potential terms in the dynamical matrix, especially in the long-wavelength limit. The required terms may be obtained by calculating the dielectric function to second order in the local pseudopotential, then keeping all terms in the dynamical matrix which are of second order in umklapp scatterings. We have not yet evaluated these terms numerically, but it appears they may give a significant contribution to the theoretical phonon spectrum for aluminum. In addition the effect on the screening of the electronic exchange and correlation has been included by the Hubbard-Sham approximation in our formulation[8]; the accuracy of this approximation is quite unknown at present. We have neglected the explicit anharmonic free energy in our calculations; it is unlikely that this neglect significantly affects the discrepancies found here.

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Quantum Theory of Diffusion with Application to Light Interstitials in Metals†

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A quantum theory of diffusion is presented and applied to the particular problem of light interstitial diffusion. The theory focuses attention on transitions among approximate localized eigenstates of the system. The diffusion rate of a light interstitial in bcc metals is shown to be determined principally by the self-trapping distortion which stabilizes the impurity at a particular interstice. A quantitative explanation of both the motion energy and the motion entropy follows from the theory. The differences between interstitial motion in bcc and fcc hosts, and also the dependence of the diffusion rate on isotopic mass, are discussed.

1. INTRODUCTION

Several efforts have been made to develop a quantum theory of diffusion since the early work of Wigner.[1] The classical theory, as developed for solid-state processes by Wert and Zener[2] and by Vineyard,[3] specifies the jump rate W in terms of Gibbs functions for different configurations of the system:

$$W=(kT/h)e^{-g/kT}.$$

Here $g\equiv G_s-G_0$, with G_0 the Gibbs function of the crystal vibrating with all atoms vibrating about points of stable equilibrium near regular lattice sites; G_s is the Gibbs function when the diffusive jump process is arrested in the saddlepoint plane between the points of stable equilibrium. Both Gibbs functions, of course, are essentially entropies of the crystal together with its enclosing constant temperature and pressure bath.

The classical formulation encounters a fundamental difficulty in that there exists no operationally satisfactory way of defining G_s. Despite this difficulty, attempts have been made to obtain quantum results in the spirit of rate theory by an explicit treatment of the motion of a representative point through a model potential barrier in configuration space. The most recent and successful of these treatments are due to Weiner[4] and to Weiner and Partom[5]; references to related work will be found in these papers. It is widely believed that the classical theory must provide a correct description of diffusion for temperatures in excess of the Debye temperature Θ_D at which the lattice vibrational energy becomes sensibly classical, and this has motivated quasiclassical discussions.

In this paper we derive an alternative and more satisfactory quantum theory of diffusion by focusing attention first on the question of the exact eigenstates of a system in which diffusion occurs. Diffusive jumps then appear as transitions which are induced by the crystal Hamiltonian among the approximate eigenstates, each of which is localized near some equilibrium point in configuration space. Detailed balance is assured by the Hermitian properties of the crystal Hamiltonian. From a formal point of view the theory is closely related to well-known treatments of the polaron problem[6] and of radiationless transitions.[7] After presenting the general theory in Sec. 2, we turn in Sec. 3 to a detailed treat-

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ment of light interstitial diffusion in metals. This particular example, in addition to being one of the cases where quantum effects are expected to be important, is also made tractable because we can use an adiabatic approximation in describing the light particle motion.

A considerable body of experimental information has accumulated concerning the diffusion of light impurities in metals, but there is no adequate theory of the dynamic or thermodynamic properties of these impurities. The interstitial impurities cause a static distortion of the lattice as the host metal relaxes to equilibrium with the impurity occupying any particular interstice. This distortion may be detected by the change of lattice parameter which accompanies hydrogen permeation into metals. Volumes of solution between 0.2 and 0.4 of the solvent atomic volume are observed[8] for hydrogen in metals. The expected dependence on isotope of the volume of solution has yet to be reported. We shall see that the volume of solution is an important measure of the interaction of the light impurity with the host lattice, and that it may be related to a number of other properties.

The infrared spectra of hydride ions in ionic crystals[9] show local modes with frequencies well above the perfect lattice bands. The local-mode frequencies for hydrogen and deuterium are roughly in the ratio predicted by the relation

$$M_H\omega_H^2 \sim M_D\omega_D^2 \tag{1.1}$$

expected for the independent motion of different mass particles in identical potentials. Whenever the impurity-mode frequencies lie well above the highest frequencies of the perfect lattice, the impurity mode becomes very localized; the amplitudes of vibration of the host-lattice atoms in these modes become very small, and it is often a good approximation to assume that only the impurity atom moves. Interstitial hydrogen atoms in metals are likely to have similar characteristics. Indeed, neutron diffraction studies on hydrogen in niobium and vanadium[10] have revealed somewhat broadened local modes with energies of $\hbar\omega_H \sim k\times 1000°$, whereas the corresponding energy for deuterons is $\hbar\omega_D \sim k\times 700°$. These energies are considerably higher than the Debye energy, which is in the range $k\times 200°$ to $k\times 300°$ for most metals, and $\hbar\omega_H$ and $\hbar\omega_D$ are roughly in the ratio expected from Eq. (1.1). Other data are available from solubility measurements.[11]

The experimental data concerning the diffusion of light impurities among the interstices of a metal lattice have recently been reviewed by Wert.[12] The temperature dependence of the diffusion coefficient is not fully known for any solvent, because of experimental difficulties, but several trends are evident. First, both the proton and the deuteron jump rates appear to exhibit Arrhenius behavior:

$$1/\tau \sim D_0 e^{-E_a/kT} \tag{1.2}$$

at least down to temperatures of the order of 150°K. Second, protons diffuse with unusual rapidity. The observed activation energies lie in the range 2–10 kcal/mode (0.1 to 0.5 eV) with frequency factors from 4.10^{-4} to 6.10^{-3} cm^2/sec. Third, large isotopic differences in diffusion rate occur at low temperatures in some cases, but in cases studied above room temperature the isotope effect usually appears close to the classical prediction of an inverse-root-mass dependence. However, conclusions drawn from the available data are sensitive to possible binding effects between impurities and to trapping by dislocation and other long-range strain fields in imperfect crystals. These effects should be particularly important at low temperatures. Although the Arrhenius behavior holds approximately, as mentioned, the diffusion data do often suggest that different diffusion mechanisms are operative in different temperature ranges.

2. QUANTUM THEORY OF DIFFUSION

Atoms generally diffuse through crystals at significant rates only in the presence of point defects which provide easy mechanisms for atomic jumps. The point defect is often a vacancy which migrates one lattice step as a neighboring atom changes position to occupy the vacant cell, leaving its former site vacant. In other cases the migrating atom may itself be an interstitial which migrates between equivalent interstices, or else the atom interacts with an interstitial to migrate by the interstitialcy mechanism. In each case the crystal configuration before and after a jump may be characterized in part by the location of some detectable inhomogeneity of the lattice. We shall consider, for simplicity, the diffusive motion of a single defect whose location is given by **R**. This simplification does not affect any essential features of the diffusion process; for example, it is trivial to generalize the treatment to cases in which the orientation as well as the location of the defect is important.

Although it is natural to develop the theory of diffusion in terms of localized defect states, it must be remembered that the exact eigenfunctions are not localized. For each state in which the defect is localized on one site there is an equivalent state related to it by one of the symmetry operators of the host lattice. The exact eigenstates are linear combinations of the equiva-

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[8] Recent data have been collected by R. A. Oriani, in *Phase Stability in Metals and Alloys*, edited by P. S. Rudman, J. Stringer, and R. I. Jaffe (McGraw-Hill, New York, 1967).

[9] See, for example, the article by M. V. Klein, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968).

[10] W. Kley, J. Peretti, R. Rubin, and G. Verdan, J. Phys. Radium **28**, C1-26 (1967).

[11] See, for example, W. Eichenauer, W. Lösser, and H. Witte, Z. Metallk. **56**, 287 (1965).

[12] C. A. Wert, in Proceedings of the International Conference on Ultrasonic Attenuation and Internal Friction, Brown University, Providence, R. I., 1969 (unpublished).

lent states which reflect the translational symmetry of the host lattice. However, the localized functions are sensibly exact eigenfunctions in the present case. The localized approximate eigenfunctions bear the same relation to the exact eigenstates that Wannier functions bear to Bloch functions: A quantum number indicating a crystal site replaces a wave vector which measures the phase change of the wave function from site to site. Just as in the construction of Wannier functions we may arrange that the localized functions on different sites be orthogonal. These localized functions are nevertheless mixed by the exact crystal Hamiltonian, and the transitions induced among these crystal configurations are the familiar hopping motions of point defects through crystals. We shall write the localized states $|p,\nu\rangle$, in which p gives the location of the defect and ν refers to the other degrees of freedom. In particular, ν gives the phonon occupation numbers for the lattice.

It is natural to ask how the propagating nature of the translationally invariant exact eigenstates has been degraded into a hopping motion. We may answer this question superficially by noting that for each state $|p,\nu\rangle$ of the whole system, with the defect localized at site p, there is only one state $|p'\nu\rangle$ which is just related to $|p\nu\rangle$ by the particular translation operator. At high temperatures there are many states degenerate with $|p'\nu\rangle$ which we may regard as differing only by a redistribution of the lattice vibrational energy among the various lattice oscillators. Consequently the transitions which are diagonal in the lattice vibrational quantum numbers, so that the initial and final states of the transition are related by a symmetry operation, are overwhelmed at high temperatures by the enormous number of off-diagonal "hopping" transitions. At low temperatures, however, it is possible that diagonal transitions may predominate and the defect motion can then take on a propagating character.

One important feature is that diffusive jump times are observed to be long compared with the characteristic times of other crystal processes. The jump times are normally longer than 10^{-10} sec even at the melting point, and may become indefinitely large at low temperatures. Thus the mean interval between jumps is long compared with typical phonon periods ($\omega^{-1}\sim 10^{-13}$ sec) and also when compared with typical phonon lifetimes. Consequently, dynamical correlations between jumps may be neglected.

In calculating the transition probability between approximate eigenstates $|p,\nu\rangle$ and $|p',\nu'\rangle$ we shall use the standard perturbation result

$$w_{pp'}(\nu,\nu')=(2\pi/\hbar)|\langle p\nu|\mathcal{H}|p',\nu'\rangle|^2\delta(E_{p\nu}-E_{p'\nu'})\,, \quad (2.1)$$

in which

$$E_{p\nu}=\langle p\nu|\mathcal{H}|p\nu\rangle\,. \quad (2.2)$$

Note that if, for preference, the localized states chosen are imperfectly orthogonalized then the transition probability can be written

$$w_{pp'}(\nu,\nu')=(2\pi/\hbar)|\langle p\nu|(\mathcal{H}-E_{p\nu})|p'\nu'\rangle|^2 \times\delta(E_{p\nu}-E_{p'\nu'})\,. \quad (2.3)$$

In writing these expressions we have recognized that the energy expectation values of the initial and final states have essentially continuous distributions, so that a density of states may be defined. Also we have assumed that the diagonal transitions are rare, so that the probability of the defect simply propagating among the equivalent states may be neglected. Detailed balance is ensured because the operator $(\mathcal{H}-E)$ is Hermitian.

We are mainly concerned with the transition probability between different sites p rather than between different states $|p\nu\rangle$. The probability that a transition takes place from an initial state $|p\nu\rangle$ to any state with site p' is obtained by summing over final states $|p'\nu'\rangle$. Further, since the populations of the states with the defect on site p are thermally distributed we must average over the thermal equilibrium distribution of quantum numbers ν. Consequently, the over-all jump rate is

$$W_{pp'}=\langle\sum_{\nu'} w_{pp'}(\nu,\nu')\rangle_\nu \quad (2.4)$$

in which $\langle\ \rangle_\nu$ denotes the thermal average over ν.

Before passing on to a detailed application of these expressions in the theory of proton migration, we shall emphasize the difference between the present view of diffusion and previous theories, both classical and quantum mechanical. The present theory focuses attention on transitions among states which differ from eigenstates only in that they are localized. There is no question of the representative point simply surmounting or penetrating a barrier in configuration space; the intermediate stages of a transition are not discussed in quantum mechanics. It is indeed satisfactory that this distinction be drawn, since it is evident that the detailed structure of the potential on either side of any barrier is needed even to determine whether or not a transition is energetically acceptable. In the quantum theory outlined above the saddlepoint plays no especially distinguished role; only the exact Hamiltonian and the localized initial and final state wave functions are relevant. However, it is true that the wave functions decrease rapidly away from the center of localization in configuration space, and that contribution to the matrix element in (2.1) may be drawn principally from a diffusion volume on the saddlepoint.

3. DIFFUSION OF LIGHT INTERSTITIALS

We now turn to an explicit evaluation of the jump rate given by Eq. (2.1) for light interstitial impurities. This case is of particular interest and complexity because of the lattice distortion, isotope effects, and possible tunneling behavior associated, for example, with hydrogen interstitials in metals. We shall find that the volume of solution is of central importance in diffusion. An Arrhenius behavior is expected at high temperatures, and deviations are expected well below the Debye temperature. Our approach also gives estimates of the activation energy E_a associated with the Arrhenius behavior, and predicts the dependence of various experimentally observable parameters on isotopic mass.

Throughout this discussion we shall use the Born-Oppenheimer approximation to separate the nuclear and electronic motion. The crystal potential energy is thus assumed to be a unique function of the nuclear coordinates. For each configuration of the nuclear coordinates we may calculate the electronic energy, and this electronic energy provides an effective potential which determines the motion of the nuclei. Since this potential is a function of the nuclear coordinates alone, and does not depend on the instantaneous positions of the electrons, it is immaterial to the theory of proton migration whether protons exist in metallic solution with a bound electron or, more plausibly, with a screening charge drawn from the conduction-electron gas by scattering. The screen is itself of interest, but its properties are not relevant in our discussion.

A. Linear Coupling Model

We write the Hamiltonian of a crystal containing one interstitial particle of mass m as

$$\mathcal{H}=\mathcal{H}_I+\mathcal{H}_{\mathrm{int}}+\mathcal{H}_L. \tag{3.1}$$

Here $\mathcal{H}_I$ is the kinetic energy of the interstitial:

$$\mathcal{H}_I=-(\hbar^2/2m)\nabla^2, \tag{3.2}$$

and $\mathcal{H}_L$ is the perfect lattice Hamiltonian:

$$\mathcal{H}_L=\sum_q \hbar\omega_q(a_q{}^+a_q+\tfrac{1}{2}), \tag{3.3}$$

which we write in the usual second-quantized form for a harmonic system. The interstitial is coupled to the lattice by the intraction term:

$$\mathcal{H}_{\mathrm{int}}=\sum_i U(\mathbf{R}-\mathbf{R}_i,\mathbf{x}_i), \tag{3.4}$$

with $\mathbf{R}$ the coordinate of the interstitial, $\mathbf{R}_i$ the position of host atom i in the perfect crystal, and $\mathbf{x}_i$ its instantaneous displacement from R_i. The explicit form of $\mathcal{H}_{\mathrm{int}}$ can only be determined by detailed calculation.

Since the interstitial hopping rates are very small compared with typical phonon frequencies, it is appropriate first to consider the particle localized at one particular interstice, and to ignore its infrequent jumps. We assume that the impurity wave function $\tilde{\phi}$ adjusts adiabatically to the instantaneous lattice configuration $\mathbf{x}$. With this assumption, which should be satisfactory for a light impurity vibrating in a highly localized mode, we can proceed without semiclassical approximations and obtain the jump rate.

Within the validity of this adiabatic approximation the wave function of the entire system containing the interstitial at site p is

$$\tilde{\Psi}_p(\mathbf{R},\mathbf{x})=\tilde{\phi}_p(\mathbf{R};\mathbf{x})a_p(\mathbf{x}). \tag{3.5}$$

The interstitial wave function $\tilde{\phi}_p(\mathbf{R};\mathbf{x})$, which is not usually orthogonal to interstitial wave functions on other sites, satisfies

$$(\mathcal{H}_I+\mathcal{H}_{\mathrm{int}})\tilde{\phi}_p(\mathbf{R};\mathbf{x})=E_p(\mathbf{x})\tilde{\phi}_p(\mathbf{R};\mathbf{x}), \tag{3.6}$$

and is seen to depend parametrically on $\mathbf{x}$. The energy $E_p(\mathbf{x})$ represents the interstitial energy when the lattice is frozen in configuration $\mathbf{x}$; it constitutes an extra term in the lattice Hamiltonian. The lattice wave function satisfies

$$[\mathcal{H}_L+E_p(\mathbf{x})]a_p(\mathbf{x})=Ea_p(\mathbf{x}), \tag{3.7}$$

with E the energy eigenvalue of the entire crystal containing the defect.

We shall find it convenient to expand $E_p(\mathbf{x})$ as a power series in the displacements $\mathbf{x}$. The distortions will be presumed small, and only the linear term in the expansion will be retained. Thus,

$$E_p(\mathbf{x})=E_{p0}+\mathbf{A}_p\cdot\mathbf{x}. \tag{3.8}$$

We shall not need to know the exact form of the vector $\mathbf{A}_p$. With some generalization, Eq. (3.8) may be applied to the related problem of the reorientation of anisotropic defects.

The term $\mathbf{A}_p\cdot\mathbf{x}$ does not intermix the normal modes, nor does it change their frequencies; it simply displaces the mean position about which the mode vibrates. If the (mass weighted) normal-mode coordinates $\mathbf{Q}_q$ are labeled by the associated wave vectors $\mathbf{q}$ and if the displacements caused by the defect at site p are written $\mathbf{Q}_q{}^p$, then the energy released by this distortion is

$$E_{\mathrm{loc}}{}^a=\tfrac{1}{2}\sum\omega_q{}^2|Q_q{}^p|^2. \tag{3.9}$$

The "localization energy" or "self-trapping energy" E_{loc} is the analog of the carrier localization energy in polaron theory.[6]

If the nth harmonic-oscillator wave function associated with mode $\mathbf{q}$ is $\chi(n,\mathbf{Q}_\mathbf{q})$, then the perfect wave function may be written

$$\prod_\mathbf{q}\chi(n_\mathbf{q},\mathbf{Q}_\mathbf{q})=\prod_\mathbf{q}|n_\mathbf{q}\rangle.$$

The lattice wave function when the impurity occupies interstice p is

$$\begin{aligned}a_p(\mathbf{x})&\equiv|p,\{n_q\}\rangle\\&=\prod_q\chi(n_\mathbf{q},\mathbf{Q}_\mathbf{q}-\mathbf{Q}_\mathbf{q}{}^p)\\&=\prod|p,n_\mathbf{q}\rangle,\end{aligned} \tag{3.10}$$

and is completely defined by the position of the interstitial, p, and the phonon occupation numbers $n_{\mathbf{q}}$.

B. Motion of Interstitials

The wave function (3.5) is inexact not only because of our adiabatic approximation but also because the interstitial atom does not remain localized indefinitely at a single site. The delocalization is precisely what we must study to determine the diffusion rate. As explained in Sec. 2, an interstitial fails to remain at site p because neighboring interstices offer equivalent states, degenerate with those associated with interstice p, but which are not orthogonal to $\tilde{\Psi}_p$ and which are mixed into $\tilde{\Psi}_p$ by $\mathcal{H}_{\text{int}}$. For future convenience we introduce wave functions Ψ_p, related to the $\tilde{\Psi}_p$, but which are orthogonal to $\Psi_{p'}$ on all other sites $p'\neq p$. It is natural to effect this orthogonalization by introducing orthogonal interstitial wave functions, $\phi_p(\mathbf{R};\mathbf{x})$, related to the $\tilde{\phi}_p(\mathbf{R};\mathbf{x})$. The $\phi_p(\mathbf{R};\mathbf{x})$ are formed by taking linear combinations of the $\tilde{\phi}_p(\mathbf{R};\mathbf{x})$ in exactly the same way that Wannier functions are constructed in the tight-binding limit of conventional band theory. In the present case the overlap between nearest-neighbor sites is small, and it suffices to introduce small components of nearest-neighbor terms into the $\tilde{\phi}_p$. We shall assume this has been done, and that the resulting orthogonal impurity functions $\phi_p(\mathbf{R};\mathbf{x})$ remain reasonably well localized. The wave functions which replace (3.5),

$$\Psi_p(\mathbf{R};\mathbf{x})=\phi_p(\mathbf{R};\mathbf{x})a_p(\mathbf{x})\,, \tag{3.11}$$

are now orthogonal:

$$\int d^3\mathbf{R}\,\Psi_p(\mathbf{R};\mathbf{x})\Psi_{p'}(\mathbf{R};\mathbf{x})=|a_p(\mathbf{x})|^2\delta_{pp'}\,. \tag{3.12}$$

Although these functions are orthogonal, they are still mixed by the Hamiltonian; the transformation from the $\tilde{\Psi}_p$ to the Ψ_p does not eliminate the delocalization of the wave function, since $\langle\Psi_p|\mathcal{H}|\Psi_{p'}\rangle$ does not vanish for all $p\neq p'$. We write

$$\begin{aligned} V_{pp'}&=\langle\Psi_p|\mathcal{H}|\Psi_{p'}\rangle\\ &=\langle a_p|a_{p'}\rangle\langle\phi_p|\mathcal{H}_{\text{int}}|\phi_{p'}\rangle \end{aligned} \tag{3.13}$$

or, equivalently,

$$V_{pp'}=J_{pp'}S_{pp'}\,, \tag{3.14}$$

with

$$J_{pp'}=\langle\phi_p|\mathcal{H}_{\text{int}}|\phi_{p'}\rangle\,, \tag{3.15}$$

$$S_{pp'}=\langle a_p|a_{p'}\rangle\,. \tag{3.16}$$

We shall at first assume that $J_{pp'}$ is independent of $\mathbf{x}$, although later we shall discuss the effect of the variation of the matrix element with lattice configuration. By analogy with a similar approximation in the theory of optical spectra,[13] we call this assumption the "Condon approximation."

We now distinguish between two temperature regimes in which the diffusive behavior is very different. These regimes are analogous to those described by Holstein[6] for polaron motion. At the lowest temperatures the lattice oscillators are not excited, and the transitions from site to site which dominate are those which do not involve changes in phonon occupation numbers. The displacements $\mathbf{Q}_{\mathbf{q}}{}^p$ change in the transition, but the phonon system is not otherwise affected. In these "diagonal" transitions the initial state and the final state are related by the lattice translation operator. The crystal momentum of the proton is conserved, and a band picture provides an appropriate description of the motion. The "nondiagonal" transitions, in which the occupation numbers of some of the lattice modes change, become more important as the temperature increases. The crystal momentum of the interstitial and of the phonon system change, and the proton mobility begins to decrease as scattering becomes more important in much the same way as electronic carrier mobilities decrease. Eventually the mobility passes through a minimum with increasing temperature, and the transport enters a hopping regime in which the mobility increases with temperature. We now discuss the low- and high-temperature regimes in more detail.

At the lowest temperatures a band picture provides a good description, and the tight-binding approximation should be adequate, since the overlaps of the $\tilde{\Psi}_p$ are small. In the band approach the bandwidth is of order $V_{pp'}$, and typical particle propagation velocities are

$$\begin{aligned} \langle|\mathbf{v}|\rangle&\sim(1/\hbar)\langle|\nabla_{\mathbf{k}}E(\mathbf{k})|\rangle\\ &\sim|V_{pp'}|/\hbar k_{\max}\,, \end{aligned} \tag{3.17}$$

in which $E(\mathbf{k})$ is the energy eigenvalue of state $\mathbf{k}$ and $k_{\max}$ is a typical value of $|\mathbf{k}|$ at the zone boundary. The time t taken for the interstitial to travel through the nearest-neighbor distance $\sim 1/k_{\max}$ is then given by

$$\begin{aligned} 1/\tau&\sim\langle|v|\rangle k_{\max}\\ &\sim|J_{pp'}|\,|S_{pp'}|/\hbar\,, \end{aligned} \tag{3.18}$$

using (3.14). We may also rewrite this by using

$$J_{pp'}\equiv\langle\phi_p|\mathcal{H}_{\text{int}}|\phi_{p'}\rangle=\langle\phi_p|(\hbar^2/2m)\nabla^2|\phi_{p'}\rangle\,, \tag{3.19}$$

which is derived from (3.6), when rewritten in terms of $\phi_{p'}$ rather than $\tilde{\phi}_p$ and integrating over $\mathbf{R}$. Evidently the lattice overlap factor $S_{pp'}\equiv\langle a_p|a_{p'}\rangle$ reduces the propagation velocity of the interstitial or, equivalently, increases the interstitial effective mass, by $S_{pp'}{}^{-1}$. As the lattice dilatation increases, the mobility decreases. However, this regime occupies a very limited temperature range which is unlikely to be of practical importance.

For the important high-temperature regime in which the impurity moves by hopping, we can calculate the average transition rate from site p to site p' using the

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[13] D. L. Dexter, Solid State Phys. 6, 355 (1958).

prescription provided by Eq. (2.4):

$$W_{pp'}=\langle\sum_{n_{\mathbf{q}}'} w_{pp'}(n_{\mathbf{q}},n_{\mathbf{q}}')\rangle. \tag{3.20}$$

The main features of the discussion here follow Holstein's treatment[6] of the small polaron. The summation in (3.20) is over all final states which conserve energy, and $w_{pp'}(n_{\mathbf{q}},n_{\mathbf{q}}')$ is the partial transition rate from the state $|p,\{n_{\mathbf{q}}\}\rangle$, with the interstitial at site p and phonon occupation numbers $n_{\mathbf{q}}$, to the state $|p'\{n_q'\}\rangle$ in which the impurity occupies interstice p' and the phonon occupation numbers are n_q'. The partial transition probabilities given by Eq. (2.1) may be rewritten in the form

$$w_{pp'}(n_q,n_q')=(2\pi/h^2)|\langle p,\{n_q\}|\mathcal{H}_{\text{int}}|p'\{n_q'\}\rangle|^2 \times D(\bar{\omega},t). \tag{3.21}$$

Here, the change in phonon energy is

$$\hbar\bar{\omega}=\sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}}(n_{\mathbf{q}}'-n_{\mathbf{q}}) \tag{3.22}$$

and the function

$$D(\bar{\omega},t)=\frac{1}{2\pi}\int_{-t}^{t} d\xi\, e^{i\bar{\omega}\xi} \tag{3.23}$$

tends to $\delta(\bar{\omega})$ at large t, to ensure that energy is conserved.

The impurity and phonon terms in the matrix elements may be separated using (3.10) and (3.15), giving

$$W_{pp'}=\left\langle\frac{|J_{pp'}|^2}{h^2}\sum_{n_q'}\prod_{q}|\sigma_{pp'}(n_q,n_q')|^2\int_{-t}^{t} d\xi e^{i\bar{\omega}\xi}\right\rangle, \tag{3.24}$$

in which

$$\sigma_{pp'}(n_q,n_q')=\langle p,n_q|p'n_q'\rangle \tag{3.25}$$

is the overlap for mode q between harmonic-oscillator wave functions with appropriate occupation numbers; the site labels p, p' are necessary because the mean displacement of mode q depends on the position of the impurity. The change in the mean value of $Q_{\mathbf{q}}$ during the transition is just

$$\Delta\mathbf{Q}_{\mathbf{q}}=\mathbf{Q}_{\mathbf{q}}^{p}-\mathbf{Q}_{\mathbf{q}}^{p'}, \tag{3.26}$$

which is of order $N^{-1/2}$, where N is the number of atoms. Consequently, we may neglect transitions with $|n_q-n_q'|>1$. Since the n_q' are independent parameters, the sum over n_q' of the product is just the product of the partial sums, so we may write

$$W_{pp'}=\left\langle\frac{|J_{pp}'|^2}{h^2}\int_{-t}^{t} d\xi\prod_{\mathbf{q}}[1-\Lambda_{pp'}(q,\xi)]\right\rangle. \tag{3.27}$$

Evaluating the overlap factors (3.25) explicitly, we have

$$\Lambda_{pp'}(q,\xi)=1-|\sigma_{pp'}(n_q,n_q)|^2-|\sigma_{pp'}(n_q,\,n_p+1)|^2e^{i\omega_q\xi} -|\sigma_{pp'}(n_q,\,n_q-1)|^2e^{-i\omega_q\xi}$$
$$=\frac{\omega_q^2|\Delta Q_q|^2}{2\hbar\omega_q}[(2n_q+1)-(n_q+1)e^{i\omega_q\xi} -n_qe^{-i\omega_q\xi}]. \tag{3.28}$$

The thermal average may now be performed explicitly, since (3.27) contains the product of terms linear in occupation numbers, n_q, which are now replaced by their thermal average values $\bar{n}_q$.

Since the $\Delta\mathbf{Q}_{\mathbf{q}}$ are small, the $\Lambda_{qq'}(\mathbf{q},\xi)$ are also small. After making the customary exponential approximation to the continued product we obtain

$$W_{pp}'=\frac{|J_{pp'}|^2}{\hbar^2}\int_{-t}^{t} d\xi\exp\left\{\sum_{\mathbf{q}}\frac{\omega_{\mathbf{q}}^2|\Delta\mathbf{Q}_{\mathbf{q}}|^2}{2\hbar\omega_{\mathbf{q}}} \times[(2\bar{n}_q+1)(\cos\omega_q\xi-1)+i\,\sin\omega_q\xi]\right\}. \tag{3.29}$$

The evaluation of the integral presents a number of problems. These have been discussed at length by Holstein[6] and, in another context, by Huang and Rhys,[7] Markham,[14] and by Pryce.[15] It is shown in an appendix that at high temperatures

$$W_{pp'}\simeq\frac{2|J_{pp'}|^2}{\hbar}\exp\left(-\sum\frac{\omega_q^2|\Delta Q_q|^2}{2\hbar\omega q}\tanh\left(\frac{\hbar\omega_q}{4kT}\right)\right)\Big/ \left(\sum_{q}\frac{\hbar\omega_q}{\pi}|\Delta Q_q|^2\operatorname{cosech}\left(\frac{\hbar\omega_q}{2kT}\right)\right)^{1/2}, \tag{3.30}$$

which tends with increasing temperature to

$$W_{pp'}\simeq\left(\frac{\pi}{4\hbar^2E_akT}\right)^{1/2}|J_{pp'}|^2e^{-E_a/kT}, \tag{3.31}$$

with

$$E_a=\tfrac{1}{2}\sum_{q}\omega_q^2|\Delta\mathbf{Q}_q/2|^2. \tag{3.32}$$

At low temperatures the jump rate becomes

$$W_{pp'}\simeq 57\,600\pi\omega_D\frac{|J_{pp'}|^2}{(\hbar\omega_D)^4}E_a^2e^{-5E_a/\hbar\omega_D}\left(\frac{T}{\Theta_D}\right)^7 \tag{3.33}$$

in the isotropic Debye approximation. The Debye temperature is Θ_D, and $\hbar\omega_D=k\Theta_D$. Equations (3.31) and (3.33) become valid in the limits $T\gg\frac{1}{2}\Theta_D$ and $T\ll\frac{1}{2}\Theta_D$, respectively. The activation energy E_a is just the lattice strain energy for displacements $\frac{1}{2}\Delta\mathbf{Q}_q$; it is the saddle-point energy of the lattice. E_a is always smaller than the localization energy E_{loc}.

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[14] J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959).

[15] M. H. L. Pryce, in *Phonons in Perfect Lattices and in Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Oliver and Boyd, London, 1966).

Our expression (3.33) for the low-temperature limit resembles a number of expressions derived in other contexts by Sussman,[16] by Silsbee[17] and by Pirc, Žekš, and Gosar.[18] These authors were mainly concerned with the reorientation of anisotropic defects. The differences result from slightly different assumptions about the form of $\mathcal{H}_{\text{int}}$. The various possibilities are compared by Sussmann, and his equation (15a) corresponds to our (3.33).

In deriving these equations we have tacitly assumed that the interstitial jumps from a state l in one well to the equivalent state in a second interstice. If we may ignore transitions in which the interstitial state changes, then the jump rate is a thermal average over the various interstitial levels: $W_{pp'}\equiv\langle W_{pp'}{}^{ll}\rangle$. Both the matrix element $J_{pp'}{}^{ll}$ and the displacements $\Delta Q_q{}^{ll}$ depend on the interstitial level l; they may also be expected to depend on isotopic mass.

We may also calculate the rate at which transitions take place between inequivalent interstitial states. This is relevent when transitions occur between different states of equivalent interstices ($l — l'\neq l$ in our previous notation) and also when the wells are rendered inequivalent by random strain fields in the lattice. Apart from the appropriate change in the matrix element J, the activation energy E_a in (3.31) is replaced by

$$E_a+\tfrac{1}{2}(E_{l'}-E_l)+(E_{l'}-E_l)^2/16E_a.$$

Here the second term ensures detailed balance while the third takes account of the increased difficulty of transferring energy between the lattice and the local mode as the coupling, and hence E_a, becomes small. The results at low temperatures, analogous to (3.33), contain an extra term from the so-called "one-phonon process" when $|E_l-E_{l'}|<k\Theta_D$. We shall not normally need this term, although it is important in reorientation problems.[16–18]

C. Lattice-Activated Diffusion

In Sec. 3 B we assume that the matrix element $J_{pp'}$ of Eq. (3.15) is independent of the lattice configuration $\mathbf{x}$. The results, given by Eqs. (3.30)–(3.33), show that the jump rate depends on $|J_{pp'}|^2$ and on a strongly temperature-dependent function which is determined by E_a, and hence by $|Q_q{}^p-Q_q{}^{p'}|^2$ for the various modes $\mathbf{q}$. Since E_a depends only on the difference between the displacements of the initial and final states, it follows for a cubically *isotropic* self-trapping dilation that the only modes which contribute to E_a are those which are antisymmetric about the midpoint of the jump path in real space. We now show that the symmetric modes can also play an important role in the jump process, and extend our discussion to include their contribution.

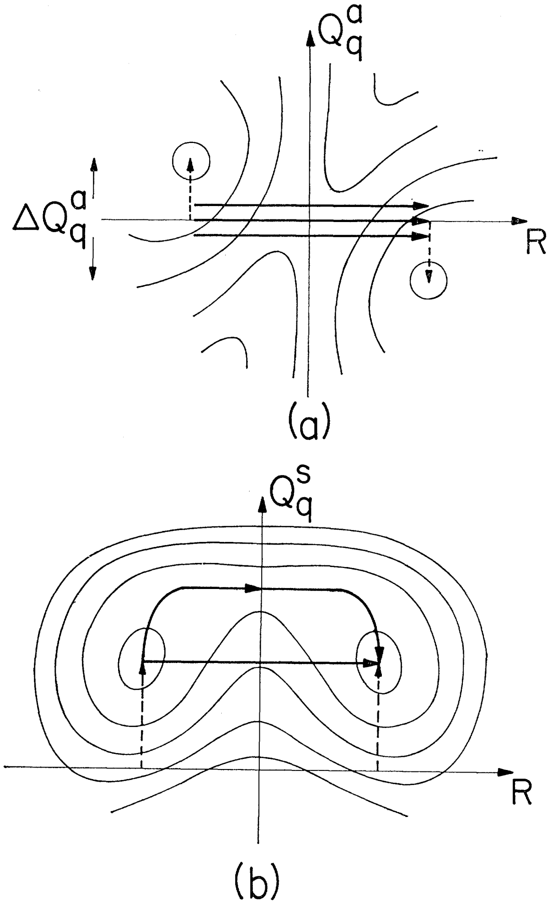

FIG. 1. (a) Sketch showing the potential-energy contours as a function of the proton location R and one antisymmetric phonon coordinate $Q_q{}^a$. The broken arrows show the self-trapping displacements for two successive interstices. The solid arrows show the direct transitions. These pass near a turning point in the potential, presumed to be a saddlepoint, and the Condon approximation is solid. The Condon approximation is not, however, improved by symmetry considerations for symmetric lattice distortions, as shown in (b). Lattice activated transitions may therefore be important.

The processes which we discuss in Sec. 3 B are shown schematically in Fig. 1(a). This shows the total potential energy of the lattice (the potential energy of the distorted perfect lattice plus the interstitial-lattice interaction energy) as a function of the interstitial coordinate $\mathbf{R}$ and an antisymmetric mode Q_a. The displacements which give the localization energy have equal magnitudes $|\Delta Q_a/2|$ but opposite directions for the adjacent sites. The saddlepoint between the wells lies at $\mathbf{R}=0$, midway between the wells, and at $\mathbf{Q}_a=0$. The transitions of interest take place at constant $\mathbf{Q}_a$, because of our adiabatic approximation, and the activation energy E_a is just the elastic strain energy required to displace the antisymmetric modes from the configuration at the minimum to the saddlepoint.

In taking $J_{pp'}$ to be independent of $\mathbf{x}$ we are assuming that $J_{pp'}$ varies only slowly with Q_a. Since the transi-

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[16] J. A. Sussman, J. Phys. Chem. Solids 28, 1643 (1967).

[17] R. Silsbee, J. Phys. Chem. Solids 28, 2525 (1967).

[18] R. Pirc, B. Žekš, and P. Gosar, J. Phys. Chem. Solids 27, 1219 (1966).

tions shown in Fig. 1(a) fall about an extremum, presumably a saddlepoint, the approximation should be quite good. However, we are also assuming that $J_{pp'}$ varies only slowly with the symmetric modes Q_s, and this is not valid. Isotropic dilatations about the initial and final sites cause equal displacements of the symmetric modes. Consequently the self-trapping displacements for these sites have the same magnitudes and directions; ΔQ_s is zero, and these modes do not contribute to E_a. The most important feature is, however, that $J_{pp'}$ is sensitive to Q_s and that, since the transition of interest does not occur near an extremum of $J_{pp'}(Q_s)$, the Condon approximation is not valid; the dependence of $J_{pp'}$ on Q_s cannot be ignored. This feature is illustrated in Fig. 1(b), where we show contours of the total potential energy as functions of Q_s and R. It is probable that the saddlepoint on this energy surface will lie at larger values of Q_s than the values for the relaxed initial and final states since, in general, an impurity moving between interstices past intervening atoms will tend to dilate the lattice further in its passage through the saddlepoint. The sketch also shows that a sufficiently large dilatation about the jump midpoint can open up an essentially unrestricted path for the impurity between the two interstices. Two transitions are shown representing extreme cases: one in which Q_s remains at its mean value, and a second in which a fluctuation in Q_s occurs which eliminates the barrier to interstitial motion. We expect that Figs. 1(a) and 1(b) are relevant to diffusion between the regular octahedral or tetrahedral interstices of the fcc lattice.

Lattice-activated transitions can be built into the theory of Sec. 3 B in a natural way by averaging $|J_{pp'}(Q_s)|^2$ over fluctuations of the symmetrical lattice coordinates. We are exploiting here the fact that the antisymmetric and symmetric nodes are distinct from each other. The average cannot be performed in general since it depends on the detailed behavior of $J_{pp'}$ as a function of Q_s. For qualitative purposes, however, we can usefully examine the two extreme cases shown in Fig. 1(b). The first case, when $J_{pp'}$ is independent of Q_s, just gives the theory of Sec. 3 B. The second case, when the transitions are dominated by the configurations for which the barrier to motion of the impurity is zero, can be treated using Bloch's theorem.[19,20] This general result shows that the distribution of Q_s is Gaussian and from the dispersion of the distribution we find the temperature dependence of the thermal average of $|J_{pp'}(Q_s)|^2$.

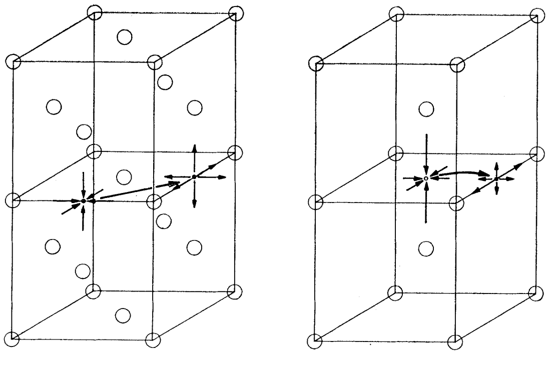
(a) (b)

FIG. 2. Jumps between octahedral interstices of (a) the fcc lattice, and (b) the bcc lattice. In case (a) the interstices have cubic symmetry and self-trapping strain is a symmetric dilatation, but in case (b) the interstices are tetragonal, as also is the self-trapping strain. The nuclei of strain shown in each figure generate the displacements ΔQ_q (see text).

If we assume that $J_{pp'}$ has a step-function form, being negligible for Q_{sq} less than a critical Q_{0q} but having a large value, J_{lim}, for Q_{sq} greater than Q_{0q}, then the thermal average is particularly easy to perform. One finds

$$\langle |J_{pp'}(Q_{\text{s}})|^2\rangle = |J_{\text{lim}}|^2 \tfrac{1}{2}\,\text{erf}\left(\left\{\sum_q \frac{\omega_q^{\,2}}{2\hbar\omega_q} Q_{0q}^{\,2} \times \coth\frac{\hbar\omega_q}{2kT}\right\}^{1/2}\right), \qquad (3.34)$$

with erf the complementary error function. If Q_0 is large, then the fluctuations which make $Q_s > Q_0$ are improbable and the asymptotic form of erf(x) may be used. The effect on W at high temperatures is to add to E_a a term

$$E_s = \tfrac{1}{2} \sum_q \omega_q^2 Q_{0q}^2, \qquad (3.35)$$

and to remove the temperature dependence of the pre-exponential factor:

$$W_{pp'} = \frac{1}{4\hbar} |J_{\text{lim}}|^2 \frac{1}{(E_a E_s)^{1/2}} \exp[-(E_a + E_s)/kT]. \qquad (3.36)$$

On the other hand, the Q_{0q} may be so small that the barrier for impurity motion is negligible in the absence of a self-trapping distortion. In this limit erf(x) tends to unity. As a crude limit in either case we may use

$$|J_{\text{lim}}| \sim \hbar\omega_E. \qquad (3.37)$$

There remains the difficult question of the detailed temperature dependence of $|J|^2$. We have considered some simple models which suggest that the qualitative features are similar to our special examples in Eqs. (3.34)–(3.37). Thus at high temperature Arrhenius behavior is observed, and at lower temperatures the matrix element becomes constant. The temperature at which the change of behavior occurs depends on the details of the model.

D. Comparison with Experiment

In this section we focus attention on the direct hopping transitions of Sec. 3 B and on the lattice-activated transitions of Sec. 3 C. The propogating mo-

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[19] F. Bloch, Z. Physik **74**, 295 (1932).

[20] R. O. Davies, in *Fluctuation, Resonance and Relaxation*, edited by D. ter Haar (Oliver and Boyd, London, 1962).

tion of interstitials will be ignored, since it does not occur at experimentally accessible temperatures. Our objective will be to reproduce, as far as possible, the observed activation energies and preexponential factors for the diffusion of light interstitials in metals. These quantities can only be obtained from first principles by a calculation of the crystal energy as a function of configuration for a wide range of configurations. Instead we use an alternate approach, and show how the lattice contribution to the motion energy can be derived from the observed lattice strain caused by the defect, in the linear coupling approximation of Sec. 3 A. This provides a useful insight into the origin of the energy of motion and the relative importance of E_a and E_s. In particular, there is a striking difference between the fcc and bcc cases.

This difference between the two cases arises directly from their differing geometries. Impurities in the octahedral interstices of the fcc lattice are impeded in their motion by atoms straddling the saddlepoint [Fig. 2(a)]. Presumably this is reflected in a substantial barrier to direct transitions in the lattice, even in the absence of self-trapping distortions. In contrast, no neighbors block direct transitions in the undistorted bcc lattice, and the saddlepoint may present interstitials with little, if any, obstacle to motion; it is mainly the self-trapping energy which localizes the defect in one interstice. Thus, in bcc solvents we anticipate that E_a will contribute the mjaor part of the activation energy, whereas this is not to be expected for fcc solvents.

For convenience we shall use isotropic elasticity theory in our calculations. There is no difficulty in principle in using more sophisticated approaches[21] provided a reasonable lattice dynamic model is available, and in practice such a development is made much easier by the relatively short range of the interaction of the interstitial with host atoms. It is clear from symmetry that the self-trapping distortion for an interstitial in the fcc lattice must then be an isotropic dilatation. Consequently the $\Delta\mathbf{Q}_\mathbf{q}$ are derived by a Fourier analysis of the difference between the displacement fields of dilatations centered on successive interstices differing in position by the jump distance d. This is not the case for bcc lattices in which the octahedral interstitial sites lack cubic symmetry. Instead the dilatation is superposed on a quadrupolar strain field. Figure 3 indicates the origins of the $\Delta\mathbf{Q}_\mathbf{q}$ in force pairs for both fcc and bcc lattices.

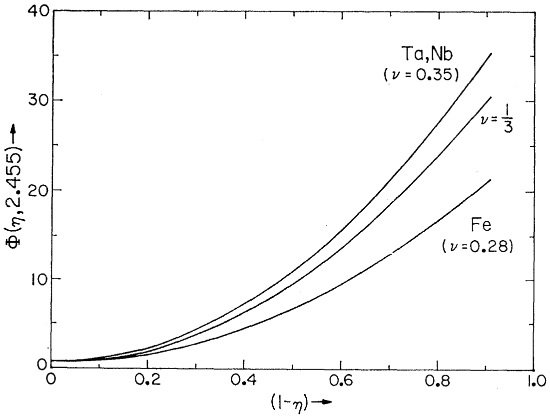

FIG. 3. The function $\Phi(\eta,\zeta)$ shown as a function of $1-\eta$ for the case of octahedral interstices of the bcc lattice ($\zeta=2.455$) and for $\nu=\frac{1}{3}$, $\nu=0.35$ (Ta,Nb), and $\nu=0.28$ (Fe). Carbon and nitrogen in iron have $1-\eta\simeq0.225$.

TABLE I. Values of the activation energy E_a, for various interstitials, according to Eq. (3.39), compared with the observed activation energies for diffusion. The results quoted are for jumps among octahedral interstices. Values of $\Delta V/\Omega$ were obtained from Ref. 8 (corrected for numerical error in the case of Nb). Debye temperatures and Poisson's ratios were obtained from K. A. Gschneidner, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16. Values of the Debye temperature derived from elastic data for 0°K were used where available, since these are most compatible with the calculation and the Zener relation (although these values should nevertheless still underestimate Q). Otherwise values derived from the specific heat for $T\rightarrow0$°K were employed. Combined uncertainties in the parameters doubtless make the calculated values of E_a unreliable to 50%.

Solvent	Impurity	θ_D (°K)	$\Delta V/\Omega$	E_a (eV)	Q (eV)
α-Fe (bcc)	H	477	0.27_5	0.06	0.08
α-Fe (bcc)	C	477	0.79	0.48	0.80
α-Fe (bcc)	N	477	0.84_5	0.55	0.91
Nb (bcc)	H	241	0.42	0.15	0.18
Ta (bcc)	H	262	0.3	0.18	0.16
β-Ti (bcc)	H	426	0.35_5	0.18	···
β-Zr (bcc)	H	289	0.36	0.17	···
Pd (fcc)	H	275	0.18_2	0.05[a]	0.26

[a] Calculated for jumps among octahedral interstices of the fcc lattice.

We have calculated the dependence of E_a on the strength of the force pairs using the standard expressions[22] for the components of the relative displacements caused by a double force; for example,

$$\begin{aligned} u_1&=\alpha_1\left(K\frac{\partial^3 r}{\partial x_1^3}+\frac{2x_1}{r^3}\right),\\ u_2&=\alpha_1 K\frac{\partial^3 r}{\partial x_1^2\partial x_2},\\ u_3&=\alpha_1 K\frac{\partial^3 r}{\partial x_1^2\partial x_3}. \end{aligned} \tag{3.38}$$

Here $K\equiv\frac{1}{2}(1-\nu)^{-1}$ with ν Poisson's ratio, and α_1 is a constant specifying the strength of the force along axis 1. The calculation of the $\Delta\mathbf{Q}_\mathbf{q}$, and hence E_a, is straightforward but tedious. The result may be written

$$E_a=\frac{M\omega_D{}^2d^2}{360}\left(\frac{1+\nu}{1-\nu}\right)^2\left(\frac{\delta V}{\Omega}\right)^2\Phi(\zeta,\eta), \tag{3.39}$$

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[21] H. Kanzaki, J. Phys. Chem. Solids 2, 24 (1957).

[22] A. E. H. Love, in *The Mathematical Theory of Elasticity* (Dover, New York, 1927).

with M the mass of a host lattice atom, ω_D the Debye frequency, d the jump distance, and $\delta V/\Omega$ the lattice dilatation caused by each defect expressed as a fraction of the solvent atomic volume Ω. The function Φ is specified by the parameter $\zeta = q_m d$; with q_m the radius of the Debye sphere in reciprocal space, and by η, which is the fraction of the volume change δV due to an isotropic dilatation (hence $1-\eta$ gives the fraction of the dilation caused by the "dipole" component of the strain field). Φ is written in full as follows:

$$\Phi = (30/\zeta^2)[\alpha + (\beta - 2\alpha)(1-\eta) + (\gamma - \beta + \alpha)(1-\eta)^2]. \tag{3.40}$$

The constants have been chosen so $\lim_{\zeta\to 0}\Phi(\zeta, \eta=1) = 1$. In these expressions we use

$$\begin{aligned}
\alpha &= \tfrac{1}{3} + (\zeta\cos\zeta - \sin\zeta)/\zeta^3 ,\\
\beta &= \tfrac{2}{3} + 3(\sin\zeta - 2\mathrm{Si}(\zeta)]/\zeta^3 ,\\
\gamma &= \frac{2}{5}\left(\frac{1}{1-K}\right)^2 + \frac{3}{5} + \frac{9}{2}\left(\frac{K}{1-K}\right)\\
&\quad \times\left[\mathrm{Si}(\zeta) + 3\left(\frac{\zeta\cos\zeta - \sin\zeta}{\zeta^2}\right)\right]\Big/\zeta^3 ,
\end{aligned} \tag{3.41}$$

with
$$\mathrm{Si}(\zeta) = \int_0^\zeta dx \sin x/x .$$

$\Phi(\zeta,\eta)$ is shown as a function of η in Fig. 3 for $\zeta = 2.46$, which is appropriate for transitions among the octahedral sites of the bcc lattice. It is apparent that the activation energy is sensitive to both the size and anisotropy of the strain introduced by the defects.

The independent components of the defect strain tensor are known in very few cases. Fortunately N and C in Fe have been studied by internal friction methods.[23] Using the volumes of solution given in Table I and the experimentally determined "dipole" strengths we find for C and N in Fe the following principal components λ of the defect strain tensor:

$$\begin{aligned}
\mathrm{C}&: \quad (\lambda_1,\lambda_2,\lambda_3) = (0.99,\ -0.07,\ -0.07) ,\\
\mathrm{N}&: \quad (\lambda_1,\lambda_2,\lambda_3) = (0.91,\ -0.06,\ -0.06) .
\end{aligned} \tag{3.42}$$

We have derived these using methods similar to those of Ref. 23. The second decimal figure is included for reasons of self-consistency rather than as a measure of experimental precision. These strain components are observed at the crystal exterior, and include image effects which differ for the isotropic dilations and for the lower symmetry quadrupolar strains. Huntington and Johnson[24] show that the image forces exaggerate the anisotropy of the strain field in an isotropic continuum by a factor

$$\frac{5}{2}\,\frac{1+\nu}{4-5\nu} .$$

On allowing for this factor and using the principal strains derived from Eqs. (3.38) to describe the dipole field we find from the experimental data for C and N

$$\begin{aligned}
\eta_{\mathrm{C}} &= 0.77 ,\\
\eta_{\mathrm{N}} &= 0.78 .
\end{aligned} \tag{3.43}$$

We have used the value $\eta = 0.775$ in calculating the values of E_a given in Table I for a variety of light interstitials. The components of the strain tensor have not been determined for hydrogen isotopes, and there remains even some doubt that the hydrogen occupies the same interstitial sites as carbon and nitrogen. Apart from this uncertainty the elastic constants of the bcc hosts follow a fairly regular pattern, and it would not be too surprising if different defects caused similar strain fields, differing for the main part only in amplitude. This expectation is borne out for interstitial H, N, and C in Fe by the observed activation energies and volumes of solution:

$$\begin{aligned}
Q_{\mathrm{C}}:Q_{\mathrm{N}}:Q_{\mathrm{H}} &= 1.00:0.81:0.08 ,\\
(\delta V/\Omega)^2_{\mathrm{C}}:(\delta V/\Omega)^2_{\mathrm{N}}:(\delta V/\Omega)^2_{\mathrm{H}} &= 1.00:0.88:0.11 .
\end{aligned} \tag{3.44}$$

Even more striking is the good order-of-magnitude agreement between the experimental values of Q and the theoretical values of E_a for hydrogen in different materials; this indicates similar strain patterns in the different solvents. The adiabatic approximation employed in Sec. 3 B has a more substantial validity for these lighter interstitials.

Note also that with $d \sim 1$ Å and $D_0 \sim 10^{-3}$ cm^2/sec, we have $W_{pp'} \sim 10^{-16} e^{-E_a/kT}$. Therefore for typical values $\hbar\omega_E \simeq E_a \simeq kT \simeq 0.1$ eV, we find $(|J|/\hbar\omega_E) \sim 1$, in agreement with Eq. (3.37).

These results show that the self-trapping distortion plays a fundamental role in the diffusion of light interstitials in bcc metals. So much is this the case that the diffusing particles, together with their associated lattice distortion could appropriately be called "dilatons" by analogy with polarons in insulators. This analogy has previously been noted by Schaumann *et al.*[25] Any temperature variation of $|J|^2$ appears to play a minor or negligible part in determining Q. This is not the case for fcc solvents. As indicated in Sec. 3 C, the geometry is such that the direct motion among sites is hindered by intervening atoms. For this reason the calculated value of E_a for H in Pd given in Table I is much smaller than the observed activation energy for diffusion. The theoretical value quoted was calculated with $\eta = 1$, since the interstices have cubic symmetry.

In some cases (e.g., Ref. 25) an isotopic dependence of Q for hydrogen and deuterium has been observed at high temperatures. This effect may represent an isotopic variation of $\delta V/\Omega$, an effect which we discuss later.

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[23] A. S. Nowick and R. W. Heller, Advan. Phys. **12**, 251 (1963).

[24] H. B. Huntington and R. A. Johnson, Acta Met. **10**, 281 (1962).

[25] G. Schaumann, J. Völkl, and G. Alefeld, Phys. Rev. Letters **21**, 891 (1968).

Another important feature of the present model is its ability to predict the Zener relationship[26] between motion entropy and motion energy for interstitials in bcc lattices. The localization energy in the linear coupling approximation is exactly equal to the increase in lattice potential energy caused by the relaxation. Consequently, the self-trapping energy may be treated as purely elastic strain energy. Moreover, the quantity E_α in (4.2) should be regarded as a Gibbs function for migration; it is both temperature and pressure dependent. The motion entropy S_m and motion volume V_m may be obtained from E_a (or E_a+E_s, where relevant) by the standard thermodynamic formula

$$\begin{aligned} S_m &= -(\partial E_a/\partial T)_P , \\ V_m &= (\partial E_a/\partial p)_T . \end{aligned} \tag{3.45}$$

Since E_a and E_s are, in effect, purely strain energy the motion entropy is obtained from the temperature dependence of the appropriate elastic constants (principally shear constants) in the Debye approximation. This explains the empirical relation between Q and S_m pointed out originally by Zener. Equations (3.32) and (3.45) show that the motion entropy may be related rather generally to the lattice mode frequencies. A similar explanation has been given[27] for the Zener relation in solvent diffusion. We note, however, than when energy contributions other than elastic strain energy are important the Zener relation may not hold. Thus for direct transitions, in which $|J_{pp'}|^2$ may be sensitive to temperature and pressure, the Zener relation need not hold. In lattice-activated processes, the pressure and temperature dependence is dominated by the dependence on the strain energies E_s and E_a; the relation should then be valid.

4. DISCUSSION

The quantum theory of diffusion outlined in Sec. 2 differs from previous theories in that attention is centered on transitions among appropriately chosen states, each localized near a particular equilibrium point in configuration space. We now remark on a number of features of this approach. First, it is commonly believed that a quantum theory of diffusion must reduce exactly to the rate and dynamical theoretic descriptions of diffusion at high temperatures when the phonon occupation numbers have a sensibly classical distribution. We have not demonstrated this equivalence here. Indeed, it is not possible to introduce a saddlepoint Gibbs function G_s satisfactorily unless a sensibly exact eigenstate can be defined for a configuration close to the saddlepoint. Second, Eq. (3.36) contains a factor $|J_{\text{lim}}|^2$ in addition to the factors (E_a+E_s) which measure more directly the size of the potential-energy fluctuation required to activate a jump. It is far from clear that the composite expression can possibly reduce at high temperatures to an Arrhenius factor containing just the required potential energy change and thus reduce to reaction rate theory. Third, the T^7 variation of the jump rate with temperature, and equivalent expressions for slightly different models, are characteristic quantum forms determined by the density of final states as a function of temperature. Thus the detailed structure of the potential-energy surface as a function of configuration is of central importance, and simple barrier penetration models are unlikely to give a satisfactory description of the hopping. Finally, the present emphasis on initial and final states, rather than intermediate configurations, may have a radical effect on current ideas concerning electromigration and thermomigration.

In its application to the motion of light interstitials the present theory has had a considerable success. It emphasizes the role of the self-trapping distortion about occupied interstices of bcc lattices in preventing easy motion. Activation energies calculated by the methods of continuum elasticity theory from the observed lattice volume changes are in good agreement with experiment, as also are the motion entropies according to the Zener theory. Better calculations of both quantities should become feasible when better models of the lattice dynamics and of the detailed impurity-lattice coupling become available. A correlation between activation energy and interstitial size has previously been explained by Ferro[28] using elasticity theory and the rather ill-defined concept of impurity and host atomic radii; in our approach the relation follows directly from the assumption of linear coupling.

The dependence of diffusion rate on isotopic mass is implicit rather than explicit in the results presented in Sec. 3. The matrix element $|J|^2$ depends on isotope mass in a way demonstrated by Eq. (3.36) for lattice-activated processes. E_s is independent of the impurity mass, but E_a depends on the $\Delta\mathbf{Q}_\mathrm{q}$ which, in turn, depend on isotopic mass through Eqs. (3.6), (3.8), and (3.39). To predict the isotope effect we need a specific model for $\mathcal{H}_{\text{int}}(\mathbf{R},\mathbf{x})$. No reliable model is available, but the following results derived from some simple models may be qualitatively useful.

The change in volume per defect is proportional to the derivative of E of (3.6) with respect to the symmetric outward displacement of the neighbors to the interstitial. Thus the mass dependence of E_a is the same as that of $|dE(x)/dx|^2$. We shall consider two simple models. The first (model I) assumes $\mathcal{H}_{\text{int}}$ to be a harmonic oscillator potential, and that the potential simply scales as the neighbors move. If the distance of the nearest neighbors from the interstitial site changes from a to λa then the potential changes from $\mathcal{H}_{\text{int}}(\mathbf{R})$ to $\mathcal{H}_{\text{int}}(\lambda\mathbf{R})$. The second (model II) is a deep square-well potential bounded by the nearest neighbors to the

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[26] C. Zener, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (Wiley, New York, 1952).

[27] C. P. Flynn, Phys. Rev. **171**, 682 (1968).

[28] A. Ferro, J. Appl. Phys. **28**, 895 (1957).

TABLE II. The isotopic mass dependence of the activation energy, E_a, and the preexponential factor for two simple models discussed in the text.

Isotope dependence	Model I (oscillator model)	Model II (well model)
E_a	M^{-1}	M^{-2}
E_s	M^0	M^0
Direct processes		
$\lvert J_{pp'}\rvert/E_a^{1/2}$	$(M)^{1/2}e^{-\xi\sqrt{M}}$	$Me^{-\zeta M}$
Lattice-activated processes		
$\lvert J_{\lim}\rvert^2/E_a^{1/2}$	$M^{-1/2}$	M^0

interstitial site. The results for these cases are given in Table II. From these predictions and our earlier results it seems likely that the preexponential factor should vary as $M^{-1/2}$ (the classical result) or possibly less rapidly. The activation energy should decrease with M, the precise dependence being sensitive to the relative sizes of E_s and E_a.

In real systems the direct and lattice activated processes may both be significant. However, if one mechanism dominates then the low temperature behavior is likely to discriminate between the processes most readily. At these low temperatures the direct processes should have a very strong and distinctive dependence on isotope mass because of the dependence of $|J_{pp'}|^2$. This dependence may be harder to see at higher temperatures where contributions from transitions between excited states in the wells may be appreciable. In either case the coupling of the interstitial to the lattice severely modifies that expected for the rigid lattice. For large values of E_a the low temperature rate (3.33) and high temperature rate (3.31) become comparable when

$$(\Theta_D/T)^{15/2}e^{-E_a/kT}=115\,200(\sqrt{\pi})(E_a/k\Theta_D)^{5/2}\times e^{-5E_a/k\Theta_D}. \quad (4.1)$$

It seems that for a range of temperature centered between $\frac{1}{3}\Theta_D$ and $\frac{1}{5}\Theta_D$, depending on E_a, the sensibly Arrhenius behavior of $W_{pp'}$ with temperature gradually transforms to the power-law dependence which dominates in the low temperature hopping regime. At much lower temperatures the lattice drops into its ground state and the propagating mechanism may prevail. As pointed out in Sec. 3, further deviations from Arrhenius behavior may appear because of the temperature dependence of the preexponential factor, both for direct and for lattice-activated processes. These deviations should become noticeable below 150°K in typical cases.

The T^7 low temperature regime is only likely to be observed for interstitials with $E_a\lesssim 10\hbar\omega_D$. Even when $|J|^2\sim(\hbar\omega_D)^2$ the jump rate is then reduced to 10^{-5} sec^{-1} for $T=\frac{1}{4}\Theta_D$. Dilatations small enough to ensure that $E_a\lesssim 0.2$ eV appear to be associated with hydrogen isotopes alone. Strong low temperature deviations from the Arrhenius relation have been seen for Nb:H,[29] where the activation energy is about 0.2 eV. Recent data suggest, however, that hydrogen in Nb at temperatures below ~150°K is almost all present as the precipitated hydride phase.[30] It appears that no firm experimental results concerning the low temperature diffusion of hydrogen isotopes are, at present, available.

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APPENDIX

We discuss briefly the calculation of the integral in (3.29). If we write $\omega_q^2|\Delta Q_q|^2/2\hbar\omega_q\equiv\Gamma_q$ then the integral is

$$\lim_{t\to\infty}\int_{-t}^{t}d\xi\,\exp\{\sum_q\Gamma_q[(2n_q+1)\cos\omega_q\xi+i\sin\omega_q\xi]\}. \quad (A1)$$

Integrals related to this one also appear in the theory of optical spectra (Huang and Rhys,[7] Markham,[14] and Pryce[15]). We shall generally follow Holstein's[6] arguments, merely emphasizing the main points of the proof and making a slight generalization.

We begin by changing the contour of integration in such a way that the term in the exponent proportional to $\sin\omega_q\xi$ vanishes. This is accomplished by letting $\xi\to u+iv$ with u equal to our old ξ and $v=\hbar/2kT$. The exponent becomes

$$\sum_q[(2n_q+1)-\cos\omega_q u\,\operatorname{cosech}\hbar\omega_q/2kT]\Gamma_q. \quad (A2)$$

The contour of integration now contains parts parallel to the imaginary axis. These contributions prove to be small. Next, we recognize that the diagonal processes cause a divergence of the integral as it stands. These processes, although strictly negligible, give an infinite term because the perturbation theory we use does not treat them adequately. Consequently, we subtract these terms off entirely, so that the integral tends to zero as the temperature tends to zero. The integral we need in the hopping regime is thus

$$\int_{-\infty}^{\infty}du\,\exp[\sum_q\Gamma_q(2n_q+1)]\times[\exp(-\sum\Gamma_q\operatorname{cosech}(\hbar\omega_q/2kT)\cos\omega_q u)-1]\equiv\exp[\sum_q\Gamma_q(2n_q+1)]I. \quad (A3)$$

We now evaluate I in two limiting cases; the low

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[29] J. Völkl, G. Schaumann, and G. Alefeld, in Proceedings of the International Conference on Ultrasonic Attenuation and Internal Friction, Brown University, Providence, R. I., 1969 (unpublished).

[30] D. G. Westlake, Trans. AIME **245**, 1969 (1969).

temperature case when the exponent in I is small, and the high temperature case where the exponential term in I dominates.

At low temperatures the exponential in I may be expanded in powers of the exponent. Thus if

$$F(q)=\Gamma_q \operatorname{cosech}\hbar\omega_q/2kT, \tag{A4}$$

then

$$\begin{aligned} I=&\sum_q F(q)\int_{-\infty}^{\infty} du \cos\omega_q v+\tfrac{1}{2}\sum_q\sum_{q'} F(q)F(q) \\ &\times\int_{-\infty}^{\infty} du \cos\omega_q v \cos\omega_{q'} v+\cdots \\ \doteq&\, 2\pi\{\sum_q F(q)\delta(\omega_q)+\tfrac{1}{4}\sum_q\sum_{q'} F(q)F(q) \\ &\times[\delta(\omega_q+\omega_{q'})+\delta(\omega_q-\omega_{q'})]+\cdots\}. \end{aligned} \tag{A5}$$

This gives us a sum of one-phonon processes, two-phonon processes, and so on. The lowest nonvanishing term is the two-phonon term; in the Debye approximation this gives

$$\begin{aligned} I\simeq&\tfrac{1}{2}\pi\sum_q\sum_{q'} F(q)F(q')\delta(\omega_q-\omega_{q'}) \\ =&\tfrac{1}{2}\pi\alpha^2\int_0^{\omega D} d\omega_q\omega_q^2\int_0^{\omega D} d\omega_{q'}\omega_{q'}^2\delta(\omega_q-\omega_q')F(q)F(q') \\ =&\tfrac{1}{2}\pi\alpha^2\int_0^{\omega D} dx x^2[F(x)]^2, \end{aligned} \tag{A6}$$

where we have written F as a function of frequency rather than wave vector, and α converts sums $\sum_q$ to integrals $\int_0^{\omega_D} d\omega\omega^2$ in the Debye approximation. At low temperatures we may let the upper limit of the integral tend to ∞ and use the asymptotic form of $\operatorname{cosech}\hbar\omega_q/2kT$; using our earlier result for E_a we find

$$I=800\pi 6!(E_a/\hbar\omega_D)^2(T/\Theta_D)^7. \tag{A7}$$

This result gives Eq. (3.33) of the text.

At high temperatures we use the method of steepest descents; essentially

$$I\simeq\int_{-\infty}^{\infty} du e^{V-Wu^2}=(\pi/W)^{1/2}e^V, \tag{A8}$$

where

$$V=-\sum_q \Gamma_q \operatorname{cosech}\hbar\omega_q/2kT, \tag{A9}$$

$$W=+\tfrac{1}{2}\sum_q \Gamma_q(\operatorname{cosech}\hbar\omega_q/2kT)\omega_q^2. \tag{A10}$$

Since $\coth x-\operatorname{cosech} x$ is just $-\tanh\frac{1}{2}x$, the original integral (A1) is just

$$\begin{aligned} &\exp(\sum_q \Gamma_q \coth\hbar\omega_q/2kT)I \\ &\quad\equiv(\pi/W)^{1/2}\exp(-\sum \Gamma \tanh\hbar\omega_a/4kT). \end{aligned} \tag{A11}$$

This expression has been used to obtain Eq. (3.31).