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Atomic Migration in Monatomic Crystals*

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A theory of the diffusion-jump process in monatomic crystals is presented. The theory treats large atomic displacements causing diffusion jumps as a summation of phonon amplitudes. By using the Debye approximation to the phonon spectrum, a theoretical basis for the empirical Zener relation is established. The elastic theory gives a satisfactory quantitative account of (a) the motion energy; (b) the motion entropy; (c) the motion volume; (d) the isotope effect. Low-temperature diffusion phenomena may be examined because the theory employs a sufficiently general description of the phonon system. Attention is drawn to some enhanced diffusion effects caused by zero-point phonons. A quantum-mechanical calculation of diffusion rates for very light impurities is made with a model potential. Anomalous isotope effects are found at temperatures below the characteristic temperature of the localized mode. The relevance of these results to low-temperature annealing of radiation damage is discussed.

I. INTRODUCTION

ATOMIC migration in crystals is an extremely complex phenomenon; lying well outside the bounds of conventional harmonic-lattice theory, its mechanisms are more grossly anharmonic than any likely fluctuations of the perfect lattice. Moreover, whether diffusion of atoms from one site to the next takes place by an interstitial process or by means of lattice vacancies, the elementary jump always occurs in a defective region of the lattice, where translational symmetry no longer prevails. The latter is, perhaps, of greater concern to the theoretical physicist than to the crystal itself, for while the crystal spectrum may often suffer only a slight distortion, the increase in mathematical complexity is very considerable. So much is this the case that the harmonic theory of defective lattices is a field of current interest, and calculations, for the main part, are still performed on model systems. A second important reason for this limitation is that the calculation of crystal free energies of perfect solids remains very difficult, and only the most intrepid tackle phonons in a defective lattice from first principles. Indeed, it has become fashionable to approach even metallic systems using two-body central-force models and a digital computer. Thus, the correct description of atomic migration processes lies in the union of three areas of major difficulty in crystal theory: cohesion, anharmonicity, and defect vibrations.

Yet, the complexity may in part be peripheral to the main problem of understanding, in reasonably quantitative terms, the factors limiting atomic diffusion. The perturbed-lattice modes near a vacancy may, in most cases, be sufficiently similar to unperturbed states for their inclusion to be a matter of detail, rather than of central interest. Moreover, a wealth of information concerning the crystal energy near equilibrium is available in the phonon spectrum itself; if as yet the spectrum cannot be calculated precisely, it is at least susceptible to experimental determination. Properties relevant to atomic migration may therefore be obtained. Finally, anharmonicity may be of direct concern only to the extent that the *magnitude* of fluctuation needed to effect an elementary atomic jump is determined by the crystal energy in a configuration containing one atom well removed from an equilibrium site. But this energy is just a parameter, which we may hope eventually to obtain from first principles and which at present appears to be well approximated by the relaxed saddlepoint energy; the essential point—the variation with thermodynamic variables of the transition probability—may well be contained in the almost harmonic vibrational structure of the normal modes near equilibrium.

Existing treatments of the diffusion-jump process in solids have fallen into two categories. The approach that has hitherto proved the more useful, due initially to Wert and Zener,[1] has been elaborated by Vineyard[2] to a form identical with that now employed in the theory of chemical reaction rates as applied to molecular transitions (see Slater[3]). It is essentially a classical treatment, not only because of the classical partition functions customarily employed, but also because its development rests upon the existence of a saddlepoint configuration in which the velocities and positions of each particle are specified simultaneously without taking due cognizance of the uncertainty principle. Some corrections to the classical statistical formulation have recently been incorporated into the theory by LeClaire,[4] but it seems likely that in those cases (diffusion of H and D) for which the statistical corrections are most necessary, the uncertainty principle makes the basis of reaction-rate theory least tenable. We consider this point in more detail below (Sec. X).

The merits and difficulties of the reaction-rate treatment are discussed in the literature.[5,6] It results in a prediction that migration parameters are associated with the relaxed crystal constrained in the saddlepoint configuration, although the configuration must be very

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* Supported in part by the Advanced Research Projects Agency under Contract No. ARPA SD-131.

[1] C. A. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

[2] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

[3] N. B. Slater, *Theory of Unimolecular Reactions* (Cornell University Press, Ithaca, N. Y., 1959).

[4] A. D. LeClaire, Phil. Mag. **14**, 1271 (1966).

[5] D. Lazarus, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. X.

[6] H. R. Glyde, Rev. Mod. Phys. **39**, 373 (1967).

short-lived. This is seen clearly in the frequency factor[2]

$$\nu=\prod_{i=1}^{3N}\nu_i\Big/\prod_{i=2}^{3N}\nu_i', \tag{1.1}$$

with ν_i and ν_i' phonon frequencies in the normal and the constrained saddlepoint configurations. Equation (1.1) measures the entropy change of the phonon system; a calculation of the entropy based on this prescription[7] falls short by several entropy units, of experimental values. Similarly, the activation "volume" for motion is found to be the equilibrium-volume change of the lattice constrained to remain in the saddlepoint. It has often been thought unsatisfactory that such equilibrium quantities for a fully relaxed configuration should appear relevant to processes occupying only a fraction of any phonon period.

An alternative formulation by Rice[8] emphasizes fluctuation processes; it has fallen into disrepute because, in the final evaluation of jump rates, necessary simplifications of the general equations lead to a predicted temperature variation of diffusion that is not in accord with experiment. However, this approach has been shown to have the same formal content as reaction-rate theory.[6] It falls down when the jump is ascribed to a particular activated mode, thereby producing a variation of D with T other than the simple Arrhenius relation.

In the present paper, we present a fresh calculation of the jump rate that is more akin in spirit to the dynamical approach than the rate-theoretic method. The reason for this choice is that it leads very simply into a quantum-statistical treatment of the lattice modes. Instead of continuing the general theory to a point where physical arguments become difficult, we choose immediately a particular reaction coordinate x on physical grounds, and then express fluctuations of this coordinate in terms of the phonon structure. On making the assumption that jumps occur when the coordinate exceeds a critical value q, one may then obtain the jump rate from Kac's equation using an approximation due to Slater. Calculations are carried through in the harmonic approximation and our final expressions contain the parameter q. For a well-chosen reaction, coordinate q is, in effect, the energy parameter we discuss in the opening paragraphs of this introduction: It measures the type and size of fluctuation needed to effect a jump.

Several interesting results follow from this approach. When the phonon spectrum is treated in the Debye approximation one obtains the motion free energy in terms of elastic constants. A theoretical basis for the empirical Zener relation[9] may then be established. Moreover, it is found that the critical quantity q is a sensibly constant fraction of the jump path for all monatomic materials with the same crystal structure. As a result, the migration energy may be predicted with fair accuracy. When quantum statistics are used to obtain the phonon amplitudes, we may also trace an anomalous diffusion behavior to be anticipated at temperatures below the lattice Debye temperature.

These and other results are presented in later sections of this article. In the next section, we consider the choice of a suitable reaction coordinate.

II. FLUCTUATIONS OF THE REACTION COORDINATE

No general prescription for calculating the motion energies of defects in solids is, as yet, available. Approximate computations using pairwise forces derived from equilibrium properties have not met with great success, particularly for metals.[10] Nevertheless, it does seem intuitively reasonable that short-range repulsions between a migrating atom and certain of its neighbors dominate the dynamics of the compressed saddlepoint configuration. These forces must therefore be emphasized in a correct selection of the reaction coordinate. Furthermore, the criterion for completion of a jump is closely tied to the position of a migrating atom with respect to its neighbors barring the jump path. The neighbors exert strong repulsive forces on the jumping atom as it approaches the saddlepoint, and the jump will be completed only if the fluctuation is sufficiently strong to force the moving atom past its neighbors towards the vacancy.

Evidently the instantaneous *relative* position of the ring of neighbors and the migrating atom is of central interest in the diffusion process. As a first crude approximation to the mechanics of atomic migration we therefore choose

$$x=\left(\mathbf{u}_d-\frac{1}{\mathfrak{N}}\sum_n \mathbf{u}_n\right)\cdot\hat{x} \tag{2.1}$$

as a suitable reaction coordinate, with $\mathbf{u}_d$ the position of the diffusing atom and $\mathbf{u}_n$ the position of the neighbor n along the jump path. In effect, the quantity $\mathfrak{N}^{-1}\sum_n \mathbf{u}_n$ defines the saddlepoint as the center of gravity of these $\mathfrak{N}$ neighbors; the scalar product selects only those displacements parallel to the unit vector $\hat{x}$ directed along the jump path.

With Eq. (2.1) we lose immediately any many-body generality of the subsequent argument; attention is focused on the behavior of a particular set of atoms crucial to the completion of a jump, and the configuration of all other atoms is ignored. Moreover, it is clear that no single choice of reaction coordinate can be ideal for all crystals and all types of defect. That the resulting predictions prove useful presumably indicates that the assumption is a satisfactory first approximation. Note

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[7] H. B. Huntingdon, G. A. Shirn, and E. S. Wadja, Phys. Rev. **99**, 1085 (1955).

[8] S. A. Rice, Phys. Rev. **112**, 804 (1958); O. P. Manley, J. Phys. Chem. Solids **32**, 1046 (1960).

[9] C. Zener, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley & Sons, Inc., New York, 1952).

[10] See, e.g., R. A. Johnson, J. Phys. Chem. Solids **28**, 275 (1966).

that these difficulties only enter into the criterion for an adequate fluctuation. The statistics of phonon fluctuations may, in principle, be treated using the exact spectrum of lattice vibrations.

Equation (2.1) is open to substantial criticism on the grounds that, even inside the assumption that certain chosen atoms alone are important, a relevant part of their motion is still ignored; for it is obvious that the lateral motion of saddlepoint neighbors is essential to minimize the required fluctuation energy. However, it is likely that this process will enter into the theory only as an adjustment of the parameter q which eventually measures the energy of motion. On the present approach this quantity is not determined from crystal theory, but is obtained by correlating observed diffusion data with theory. We proceed in the belief that future elaboration of this theory will clarify the question raised here.

The theory now develops according to the following argument:

In the harmonic approximation[11] we may resolve lattice vibrations into a spectrum of normal modes with eigenfunctions

$$\mathbf{u}_{\omega\lambda}(\mathbf{r}_n,t)=\boldsymbol{\varepsilon}_{\omega\lambda}u_{\omega\lambda}(\mathbf{r}_n)e^{i\omega t} \qquad (2.2)$$

having frequencies ω and polarizations $\boldsymbol{\varepsilon}_{\omega\lambda}$, with λ identifying a branch of the spectrum, and $\mathbf{r}_n$ locating the atom in the nth cell. The modes have an average thermal equilibrium energy

$$\mathcal{E}_\omega=\tfrac{1}{2}\hbar\omega\coth(\hbar\omega/2kT)\,. \qquad (2.3)$$

The classical peak amplitudes in a perfect lattice of N ions with mass M may be obtained as

$$|u_{\omega\lambda}{}^0|^2=2\mathcal{E}_\omega/NM\omega^2\,. \qquad (2.4)$$

Consider a particular atom which is free to migrate, either by virtue of its interstitial location, or because it neighbors a lattice vacancy. Each harmonic mode gives rise to a motion of this atom along the reaction coordinate x. The mode $(\omega\lambda)$ will contribute to the fluctuation of x according to

$$x_{\omega\lambda}=x_{\omega\lambda}{}^0e^{i\omega t}, \qquad (2.5)$$

where $x_{\omega\lambda}{}^0$ may be obtained from the phonon structure and Eq. (2.1). Thus,

$$x(t)=\sum_{\omega\lambda}x_{\omega\lambda}=\sum_{\omega\lambda}x_{\omega\lambda}{}^0e^{i\omega t}. \qquad (2.6)$$

In the harmonic approximation, x fluctuates wildly with peak amplitudes $\sim 10^{10}\,a$ for a crystal with $\sim 10^{24}$ lattice points. Fluctuations with $x\simeq a$ sufficient to cause a diffusion jump, occur substantially more frequently.

The criterion for a jump is that $x(t)-q$ have an "upzero" (i.e., swing through zero in an increasing sense). Upzero frequencies of sums such as (2.6) may be obtained from Kac's[12] equation, and the enormous number of modes involved makes an approximation due to Slater particularly attractive. When

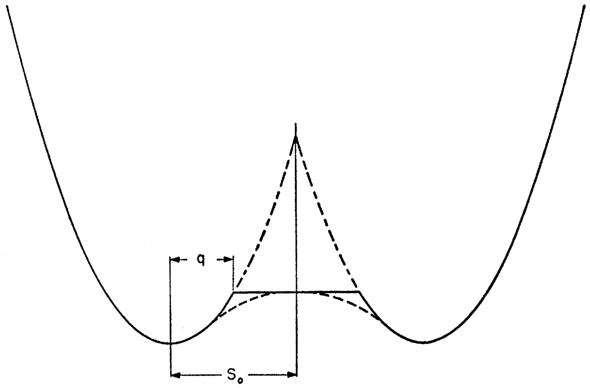

FIG. 1. Hypothetical potential energy of a migrating atom as the reaction coordinate varies. The harmonic potential and a potential cut off at $V(q)$ so as to be consistent with the harmonic assumption are shown.

$$q\ll\sum_{\omega\lambda}x_{\omega\lambda}{}^0, \qquad (2.7)$$

one may represent displacements by a Gaussian distribution, under which conditions the upzero frequency is[13]

$$w=\left[\frac{\sum_{\omega\lambda}\omega^2|x_{\omega\lambda}{}^0|^2}{\sum_{\omega\lambda}|x_{\omega\lambda}{}^0|^2}\right]^{1/2}\exp\left[-\frac{q^2}{\sum_{\omega\lambda}|x_{\omega\lambda}{}^0|^2}\right]. \qquad (2.8)$$

In the present case it is obvious that

$$q\sim N^{1/2}x_{\omega\lambda}{}^0, \qquad (2.9)$$

since, typically, atoms in solids have vibrational amplitudes reaching a fraction of the lattice spacing at the melting point. The lattice potential associated with the migrating atom, as approximated by our present model, is shown in Fig. 1. It is harmonic up to $x=q$, and for any displacement larger than q the jump proceeds to completion. Note that one need not pay attention to the velocity of the migrating atom. Atomic motion is so rapid, and jumps so rare, that it is sufficient to regard diffusion jumps as being effected with the frequency of appropriate fluctuations.

Equation (2.8) has been applied to jump processes previously[5]; the novel part of the present theory lies in its application to a particular reaction coordinate with a simple model of the phonon system.[14]

III. PLANE-WAVE APPROXIMATION

To obtain the jump frequencies from Eq. (2.8) we need values of the $x_{\omega\lambda}{}^0$. These may be obtained in prin-

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[11] J. M. Ziman, *Phonons and Electrons* (Oxford University Press, Oxford, England, 1960).

[12] M. Kac, Am. J. Math. **65**, 609 (1943).

[13] This is strictly true only for cases where the $x_{\omega\lambda}{}^0$ are equal (see Ref. 3).

[14] Two further articles in which an inappropriate reaction coordinate is used have recently come to the author's attention. They are (a) G. O. Alefeld, Phys. Rev. Letters **12**, 372 (1964); (b) H. R. Glyde, J. Phys. Chem. Solids **28**, 2061 (1967).

ciple from the crystal phonon spectrum, but it must be recalled that the migrating atom is found in a disturbed region of the crystal, either neighboring a vacant site (vacancy mechanism) or being itself an interstitial atom (interstitial mechanism). Calculations of phonon spectra for such atoms have been of intense interest in recent years,[15,16] but have not yet reached a level of accuracy sufficient for reliable polarizations, amplitudes, and frequencies to be generally available. The main difficulty lies in evaluating the energy of real crystals as a function of the ionic displacements.

In the absence of detailed and general information, we make the assumption that the phonon spectrum is little altered by the defect, and we represent the eigenfunctions by plane waves with atoms occupying sites of the perfect crystal lattice:

$$\mathbf{u}_{\omega\lambda}(\mathbf{r})=\boldsymbol{\varepsilon}_{\omega\lambda}u_{\omega\lambda}{}^{0}e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{3.1}$$

Suppose in addition that the saddlepoint is defined by the location of atoms separating the migrating atom from the final site. According to the discussion of Sec. II, a reasonable choice for the reaction coordinate is then the quantity

$$\begin{aligned}x(t)&=\sum_{\omega\lambda} x_{\omega\lambda}{}^{0}e^{i\omega t}\\&=\sum_{\omega\lambda}\left[\mathbf{u}_{\omega\lambda}(\mathbf{r}_d)-\frac{1}{\mathfrak{N}}\sum_{n=1}^{\mathfrak{N}}\mathbf{u}_{\omega\lambda}(\mathbf{r}_n)\right]\cdot\hat{x}e^{i\omega t},\end{aligned} \tag{3.2}$$

where $\mathbf{r}_d$ is the equilibrium position of the diffusing atom, and the $\mathbf{r}_n$ locate the equilibrium sites of the $\mathfrak{N}$ atoms surrounding the saddlepoint. The scalar product selects only those relative displacements parallel to the unit vector $\hat{x}$ along the jump direction.

It is instructive first to carry out the calculation of w for a specific lattice, for which purpose the fcc structure serves as a useful example. Four atoms bar a direct migration jump; they are situated on the plane perpendicularly bisecting the jump distance, each lying a distance $\rho=(\frac{1}{2}\sqrt{\frac{3}{2}})a$ from the jump path (Fig. 2). The two opposite pairs lie at $\pm\boldsymbol{\rho}_1$ and $\pm\boldsymbol{\rho}_2$ with $\boldsymbol{\rho}_1\cdot\boldsymbol{\rho}_2=\frac{1}{3}\rho^2$. We have, from Eq. (3.2),

$$x_{\omega\lambda}{}^{0}=u_{\omega\lambda}{}^{0}\{1-\tfrac{1}{2}e^{i\mathbf{k}\cdot\mathbf{s}_0}[\cos(\mathbf{k}\cdot\boldsymbol{\rho}_1)+\cos(\mathbf{k}\cdot\boldsymbol{\rho}_2)]\}\times(\boldsymbol{\varepsilon}_{\omega\lambda}\cdot\hat{x})e^{i\mathbf{k}\cdot\mathbf{r}_d}, \tag{3.3}$$

where $\mathbf{s}_0$ is one-half the jump path. Thus,

$$\begin{aligned}|x_{\omega\lambda}{}^{0}|^2=|u_{\omega\lambda}{}^{0}|^2\{1&+\tfrac{1}{4}\cos^2(\mathbf{k}\cdot\boldsymbol{\rho}_1)+\tfrac{1}{4}\cos^2(\mathbf{k}\cdot\boldsymbol{\rho}_2)\\&+\tfrac{1}{2}\cos(\mathbf{k}\cdot\boldsymbol{\rho}_1)\cos(\mathbf{k}\cdot\boldsymbol{\rho}_2)-\cos(\mathbf{k}\cdot\mathbf{s}_0)\\&\times[\cos(\mathbf{k}\cdot\boldsymbol{\rho}_1)+\cos(\mathbf{k}\cdot\boldsymbol{\rho}_2)]\},\end{aligned} \tag{3.4}$$

in which

$$|u_{\omega\lambda}{}^{0}|^2=2\mathcal{E}_{\omega}/NM\omega^2. \tag{3.5}$$

For an isotropic crystal we may obtain approximate values of the sums $\sum_{\omega\lambda}|x_{\omega\lambda}{}^{0}|^2$ and $\sum_{\omega\lambda}\omega^2|x_{\omega\lambda}|^2$ quite easily because the polarization vectors may be chosen for convenience. We take N of the $3N$ modes to be polarized parallel to $\hat{x}$, and find the average of $|x_{\omega\lambda}{}^{0}|^2$ over all directions of $\mathbf{k}$ for a fixed k (and ω), finally summing over the crystal frequency spectrum. The average over $\mathbf{k}$ in Eq. (3.4) may be performed using the following results:

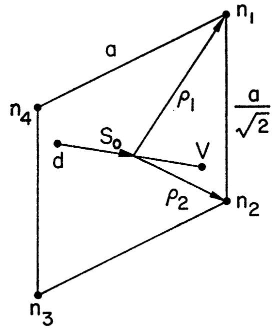

FIG. 2. Geometry of the atomic jump into a vacant site in the fcc lattice.

$$\begin{aligned}\langle\cos^2(\mathbf{k}\cdot\boldsymbol{\rho}_1)\rangle&=\langle|\sum_l(-1)^l(4l+1)j_{2l}(k\rho_1)P_{2l}(\cos\theta_{k\rho})|^2\rangle\\&=\sum_l(4l+1)j_{2l}{}^2(k\rho),\end{aligned} \tag{3.6}$$

$$\langle\cos(\mathbf{k}\cdot\boldsymbol{\rho}_1)\cos(\mathbf{k}\cdot\boldsymbol{\rho}_2)\rangle=\sum_l(4l+1)j_{2l}{}^2(k\rho)P_{2l}(\tfrac{1}{3}), \tag{3.7}$$

since

$$|\boldsymbol{\rho}_1|=|\boldsymbol{\rho}_2|=\rho\quad\text{and}\quad\boldsymbol{\rho}_1\cdot\boldsymbol{\rho}_2=\tfrac{1}{3}\rho^2,$$

and

$$\langle\cos(\mathbf{k}\cdot\boldsymbol{\rho}_1)\cos(\mathbf{k}\cdot\mathbf{s}_0)\rangle=\sum_l(4l+1)j_{2l}(k\rho_1)\times j_{2l}(ks_0)P_{2l}(\tfrac{1}{2}\pi) \tag{3.8}$$

(since $\boldsymbol{\rho}_1\cdot\mathbf{s}_0=\boldsymbol{\rho}_2\cdot\mathbf{s}_0=0$). In Eq. (3.6), $\theta_{k\rho}$ signifies the angle between $\mathbf{k}$ and $\boldsymbol{\rho}$. On collecting terms one finds

$$\begin{aligned}\langle|x_{\omega\lambda}{}^{0}|^2\rangle/|u_{\omega\lambda}{}^{0}|^2=1&+\tfrac{1}{2}\sum_l(4l+1)j_{2l}(k\rho)\\&\times\{[1+P_{2l}(\tfrac{1}{3})]j_{2l}(k\rho)-4P_{2l}(\tfrac{1}{2}\pi)j_{2l}(ks_0)\}.\end{aligned} \tag{3.9}$$

The remarkable feature of Eq. (3.9) is that almost the same result is obtained by assuming that the saddlepoint position is displaced by the plane-wave amplitude at a position $\mathbf{s}\simeq\mathbf{s}_0$, in which case we find

$$|x_{\omega\lambda}{}^{0}|^2=4|u_{\omega\lambda}{}^{0}|^2\sin^2(\mathbf{k}\cdot\mathbf{s}/2) \tag{3.10}$$

and

$$\langle|x_{\omega\lambda}{}^{0}|^2\rangle/|u_{\omega\lambda}{}^{0}|^2=2(1-j_0(ks))\simeq\tfrac{1}{3}(ks)^2, \tag{3.11}$$

where the approximate equality follows because ks is only ~ 2 even for the maximum crystal k. Equations (3.9) and (3.11) are shown, in Fig. 3, as functions of k for $s\simeq 1.2s_0$. Evidently, Eq. (3.11) is quite adequate; it is as if the saddlepoint fluctuation were given by the plane-wave amplitude at a point slightly beyond the saddlepoint. Consequently, we may take

$$\sum_{\omega\lambda}|x_{\omega\lambda}{}^{0}|^2=\tfrac{1}{3}s^2\sum_{\omega\lambda}k^2|u_{\omega\lambda}{}^{0}|^2, \tag{3.12}$$

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[15] See, e.g., A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3.

[16] R. F. S. Hearmon, in *Landolt-Börnstein Tables*, edited by K. H. Hellwege (Springer-Verlag, Berlin, 1966).

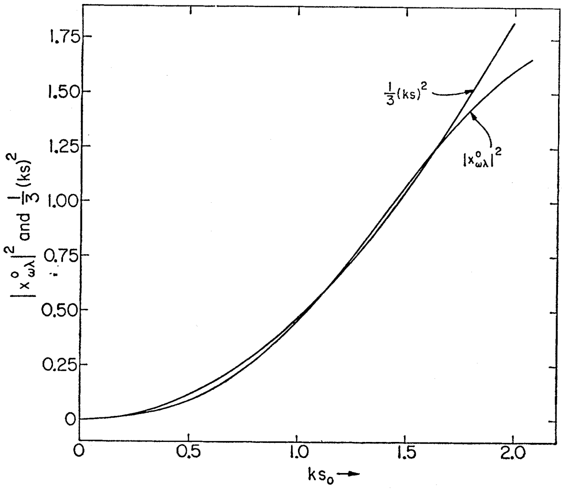

FIG. 3. Comparison of $\sum_{\omega\lambda}|x_{\omega\lambda}^{0}|^2$ and $\frac{1}{3}(ks)^2$ for $s \simeq 1.2s_0$.

and from Eq. (3.5) find

$$\sum_{\omega\lambda} |x_{\omega\lambda}^{0}|^2 = (2s^2/3NM)\sum_{\omega\lambda} k^2 \varepsilon_\omega/\omega^2. \tag{3.13}$$

The summation in Eq. (3.13) can always be performed if the dispersion curves of the crystal are known; it may be obtained trivially for a Debye crystal. In the isotropic Debye approximation $k^2/\omega^2 = v^{-2}$, where v is the sound velocity. For a crystal with all elastic constants equal,

$$\sum_{\omega\lambda} |x_{\omega\lambda}^{0}|^2 = (2s^2/3Mv^2)\varepsilon_D, \tag{3.14}$$

where ε_D is the vibrational energy per mode of the spectrum. The small discrepancy between Eqs. (3.9) and (3.11) at high frequency may be regarded as simulating dispersion in the relation between k and ω. In the same approximation, but limited to high temperatures where $\varepsilon = kT$, we may also evaluate

$$\frac{\sum_{\omega\lambda} \omega^2 |x_{\omega\lambda}^{0}|^2}{\sum_{\omega\lambda} |x_{\omega\lambda}^{0}|^2} = \tfrac{3}{5}\nu_D^2, \tag{3.15}$$

with ν_D being the Debye frequency. The jump frequency follows from Eq. (2.8):

$$w = (\tfrac{3}{5})^{1/2}\nu_D e^{-3Mv^2q^2/\varepsilon_D s^2}. \tag{3.16}$$

Turning now to the case of crystals with several elastic constants, we find that the summations cannot be effected without much more detailed calculation. However, the Debye approximation may be employed for longitudinal and transverse waves of different velocities. For longitudinal waves in the approximation of Eq. (3.11), we find

$$\sum_{\omega\lambda(\text{long})} |x_{\omega\lambda}^{0}|^2 = (2s^2/5Mv_l^2)\varepsilon_l, \tag{3.17}$$

and for transverse waves summed over both polarizations

$$\sum_{\omega\lambda(\text{trans})} |x_{\omega\lambda}^{0}|^2 = (4s^2/15Mv_t^2)\varepsilon_t, \tag{3.18}$$

where ε_l and ε_t are, respectively, the vibrational energy per atom in longitudinal modes and in each polarization of transverse modes. The jump frequency is therefore found to be

$$w = (\tfrac{3}{5})^{1/2}\tilde{\nu}_D \exp\left\{-\frac{15Mv_l^2v_t^2q^2}{2(3\varepsilon_l v_t^2 + 2\varepsilon_t v_l)^2 s}\right\}. \tag{3.19}$$

The preexponential factor, when evaluated at high temperatures with $\varepsilon_t = \varepsilon_l = kT$, contains

$$\tilde{\nu}_D^2 = \langle\omega_D^3\rangle/4\pi^2\langle\omega_D\rangle, \tag{3.20}$$

with averages taken over mode polarizations at the Debye limit. Given the detailed crystal vibrational spectrum the summations could be effected more accurately. The pre-exponential factor, although derived for $T > \Theta_D$, is so insensitive to temperature that we are justified in presuming throughout that it is temperature-independent, and that the entire pre-exponential factor is just

$$w_0 = (\tfrac{3}{5})^{1/2}\nu_D, \tag{3.21}$$

where ν_D is the average Debye frequency obtained from specific-heat data.

Through use of the Debye approximation we have now obtained an expression for the migration rate of atoms in a monatomic crystal, in terms of measurable quantities and one parameter q that measures the energy fluctuation needed for the jump to continue to completion.

IV. ELASTIC THEORY: METALS

It has been realized for some years that there exists a connection between the diffusion rate in a solid and its elastic constants; however, the basis of this observation has not been fully understood. Zener[9] has pointed out a most useful relationship between D_0 and the shear modulus $\mu(T)$. For interstitial impurities he gives

$$D_0 = \nu a^2 Q\left[\frac{-1}{\mu_0}\frac{\partial\mu_0}{\partial T}\right], \tag{4.1}$$

where Q is the activation energy for self-diffusion, and ν is a frequency factor often associated with the lattice Debye frequency. For solvent vacancy diffusion, a similar equation gives quite good results when a factor of $0.55f$ is inserted on the right, with f being the correlation factor. The qualitative interpretation of this equation usually offered is that μ measures the lattice strain at the saddlepoint.

With Eq. (3.19) we have already made contact with the elastic theory, for the sound velocities may be written

$$v_l^2 = (\lambda + 2\mu)/\rho \tag{4.2}$$

and

$$v_t^2 = \mu/\rho. \tag{4.3}$$

Here, ρ is the density and λ, μ the Lamé elastic con-

TABLE I. Elastic theory applied to fcc metals. Elastic data are obtained from Hearmon (Ref. 16) and activation energies from Lazarus (Ref. 5) and Corbett (Ref. 33) unless otherwise noted. Theoretical values of E_M obtained using $\delta^2=0.104$ (column 5) are to be compared experimental values (column 6).

	c_{11}	$(c_{11}-c_{12})$ $(10^{12}$ dyn cm$^{-2})$	c_{44}	E_M (eV)	Experimental values E_M	 E_F (eV)	 Q
Cu	1.762	0.256	0.818	0.84	0.88[a]	1.17	2.05
Ag	1.315	0.171	0.511	0.83	0.82[a]	1.08	1.91
Au	2.016	0.159	0.454	0.82	0.83[a]	0.98	1.81
Ni	2.612	0.552	1.317	1.42	~1.3	···	2.90
Al	1.143	0.262	0.316	0.83	?	0.73[b]	1.48−1.28[c]
Pb	0.555	0.050	0.194	0.48	0.56[a]	0.49[d]	1.05

[a] Values obtained directly or indirectly from E_F and Q.
[b] J. Bass, Phil. Mag. **15**, 717 (1967).
[c] F. Y. Fradin and T. J. Rowland (Ref. 22).
[d] R. Feder and A. S. Nowick, Phil. Mag. **15**, 805 (1967).

stants. With these substitutions Eq. (3.19) may be obtained in the form

$$w=(\tfrac{3}{5})^{1/2}\nu_D \exp\left\{-\frac{15\Omega\delta^2}{6\varepsilon_l/(\lambda+2\mu)+4\varepsilon_t/\mu}\right\}, \tag{4.4}$$

where $\delta^2=q^2/s^2$ and the atomic volume $\Omega=M/\rho$. But at high temperatures

$$\varepsilon_l=\varepsilon_t=kT. \tag{4.5}$$

Therefore,

$$w=(\tfrac{3}{5})^{1/2}\nu_D e^{-(c\Omega\delta^2/kT)}, \tag{4.6}$$

where c is an average elastic constant for migration given by

$$c=\frac{15\mu(\lambda+2\mu)}{2(2\lambda+7\mu)}. \tag{4.7}$$

Even cubic crystals are, in reality, anisotropic. We then use in place of Eq. (4.7) an average reciprocal modulus:

$$\frac{15}{2c}=\frac{3}{c_{11}}+\frac{2}{c_{11}-c_{12}}+\frac{1}{c_{44}}, \tag{4.8}$$

which has weighting factors in accordance with Eq. (3.19).

The quantity $\phi=c\Omega\delta^2$ plays the part of a Gibbs function for migration. We therefore need elastic constants at 0°K and zero pressure to obtain the motion energy E_M (assuming that c varies linearly with T and p). Elastic moduli[16] are given for various fcc metals in Table I, together with measured and deduced experimental values of Q, E_F and E_M. The theoretical estimates of E_M obtained by assuming $\delta^2=0.104$ for the fcc lattice are in remarkably good agreement with experiment, and we show in Sec. V that nonmetallic fcc crystals also fall within the scope of this theory. While an approximately constant value of δ^2 may be expected if pairwise repulsive forces invariably predominate, the present results suggest a surprising degree of uniformity among these crystals.

TABLE II. Elastic theory applied to bcc metals. Elastic data are obtained from Hearmon (Ref. 16) and activation energies from Ref. 23 unless otherwise noted. Theoretical values of E_M are obtained using $\delta^2=0.067$.

	c_{11}	$\frac{1}{2}(c_{11}-c_{12})$ $(10^{12}$ dyn cm$^{-2})$	c_{44}	E_M (eV)	Experimental values E_M	 E_F (eV)	 Q
Li	0.134	0.011	0.100	0.031	···	···	
Na	0.062	0.008	0.059	0.039	~0.025[a]	0.42	0.445[b]
K	0.046	0.0042	0.038	0.042	···	···	0.42
Cr	3.50	1.41	1.01	0.85	···	···	3.2
V	2.325	0.565	0.460	0.62	···	···	~3.6
Fe	2.43	0.606	1.381	0.70	···	···	2.6
Mo	4.80	1.58	1.087	1.73	···	···	4.0
Ta	2.665	0.541	0.873	0.95	···	···	4.8
Nb	2.46	0.56	0.287	0.68	···	···	4.1
W	5.326	1.616	1.631	2.8	2.85[a]	3.15[c]	5.9

[a] Values obtained from E_F and Q.
[b] See Ref. 37.
[c] Ya. A. Kraftmakher and P. G. Strelkov, Fiz. Tverd. Tela **4**, 2271 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1662 (1963)].

Much less is known about bcc crystals. Table II gives elastic data for various bcc crystals, and values of E_M obtained by fitting δ^2 to the two cases, sodium and tungsten, for which the motion energy is known approximately. Once more a single value, $\delta^2=0.067$, explains these data, and it is remarkable that materials so different as Na and W should be amenable to so simple a procedure.[17] The anomalously small fraction of Q taken by the motion energy of sodium is thus explained by the small shear modulus C'. Predicted values of E_M for other bcc crystals are also shown in Table II. It appears that small motion energies are to be anticipated in all alkali metals, because of the anomalously large amplitude of shear modes polarized in ⟨110⟩ directions.

The deduced values of δ are only 30% of the saddle-point displacement, and one must inquire why such small fluctuations are sufficient to cause a diffusion jump. The meaning becomes clear when the saddle-point energy of the cusped harmonic potential is calculated: $M\omega^2 s_0^2 \sim 10$ eV. The potential is cut off at the motion energy, so the cutoff distance is small. Why, then, does the harmonic approximation give sensible results? The following argument seems to offer at least a partial justification: Although we have calculated the probability of certain displacements, and therefore of certain potential-energy fluctuations, occurring we could equally well have discussed kinetic-energy fluctuations. The kinetic energy is largest near equilibrium, where a harmonic approximation is valid, and the effect of neighbors barring the jump of an atom with sufficient kinetic energy is just to slow it down to an extent measured by the barrier height. Rather than being carried by a cooperative motion, the atom is thrown over the barrier by an energy fluctuation achieved at small displacements.

We obtain from the temperature dependence of ϕ an estimate of the motion entropy. On writing

$$\phi(T)=\phi(0)+T\left(\frac{\partial\phi}{\partial T}\right)_p, \tag{4.9}$$

---

[17] This result is to be contrasted with that of Ref. 14(b), in which E_F and E_M are found to vary in a fixed proportion between different crystals.

the results

$$E_M=\phi(T)-T\left(\frac{\partial\phi}{\partial T}\right)_p=\phi(0) \tag{4.10}$$

and

$$S_M=-\frac{1}{\phi(0)}\left(\frac{\partial\phi}{\partial T}\right)_p E_M \tag{4.11}$$

follow very easily. The first we have used above to obtain E_M; the second is essentially Zener's empirical result, for the derivative of ϕ depends principally on $(\partial c/\partial T)_p$, and c is dominated by the shear modulus. In place of $0.55Q$ we have E_M, which is usually a satisfactory approximation when some allowance is made for the effect of formation entropy on D_0. The success of the empirical relation has provoked sufficient comment[5,18] to make further tabulation unnecessary. It is, however, worth noting that the existing correlations make use of data obtained by Köster[19] from measurements of Young's modulus. When sufficient information concerning high-temperature elastic moduli has accumulated it would be of interest to compare more exact calculations of S_M with experiment. There is a second, more obscure point, concerning the need for such data, to which we return below.

It is interesting to consider further the anomalous case of Na for which the motion energy is only a small fraction of Q.[20] This feature is well represented in the elastic theory, as we have demonstrated. A second anomaly is that the motion entropy appears to be small or slightly negative, the experimental result being $S_M=-2.3\pm1.8$ eu. But since the temperature derivative $\phi(0)^{-1}(\partial\phi/\partial T)$ is observed to be normal for Na, and E_M is small, we should, from Eq. (4.11), anticipate the approximately zero motion entropy, which is determined by direct experiment. However, the small motion energy must make the region almost fluid and so give rise to a complex pattern of motion that makes the choice of reaction coordinate questionable.

In this discussion of entropy we have tacitly assumed that the Debye approximation at any given temperature gives a correct account of the vibrational structure, and that the mode frequencies shift with the elastic constants. This appears obviously true for low-frequency modes, but it may be in error at high frequencies. Theoretical insight into this relationship is obscured by the complexity of anharmonic effects, while experiments at temperatures near the melting point are made impracticable by short phonon lifetimes. Recent experiments performed below the Debye temperature on copper crystals[21] suggest that, up to the Debye temperature at least, high-frequency modes shift considerably less than low-frequency modes; on the other hand, the optical-mode frequencies of ionic crystals are observed[22] to suffer quite large shifts with temperature. Thus, it is not possible at present to assess fully the degree to which temperature coefficients of elastic moduli give a satisfactory measure of the average mode frequency changes. Certainly, the Gruneissen assumption predicts a shift of $\bar{\omega}^2$ with temperature comparable to the observed change in elastic constants.

The intimate connection between elastic constants and diffusion rates is found not only for the motion energy as given by the present theory, and the Zener relationship, but also for more subtle features. In Sec. V, we show that the elastic constants also account for the "motion volume".

In recent years, curved Arrhenius plots for diffusion have been obtained in certain metals and the origin of these effects, if real, remains obscure. The bcc metals have provided well-documented examples,[23] but the combination of several independent investigations of diffusion in aluminum apparently points to equally nonlinear behavior.[24] It is interesting to note that at high temperature the elastic constants of bcc tungsten vary with temperature in a markedly nonlinear fashion[25] and that, from Eqs. (4.10) and (4.11), one finds a corresponding curvature of the Arrhenius plot, which indicates larger values of the E_M at the higher temperatures, as is observed in many systems. If similar curvature is found in the elastic constants of other bcc metals then it may be that anomalous diffusion effects that have not been understood will find a natural explanation on the elastic theory. We have been able to fit the combined diffusion data for aluminum remarkably well using $\phi(T)$ estimated from Köster's[16] measurements of elastic properties of aluminum at high temperature. However, since these data are obtained from polycrystalline samples, and are therefore uncertain at high temperatures to the extent of possible grain-boundary effects, the presentation of detailed results would appear premature. Single-crystal data are at present available only at temperatures less than 780°K,[14] which unfortunately lies below the region of greatest interest. One should notice that the formation energy also varies with the elastic constants and may, therefore, contribute to curvature. In the Appendix, we offer a rough estimate of this effect. It is shown that E_F is only one-third as sensitive as E_M to fractional changes of the elastic constants.

It is appropriate to conclude this discussion of the elastic theory applied to metals with some general remarks concerning well-known empirical formulas[5] that provide good estimates of the activation energy for self-diffusion, namely,

$$Q=34T_m \tag{4.12}$$

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[18] A. D. LeClaire, Acta Met. **1**, 438 (1953).

[19] W. Köster, Z. Metallk. **39**, 1 (1948).

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

[21] R. M. Nicklow, G. Gilat, H. G. Smith, and L. J. Raubenheimer, Phys. Rev. **164**, 922 (1967).

[22] G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London) **A261**, 10 (1961).

[23] Various tabulations of activation energies in bcc metals are to be found in *Diffusion in Body-Centered Cubic Metals* (American Society for Metals, Cleveland, Ohio, 1965).

[24] F. Y. Fradin and T. J. Rowland (to be published).

[25] R. Lowrie and A. M. Gonas, J. Appl. Phys. **38**, 4505 (1967).

TABLE III. Elastic theory applied to valence crystals. Elastic data are taken from Hearmon (Ref. 16). Theoretical values of E_M are obtained using $\delta^2=0.087$. Values in parenthese are theoretical (see footnotes).

					Other data		
	c_{11}	$\frac{1}{2}(c_{11}-c_{12})$	c_{44}		E_M	E_F	Q
		(10^{12} dyn cm^{-2})		E_M		(eV)	
C	10.2	2.59	2.5	1.56	(1.85[a]; 2.0[b])	(3.15[a]; 4.2[b])	...
Si	1.676	0.512	0.80	1.17	(1.09[a]; 1.06[b])	(2.13[a]; 2.32[b])	5.13[c]
Ge	1.32	0.405	0.686	1.06	~1[d] (0.98[a]; 0.95[b])	~2[d] (1.91[a]; 2.07[b])	2.98[d]

[a] K. H. Benneman (Ref. 34).
[b] R. A. Swalin (Ref. 35).
[c] J. M. Fairfield and B. J. Masters, J. Appl. Phys. 38, 3148 (1967). Note that this activation energy is not compatible with the cohesive energy of Si and low migration energies quoted in the literature (Ref. 33).
[d] See Ref. 33.

and

$$Q=16.5L_m, \tag{4.13}$$

where T_m is the melting temperature and L_m is the latent heat of melting. The physical basis of these correlations is surely this: The vacancy-formation energy[26,27] and (through the elastic constants) the motion energy, are largely determined by the plasma interaction between conduction electrons and the positive ionic background of the lattice. The melting temperature also depends on the plasma interaction,[28] and, furthermore, it appears likely that the latent heat of melting measures mainly the effect on plasma energy of the volume change on melting, through effects similar to those that limit liquid expansion.[29] Thus Eqs. (4.12) and (4.13) essentially interrelate plasma properties, and it seems quite probable that their general validity in metals will eventually be traced to this common link. This explanation also makes self-evident the reason why the correlations are successful for metals.

The case of Na also points to a validity of the Zener relationship more broadly based than is indicated by a separate analysis of E_M and E_F; for the diffusion entropy is given rather well despite the anomalous division of Q between these components. As we have pointed out, the underlying connection between these variables appears to be the plasma interaction.

V. DIFFUSION IN NONMETALLIC CRYSTALS

The elastic theory is limited to monatomic crystals, but not to metals alone; polyatomic crystals have a more complex vibrational structure to which elastic constants certainly do not provide a reasonable guide. We shall consider diatomic crystals elsewhere; the following discussion for fcc materials is restricted to solid argon, for which both elastic[30] and diffusion[31] measurements have been completed, although with limited precision. Diffusion has been studied in Xe, but the elastic constants have not.

At 0°K, the elastic constants of Ar (in units of 10^{10} dyn/cm^2) are believed to be: $c_{11}=4.819$, $c_{12}=1.277$, and $c_{44}=1.235$. Consequently, $c(0)$ from Eq. (4.8) is 2.50×10^{10} dyn/cm^2. With $\delta^2=0.052$ for the fcc structure, we thus obtain

$$E_M=0.091 \text{ eV}.$$

Q is observed to be 0.168 eV and theoretical arguments[32] support a value of E_M somewhat less than $Q/2$, in good order-of-magnitude agreement with our result. It is remarkable that structures having such different cohesive properties as, e.g., Cu and Ar are equally well described by the present theory. Bernè *et al.* have noted previously that the Zener relationship appears to hold satisfactorily for solid Ar. From our present viewpoint, this result is not unexpected.

Table III shows elastic constants of the valence crystals C (diamond), Si, and Ge.[16] Only for the case of Ge has the motion energy been obtained from experiment.[33] A value of $\delta^2\simeq0.087$, midway between its values of the fcc and bcc lattices, appears to reproduce in a satisfactory manner the *theoretical* motion energies due to Benneman[34] and to Swalin[35] who, respectively, employ a pseudopotential approach and the Lennard-Jones potential in crystal-energy calculations.

VI. ACTIVATION VOLUME FOR MOTION

It is observed experimentally[5] that the application of hydrostatic pressure to crystals modifies the diffusion rate. For crystals dominated by vacancy diffusion, this change occurs mainly because lattice vacancies (which increase the crystal volume) are suppressed, and to a smaller extent from modification of the jump rate. From our present standpoint, the crystal-volume change during a diffusion jump is zero, for the atomic displacement is just a phase coincidence among the phonons. We must examine the change in elastic constants caused by pressure to find the effect on vacancy migration.

The activation "volume" for migration is a useful parameter with which to measure pressure changes of

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[26] F. C. Fumi, Phil. Mag. 46, 1007 (1955).
[27] C. P. Flynn, Phys. Rev. 125, 881 (1962).
[28] J. E. Enderby and N. H. March, Advan. Phys. 16, 691 (1967).
[29] C. P. Flynn, J. Appl. Phys. 35, 1641 (1964).
[30] H. R. Moeller and C. F. Squires, Phys. Rev. 151, 689 (1967).
[31] A. Bernè, G. Boato, and M. dePaz, Nuovo Cimento 46, 182 (1966).
[32] J. J. Burton and G. Jura, J. Phys. Chem. Solids 28, 705 (1967).
[33] J. W. Corbett, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Suppl. 7.
[34] K. H. Benneman, Bull. Am. Phys. Soc. 9, 298 (1964).
[35] R. A. Swalin, J. Phys. Chem. Solids 18, 290 (1961).

migration rates. Thus, if

$$w = w_0 e^{-G_M/kT}, \tag{6.1}$$

then

$$V_M = \left(\frac{\partial G_M}{\partial p}\right)_T = -\frac{kT}{w}\left(\frac{\partial w}{\partial p}\right)_T, \tag{6.2}$$

provided w_0 is pressure-independent. V_M is the required activation volume. According to the preceding results,

$$G_M = \phi = c\Omega\delta^2. \tag{6.3}$$

Thus,

$$V_M = \left(\frac{\partial \phi}{\partial p}\right)_T = (c^P - \kappa_T)\phi(0), \tag{6.4}$$

where

$$c^P = \frac{1}{c(0)}\left(\frac{\partial c}{\partial p}\right)_T \tag{6.5}$$

and

$$\kappa_T = -\frac{1}{\Omega}\left(\frac{\partial \Omega}{\partial p}\right)_T. \tag{6.6}$$

To our knowledge, the motion volume has been measured directly only for the case of gold at room temperature, for which the measured motion volume, $V_m = 1.5 \pm 0.14$ cm^3/mole, is about 15% of the molar volume.[36] There is, however, evidence from diffusion measurements that this volume is reasonably typical of motion volumes in metals.[37] Using c_{44} and $\frac{1}{2}(c_{11} - c_{12})$ as shear moduli, one may obtain an estimate of $c^P \sim 3 \times 10^{-12}$ cm^2/dyn from data listed in Ref. 16. In addition, $\kappa_T = 0.5 \times 10^{-12}$ cm^2/dyn, and E_M is observed to be 0.7 eV.[36] We therefore obtain, from Eq. (6.4),

$$V_m \sim 3 \times 10^{-24} \text{ cm}^3/\text{atom} \sim 2 \text{ cm}^3/\text{mole},$$

in quite good agreement with the observed value of 1.5 cm^3/mole. Activation volumes for migration in other metals should, in general, occupy a similar proportion of the atomic volume.

For sodium, $\kappa_T = 16 \times 10^{-12}$ cm^2/dyn and $c^P \simeq 40 \times 10^{-12}$ cm^2/dyn. With $E_M \simeq 6 \times 10^{-14}$ erg, $V_M \simeq 1$ cm^3/mole. This is small compared to the atomic volume of 24 cm^3/mole. The formation volume, 0.48 Ω, obtained by correcting the measured activation volume of 0.52 Ω for self-diffusion in sodium is thus not very different from those observed in fcc metals.

It is interesting to note that V_M is not necessarily positive. For highly compressible crystals it is possible that $\kappa_T > c^P$, so that $V_M < 0$.

Finally, attention is called to the fact that the changes of elastic constants with pressure, which reproduced the motion volumes, are being used to represent the frequency shifts of the normal modes. This is, once more, a sound assumption for low-frequency modes, but its use for high-frequency modes may be questioned. In a future publication we shall show how a more direct consideration of the high-frequency mode shifts reproduces observed pressure effects in silver halides.

VII. ISOTOPE EFFECT

Careful measurements of the relative diffusion coefficients of isotopes having different masses, has revealed that the migration rate varies with isotopic mass.[38] This effect obviously depends on the detailed lattice dynamics of imperfect crystals and, as such, is a complex problem for which no exact description is as yet available. Model calculations show that very heavy and very light "isotopic impurities" give rise respectively to low-frequency resonances and to localized modes. Both light and heavy impurities have a reduced vibrational amplitude in high-frequency band modes, but for light isotopes this is compensated by the local mode.[39]

While a precise account of isotope effects is thus not possible at present, we can arrive at quite satisfactory predictions from a study of the reaction coordinate defined in Sec. II.

We should expect the quantity $\sum_{\omega\lambda} |x_{\omega\lambda}^0|^2$, which occurs in the exponent of Eq. (2.7) for the jump rate, to be independent of atomic mass. To the extent that the potential energy of a migrating atom is defined by its displacement towards the saddlepoint, the mean-square displacement given by the summation measures an average potential energy. A similar but not identical result, which has been proved by Dawber and Elliott[39] shows that the mean-square amplitude around the equilibrium position is independent of isotopic mass. The matter is seen much more clearly on the reaction-rate model, where the exponent is found to be proportional to the saddlepoint energy and thus depends only on chemical properties of an ion. In addition, this conclusion appears to be in accordance with experiment.[4]

The influence of isotopic mass on diffusion is then contained entirely in the term $\{\sum_{\omega\lambda} \omega^2 |x_{\omega\lambda}^0|^2\}^{1/2}$ of the pre-exponential factor. On writing $\mathbf{u}_d \cdot \hat{x} = \xi^d$ and $\mathbf{u}_n \cdot \hat{x} = \xi^n$, we may expand the summation as

$$\sum_{\omega\lambda} \omega^2 |x_{\omega\lambda}^0|^2 = \sum_{\omega\lambda} \omega^2 |\xi_{\omega\lambda}^d|^2 + \frac{1}{\mathfrak{N}^2} \sum_n \sum_{\omega\lambda} \omega^2 |\xi_{\omega\lambda}^n|^2 + \frac{2}{\mathfrak{N}} \sum_n \sum_{\omega\lambda} \omega^2 \xi_{\omega\lambda}^n \xi_{\omega\lambda}^d + \frac{2}{\mathfrak{N}^2} \sum_{n \neq n'} \sum_{\omega\lambda} \omega^2 \xi_{\omega\lambda}^n \xi_{\omega\lambda}^{n'}. \tag{7.1}$$

Now $\sum_{\omega\lambda} \omega^2 |\xi_{\omega\lambda}^d|^2$ is identical with $\sum_{\omega\lambda} |\dot{\xi}_{\omega\lambda}^d|^2$ for harmonic time variations, and the latter summation is just twice the mean-square velocity of the migrating atom d. Thus, at high temperatures,

$$\sum_{\omega\lambda} \omega^2 |\xi_{\omega\lambda}^d|^2 = 2kT/M_d. \tag{7.2}$$

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[36] R. M. Emrick, Phys. Rev. **122**, 1720 (1961).

[37] L. W. Barr and J. N. Mundy, in *Diffusion in Body Centered Cubic Metals* (American Society for Metals, Cleveland, Ohio, 1965).

[38] L. W. Barr and A. D. LeClaire, Proc. British Ceram. Soc. **1**, 109 (1964).

[39] P. G. Dawber and R. J. Elliott, Proc. Roy. Soc. (London) **273**, 222 (1963).

Similarly,

$$\frac{1}{\mathfrak{N}^2}\sum_n\sum_{\omega\lambda}\omega^2|\xi_{\omega\lambda}{}^n|^2=\frac{2kT}{\mathfrak{N}M_n}. \tag{7.3}$$

The remaining terms in Eq. (7.1) are identically zero, leaving

$$\sum_{\omega\lambda}\omega^2|x_{\omega\lambda}{}^0|^2=2kT\left(\frac{1}{M_d}+\frac{1}{\mathfrak{N}M_n}\right). \tag{7.4}$$

We can show that the sums over cross terms in Eq. (7.1) are zero, by considering the orthonormal eigenvectors $v_{\omega\lambda}{}^m$ of the dynamical matrix. Modes with these amplitudes have mean kinetic energies

$$\tfrac{1}{2}\epsilon_\omega=\tfrac{1}{4}\sum_m\omega^2(v_{\omega\lambda}{}^m)^2, \tag{7.5}$$

where the summation extends over all atoms. Modes in equilibrium at high temperature have $\varepsilon_\omega=kT$ and therefore contain an amplitude-weighting factor $(kT/\omega^2)^{1/2}$; the $\xi_{\omega\lambda}{}^m$ are such thermal-equilibrium modes. Therefore

$$\sum_{\omega\lambda}\omega^2\xi_{\omega\lambda}{}^d\xi_{\omega\lambda}{}^n\propto kT\sum_{\omega\lambda}v_{\omega\lambda}{}^dv_{\omega\lambda}{}^n. \tag{7.6}$$

But the last summation must vanish because the $v_{\omega\lambda}{}^m$ are orthonormal. We may show by an identical argument that the remaining summations in Eq. (7.1) are also zero and that the diffusion rate is, in the Debye approximation, therefore proportional to

$$\{M_d{}^{-1}+(\mathfrak{N}M_n)^{-1}\}^{1/2}$$

from Eq. (7.4).

For light impurities, $M_d{}^{-1}\gg(\mathfrak{N}M_n)^{-1}$; the jump rate is then proportional to $M_d{}^{-1/2}$, giving a simple isotope effect as observed.[40] For $M_d=M_n+\delta M$ with $\delta M/M$ small, we may write the jump rate in an obvious notation as

$$1-\frac{w(M+\delta M)}{w(M)}=\frac{\mathfrak{N}}{\mathfrak{N}+1}\frac{\delta M}{2M}=\Delta K\frac{\delta M}{2M}, \tag{7.7}$$

to show that the isotope effect is reduced to a fraction $\mathfrak{N}/(\mathfrak{N}+1)$ of its value for the simple effect. The change in diffusion coefficient is then obtained by substituting D for w and $f\Delta K$ for ΔK in Eq. (7.7), with f the correlation factor (see, e.g., Ref. 4). The factor $\mathfrak{N}/(\mathfrak{N}+1)$ is precisely the fraction of kinetic energy that resides in the migrating atom for a normal mode obtained by coupling the $\mathfrak{N}$ saddlepoint atoms rigidly together and connecting them by a spring to the jumping atom. To this extent the present approach may be reconciled with rate-theory results. An interesting prediction is that isotopic impurities much heavier than solvent atoms should exhibit only a small isotope effect.

Equation (7.8) indicates that true isotopic impurities ($\delta M/M$ small) should have isotope effects 20 and 25% smaller than the $M^{-1/2}$ value, for fcc and bcc crystals, respectively. These values appear to lie near the range of the experimental observations, except for Na in which a larger, 50% reduction is found.[37] We examine this interesting anomaly in what follows.

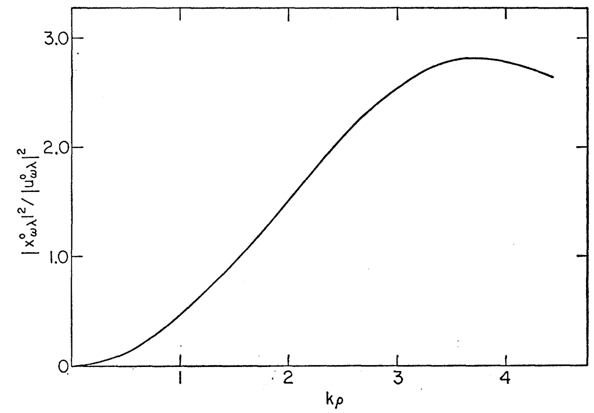

FIG. 4. $|x_{\omega\lambda}{}^0|^2/|u_{\omega\lambda}{}^0|^2$ as a function of $k\rho$ for $\mathbf{k}$ in the (111) plane of the bcc lattice and the polarization vector in the [111] direction. The ratio is considerably larger than unity, because atoms definining the saddlepoint move out of phase with the diffusing atom for large k.

Vacancy jumps occur in ⟨111⟩ directions in bcc metals. The [111] direction contains three {110} planes in which the weak shear moduli of Na will give rise to anomalously large amplitudes of shear modes. We therefore expect an overwhelming contribution to the jump probability from transverse phonons with k near the (111) plane. Now, Eq. (2.8) is only valid when the $x_{\omega\lambda}{}^0$ are all of comparable size. If this condition breaks down we should expect the value of w_0 to reflect properties of the packet of modes which activates most jumps; in the present case we should pay careful attention to the large-amplitude shear modes.

From our present viewpoint, neighbors influence the sotope effect only because the saddlepoint is in motion. For the phonons with k large, and which, through multiplicity, dominate the diffusion, the distance between neighbors approaches one-half a phonon wavelength. The *relative* velocity $\dot{x}$ of diffusing atom and saddlepoint is therefore increased; consequently, it becomes less sensitive to changes caused by isotopic substitution. The result (7.7) states essentially that $\langle|\dot{x}|^2\rangle^{1/2}$ is increased about 25% by this correlated motion in relatively isotropic lattices. However, for shear modes in the (111) plane polarized in the [111] direction, the correlation is very much greater. The neighbors may for convenience be spread into a uniform ring of radius $\rho=a(\frac{2}{3})^{1/2}$ encircling the [111] axis. Then

$$|x_{\omega\lambda}{}^0|^2=|u_{\omega\lambda}{}^0|^2\langle|1-e^{i\mathbf{k}\cdot\boldsymbol{\rho}}|^2\rangle, \tag{7.8}$$

where the average is over directions of $\boldsymbol{\rho}$. On writing

$$e^{i\mathbf{k}\cdot\boldsymbol{\rho}}=\sum_l i^l\epsilon_lJ_l(k\rho)\cos l\phi, \tag{7.9}$$

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[40] See W. Eichenauer, W. Löser, and H. Witte [Z. Metallk. **56**, 287 (1965)] for some collected data.

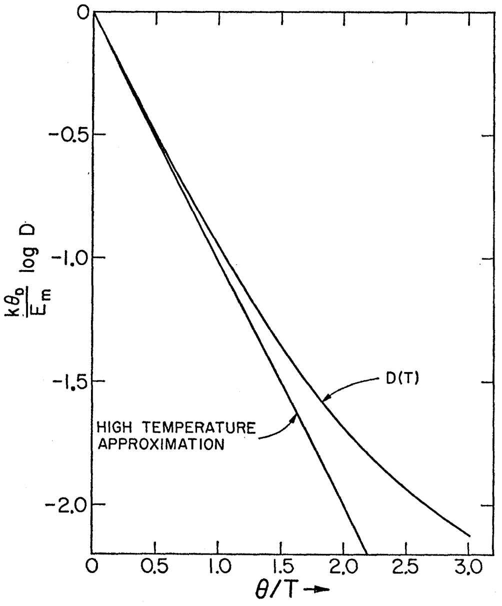

FIG. 5. The jump rate w as a function of T^{-1} for classical statistics and for a quantum-statistical treatment of the migration process. (The base of the logarithms is 10.)

with

$$\epsilon_l = 2 - \delta_{l0}, \qquad (7.10)$$

we readily obtain

$$\langle |x_{\omega\lambda}^0|^2\rangle / |u_{\omega\lambda}^0|^2 = 2(1 - J_0(k\rho)). \qquad (7.11)$$

This function is shown in Fig. 4. In the important region $k > \frac{1}{2}k_D$, $|x_{\omega\lambda}^0|^2/|u_{\omega\lambda}^0|^2$ lies between 2 and 3, whereas the isotropic lattice shows an average value of about 1.6. This motion of the saddlepoint greatly increases the relative velocity of the diffusing atom and makes the jump rate correspondingly less sensitive to isotopic mass. We believe that the small observed isotope effect in sodium metal may be a direct consequence of this feature of shear modes polarized along the [111] axis. It is possible, however, that the neighborhood of a vacancy in Na is so relaxed that a normal-mode analysis in terms of crystal properties becomes meaningless.

VIII. DIFFUSION AT LOW TEMPERATURES

In the preceding sections, we have restricted the discussion of particular cases to high-temperature phenomena where $\varepsilon_\omega \simeq kT$. However, the equations developed in Secs. III and IV have the additional merit that they apply to nontunneling motion at all temperatures.[41] Thus the entire temperature range may be spanned by the equation

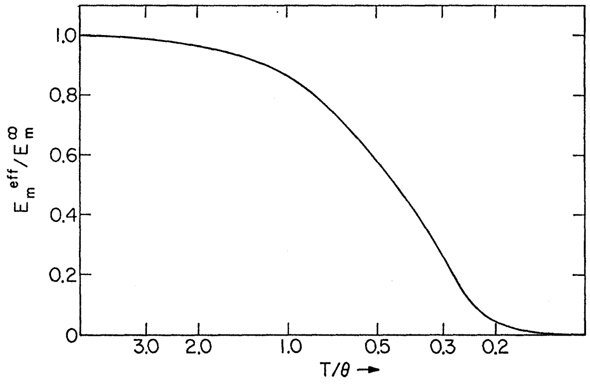

FIG. 6. The effective migration energy as a function of reduced temperature for the isotropic Debye crystal (quantum-statistical treatment).

$$w = (\tfrac{3}{5})^{1/2}\tilde{\nu}_D \times \exp\left\{-\frac{15\Omega\delta^2}{6\varepsilon_l/c_{11} + 4\varepsilon_{t_1}/(c_{11}-c_{12}) + 2\varepsilon_{t_2}/c_{44}}\right\} \qquad (8.1)$$

(the pre-exponential factor exhibits a negligibly small temperature variation). For the isotropic case, we have

$$w = (\tfrac{3}{5})^{1/2}\tilde{\nu}_D \exp(-c\Omega\delta^2/\varepsilon), \qquad (8.2)$$

where c is an average elastic constant and

$$\varepsilon = \frac{1}{3N}\sum_\omega \tfrac{1}{2}\hbar\omega \coth(\hbar\omega/2kT). \qquad (8.3)$$

Figure 5 shows Eq. (8.2) as a function of Θ_D/T, where Θ_D is the crystal Debye temperature. Figures 6 and 7 give the effective energy of motion E_M^{eff} and the effective preexponential factor w_{eff}, obtained by assuming $c\Omega\delta^2$ remains constant as the temperature is varied, and by writing

$$w = w_{\mathrm{eff}} e^{-E_M^{\mathrm{eff}}/kT}. \qquad (8.4)$$

The diffusion rate achieves a constant value at a temperature that is small compared to the Debye temperature, because the lattice falls into a sensibly temperature-independent vibrational state. This residual migration at low temperatures occurs because the zero-point phonons can coincide in phase at suitable sites to cause diffusion jumps into vacant lattice sites. Note that this is *not* a tunneling effect; it is the result of summed positive energy displacements. The occurence of this migration is, of course, contingent upon the presence of vacancies for the case of a vacancy mechanism. The residual jump rate is

$$w = w_0 e^{-8E_M/3k\Theta_D}, \quad (T \to 0) \qquad (8.5)$$

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[41] The author has recently chanced upon a letter by Alefeld [Ref. 14(a)] which appears to have been dropped from the current literature. Alefeld draws attention to the possibility of striking quantum effects occurring at low temperatures, but, through an inappropriate choice of reaction coordinate, arrives at an incorrect result for the variation of W with T. In addition, Ref. 14(a) fails to make clear the type of behavior to be expected at low temperature in solids. To the author, the thermal energy (as opposed to the total vibrational energy) appears irrelevant to the theory. It should be noted that the present analysis deals only with positive-energy excursions, not tunneling, but the use of a model potential leaves the applicability of these results open to serious question. A correct analysis would treat explicitly the many-body wave function propagating between configurations.

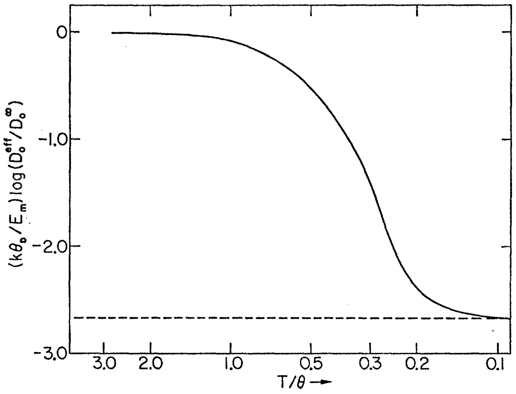

FIG. 7. The effective pre-exponential factor as a function of reduced temperature for the isotropic Debye crystal (quantum-statistical treatment). (The base of the logarithms is 10.)

in an isotropic crystal. In real crystals one may expect a smaller effective Θ_D due to the dominant effect of lower-frequency branches of the spectrum.

No very striking evidence for the existence of this low-temperature migration has been found by the author, although according to Eq. (8.2) the influence of zeropoint motion on migration in crystals such as neon with $\Theta_D > T_M$ should be very appreciable. Of metallic crystals, those, such as Al, with Θ_D a relatively large fraction of $T_M(\sim 0.4)$ appear the most likely source of such evidence. Indeed, it is necessary to include a correction to the diffusion coefficient above room temperature. Thus, the temperature range of interest for annealing quenched Al samples is between Θ_D and $0.5\Theta_D$. Migration has been observed at $-80°\mathrm{C}$, and it is interesting to note that at -50 to $-60°\mathrm{C}$ Doyama and Koehler[42] report E_M values decreasing through 0.47 and 0.43 eV for a sample in the later stages of annealing. According to the present theory, experiments employing protracted annealing periods below these temperatures may possibly reveal a persistance of atomic migration at low temperatures.

IX. DIFFUSION OF VERY LIGHT INTERSTITIALS

Diffusion, at normal temperatures, of interestitial impurities much lighter than solvent atoms (e.g., H and D in metals) is, from a theoretical viewpoint, profoundly different from solvent diffusion, because these atoms vibrate in localized modes outside the spectrum of lattice modes. It seems likely (contrary to accepted doctrine) that the diffusion process cannot be described adequately outside a quantum-mechanical framework. Three features of the problem may be mentioned specifically: (a) Impurities vibrate in an Einstein-like fashion with characteristic temperatures $\sim 1000°\mathrm{K}$, so at normal temperatures less than $\sim 1000°\mathrm{K}$ there appears little value in using a classical heat-capacity approximation; (b) a particle with mass $\sim 10^{-24}$ g oscillating at 10^{13} cps in its ground state has a *classical* amplitude of ~ 0.3 Å and a wave function that remains appreciable at distances ~ 1 Å, which represent a typical saddlepoint displacement; (c) the notion of a saddlepoint "velocity" becomes quite meaningless, because in locating a saddlepoint to any precision, say $\delta x \sim 10^{-9}$ cm, the resulting momentum uncertainty becomes $\hbar/\delta x \sim 10^{-18}$ dyn sec, and the velocity uncertainty therefore $\sim 10^{6}$ cm/sec. This uncertainty is greater than the required quantity, namely, the velocity through the saddlepoint, which presumably is roughly the rms velocity of the particle in its ground state. The latter has a magnitude $(\hbar\omega/M)^{1/2} \simeq 3\times 10^{5}$ cm/sec, so that the calculation of jump rates from the saddlepoint velocity becomes hazardous. In what follows, we give a model quantum-mechanical treatment of interstitial diffusion, in the belief that the chosen model has enough in common with the problem at hand for the results to be at least of qualitative interest. Some estimated results have previously been obtained by Heller.[43]

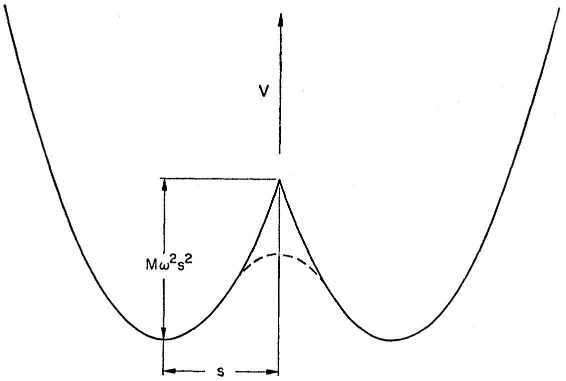

FIG. 8. The model potential for light interstitial diffusion.

The calculation may be performed in one dimension for a particle trapped in a classical potential. For simplicity, we assume that only two alternative configurations are possible and that the potential near the equilibrium point in each well is harmonic. The potential is shown in Fig. 8; the problem is to determine the rate at which transitions from one equilibrium point to its neighbor take place. This transition rate should be similar to the jump rate of the particle from one site to the next of an infinite linear chain of sites, provided the particle energy is much less than the barrier energy.

If the particle remains in one well for a time that is long compared to the vibrational period, then the one center-wave function, $\psi_\alpha(\xi)$ (say, in potential well α) becomes well defined. However, in principle, we should acknowledge two wave functions, ψ_g and ψ_u, which spread out over both wells and which are, respectively, symmetric and antisymmetric around the saddlepoint. Obviously,

$$\psi_g \simeq (1/\sqrt{2})(\psi_\alpha+\psi_\beta)e^{-(i/\hbar)E_g t} \qquad (9.1)$$

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[42] M. Doyama and J. S. Koehler, Phys. Rev. **127**, 21 (1962).

[43] W. R. Heller, Acta Met. **9**, 600 (1961).

and

$$\psi_u \simeq (1/\sqrt{2})(\psi_\alpha - \psi_\beta)e^{-(i/\hbar)E_u t}, \tag{9.2}$$

with E_g and E_u being the energies of the states g and u.

If we wish to place the particle in well α at time $t=0$, we must take the appropriate combination

$$\psi = (1/\sqrt{2})(\psi_g + \psi_u) \tag{9.3}$$

of these wave functions, and the variation of ψ with time then gives the jump rate. ψ develops in time as

$$\psi = [\psi_\alpha \cos(E_u - E_g)t/2\hbar + \psi_\beta \times \sin(E_u - E_g)t/2\hbar]e^{-(E_u+E_g)t/2\hbar}; \tag{9.4}$$

the particle then jumps from one well to the next in a time τ such that

$$\cos(E_u - E_g)\tau/2\hbar = 0 \tag{9.5}$$

or

$$w = 1/\tau = (E_u - E_g)/\pi\hbar. \tag{9.6}$$

It is readily shown[44] that the difference in energy of the two states ψ_g and ψ_u is

$$E_g - E_u = (2\hbar^2/M)\psi_\alpha(s)\psi_\alpha'(s), \tag{9.7}$$

where s denotes the saddlepoint displacement. Thus,

$$w = -(2\hbar/\pi M)\psi_\alpha(s)\psi_\alpha'(s). \tag{9.8}$$

For the chosen potential (Fig. 8), the states ψ_α of interest are just the succession of harmonic-oscillator states

$$\psi_n = \left(\frac{\alpha^2}{\pi}\right)^{1/4} \frac{H_n(\alpha\xi)}{2^{n/2}(n!)^{1/2}} e^{-\alpha^2\xi^2/2} \tag{9.9}$$

(note that we now use a subscript on ψ to indicate the particular quantum state in one well), with $\alpha^2 = M\omega/\hbar$ and H_n the nth Hermite polynomial. Now, the ψ_n are real; we may therefore write

$$\psi_n(s)\psi_n'(s) = \tfrac{1}{2}[(d/d\xi)\psi^2(\xi)]_s = \frac{1}{2}\left(\frac{\alpha^2}{\pi}\right)^{1/2} \frac{1}{2^n n!}\left[\frac{d}{d\xi}\left(e^{-\alpha^2\xi^2}H_n^2(\alpha\xi)\right)\right]_s. \tag{9.10}$$

The probability of state n being occupied is

$$p_n = e^{-n\hbar\omega/kT}(1 - e^{-\hbar\omega/kT}) \tag{9.11}$$

and the mean jump rate

$$w = \sum_n w_n p_n \tag{9.12}$$

is thus

$$w = -\left(\frac{\alpha^2}{\pi}\right)^{1/2} \frac{\hbar}{\pi M}(1 - e^{-\hbar\omega/kT}) \times \left[\frac{d}{d\xi} e^{-\alpha^2\xi^2} \sum_{n=0}^{\infty} \frac{e^{-n\hbar\omega/kT}}{2^n n!} H_n^2(\alpha\xi)\right]_s. \tag{9.13}$$

The addition theorem[45]

$$(1-z^2)^{-1/2} \exp[(x^2+y^2-2xyz)/(1-z^2)] = \exp[-(x^2+y^2)] \sum_{n=0}^{\infty} \frac{z^n}{2^n n!} H_n(x)H_n(y) \tag{9.14}$$

may be employed, with $x = y = \alpha\xi$ and $z = \exp(-\hbar\omega/kT)$, to find

$$e^{-2\alpha^2\xi^2} \sum_{n=0}^{\infty} \frac{e^{-n\hbar\omega/kT}}{2^n n!} H_n^2(\alpha\xi) = (1 - e^{-2\hbar\omega/kT})^{-1/2} \times \exp[-2\alpha^2\xi^2(1 + \exp(-\hbar\omega/kT))^{-1}]. \tag{9.15}$$

When this is substituted into Eq. (9.13), together with $\alpha^2 = M\omega/\hbar$, only a little manipulation is needed to obtain the required result:

$$w = 2\left(\frac{2\omega E_M}{\pi^3\hbar}\right)^{1/2} \frac{(1 - e^{-\hbar\omega/kT})}{(1 - e^{-2\hbar\omega/kT})^{1/2}} \times \tanh\left(\frac{\hbar\omega}{2kT}\right) e^{-E_M/\varepsilon}, \tag{9.16}$$

with the mean oscillator energy

$$\varepsilon = \tfrac{1}{2}\hbar\omega \coth(\hbar\omega/2kT) \tag{9.17}$$

and the saddlepoint energy

$$E_M = M\omega^2 s^2/2. \tag{9.18}$$

The last factor on the right of this equation is the important one; it has the same form found for solvent diffusion, with the average lattice energy per mode replaced by the local-mode energy. Eq. (9.16) reduces correctly to the ground-state tunneling rate, for which

$$\psi_0(s)\psi_0'(s) = (\alpha^3 s/\pi^{1/2})e^{-\alpha^2 s^2}, \tag{9.19}$$

and w may be written

$$w_0 = (2\hbar\alpha^3 s/\pi^{3/2}M)e^{-E_M/\varepsilon_0}, \tag{9.20}$$

with $\varepsilon_0 = \frac{1}{2}\hbar\omega$.

Only the variation with temperature and atomic mass of the exponential is worth numerical attention, for at low temperatures the remaining functions of temperature tend to unity, leaving a preexponential factor typically $\sim 10^{14}$. At high temperature, many additional complications arise through interaction with the lattice, and we may in addition expect jumping *over* the barrier to augment the essentially tunneling motion considered here. Figure 9 shows $\exp(-E_M/\varepsilon)$ for the same potential and several different interstitial masses, as a function of Θ_1/T, Θ_1 being the Einstein temperature of the lightest mass, and with $E_M = 5k\Theta_1$. The limiting form for infinite mass, and the classical result for our chosen potential, are also shown.

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[44] L. D. Landau and I. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958).

[45] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Co., New York, 1953).

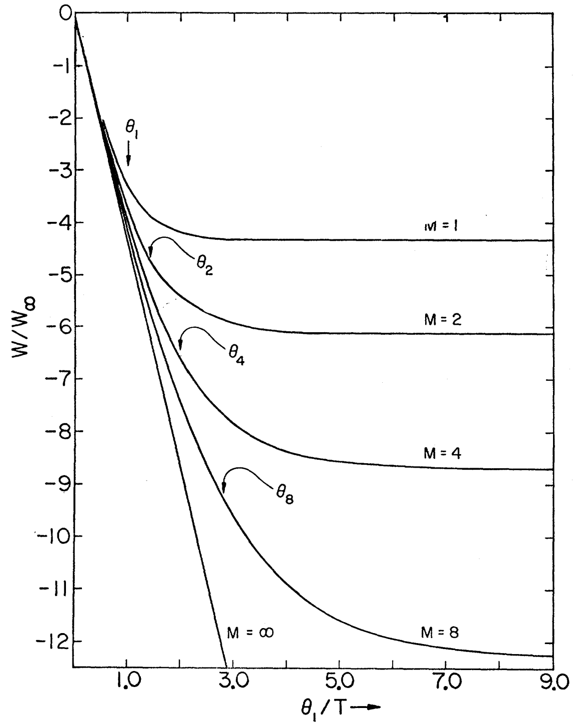

FIG. 9. The diffusion rate for light interstitials vibrating in local modes, above the lattice spectrum for various interstitial masses (see text for details of the model potential used).

Three features of Fig. 9 may be noted: (a) Large isotope effects occur at low temperatures as the oscillator falls into its ground state; (b) at $T\sim\Theta_1$, the diffusion coefficient ($\sim10^{-16}w$) is $\sim10^{-5}$–10^{-6} cm^2/sec, which is typical of H diffusion in metals at normal temperatures[40]; and (c) the classical jump rate is much smaller than the tunneling rate. It is unfortunate, however, that this most interesting comparison between classical and quantum rates is very sensitive to the chosen potential; but this obviously must always be the case, since by inserting a δ function we may inhibit classical diffusion entirely. By suitable choice of different potentials one could vary the ratio between classical and tunneling rates, although the low-temperature classical rate can probably not exceed a correctly calculated quantum rate including tunneling and zeropoint effects. At sufficiently low temperatures, the classical rate must become negligible, while the quantum rate tends to a constant value as the oscillator falls into its ground state.

While our model is thus not suited to precise calculation of jump rates, it makes one point strikingly clear: It is not possible to prevent interstitials moving at low temperatures other than by trapping processes which bind the defects to a particular set of sites, thereby inhibiting diffusion by eliminating long-range migration. After all, the model places an unreasonably large potential between the equilibrium sites, and even this potential is incapable of preventing motion at zero temperature. In the absence of traps, the results of this section suggest even for the cusped potential a zero-point diffusion rate of H in metals within a few orders of magnitude of 10^{-19} cm^2/sec, or a jump rate $\gtrsim10^5$ sec^{-1}. Internal friction peaks at ~1 sec^{-1}, such as those observed by Heller, can best be ascribed to trapped interstitials, according to the present theory. Since the mixing entropy goes to zero at 0°K, such trapping becomes quite probable. Estimates of actual diffusion rates from the theory are, however, made insecure by the use of a model potential, as errors will occur in the *exponent* of Eq. (9.20).

Interstitial diffusion at higher temperatures is likely to prove much more complex than the simple model, as the following three considerations show. First, the interstitials exert a very large pressure on neighboring solvent atoms.[46] The rms acceleration, even in the ground state, is

$$f=\langle\omega^4s^2\rangle^{1/2}\simeq(\hbar\omega^3/4M)^{1/2}, \tag{9.21}$$

so the pressure on neighboring atoms, if reckoned as an area of several Å^2, is of the order of 10 kbar, and it presumably causes strain. The strain varies with $M^{-5/4}$ and may give rise to isotopic effects. It would be interesting to observe directly isotope effects in the dilatation caused by interstitials. Second, we have considered an impurity completely decoupled from the lattice modes. Now, the effect of solvent motion in lattice modes is (a) to frequency-modulate the interstitial by varying the solvent-interstitial interaction, and (b) to modulate the energy barrier. Since the lighter interstitials tend to have less localized wave functions, an isotopic effect may result from these modulations. Too little is at present understood about these processes for their effect on diffusion to be estimated. Finally, we have assumed in our model that the interstitial motion is confined to a narrow localized mode. However, the calculations of Dawber and Elliot[39] show that this is only true in the limit $M\rightarrow0$. The impurities also have vibrational amplitudes *inside* the lattice band; these modes will be excited at temperatures typically well below the impurity Einstein temperature and will contribute to the diffusion jump rate at intermediate temperatures in a way that is not understood at present. In addition, anharmonic forces may be expected to broaden the local mode.

A measure of the influence of these effects on interstitial diffusion at high temperatures may, perhaps, be obtained from the observed isotope effect at $T\simeq\theta_E$, where our model calculation, though not strictly applicable, shows an isotope effect several times larger than the classical value. Experimental results are generally smaller than the classical value. It is interesting to note that LeClaire,[4] using an approximate quantum-partition function in classical reaction-rate theory, finds

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[46] I am indebted to Professor R. O. Simmons for drawing my attention to this point.

relatively good agreement with the experimental isotope effects. As we have shown, the use of reaction-rate theory is, in any event, not obviously justifiable for very light impurities, but it may be that at elevated temperatures the coupling with lattice modes in real crystals is strong enough to dominate the jump process. At low temperatures, as for the *U* center in ionic crystals, we expect the localized mode to be well defined, and the results obtained here to be at least qualitatively correct.

X. IRRADIATED CRYSTALS

Two aspects of the present work are relevant to the annealing processes observed in crystals irradiated at low temperatures. They pertain, respectively, to the observed first and third stages.

Residual resistivity caused by radiation damage is found to decrease markedly at temperatures typically ~30°K, with certain well-defined structure at lower temperatures.[33] In view of our previous discussion, in which diffusion processes are found to persist at low temperatures when the lattice falls to its ground state, this structure at temperatures only a few percent of Θ_D is remarkable. According to the present theory, it is most unlikely that the migration is excited by band modes, for the influence of temperature on fluctuation probabilities among band phonons is negligible at these temperatures. Whatever the activation energy may be, we expect from band modes a jump rate proportional to $\exp(-E_M/\varepsilon_D)$, and this varies little with temperature at $T \ll \Theta_D$. Thus, the presence of a low migration energy does not imply that the defects will suddenly become mobile at a *proportionately* low temperature. For this to occur, the migrating atoms must vibrate mainly in modes decoupled from the lattice modes, and must have a jump rate of the approximate form $\exp(-E_M/\theta_E)$, which, for sufficiently small θ_E, may give rise to rapid changes in annealing rate even at low temperatures.

This isolation from the band modes can be arranged in two ways: The atoms may lie in a sharply curved potential, which gives rise to vibrations above the band; or, otherwise, the potential well may be very shallow, so the vibration falls in the low-frequency tail of the phonon spectrum as a resonance mode coupled only to a small fraction of the phonons, thereby inhibiting zero-point fluctuations capable of causing migration. However, one must also recall that whatever the potential may be, the atom must be excited at temperatures $\sim\Theta_D/20$ sufficiently for many migration jumps do occur in a period $\sim 10^3$ sec. The most likely configuration appears to be some interstitial configuration, lying in a shallow potential well and being essentially decoupled from the lattice at low temperatures by virtue of its low frequency. Some calculations[47] have indeed indicated that the interstitial has a small migration energy. In addition, recent experiments[48] suggest that long-range migration occurs in stage I, as if the interstitial were free to move when isolated. Any lower-temperature structure then corresponds to excitation of recombination transitions[49] between neighboring interstitials and vacancies, for which configurations the resonant-mode frequency would presumably lie still lower. The present viewpoint is thus consistent with the model proposed by Corbett *et al.*[49] It is possible in light materials containing several isotopic species, that isotopic structure in the annealing spectrum may occur. Isotopically enriched Li metal could be interesting in this respect.

It follows from the present theory that interstitials with low migration energies should have small pre-exponential factors for migration. A motion energy of 0.1 eV gives rise to a negligible motion entropy (particularly at low temperatures), and for an Einstein frequency $\sim 3\times10^{11}$ sec^{-1}, the pre-exponential factor is $\sim 5\times10^{-4}$ cm^2/sec.

The stage-III annealing process has often been ascribed to vacancy migration, but this assignment encounters difficulty in that the motion energy has, in several cases, been measured at a smaller value than that observed in vacancy diffusion at high temperatures.[33] This difficulty may eventually prove more apparent than real, for the motion energy may indeed be smaller at low temperature than near the melting point. This will be the case, for example, if the vibrational-mode frequencies (or the elastic constants) prove to have a nonlinear variation with temperature, such that at high temperature the negative temperature derivative has a larger value than that at low temperatures. This possibility cannot be assessed at present owing to the paucity of experimental data. In addition, for those materials in which stage III occurs below the Debye temperature, a further decrease in E_M, caused by enhanced low-temperature migration effects (Sec. IX), is to be anticipated.

XI. CONCLUDING REMARKS

A theory of the atomic-migration process has been developed from the following assumptions: (a) The jump probability can be calculated from the phonon structure of the harmonic lattice. (b) Anharmonicity enters into the jump probability only to the extent that the migration energy is determined from a configuration in which one atom lies far from its equilibrium site. (c) Simple repulsive forces dominate from the saddlepoint configuration so that a simple reaction coordinate may be postulated. That the elastic approximation to the theory is so successful in accounting for diverse features of the migration process is, in the author's opinion, only partially warranted by the soundness of these assumptions.

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[47] H. B. Huntingdon and F. Seitz, Phys. Rev. **61**, 315 (1942).

[48] R. R. Coltman, Jr., C. E. Klabunde, and J. K. Redman, Phys. Rev. **159**, 521 (1967).

[49] J. W. Corbett, R. B. Smith, and R. M. Walker, Phys. Rev. **114**, 1452 (1959).

Use of the Debye approximation with low-temperature elastic constants gives a surprisingly good measure of the motion energy. This approximation should certainly give a reasonable description of the phonons and so provide a useful estimate of the fluctuation probability in terms of elastic constants in a way that is independent of the particular cohesive forces that prevail with a solid. All the known motion energies in monatomic solids, with values ranging over two orders of magnitude, may be explained in terms of a fluctuation parameter δ^2 characteristic of the lattice structure, which takes approximate values of 0.104 (fcc), 0.067 (bcc), and 0.087 (diamond structure). Presumably, this reflects favorably on the chosen reaction coordinate, and indicates an unexpected degree of uniformity in diffusion behavior. The description of isotopic effects at high temperatures also depends to a great extent on the reaction coordinate, and the results give substantial support for the choice made in this paper.

Although the elastic theory gives the most satisfactory available account of the temperature and pressure dependence of the Gibbs function for motion, the agreement secured in Secs. IV and VI (i.e., the Zener empirical relationship and the numerical values of V_M) cannot serve entirely as a measure of the theory until the relationship between elastic constants and lattice frequencies is clarified. The elastic constants are, after all, used only to approximate the lattice-mode frequencies, and it is unlikely that they provide a completely satisfactory description of the mode shifts with temperature and pressure. Evidently, the result of future investigations of high-temperature anharmonic effects will have considerable relevance to the theory of diffusion.

There is a second interesting viewpoint on the elastic theory. In the most simpleminded sense, a diffusion jump does introduce a lattice strain as a migrating atom moves through the saddlepoint. We may expect this strain to be mainly a shear, if the saddlepoint lifetime is sufficient for the configuration of atoms to become established in equilibrium. Now, to estimate the energy in this shear strain we may use the formula

$$E_M = 8\pi a^3 c' \epsilon^2, \tag{11.1}$$

where a will provide a measure of the atomic spacing, c' is a suitable average shear modulus, and ϵ is the strain caused by the jump. But Eq. (11.1) may obviously be written

$$E_M = c'\Omega\delta^2, \tag{11.2}$$

with $\delta^2 = 6\epsilon^2 a^3/r_s^3$, and r_s the atomic radius. Both the elastic constant c we use in Sec. IV, and c' in Eq. (11.2) are essentially shears, and any agreement we secure in the elastic theory could be reproduced approximately by Eq. (11.2), with the dimensionless parameter ϵ suitably chosen to fit the lattice structure, as we have previously chosen δ. This is the "strain energy" model,[50] which leads to equations similar to those obtained from the elastic approximation. What, then, is there to choose between Eq. (11.2) and the theory of Sec. IV?

In a certain sense, the two approaches are identical for high-temperature processes. The elastic theory developed in Sec. IV simply parametrizes the energy change as an atom moves toward the saddlepoint in terms of a scaling factor and the elastic constants; so also does Eq. (11.2), although the correct choice of elastic constant is obscure. The shifts of lattice-mode frequencies with temperature also have their analog in the difficulty in selecting c' in Eq. (11.2) to give energy changes for a transient saddlepoint. But while Eq. (11.2) does not permit elaboration, the present theory is a starting point for which the elastic approximation represents a crude first approximation; it is an approach in which we may hope eventually to incorporate an accurate phonon spectrum and precise crystal energies.

Equation (11.2) is useful in drawing attention to an additional complication present when G_M varies with p and T. While it is reasonable that geometrically similar systems should have much the same value of δ^2, it is not to be expected that the motion Gibbs function changes with p and T in such a way that δ^2 remains quite constant. It may be that through the similarity between Eq. (11.2) and our previous expression for G_M, we have fortuitously taken better account of the change of G_M with temperature and pressure than would be the case had we left the jump rate written in terms of phonon frequencies and a presumed constant value of δ. However, since the theory gives a good account of diffusion in ionic crystals when applied directly to the mode frequencies, it appears most unlikely that this effect does give a major contribution to the entropy. That a changing saddlepoint energy could enter into the jump rate in this way does not, of course, contradict our assumption that the phonon amplitudes are of primary importance; it simply means that δ is not independent of temperature and pressure. The influence of phonon amplitudes may be discerned most clearly in the low-temperature effects discussed in Sec. IX.

Of other results obtained in this article, we may draw particular attention to these predictions concerning low-temperature diffusion. Atomic migration between degenerate sites would appear to persist at 0°K with a frequency appropriate to classical diffusion processes at temperatures somewhat less than one-half the characteristic temperature of the vibrational modes that cause diffusion. This prediction may, however, be quite sensitive to the model employed. Very light impurities have a diffusion rate augmented by tunneling.

ACKNOWLEDGMENTS

The author wishes to thank many colleagues for stimulating discussions; those with Professor H. Birnbaum, Professor J. J. Burton, Professor M. V. Klein, Professor J. S. Koehler, Professor D. Lazarus, and Pro-

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

fessor R. O. Simmons proved particularly helpful. The cooperation of Professor T. J. Rowland and Professor T. G. Stoebe, in allowing the author access to their unpublished manuscripts, are most gratefully acknowledged.

APPENDIX: CURVATURE FOR VACANCY DIFFUSION

When the elastic constants change nonlinearly with temperature it is to be expected that the vacancy-formation energy also changes with temperature. In this section, we make an order of magnitude estimate of the effect on D of the combined changes in motion and vacancy activation energies.

Most of the vacancy energy in metals comes from the plasma interaction with the nonuniform background charge of the lattice. In the Born approximation, the free energy needed to form an unrelaxed vacancy in a metal of valence Z is

$$F_F{}^0=(4/15)ZE_{\max} \tag{A1}$$

with $E_{\max}$ the Fermi energy; Eq. (A1) provides a sensible estimate for low-valence metals, but is too large for higher valences because the Born approximation becomes inadequate.

We may in addition include relaxation effects by inserting $Z'=ZV/\Omega$ in Eq. (A1), with V the vacancy volume, and adding the elastic energy of lattice distortion to find the total formation energies. The result is

$$F_F=\frac{4ZVE_{\max}}{15\Omega}+\frac{8}{9}\pi a^3\mu(V-\Omega)^2 \tag{A2}$$

or

$$F_F=F_F{}^0+F_F{}^0\frac{\delta V}{V}+\tfrac{2}{3}\Omega\mu\left(\frac{\delta V}{V}\right)^2. \tag{A3}$$

This has a minimum when

$$\frac{\delta V}{V}=-\frac{3F_F{}^0}{4\mu\Omega}. \tag{A4}$$

The formation energy is thus

$$F_F=F_F{}^0\left(1+\frac{\delta V}{V}\right). \tag{A5}$$

Now $\delta V/V$ is typically $\sim-\frac{1}{2}$, so $F_F{}^0\simeq\frac{4}{3}F_F$. It follows from (A4) and (A5) that

$$\frac{1}{F_F}\left(\frac{\partial F_F}{\partial T}\right)=-\frac{1}{3\mu\Omega}\frac{\partial(\mu\Omega)}{\partial T}. \tag{A6}$$

Thus, changes in elastic constants affect the formation energy only to $\frac{1}{3}$ the fractional extent to which the migration energy is changed. The argument is far from exact, since neither the elastic nor the plasma contribution to Eq. (A2) bears close scrutiny. It does, however, provide an estimate in the elastic approximation of the diffusion coefficient at any chosen temperature T, in terms of the diffusion coefficient at the melting temperature T_m by means of the following relationship:

$$\frac{D(T)}{D(T_M)}=\exp[f(T_m)/kT_m-f(T)/kT] \tag{A7}$$

with

$$f(T)=\tfrac{1}{3}[2E_F+(E_F+3E_M)\phi(T)/\phi(T_m)], \tag{A8}$$

in which E_F and E_M denote quantities appropriate to the melting point. Equations (A7) and (A8) have been used with elastic data due to Köster to obtain a satisfactory fit of the combined diffusion data available for aluminum at high temperatures.[24] It will be interesting, when suitable values of elastic constants become available, to see whether these equations can account for anomalous Arrhenius plots in other materials also.