in Cd turn out

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[22] Most of these data are collected by Y. ADDA and J. PHILIBERT, La Diffusion dans les Solides, Universitaires de France, Paris 1966.

[23] M. J. NORGETT and A. B. LIDIARD, Phil. Mag. **18**, 156, 1193 [1968]; Radiation Damage in Reactor Materials VI (IAEA, Vienna, 1969).— M. J. NORGETT, A.E.R.E.T.P. 412 (to be published in J. Phys. C).

[24] See e. g. the discussion of Ref. [10].

to be equal at about $T = 0.8\,T_{\mathrm{m}}$. The sensitivity of this test may, however, be judged from the fact that $w_{\mathrm{A}}/w_{\mathrm{B}}$ does not differ from unity by more than a factor 1.5 in the entire temperature range shown in Fig. 7 and this factor corresponds to a temperature change of only $\sim 10\,^{\circ}\mathrm{K}$ in either jump processes. In cases where q_{A} and q_{B} differ considerably the jump rates do not become equal for reasons made evident by Eq. (23).

4. Conclusion

The important influence of temperature and pressure change on the formation and motion Gibbs functions $g(\tilde{V}\,T)$ and $\hat{g}(\tilde{V},T)$ has been stressed. To be compatible with quasi-harmonic theory, pair-force models must employ forces fitted to the quasi-harmonic behaviour of the perfect crystal. The lack of data needed to fit modified forces near defects makes these procedures impractical for imperfect crystals. Indeed, it is not clear that any seriously quantitative calculation can be carried through at present for any category of crystal. This paper describes an exploratory study of the surfaces $g(V,T)$ and $\hat{g}(V\,T)$ directed mainly, but not entirely, towards the case of ionic crystals, in which the optic modes play an important part. It is suggested that the future development of defect calculations may most usefully be directed towards a further study of these surfaces throughout areas of the $\tilde{V},T$ plane relevent to experimental defect studies.

Note added in proof:

The Formation Volumes of Charged Defects

Consider a quasi-harmonic material of undeformed volume V_0, having a bulk modulus $B(V)$ and dielectric constant $\in(V)$, exposed to a homogeneous electric displacement field D. The energy change caused by inserting the crystal (which leaves the displacement field undisturbed) is:

$$\varepsilon = \frac{B}{2\,V_0}\,(V-V_0)^2 + \frac{V}{8\,\pi}\left(\frac{1}{\in} - 1\right) D^2,$$

and the equilibrium volume $\overline{V}$ obtained by setting $\partial\varepsilon/\partial V = 0$, is given by

$$\frac{\overline{V}-V_0}{V_0} = + \left\{\left(\frac{\partial\in}{\partial V}\right)_{V_0} + \frac{\in^2}{V_0}\left(1-\frac{1}{\in}\right)\right\}\cdot\frac{E^2\,V_0}{8\,\pi\,B} \simeq -\frac{E^2}{8\,\pi}\left(\frac{\partial\in}{\partial P}\right)_T,$$

in which the volume dependence of B is ignored during differentiation. The volume therefore depends on E^2 as in the analogous case of volume magnetostriction.

The summed dilatations of crystal elements exposed to the field $E = e^2/\in r^2$ of a charged defect contribute a volume

$$\delta v = \int_R^{\infty} 4\,\pi\,r^2 \left\{\frac{\overline{V}-V_0}{V_0}\right\} \mathrm{d}r = -\frac{e^2}{2\in R}\cdot\frac{1}{\in}\left(\frac{\partial\in}{\partial P}\right)_T.$$

This is just the pressure derivative of g given by Eq. (15), when the small pressure variation of R is ignored. Note that to the extent that the field-induced dilatations can be considered to lie in a self-strained elastic continuum they do simply add to give the total volume change. However, some fraction of δv appears at R and the remainder takes the form of a change in volume enclosed within the crystal exterior. (For a discussion of self-strained continua see J. D. ESHELBY (Solid State Physics V. 3 Academic Press, London 1956). With $\in^{-1}(\partial\in\,\partial P)_T \sim -10^{-11}\ \mathrm{cm}^2/\mathrm{dyne}$ at room temperature (see Ref. [7]) this adds $\sim 30\times10^{-24}$ cc to v for a Schottky pair with $g = e^2/2\in R \sim 2$ eV. The observed formation volumes are indeed unexpectedly large, as stressed in the accompanying article by Faux and Lidiard.

Two further points are worthy of note. First, observed non-linear variaitons of $\in(V)$ with V tend to make the volumes of charged defects increase with temperature. The experimental evidence for just such a temperature-dependent volume for the case of vacancy-divalent impurity pairs in NaCl has been pointed out by R. D. FOUCHAUX (J. Physic. Chem. Solids **31**, 1113 [1970]) on the basis of studies by W. ZIETEN (Z. Phys. **146**, 451 [1956]). Finally, coupling between axial stress fields and electric fields near charged defects may cause further volume adjustments having a temperature dependent character within the quasi-harmonic approximation.