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Lattice-Dynamical Theory of the Diffusion Process. I. Isotope Effect in Cubic Metals†

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A lattice-dynamical theory of diffusion based on the fluctuations in a certain reaction coordinate first used by Flynn is presented. The theory of vibrations of isotopic impurities in a crystal is applied to evaluate the parameter ΔK that describes the isotope effect in diffusion. Numerical results for Cu, Ag, Au, Al, Ni, Co, Pb, Na, and α-Fe are presented. The effect of both relaxation near the vacancy and temperature on ΔK are also studied.

I. INTRODUCTION

Recently, there has been renewed interest in the study of diffusion phenomena in metals, and the state of the art has been described by Peterson.[1] The degree of accuracy and sophistication that has been achieved experimentally, with the advent of tracer techniques, is paralleled by some significant theoretical developments. Glyde,[2] while examining the theories of rate processes in solids, showed that the dynamical approach used by Rice, and Rice and Frisch[3] is equivalent in formal content to the equilibrium statistical-mechanical approach used by Vineyard.[4] Franklin[5] formulated an anharmonic theory of atomic migration that resembles the equilibrium statistical-mechanical approach. Flynn[6] presented a dynamical theory of diffusion in the elastic continuum limit. His theory, based on fluctuations in a specific reaction coordinate, has met with considerable success in accounting for the diverse features of atomic migration. Impressive as these efforts are, quantitative calculation of specific parameters that appear in the theory of diffusion have been largely unsatisfactory. One example is ΔK, which, together with a correlation factor f, is a measure of the isotope effect in diffusion. Although accurate experimental measurements of the dependence of tracer diffusion rate on isotopic mass have been available for quite some time,[1] theoretical calculations of ΔK with a comparable degree of sophistication have not been available. In a recent paper, Glyde[7] rederived the expression for the classical jump rate Γ for tracer diffusion to demonstrate clearly its mass dependence; however, no numerical application to real systems was made. Huntington *et al.*[8] have attempted to calculate several fundamental parameters involved in the diffusion phenomena by computer simulation of atomic migration. They evaluated the parameter ΔK on the basis of the reaction rate theory, where ΔK is equal to the ratio of the kinetic energy of the moving atom, in the dissolution normal mode at the saddle point, to the total kinetic energy. The dissolution mode has an imaginary frequency, in terms of the normal mode analysis, and, therefore, could be distinguished in the computer program. The values of ΔK obtained in this study were very close to unity ($|\Delta K - 1| < 0.05$ in all cases). This is in conflict with the experimental values of ΔK for fcc metals[1] (~ 0.8–0.9) and for bcc metals[1] (~ 0.5). Huntington *et al.* suggested that the discrepancy might be due to the inadequacy of the reaction rate formalism.

The object of the present investigation is to develop a lattice-dynamical theory of atomic migration that can yield trustworthy values of ΔK. Flynn's reaction coordinate was utilized in this study, and the fluctuations of the coordinate are expressed in terms of the phonon spectrum of the perfect crystal. It is assumed that the mechanism of diffusion is the vacancy, and that the atomic jump occurs when the fluctuation in the reaction coordinate exceeds a certain critical value. The atomic jump frequency is obtained by using Kac's solution for "up-zero" frequencies of fluctuations that exceed the critical value. The lattice-dynamical theory of impurity modes due to isotopic defects is applied to evaluate ΔK. The harmonic approximation is assumed throughout. Numerical results are presented for Cu, Ag, Au, Al, Ni, Co, and Pb among the fcc metals and Na and α-Fe among the bcc metals. The effect of relaxation around the vacancy on ΔK in Cu and the effect of temperature on ΔK in Al and Ag are also studied.

II. REACTION COORDINATE

Our attention will be restricted to diffusion by the vacancy mechanism in a cubic metal. An atom moves through the crystal by means of a series of jumps, each jump involves the atom and an adjacent vacancy. The jump would occur as a result of the fluctuations in the energy and momentum of the atom due to thermal vibrations. The jump would be completed only if the amplitude of the fluctuation is sufficiently large, and only if the neighboring atoms, which form a barrier to the migrating atom, move away from the jumping atom. Both conditions can be met simultaneously by considering fluctuations of a reaction coordinate. The instantaneous relative displacement of the jumping atom and the nearest neighbors along the jump direction was used as the reaction coordinate.[9] If $\mathfrak{N}$ neighbors obstruct the jumping atom, the reaction coordinate can be expressed as

$$X = \left(\vec{U}^{\alpha} - \frac{1}{\mathfrak{N}} \sum_{i} \vec{U}^{i}\right) \cdot \hat{X}. \tag{1}$$

Here $\vec{U}^{\alpha}$ is the displacement of the diffusing atom, $\vec{U}^{i}$ is the displacement of the ith atom in the ring of $\mathfrak{N}$ neighbors from their equilibrium positions, respectively, and $\hat{X}$ is a unit vector along the jump direction. This reaction coordinate implies that the motion of only certain atoms is important in determining the atomic jump The lateral motion of atoms in a direction perpendicular to $\hat{X}$ is not considered. It is expected, however, that lateral motion will be involved in the determination of the critical amplitude, which is a measure of the motion energy. In the harmonic approximation, this parameter cannot be determined from theoretical considerations but can be adjusted to fit experimental values. Perhaps, if anharmonic effects were included in an extension of the theory, a theoretical calculation of the critical amplitude could be made. Section III describes how the atomic jump rate can be obtained by expressing the displacements $\vec{U}^{\alpha}$ and $\vec{U}^{i}$ from Eq. (1) in terms of the phonon spectrum of the metal.

III. ATOMIC JUMP RATE

For a lattice-dynamical description of the fluctuations in the reaction coordinate, we specify the equilibrium position of an atom by

$$\vec{R}(\vec{l}) = l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3 , \tag{2}$$

where $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are the primitive translation vectors. Thermal vibrations cause a displacement of the atom from its equilibrium position. If cyclic boundary conditions and the harmonic approximation are assumed, the displacement of the atom can be expressed as[10]

$$\vec{U}(\vec{l}) = \frac{1}{(NM)^{1/2}} \sum_{\vec{q},\lambda} \vec{e}(\vec{q},\lambda) Q(\vec{q},\lambda)\, e^{i\vec{q}\cdot\vec{R}(\vec{l})} , \tag{3}$$

where $\vec{e}(\vec{q},\lambda)$ is the polarization vector and $Q(\vec{q},\lambda)$ is the normal coordinate corresponding to the mode of frequency ω, wave vector $\vec{q}$, and branch λ given by

$$Q(\vec{q},\lambda) = \left(\frac{\hbar}{2\omega(\vec{q},\lambda)}\right)^{1/2} [a^{\dagger}(-\vec{q},\lambda) + a(\vec{q},\lambda)] \tag{4}$$

in terms of the phonon creation and destruction operators. The phonon occupation number is given by

$$n(\vec{q},\lambda) = \langle a^{\dagger}(\vec{q},\lambda) a(\vec{q},\lambda)\rangle = (e^{(\hbar\omega/kT)} - 1)^{-1}. \tag{5}$$

By substituting the quantities $\vec{U}^{\alpha}$ and $\vec{U}^{i}$ in Eq. (2), the reaction coordinate can be written as

$$X = \sum_{\vec{q},\lambda} X(\vec{q},\lambda) , \tag{6}$$

where $X(\vec{q},\lambda)$ is the contribution to the fluctuation in the reaction coordinate due to the $(\vec{q},\lambda)$ mode. The particular form of $X(\vec{q},\lambda)$ will depend on the lattice geometry of the material and the number of neighbors that obstruct the jumping atom.

The atomic jump occurs when the fluctuation in X exceeds a certain critical value X_c. The rate at which X_c occurs, when X is the sum of $X(\vec{q},\lambda)$

terms, is given by the frequency of "up-zeros," i.e.,

$$\sum X(\vec{q}, \lambda) - X_c = 0.$$

Following the solution of Kac,[11] the frequency of "up-zeros" is given by

$$\Gamma = \Big[\sum_{\vec{q},\lambda} \omega^2(\vec{q}, \lambda) \,|X(\vec{q}, \lambda)|^2 \Big/ \sum_{\vec{q},\lambda} |X(\vec{q}, \lambda)|^2\Big]^{1/2} \times \exp\Big[-X_c^2 \Big/ \sum_{\vec{q},\lambda} |X(\vec{q}, \lambda)|^2\Big]. \qquad (7)$$

Equation (7) yields the atomic jump frequency when the frequency of fluctuations is much greater than the frequency of a jump.

Equation (7) is the basic equation in the present theory. It was first applied to atomic jump processes by Rice,[3] and subsequently by others.[6,12–14] The velocity of the jumping atom need not be considered in the expression for the jump frequency. Equation (7) resembles the familar equation

$$\Gamma = \Gamma_0 e^{-\Delta E_M / RT} \qquad (8)$$

that was used in the reaction rate theory. The preexponential factor is an average of the frequency values over the entire spectrum of fluctuations.

IV. ISOTOPE EFFECT

The isotope effect in cubic metals is a measure of the dependence of the tracer diffusion rate on the isotopic mass. The parameter ΔK that describes this effect is defined[15] by

$$\Delta K = \left(\frac{\Gamma_\alpha/\Gamma_\beta - 1}{(M_\beta/M_\alpha)^{1/2} - 1}\right), \qquad (9)$$

where Γ_α and Γ_β are the jump frequencies of the isotopic masses M_α and M_β, respectively. The atomic jump rate Γ_α for the isotope of mass M_α can be calculated in a straightforward manner by using the appropriate expression for $\vec{U}^\alpha$ in Eq. (1). This result is well known in the theory of vibrations of isotopic impurities in crystal lattices.[16] Accordingly, the square of the amplitude of the isotopic impurity M_α in the $(\vec{q}, \lambda)$ mode is given by

$$|\vec{U}^\alpha(\vec{q},\lambda)|^2$$

$$= (NM)^{-1}\{[1 - \epsilon\omega^2(\vec{q},\lambda)\tilde{G}_0(\omega^2)]^2 + \pi^2\epsilon^2\omega^2(\vec{q},\lambda) G_0^2(\omega^2)\}^{-1} \quad [0 < \omega^2(\vec{q},\lambda) < \omega_{\max}^2] \quad (10)$$

$$= (\epsilon M)^{-1}\left(\epsilon\omega^2(\vec{q},\lambda)\int_0^{\omega_{\max}^2} \frac{G_0(\omega'^2)d\omega'^2}{(\omega^2 - \omega'^2)} - 1\right)^{-1} \quad [\omega_{\max}^2 < \omega^2(\vec{q},\lambda)]. \quad (11)$$

In Eqs. (10) and (11), M is the mass, N is the number of atoms in the crystal, $\epsilon = 1 - M_\alpha/M$ is the mass difference factor, $G_0(\omega^2)$ is the distribution function for the squared frequencies, and $\tilde{G}_0(\omega^2)$ is the Hilbert transform of $G_0(\omega^2)$. Equation (10) yields the square of the relative amplitude when the frequency $\omega(\vec{q},\lambda)$ lies within the allowed band of frequencies, and Eq. (11) yields the same factor when a localized mode occurs beyond the maximum allowed frequency of the perfect cyrstal. If $M_\alpha = M$, $\epsilon = 0$, the square of the amplitude reduces to $|U^\alpha(\vec{q},\lambda)|^2 = (NM)^{-1}$. Localized modes are known to occur only when there is a light impurity with $\epsilon \geq \epsilon_{cr} \approx 0.24$.[16] In most of the work concerned with the isotope effect in self-diffusion, the mass difference factor ϵ seldom reaches the critical value that will give rise to localized modes. Only Eq. (10) is needed to compute Γ_α. Although the normal mode frequencies in a crystal with an isotopic impurity are slightly different from those of the perfect crystal, a first approximation that the eigenvectors are essentially the same can be made. If this assumption is used, Γ_α, the atomic jump rate for the isotope M_α, can be calculated by using Eqs. (7) and (10). A similar computation of Γ_β for the isotope M_β leads to a straightforward calculation of ΔK through the use of Eq. (9). The numerical application to fcc and bcc metals will be discussed.

V. NUMERICAL APPLICATION

The numerical application to self-diffusion in Cu, Ag, Au, Al, Ni, Co, and Pb among the fcc metals, and Na and α-Fe among the bcc metals will be discussed.

A. fcc Metals

The geometry of the atomic jump in an fcc metal is shown in Fig. 1. The jumping atom (shaded circle) is located at the center of a face and is a nearest neighbor to the vacancy (square). The atoms at the corners of the rectangle form a barrier to the jumping atom.

The primitive translation vectors $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are given by

$$\vec{a}_1 = \tfrac{1}{2}a(\vec{j} + \vec{k}),$$
$$\vec{a}_2 = \tfrac{1}{2}a(\vec{i} + \vec{k}), \qquad (12)$$
$$\vec{a}_3 = \tfrac{1}{2}a(\vec{i} + \vec{j}),$$

where $\vec{i}$, $\vec{j}$, and $\vec{k}$ are the unit vectors along the cube edges. The corresponding reciprocal lattice

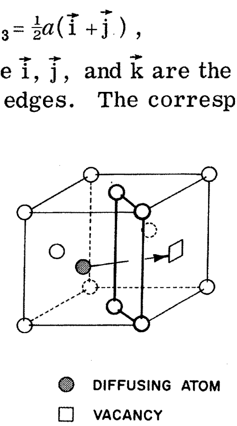

FIG. 1. Geometry of the atomic jump in a fcc crystal by the vacancy mechanism.

has the following base vectors:

$$\vec{b}_1 = a^{-1}(-\vec{i} + \vec{j} + \vec{k}),$$
$$\vec{b}_2 = a^{-1}(\vec{i} - \vec{j} + \vec{k}), \qquad (13)$$
$$\vec{b}_3 = a^{-1}(\vec{i} + \vec{j} - \vec{k}).$$

If the origin is at the diffusing atom and the vacancy is at $\frac{1}{2}a(110)$, the four atoms barring the diffusing atom are at the corners $\frac{1}{2}a(10\bar{1})$, $\frac{1}{2}a(01\bar{1})$, $\frac{1}{2}a(011)$, and $\frac{1}{2}a(101)$. The components of unit vector along the jump direction are $(1/\sqrt{2},\ 1/\sqrt{2},\ 0)$.

The contribution to the fluctuation in the reaction coordinate due to the $(\vec{q}, \lambda)$ mode is given by

$$X(\vec{q}, \lambda) = (\vec{e}(\vec{q}, \lambda) \cdot \hat{X})\, Q(\vec{q}, \lambda)\, [U^{\alpha}(\vec{q}, \lambda) - \tfrac{1}{2} U^{0}(\vec{q}, \lambda) \times \cos(\tfrac{1}{2} q_3 a)\, (e^{iaq_1/2} + e^{iaq_2/2})], \qquad (14)$$

where the wave vector $\vec{q}$ is given by

$$\vec{q} = q_1 \vec{b}_1 + q_2 \vec{b}_2 + q_3 \vec{b}_3, \qquad (15)$$

where

$$q_1 = 2\pi n_1/N_1, \quad n_1 = 0, 1, \ldots N_1 - 1, \ldots$$

and

$$N = N_1 N_2 N_3.$$

The expression for $U^{\alpha}(\vec{q}, \lambda)$ is given in Eq. (10).

A Born-Karman force-constant model is used to describe the phonon spectrum of the metal. In Cu and Ni, phonon dispersion curves have been obtained from neutron-scattering data,[17,18] and have been analyzed in terms of Born-Karman models. When interactions up to the sixth-nearest neighbors in Cu and up to the fourth-nearest neighbors in Ni are included, the theoretical calculations are in good agreement with the experimental phonon dispersion curves. A model of this type enables one to compute both the eigenfrequencies and the eigenvectors of the normal modes of vibration that are required to evaluate the sums

$$\sum_{\vec{q}, \lambda} X(\vec{q}, \lambda).$$

If the eigenfrequencies can be obtained experimentally for some of the modes, then the model helps to extrapolate to other values of the wave vector, and a larger sampling is available for the summations. A Born-Karman model is simple to use and reproduces the experimentally measured dispersion relations fairly well when the model parameters are fitted to the dispersion curves. A simpler Born-Karman model, with general nearest-neighbor interactions only, can be used when neutron-scattering data or model parameter analyses are not available. The three parameters involved in this simpler model can be fitted to the three elastic constants. Two models have been used to compare the ΔK calculations for Cu: (a) a sixth-neighbor force-constant model, derived from experimental phonon dispersion data, and (b) a nearest-neighbor general force-constant model, fitted to the elastic constants.

The form of the force-constant matrices is listed in Table I. The values of the force-constant parameters for Cu and Ni are listed in Table II. Table III lists the elastic constants of Al, Ag, Au, Pb, and Co (8% Fe) and the values of the three general force constants. The phonon spectrum was obtained by solving the secular equation for normal modes at 22 931 points in the irreducible section of the first Brillouin zone. The Hilbert transform of the squared frequency distribution was then calculated at 100 points between zero and the maximum squared frequency. The quantities

$$\sum_{\vec{q}, \lambda} |X(\vec{q}, \lambda)|^2 \quad \text{and} \quad \sum \omega^2(\vec{q}, \lambda) |X(\vec{q}, \lambda)|^2$$

were evaluated by solving the secular equation at 261 points in the irreducible part of the first Brillouin zone, and by summing over all the modes. The ratio of the Debye frequency of the crystal to the factor

$$[\sum \omega^2(\vec{q}, \lambda) |X(\vec{q}, \lambda)|^2 / \sum |X(\vec{q}, \lambda)|^2]^{1/2}$$

was also calculated. Theoretical estimates of the motion energy are presented by assuming that the critical amplitude is a definite fraction of the atomic radius of the crystal (0.275). The results are presented in Table IV. The values of ΔK calculated for Cu, Ag, Ni, Al, and Co (8% Fe) are listed in Table V. The isotope effect for Cu, calculated on the basis of the simpler nearest-neigh-

TABLE I. Force-constant matrices between the atom at (0, 0, 0) and the atom at *Rn* in fcc metals.

Rn	$\Phi(0, Rn; ij)$
$\frac{1}{2}a(110)$	$\begin{pmatrix} \alpha_1 & \gamma_1 & 0 \\ \gamma_1 & \alpha_1 & 0 \\ 0 & 0 & \beta_1 \end{pmatrix}$
$\frac{1}{2}a(200)$	$\begin{pmatrix} \alpha_2 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \beta_2 \end{pmatrix}$
$\frac{1}{2}a(211)$	$\begin{pmatrix} \alpha_3 & \delta_3 & \delta_3 \\ \delta_3 & \beta_3 & \gamma_3 \\ \delta_3 & \gamma_3 & \beta_3 \end{pmatrix}$
$\frac{1}{2}a(220)$	$\begin{pmatrix} \alpha_4 & \gamma_4 & 0 \\ \gamma_4 & \alpha_4 & 0 \\ 0 & 0 & \beta_4 \end{pmatrix}$
$\frac{1}{2}a(310)$	$\begin{pmatrix} \alpha_5 & \delta_5 & 0 \\ \delta_5 & \beta_5 & 0 \\ 0 & 0 & \gamma_5 \end{pmatrix}$
$\frac{1}{2}a(222)$	$\begin{pmatrix} \alpha_6 & \beta_6 & \beta_6 \\ \beta_6 & \alpha_6 & \beta_6 \\ \beta_6 & \beta_6 & \alpha_6 \end{pmatrix}$

TABLE II. Atomic force constants between *n*th-nearest neighbors in copper and nickel (dyn cm^{-1}).

Metal	n	α_n	β_n	γ_n	δ_n
Copper (Ref. 16)	1	13 478	−1215	14 982	•••
	2	18	− 48	•••	•••
	3	507	237	159	378
	4	267	− 32	− 36	•••
	5	− 110	− 203	37	18
	6	− 157	− 58	•••	•••
Nickel (Ref. 18)	1	17 178	− 26	19 316	•••
	2	880	− 519	•••	•••
	3	626	320	− 710	453
	4	270	− 160	424	•••

bor model by using the elastic constants data only, is also listed in Table V.

The neighboring atoms of a vacancy may undergo relaxation displacements from their "ideal" lattice positions. Calculations of such relaxation displacements in Cu have been available.[19] The effect of such relaxations on ΔK was studied by allowing all the atoms involved in the expression for the reaction coordinate X to undergo the respective displacements. There was no appreciable change in the value of ΔK ($< 0.5\%$).

The ΔK effect may depend on temperature. This may arise because the phonon spectrum exhibits a temperature dependence. Unfortunately, no experimental phonon dispersion data are available for the temperatures involved in diffusion experiments. Even the high-temperature elastic constants data are scarce; however, one set of measurements of the elastic constants of Al[20] up to its melting point has been made. The ΔK effect at 900 °K was calculated by using the elastic constants at that temperature, assuming a quasiharmonic approximation. A similar calculation was made for Ag by extrapolating the room-temperature elastic constant data[21] to 1000 °K. These results are shown in Table VI.

B. bcc Metals

The geometry of the diffusion jump in a bcc metal is shown in Fig. 2. The diffusing atom is shown as a black circle and the vacancy by a square. When the atom jumps into the vacancy, it passes through one triad of atoms at one-third the jump distance and through a second triad of atoms at two-thirds the jump distance. If the diffusing atom is able to pass through the first triad of atoms, the jump will probably be completed, and the first triad is used to evaluate the fluctuations in the reaction coordinate.

The primitive translation vectors for the bcc lattice are given by

$$\vec{a}_1 = \tfrac{1}{2}a(-\vec{i}+\vec{j}+\vec{k}),\quad \vec{a}_2 = \tfrac{1}{2}a(\vec{i}-\vec{j}+\vec{k}),\quad \vec{a}_3 = \tfrac{1}{2}a(\vec{i}+\vec{j}-\vec{k}), \tag{16}$$

with respect to $\vec{i}$, $\vec{j}$, $\vec{k}$, an orthonormal set of vectors along the cube axes.

The base vectors of the reciprocal lattice are given by

$$\vec{b}_1 = a^{-1}(\vec{j}+\vec{k}),\quad \vec{b}_2 = a^{-1}(\vec{i}+\vec{k}),\quad \vec{b}_3 = a^{-1}(\vec{i}+\vec{j}). \tag{17}$$

Neutron-scattering data are available for both Na and α-Fe, and the phonon dispersion data have been analyzed in terms of Born-Karman models.[22,23] In the case of Na, the model includes interactions up to the fifth-nearest neighbors, and, in the case of Fe, only up to the third-nearest neighbors. The form of the force-constant matrices and the values of the force-constant parameters are listed in Tables VII and VIII, respectively.

If the diffusing atom is assumed to be at the origin and the vacancy at $\frac{1}{2}a(111)$, the first triad of atoms that obstructs the diffusing atom has the coordinates $\frac{1}{2}a(11\bar{1})$, $\frac{1}{2}a(\bar{1}11)$, and $\frac{1}{2}a(1\bar{1}1)$. The

TABLE III. Lattice constants, elastic constants, and atomic force constants for fcc metals. Lattice constants (10^{-8} cm) are taken from Pearson's handbook[a] and the elastic constants (10^{12} dyn cm^{-2}) from Huntington.[b]

Metal	Lattice constant	Elastic constants C_{11}	C_{12}	C_{44}	Atomic force constants (dyn cm^{-1}) α_1	β_1	γ_1
Cu	3.61	1.684	1.214	0.754	15 902	−1 137	18 654
Ag	4.08	1.240	0.934	0.461	12 648	−3 244	14 229
Au	4.07	1.86	1.57	0.42	18 926	−10 379	20 248
Al	4.04	1.082	0.613	0.285	10 928	−5 171	9 069
Co (8% Fe)	3.56	2.343[c]	1.613[c]	1.251[c]	20 852	1 415	25 489
Pb	4.94	0.466	0.392	0.144	5 755	−2 198	6 620

[a] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, New York, 1958).

[b] H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. VII, p. 213.

[c] T. C. Fritz and K. Brugger (private communication to E. S. Fisher).

TABLE IV. Lattice theory applied to diffusion in fcc metals. Atomic radii (10^{-8} cm) are taken from Ziman,[a] Debye temperature data from Gschneidner,[b] and experimental values of motion energy from Peterson.[c]

Metal	Atomic radius	Debye temp.	Γ_0/ω_D	E_m(eV) (Theor)	E_m(eV) (Expt)
Cu	1.41	342	0.65	1.04	1.08
Ag	1.59	228	0.65	0.99	0.83
Au	1.59	165	0.70	0.88	0.82
Al	1.58	423	0.63	0.80	0.62
Ni	1.38	427	0.67	1.47	1.50
Co(8% Fe)	1.38	452	0.64	1.52	1.6
Pb	0.93	102	0.64	0.64	0.56

[a] J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, England, 1960).

[b] K. A. Gschneidner, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. XVI, p. 276.

[c] Reference 1.

components of the unit vector along the jump direction are $X = (1/\sqrt{3},\ 1/\sqrt{3},\ 1/\sqrt{3})$. The contribution to the fluctuation in the reaction coordinate due to the $(\vec{q}, \lambda)$ mode is given by

$$X(\vec{q},\lambda) = \hat{e}(\vec{q},\lambda)\cdot X(\vec{q},\lambda)Q(\vec{q},\lambda)\,\{U^\alpha(\vec{q},\lambda) - \tfrac{1}{3}U^0(\vec{q},\lambda) \times[\exp(\tfrac{1}{2}ia(q_1+q_2-q_3)) + \exp(\tfrac{1}{2}ia(q_1-q_2+q_3)) + \exp(\tfrac{1}{2}ia(-q_1+q_2+q_3))]\}\ . \tag{18}$$

The appropriate expression for $U^\alpha(\vec{q}, \lambda)$ is used in calculating the various quantities

$$\sum |X(\vec{q},\lambda)|^2,\quad \sum \omega^2(\vec{q},\lambda)|X(\vec{q},\lambda)|^2,$$

and ΔK. The frequency spectrum was obtained by solving the secular equation for normal modes at 44 251 points in the irreducible part of the first Brillouin zone, and the Hilbert transform of the squared frequency distribution was evaluated at 100 points between zero and the maximum squared frequency. The fluctuation quantities were evaluated by solving the secular equation for normal modes at 451 points in the irreducible part of the first Brillouin zone for eigenfrequencies and eigenvectors and by summing over all the modes. The results for ΔK in Na and α-Fe are presented in Table V.

TABLE V. Isotope effect calculations.

Metal	Isotopes	ΔK (Theor)	ΔK (Expt)
Cu	Cu^{64}, Cu^{67}	0.82 0.79[b]	0.87 ± 0.02[a]
Ag	Ag^{105}, Ag^{111}	0.80	0.86 ± 0.05[c]
Al	Al^{26}, Al^{29}	0.88	···
Ni	Ni^{57}, Ni^{63}	0.76	···
Co	Co^{55}, Co^{60}	0.68	···
Na	Na^{22}, Na^{24}	0.54	0.50 ± 0.05[d]
α-Fe	Fe^{52}, Fe^{59}	0.51	0.46 ± 0.01[c] (in δ-Fe)

[a] S. J. Rothman and N. L. Peterson, Phys. Status Solidi 35, 309 (1969).

[b] Calculated from elastic data only. See text for explanation.

[c] Reference 1.

[d] J. N. Mundy, L. W. Barr, and F. A. Smith, Phil. Mag. 14, 785 (1966).

TABLE VI. Effect of temperature on the isotope effect.

Metal	Temp. (°K)	Elastic constants (10^{12} dyn cm^{-2}) C_{11}	C_{12}	C_{44}	ΔK
Al	300	1.082	0.613	0.285	0.88
	900[a]	0.808	0.539	0.186	0.87
Ag	300	1.240	0.934	0.461	0.80
	1300[b]	0.942	0.784	0.272	0.84

[a] High-temperature data from Ref. 19.

[b] Extrapolation to 1300 °K from the data at 300 °K from Ref. 20.

V. DISCUSSION

Our theoretical calculations of ΔK indicate that its theoretical value is of the correct order of magnitude and is in good agreement with experiment. The value of ΔK is always less than unity for self-diffusion in cubic metals by the vacancy mechanism. The ΔK values for the fcc metals range from 0.88 in Al to 0.68 in Co, and for the bcc metals the values range from 0.51 in α-Fe to 0.54 in Na. This is contrasted with previous theoretical calculations of ΔK, where the value was always close to unity.[8] The relaxation near the vacancy has very little effect on ΔK in Cu. This is perhaps true for all the fcc metals. In the bcc

TABLE VII. Force-constant matrices between the atom at (0, 0, 0) and the atom at *Rn* in bcc metals.

Rn	$\Phi(0, Rn;\ ij)$
$\frac{1}{2}a(111)$	$\begin{pmatrix}\alpha_1 & \beta_1 & \beta_1\\ \beta_1 & \alpha_1 & \beta_1\\ \beta_1 & \beta_1 & \alpha_1\end{pmatrix}$
$\frac{1}{2}a(200)$	$\begin{pmatrix}\alpha_2 & 0 & 0\\ 0 & \beta_2 & 0\\ 0 & 0 & \beta_2\end{pmatrix}$
$\frac{1}{2}a(220)$	$\begin{pmatrix}\alpha_3 & \gamma_3 & 0\\ \gamma_3 & \alpha_3 & 0\\ 0 & 0 & \beta_3\end{pmatrix}$
$\frac{1}{2}a(311)$	$\begin{pmatrix}\alpha_4 & \delta_4 & \delta_4\\ \delta_4 & \beta_4 & \gamma_4\\ \delta_4 & \gamma_4 & \beta_4\end{pmatrix}$
$\frac{1}{2}a(222)$	$\begin{pmatrix}\alpha_5 & \beta_5 & \beta_5\\ \beta_5 & \alpha_5 & \beta_5\\ \beta_5 & \beta_5 & \alpha_5\end{pmatrix}$

2

TABLE VIII. Atomic force constants between *n*th-nearest neighbors in sodium and α-iron (dyn cm^{-1}).

Metal	n	α_n	β_n	γ_n	δ_n
	1	1180	1320	···	···
	2	470	130	···	···
Na[a]	3	− 38	27	− 65	···
	4	9.9	− 4.1	3.0	9.0
	5	20	25	···	···
	1	15200	18600	···	···
α-Fe[b]	2	15000	2300	···	···
	3	− 1100	275	−1375	···

[a] Reference 22.

[b] Reference 23.

metals, however, relaxation does change the value of ΔK. A detailed investigation of this effect in Na and also of the role played by the second triad of atoms in determining the isotope effect is under way. Temperature appears to have little effect on the value of ΔK when the calculations are made in a quasiharmonic approximation, using the high-temperature elastic data, to obtain the frequency spectrum. The small change in the value of ΔK, apparent in Ag, is probably due to poor extrapolation of the elastic-constants data.

It is not possible to associate a simple physical significance to ΔK, on the basis of the present theory. ΔK is a many-mode effect that is determined by the phonon spectrum and by the geometry of the diffusion jump. The diffusion mechanism determines the geometry of the jump, which, in turn, determines the appropriate reaction coordinate. The fluctuations of the reaction coordinate are determined by the phonon spectrum. Since ΔK depends on the frequency spectrum and its Hilbert transform, a study of the effect of resonance and localized modes on ΔK would be of interest. Experimentally this could be accomplished by an investigation of ΔK effect for diffusion of heavy and light impurities. Finally, the present theory does not set any limits to the value of ΔK, since it does not associate any specific ratio of kinetic energies with ΔK.

The preexponential factor

$$\Gamma_0=(\sum \omega^2|X|^2/\sum |X|^2)^{1/2}$$

bears a practically constant ratio of 0.65 to the Debye frequency, and a single adjustable parameter for the critical amplitude gives estimates of motion energy that are in good agreement with experimental values. The single adjustable parameter for fcc crystals is 0.275 of the atomic radius. The preexponential factor is an average frequency and the weighting factors are determined by the geometry of the diffusion jump. Therefore, its value lies between the minimum and the maximum frequencies of the spectrum. Although the critical amplitude required for the jump is not calculated by the theory, when it is a specific fraction of the atomic radius good estimates of motion energy can be obtained. Although the present theory is more general than Flynn's theory, both are in agreement. His value of $(\frac{3}{5})^{1/2}=0.77$ for the preexponential factor is due to his continuum approximation. Flynn also uses a single adjustable parameter δ to estimate motion energy, δ is given by q_c/s, where q_c is the critical amplitude, but s is difficult to define exactly. However, the actual significance of s is not important in his theory, since it appears only as an adjustable parameter.

The present theory uses the harmonic approximation or, at best, quasiharmonic approximation. The vacancy mechanism is assumed to be the diffusion mechanism. Except for determining the geometry of the jump, the vacancy plays a rather passive role in the theory. The changes introduced by the vacancy on the phonon spectrum are completely neglected, but the changes may not be important, as shown by Land and Goodman.[24] The effect of the isotopic impurity is treated in a rather sophisticated way in calculating ΔK. The fact that the critical amplitude required for the atomic jump is such a small fraction of the atomic radius is perhaps a justification and an explanation at the same time for the use of harmonic approximation. The theory works quite well in spite of all these approximations.

Future work should certainly consider the effects introduced by the vacancy on the phonon spectrum and also the effects of anharmonicity. The latter could perhaps allow a calculation *a priori* of the critical amplitude for atomic jump and thus enable a theoretical calculation of the motion energy.

VI. CONCLUSION

A lattice-dynamical theory of diffusion in the harmonic approximation has been developed, under the assumption that the jump probability can be calculated from the phonon spectrum of the lattice. Fluctuations in a reaction coordinate based on simple geometrical considerations have been used. The isotope effect ΔK and other features of the diffusion process are successfully accounted for by

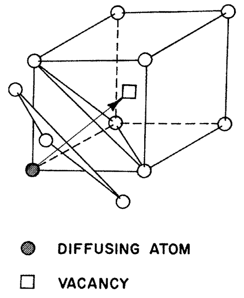

FIG. 2. Geometry of diffusion in bcc metals.

the theory. Future refinements should include anharmonicity to enable a theoretical estimation of the motion energy.

Note added in proof. Calculations of ΔK have also been made using the same reaction coordinate defined in Eq. (1) and also the procedure of Sec. IV, but Eqs. (16)–(19) of the paper by Rice[3] have been used to calculate the atomic jump rate Γ. The normal coordinates are now expressed as cosine terms, and the summations are carried through the entire first Brillouin zone, rather than only through the irreducible part. The value of ΔK obtained by this modified procedure are 0.78, 0.78, 0.75, 0.77, 0.80, 0.85, and 0.75 for Cu, Ag, Al, Ni, Co, Na, and α-Fe, respectively. Although this modification involves a more rigorous treatment of the atomic jump rate by including integration over all values of energy, the procedure yields values of ΔK that have poor agreement with experiment, especially the bcc metals.

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