

(1968)]. Value used is average of high-coverage-limit work functions for Li deposited on various faces of W and Re.

²⁸J. C. Rivière, in *Solid State Surface Science*, edited by M. Green (Dekker, New York, 1969), Vol. 1.

²⁹C. Herring and M. H. Nichols, *Rev. Mod. Phys.* **21**, 185 (1949).

³⁰It might be mentioned that T. Schneider [*Phys. Status Solidi* **32**, 323 (1969)] has shown second-order effects in δv to reduce $-\bar{\mu}$, the bulk contribution to the work function, by 0.1–0.2 eV for the alkalis and by 0.3 and 0.8 eV for Al and Mg, respectively. The second-order effect of δv on the surface term $\Delta\phi$ must be determined, however, before any conclusions can be drawn concerning

the net importance of $(\delta v)^2$ terms in Φ .

³¹Reference 19 gives also a second, much larger, value of r_c for each of these metals, which leads to somewhat less satisfactory results for bulk properties. The work functions calculated with these r_c 's are about 1 eV lower than those corresponding to the preferred set, giving an even greater discrepancy with experiment.

³²Cu and Ag: D. E. Eastman, *Phys. Rev. B* **2**, 1 (1970); Au: E. E. Huber, *Appl. Phys. Letters* **8**, 169 (1966).

³³There is some theoretical evidence suggesting the existence of occupied surface states in the noble metals; this could of course also affect $\Delta\phi$. See F. Forstmann and J. B. Pendry, *Z. Physik* **235**, 75 (1970).

Some Formal Aspects of a Dynamical Theory of Diffusion*

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A classical dynamical theory of diffusion is presented in which the reaction coordinate and its critical value are expressed in terms of a $3N$ -dimensional vector \underline{R} . The Slater approximation to the Kac equation is shown to be exact for classical statistics, and the jump rate is calculated accordingly. The jump rate can be expressed in terms of the vector \underline{R} and the dynamic matrix; this leads to a frequency factor different from that obtained from the reaction-rate theory, and an indication that the system does not jump through the relaxed saddle-point configuration. The self-diffusion isotope effect is also considered. It is shown explicitly that the migration energy is mass independent, and that the effect may be expressed simply in terms of the reaction coordinate. In terms of the phonons, the isotope effect depends on a weighted average of the fraction of the energy carried by the jumping atom in each mode. Quantum corrections are discussed and a connection is made between the isotope effect and thermomigration.

I. INTRODUCTION

There has been increasing interest in recent years in formulating the theory of diffusion jump rates in a way that avoids some of the conceptual difficulties of the absolute-rate theory.¹ The rate theory was applied to diffusion by Wert and Zener,² and elegantly formulated by Vineyard³ to show explicitly how the motions of many atoms are involved in the jump process. This can be seen in Vineyard's form for the preexponential or frequency factor

$$\frac{\omega_0}{2\pi} = \prod_{i=1}^{3N} \nu_i \bigg/ \prod_{i=2}^{3N} \nu_i' \quad (1.1)$$

in which ν_i and ν_i' are the normal-mode frequencies of the equilibrium and saddle-point configurations, respectively, with the unstable "mode" of the saddle point left out of the product in the denominator. The many-body nature is also apparent in the identification of the migration energy with the potential-energy difference of the relaxed saddle-point and

equilibrium configurations.

The troubling aspect of rate theory is that it focuses so strongly on properties of the relaxed saddle-point configuration. In a quantum-mechanical theory it would not only be impossible to treat positions and velocities independently, but, more significantly, it would be completely inappropriate to speak of the properties of the intermediate state, as has been pointed out by Flynn and Stoneham.⁴

Attempts to circumvent these difficulties have been made by several authors.^{5–8} These "dynamical" theories view the jump process as resulting from a special kind of fluctuation from equilibrium, and attempt to calculate the frequency of such fluctuations. In the earlier work, fluctuations were considered that carried the system to a definite configuration, e.g., the relaxed saddle-point configuration. Glyde⁷ has shown that, for this case, the dynamical and rate theories have the same formal content. More recently, Flynn⁸ has considered fluctuations in a reaction coordinate, made up of a linear combination of particle displacements,

whose significance is that a jump is guaranteed if the magnitude of the fluctuation exceeds a critical value. This approach is probably preferable to the earlier one since the contributions of all sets of displacements that move the system in the correct phase-space direction are included; it is the approach that will be used in the present paper.

An appropriate reaction coordinate will be determined largely by the crystal structure; e.g., Flynn chose the relative separation of the jumping atom from the center of mass of the barrier atoms. The problem then reduces to calculating the frequency with which this reaction coordinate, due to atomic vibrations, exceeds the critical value. The critical value determines the size of the energy fluctuation needed to effect the jump, and therefore determines the migration energy.

Aside from the jump rate itself, it is of interest to study the motion volume and the diffusion-isotope effect. The motion volume can be simply interpreted, according to rate theory, as the change in crystal volume upon activation of the defect. In the dynamic theory,⁸ however, it depends mainly on shifts in the normal-mode frequencies as represented by the pressure dependence of the elastic constants. We shall not pursue this subject in the present paper; we shall consider the isotope effect for self-diffusion. The relative change in the jump rate due to a small change in the mass of the jumping atom is important because it is a direct indication of the many-body nature of diffusion. Since a number of atoms participate in the jump process, the mass dependence of the jump rate is reduced from the inverse-square-root dependence of a simple oscillator. As is well known, the rate theory predicts that this reduction depends only on the fraction of kinetic energy carried by the migrating atom in the unstable "mode" of the relaxed saddle-point configuration. Calculations⁹ based on this prescription appear to give a larger mass dependence than is found experimentally.¹⁰

In the present paper we explore some general features of a classical-dynamical theory of the jump process. In Sec. II, we start from a general form for the reaction coordinate and show that the Slater approximation¹¹ to the Kac equation¹² for the up-zero frequency of trigonometric sums is rigorously valid for classical statistics. The jump rate is calculated accordingly in terms of the reaction coordinate and a definite critical fluctuation value. This leads to an effective frequency different from that of rate theory and to the prediction that, on average, the system does not pass through the relaxed saddle-point configuration when making a jump.

In Sec. III, the previous results are generalized to the case of unequal atomic masses so that the isotope effect can be treated. It is shown explicitly

that the migration energy is mass independent so that the effect depends only on the mass dependence of the preexponential factor. This dependence takes on a simple form when expressed in terms of the atomic displacements; in terms of the phonons, it involves a weighted average of the fraction of energy carried by the jumping atom in each mode. Quantum corrections to this result are discussed, and, finally, a connection is made to the theory of thermomigration. In Sec. IV, these results are discussed and a model calculation is described.

II. REACTION COORDINATE AND CRITICAL VALUE

The dynamic approach rests on the assumption that there exists a particular unique type of fluctuation, called the reaction coordinate $x(t)$, such that if the magnitude of this fluctuation exceeds a certain critical value q , the jump is guaranteed. We may, without approximation, express the reaction coordinate as the projection of the actual motion of the system onto a phase-space vector \underline{R} which we write in terms of the phonon eigenvectors \underline{e}_n as

$$\underline{R} = \sum_n A_n \underline{e}_n \quad , \quad (2.1)$$

where the sum extends over all phonon modes. We make no assumption as to the form of the eigenvectors, and let the A_n , for generality, be complex numbers so that the reaction coordinate will measure fluctuations of both kinetic and potential energy. The relative sizes of the coefficients A_n determine the structure of the reaction coordinate, while their absolute magnitudes specify the size of the harmonic-energy fluctuation ΔE necessary to carry the system to the point \underline{R} in phase space:

$$\Delta E = \frac{1}{2} m \sum_n |A_n|^2 \omega_n^2 \quad . \quad (2.2)$$

The reaction coordinate is then $x(t) = \underline{y}(t) \cdot \underline{R}$, where

$$\underline{y}(t) = \sum_n u_n \underline{e}_n e^{i\omega_n t} \quad (2.3)$$

describes the thermal motion of the system. We wish to find the frequency with which $x(t)$ exceeds the critical value q , i.e., the up-zero frequency of

$$x(t) - q = \sum_n A_n u_n e^{i\omega_n t} - q \quad . \quad (2.4)$$

This problem has been solved by Kac¹² who gives the frequency $\nu(q, \{u_n\})$ corresponding to the critical value q and the set of phonon amplitudes $\{u_n\}$ as

$$\nu(q, \{u_n\}) = (2\pi)^{-2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{d\xi d\eta}{\eta^2} \cos q\xi \left[\prod_n J_0 \left(|A_n u_n| \xi \right) - \prod_n J_0 \left(|A_n u_n| (\xi^2 + \omega_n^2 \eta^2)^{1/2} \right) \right] \quad . \quad (2.5)$$

The most useful form of this equation, for our purposes, was derived by Slater,¹¹ and also used by Flynn,⁸ under the approximation that all the phonon amplitudes are essentially equal. The desired

equation, however, has a more general validity as can be seen by considering the system as a canonical ensemble, thereby allowing for energy fluctuations. The ensemble average jump rate Γ is found by averaging over all possible sets of phonon amplitudes:

$$\Gamma = \int_0^\infty \nu(q, \{u_n\}) \prod_n P(\epsilon_n) d\epsilon_n / kT, \quad (2.6)$$

where

$$P(\epsilon_n) = e^{-\epsilon_n / kT} = e^{-1/2m\omega_n^2 u_n^2 / kT} \quad (2.7)$$

gives the distribution of the amplitudes $\{u_n\}$. The resulting integrals are easily evaluated using

$$\int_0^\infty J_0(\alpha\sqrt{x}) e^{-x} dx = e^{-\alpha^2/4}. \quad (2.8)$$

The resulting jump rate is

$$\Gamma = (\omega_0 / 2\pi) e^{-E_m / kT}, \quad (2.9)$$

where

$$\omega_0^2 = \sum_n |A_n|^2 / \sum_n \left(\frac{|A_n|}{\omega_n} \right)^2 \quad (2.10)$$

and

$$E_m = \frac{1}{2} m \omega_0^2 q^2 / \sum_n |A_n|^2, \quad (2.11)$$

which is exactly the same form as obtained from Flynn's equation (2.8) after inserting the thermal-average amplitudes $|u_n|^2 = 2kT/m\omega_n^2$.

Since the reaction coordinate is a projection of the system motion onto a phase-space vector \underline{R} whose magnitude determines the energy fluctuation involved, we may reasonably assume that a critical value is reached when this projection has magnitude $|\underline{R}|$. That is, a jump will take place if the system starts off in the right direction in phase space with just enough energy. Thus, we take $q = |\underline{R}|^2 = \sum_n |A_n|^2$ so that Eq. (2.11) for the migration energy becomes

$$E_m = \frac{1}{2} m \omega_0^2 |\underline{R}|^2. \quad (2.12)$$

We may also rewrite Eq. (2.10) in bra-ket notation as

$$\omega_0^2 = m^{-1} |\underline{R}|^2 / \langle \underline{R} | \underline{D}^{-1} | \underline{R} \rangle \quad (2.13)$$

to show how ω_0^2 depends on the reaction coordinate and the force constants. In this last equation, \underline{D} is the dynamic matrix.

There are two interesting observations about these formal expressions [Eqs. (2.9), (2.10), and (2.12)] that can be made immediately.

The preexponential factor looks quite different from that of rate theory [Eq. (1.1)]. In the rate theory, each of the equilibrium and saddle-point "normal-mode" frequencies enters on an equal basis. In the present picture, ω_0 is a weighted average of the equilibrium frequencies with those modes most important to making a jump weighted the heaviest.

However, we have to be careful because the effective frequency of rate theory is a product of an attempt frequency and the entropy term $e^{\Delta S_m / k}$, where ΔS_m is the entropy of motion. Vineyard³ separated these factors by imagining a hypersurface S_0 passing through the equilibrium point and similar to the saddle-point surface S . The attack frequency then is the effective frequency of oscillations out of S_0 , and the activation term depends on the free energy needed to reversibly carry the system from S_0 to S . The important point is that the attack frequency depends only on those normal modes whose eigenvectors do not lie in S_0 . In analogy, our ω_0 is determined only by those normal modes whose eigenvectors do not lie in the hyperplane normal to \underline{R} . So we are led to interpret ω_0 as an attempt frequency, an interpretation reinforced by the fact that our E_m in Eq. (2.11) is temperature dependent and leads naturally to an entropy term. Despite this similarity, we expect the dynamic theory attempt frequency to be larger than that of rate theory. This is because the weighting factors $|A_n|^2$, as shown by Flynn,⁸ favor the high-frequency modes, while the average of rate theory is practically unweighted.

A quantitative observation can be made about the activation energy E_m . From Eqs. (2.2) and (2.12), we can easily show that

$$\Delta E > E_m, \quad (2.14)$$

unless only one mode is involved in the reaction coordinate or all the frequencies are equal, in which case the two energies are equal. Notice that this relation is true at all temperatures. That is, the migration energy is less than the harmonic-energy fluctuation corresponding to the critical value of reaction coordinate. If the migration energy represents the potential-energy difference of the relaxed saddle-point and equilibrium configurations, the system will not jump through the relaxed saddle point, but, instead, through a slightly higher-potential configuration. This conclusion is physically reasonable since, at finite temperature, there is a region of phase space around the relaxed saddle point through which the system can jump. The slightly higher-potential configurations are favored, on the average, because of their large number. This is to say that the system will be vibrating in the saddle-point surface while crossing it.

We can write Eq. (2.9) in a more familiar form by treating E_m as a free energy, as mentioned above, and by explicitly writing out its temperature dependence,

$$\begin{aligned} E_m(T) &= E_m(0) + T \left(\frac{\partial E_m}{\partial T} \right)_p \\ &= E_m(0) - TE_m(0) \left(\frac{\partial \ln \langle \underline{R} | \underline{D}^{-1} | \underline{R} \rangle}{\partial T} \right)_p, \end{aligned} \quad (2.15)$$

by Eq. (2.13). It is seen that the migration enthalpy ΔH_m is to be identified with $E_m(0)$ and the entropy ΔS_m with

$$\Delta S_m = \Delta H_m \left(\frac{\partial \ln \langle \underline{R} | \underline{D}^{-1} | \underline{R} \rangle}{\partial T} \right)_p. \quad (2.16)$$

This last expression correlates the migration entropy with the migration enthalpy and the temperature dependence of the force constants; it is essentially the Zener relation.

III. ISOTOPE EFFECT

The effect on the jump rate Γ of a small change in the mass of the jumping atom appears rather complicated in this model. Not only must we know the mass dependence of the phonon frequencies, but also that of the coefficients A_n . The problem can be simplified, as we shall see, by using the atom-coordinate rather than the normal-mode representation.

It is not difficult to carry through the analysis of Sec. II for the case where the atomic masses m_α ($\alpha = 1 \rightarrow 3N$) are different. The main difference is that each normal mode n has associated with it a reduced mass¹³ m_n ,

$$m_n = \sum_{\alpha=1}^{3N} m_\alpha e_{n\alpha}^2, \quad (\underline{D} - m_n \omega_n^2) \hat{e}_n = 0, \quad (3.1)$$

where $e_{n\alpha} = \hat{e}_n \cdot \hat{x}_\alpha$. The frequencies are determined by the equation

$$(\underline{D}' - \omega_n^2) \hat{e}_n = 0. \quad (3.2)$$

Here $\underline{D}' = \underline{m}^{-1/2} \cdot \underline{D} \cdot \underline{m}^{-1/2}$ is the mass-weighted dynamic matrix and \underline{D} is the usual dynamic matrix. The mass-weighted orthonormal eigenvectors \hat{e}_n are related to the nonorthogonal normalized eigenvectors $\hat{\epsilon}_n$ through the mass matrix \underline{m} :

$$m_n^{1/2} \hat{e}_n = \underline{m}^{1/2} \hat{\epsilon}_n. \quad (3.3)$$

We may write the vector \underline{R} in terms of the $\hat{\epsilon}_n$ or the \hat{x}_α ,

$$\underline{R} = \sum_n A_n \hat{\epsilon}_n \equiv \sum_\alpha V_\alpha \hat{x}_\alpha; \quad (3.4)$$

the A_n reduce to their value in Sec. II when all the masses are equal. The motion of the system is given by

$$\underline{y}(t) = \sum_n u_n \hat{\epsilon}_n e^{-i\omega_n t}. \quad (3.5)$$

As before, we choose $\underline{y}(t) \cdot \underline{R}$ as the reaction coordinate and $q = \sum_n |A_n|^2$ as the critical value. Some care has to be taken because the vectors $\hat{\epsilon}_n$ are not orthogonal. Thus, the form of the reaction coordinate is [compare Eq. (2.4)]

$$x(t) = \sum_n B_n u_n e^{-i\omega_n t}, \quad (3.6)$$

where

$$B_n = \sum_{k\alpha} A_k \left(\frac{m_\alpha}{m_k} \right)^{1/2} e_{n\alpha} e_{k\alpha} = \sum_\alpha V_\alpha e_{n\alpha}. \quad (3.7)$$

The analysis proceeds just as before; we find

$$\omega_0^2 = \left(\sum_n \frac{|B_n|^2}{m_n} \right) / \left(\sum_n \frac{|B_n|^2}{m_n \omega_n^2} \right) \quad (3.8)$$

and

$$E_m = \frac{1}{2} \omega_0^2 (\sum_n |A_n|^2) / (\sum_n |B_n|^2 / m_n). \quad (3.9)$$

We need to find the mass dependence of these expressions.

We will assume that the vector \underline{R} is mass independent, i. e., that the V_α 's are mass independent. Consider the numerator of Eq. (3.8). We have that

$$\begin{aligned} \sum_n \frac{|B_n|^2}{m_n} &= \sum_{n\alpha\beta} V_\alpha^* V_\beta \frac{e_{n\alpha} e_{n\beta}}{m_n} \\ &= \sum_{n\alpha\beta} \frac{V_\alpha^* V_\beta}{(m_\alpha m_\beta)^{1/2}} \epsilon_{n\alpha} \epsilon_{n\beta} \\ &= \sum_\alpha \frac{|V_\alpha|^2}{m_\alpha}. \end{aligned} \quad (3.10)$$

The mass dependence in Eq. (3.10) is completely explicit. We may write this result in bra-ket notation as

$$\sum_n \frac{|B_n|^2}{m_n} = \langle \underline{R} | \underline{m}^{-1} | \underline{R} \rangle. \quad (3.11)$$

The denominator of (3.10) can be treated similarly:

$$\begin{aligned} \sum_n \frac{|B_n|^2}{m_n \omega_n^2} &= \sum_{n\alpha\beta} \frac{V_\alpha^* V_\beta}{(m_\alpha m_\beta)^{1/2}} \frac{\epsilon_{n\alpha} \epsilon_{n\beta}}{\omega_n^2} \\ &= \langle \underline{R} | \underline{D}^{-1} | \underline{R} \rangle. \end{aligned} \quad (3.12)$$

Since both \underline{R} and the dynamic matrix \underline{D} are mass independent, the mass dependence of ω_0^2 arises solely from $\langle \underline{R} | \underline{m}^{-1} | \underline{R} \rangle$. Further, since $\sum_n |A_n|^2 = |\underline{R}|^2$, it follows that the migration energy [Eq. (3.9)] is mass independent, as one would suspect.

Thus, if we let the jumping atom ($\alpha = 1 \rightarrow 3$) have mass $m + \delta m$, and call

$$|v_1|^2 = \sum_{\alpha=1}^3 |V_\alpha|^2, \quad (3.13)$$

the change in jump rate is found from

$$\omega_0^2(\delta m) / \omega_0^2(0) - 1 = -(\delta m / m) \Delta K, \quad (3.14)$$

where

$$\Delta K = (|v_1|^2 / |\underline{R}|^2) (1 + \delta m / m)^{-1}. \quad (3.15)$$

The experimentally observed isotope effect for the diffusion constant is equal to the product of ΔK with the correlation factor f . Equation (3.15) shows that ΔK is simply related to the fractional part of \underline{R} that

refers to the jumping atom. We can gain some insight by recasting it in terms of the normal modes. Note that

$$|v_1|^2 = \langle \underline{R} | \Delta K | \underline{R} \rangle, \quad (3.16)$$

where

$$\Delta K = |x_1\rangle\langle x_1| + |x_2\rangle\langle x_2| + |x_3\rangle\langle x_3| \quad (3.17)$$

is a projection operator onto the space of the jumping atom. We see that

$$\frac{|v_1|^2}{|\underline{R}|^2} = \sum_{nk} A_n^* A_k (m + \delta m)(m_n m_k)^{-1/2} \Delta K_{nk} / \sum_n |A_n|^2, \quad (3.18)$$

where

$$\Delta K_{nk} = \langle n | \Delta K | k \rangle = \sum_{\alpha=1}^3 e_{n\alpha}^* e_{k\alpha}. \quad (3.19)$$

It is seen that, in this mode representation, the diagonal elements ΔK_{nn} represent the squared amplitude of the jumping atom in mode n (that is, the fraction of energy in mode n carried by the jumping atom). In particular, if the reaction coordinate were to involve only one mode, ΔK would be determined by the energy sharing in that mode.

There are several things to notice about the above result. First, recall that no assumptions were made about the structure of the eigenvectors, i. e., that they are plane waves or that local modes do or do not occur. Thus, this formal result applies to both the perfect and defective lattices. In fact, the most surprising aspect of Eq. (3.15) is that the isotope effect is dependent only on the form of the reaction coordinate. Since the appropriate reaction coordinate is largely determined by the crystal structure, one thus expects crystals of the same structure to have about the same self-diffusion isotope effect, consistent with experiment.

The especially simple form for ΔK found above is a result of using classical statistics. In a quantitative calculation, quantum statistics should be used since, for the highest frequencies (where the density of states is largest), the occupation numbers are only about 2. In the quantum case, the isotope effect will depend on the frequency spectrum as well as on the form of the reaction coordinate. A recent quantum calculation by Achar¹⁴ using the Slater approximation to Kac's equation, Flynn's reaction coordinate, and realistic phonon spectra has, indeed, given a good quantitative account of the isotope effect in several fcc and bcc metals.

Notice also that both the reaction-rate theory and the above formalism depend on a special direction in phase space. In the rate theory, one looks at the flux of representative points across the saddle-point hypersurface (i. e., along the normal to this surface), while in the dynamic theory one considers

fluctuations in the direction \underline{R} . Each direction in phase space can be associated with an effective mass as in Eq. (3.1), and the isotope effect is determined by the dependence of this effective mass on the mass of the diffusing atom. Since the rate-theory preferred direction corresponds to a single normal mode (the saddle-point dissolution mode), it is only the effective mass of this mode that enters, and ΔK equals the fraction of kinetic energy carried by the jumping atom in this mode. The reaction coordinate of the dynamic theory is, in general, a linear combination of many modes so that ΔK is an average of the energy sharing in these modes [Eq. (3.18)].

The dynamic picture also implies a close connection between the isotope effect and the β factor of the Wirtz-Brinkman¹⁵ theory of thermomigration which measures the fraction of the migration energy that is actually transported across the barrier by a diffusion jump. The classical calculation of β for fcc lattices in Ref. 9 gave about 0.8 for several interatomic potentials; this is just the value of ΔK one finds with the present formalism and Flynn's reaction coordinate.

IV. DISCUSSION

A basic question to be asked of a dynamic theory based on critical fluctuations is whether there exists a "best"-reaction coordinate to be used. Unfortunately, this question cannot be answered as yet. However, some ingredients of a good reaction coordinate are apparent. For example, the relative separation of the jumping atom from the barrier atoms is clearly important. Likewise, the motion of the barrier atoms transverse to the jump direction is significant since the barrier has to open up at just the right time to let the migrating atom through.

One possible way to find a reaction coordinate, provided the effective interatomic potential is known, is to start the system in the saddle-point dissolution mode with very small kinetic energy and follow the backwards jump down the potential hill by integrating the equations of motion.¹⁶ At the bottom, the velocities are reversed, and the resulting positions and velocities are taken as the necessary initial conditions for a jump which determine a unique reaction coordinate. The reaction coordinate so derived depends not only on the potential around the equilibrium and saddle-point configurations, but on the potential in the entire region of phase space traversed during a jump.

To illustrate this method, we carried out a model calculation for a two-dimensional hexagonal lattice, containing a vacancy, with Born-Mayer interactions (the boundary atoms were held fixed). Several interesting results were obtained. First, that part of the reaction coordinate involving displacements

in the jump direction (x axis) was almost precisely the reaction coordinate of Flynn.⁸ Instead of being proportional to $x_1 - \frac{1}{2}(x_2 + x_3)$, where x_1 , x_2 , and x_3 are the x components of position of the jumping atom and ring atoms, respectively, this part of \underline{R} had the factor of $\frac{1}{2}$ replaced by 0.446.

Of course, the total reaction coordinate also involved transverse displacements and initial velocities. We can, however, treat each of the coefficients $|A_n|^2$ as arising from pure displacements, and find an equivalent real \underline{R} . In this procedure, the sign of each A_n is undetermined. This reflects the fact that in a harmonic well of N dimensions, a given direction (not along a mode axis) is equivalent to $2^N - 1$ other directions. Choosing as reaction coordinate the vector that points most directly in the saddle-point direction, we find an equivalent reaction coordinate proportional to

$$x_1 - 0.432(x_2 + x_3) + 0.802(y_2 - y_3).$$

Again, the part dealing with the jump direction is almost the same as Flynn's reaction coordinate. The last term shows the importance of transverse (y -axis) motion; the ring has to open up in order to let the jumping atom through.

This is an important result. It indicates that the simple reaction coordinate suggested by intuition is appropriate even for very anharmonic potentials. This is so because one is actually looking for large fluctuations of kinetic energy near the equilibrium configuration where the harmonic description is valid. The fluctuation involved moves the jumping atom and ring toward each other while opening the ring.

The jump rate was calculated according to both the rate-theory prescription and Eqs. (2.10) and (2.12). The migration energies were slightly different (that of the dynamic approach being about 6% smaller than the rate-theory value), but this may be attributed to the lack of vibrational energy in the hypersurface modes at the beginning of the back jump as suggested in Sec. II. More interesting is the result that the dynamic-theory attempt frequency $\omega_0/2\pi$ was about twice the effective frequency of rate theory given in Eq. (1.1). This is sugges-

tive because rate-theory calculations¹⁷ appear to give too small a value for the effective frequency. If we write the dynamic-theory effective frequency in terms of the rate-theory quantities as in Eq. (4.1) below,

$$\nu_{\text{eff}} = (\omega_0/2\pi) e^{\Delta S_d/k} \simeq \nu e^{(k \ln 2 + \Delta S_r + \Delta S_d)/k}, \quad (4.1)$$

we see that, effectively, we have increased the rate-theoretic motion entropy by several entropy units. Here ΔS_d is the migration entropy of Eq. (2.16), ΔS_r is the migration entropy of rate theory, and ν is the attempt frequency of rate theory.

The physical origin of this difference lies partly in the difference in the preferred directions singled out by rate and dynamic theories. The direction normal to the saddle-point hypersurface involves motion of the barrier atoms only to a very limited degree⁹ so that all modes that move the migrating atom in the jump direction contribute to the jump rate. The dynamic picture, on the other hand, looks for modes that move the jumping atom against the barrier. In a monatomic lattice, only the high-frequency modes are effective in doing this and a higher effective frequency results.

As for the isotope effect, use of Eq. (3.14) leads to values of ΔK in better agreement with experiment than those of Ref. 9. Achar's calculations show that this agreement is made much better by treating the phonons quantum mechanically.

We have shown how the viewpoint that diffusion jumps result from fluctuations along a certain phase-space direction leads directly, classically at least, to simple expressions for the jump rate and the ΔK factor of the isotope effect in terms of the dynamic matrix and the vector \underline{R} . The rate and dynamical theories are analogous in that both pick out a preferred direction in phase space; this choice determines the attack frequency and isotope effect.

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¹S. Glasstone, K. J. Laidler, and H. Eyring, *Theory of Rate Processes* (McGraw-Hill, New York, 1941).

²C. A. Wert and C. Zener, *Phys. Rev.* **76**, 1169 (1949).

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

⁴C. P. Flynn and A. M. Stoneham, *Phys. Rev. B* **1**, 3966 (1970).

⁵S. A. Rice, *Phys. Rev.* **112**, 804 (1958).

⁶O. P. Manley, *J. Phys. Chem. Solids* **13**, 244 (1960).

⁷H. R. Glyde, *Rev. Mod. Phys.* **39**, 373 (1967).

⁸C. P. Flynn, *Phys. Rev.* **171**, 682 (1968).

⁹H. B. Huntington, M. D. Feit, and D. Lortz, *Cryst. Lattice Defects* **1**, 193 (1970).

¹⁰See, for example, the compilation of N. L. Peterson, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968), Vol. XXII, p. 409.

¹¹N. B. Slater, *Theory of Unimolecular Reactions* (Cornell U. P., Ithaca, N. Y., 1959).

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

¹³In what follows we use Greek subscripts to denote atomic masses and Latin subscripts to denote the reduced mass of a normal mode.

¹⁴B. N. N. Achar, *Phys. Rev.* (to be published).

¹⁵K. Wirtz, Z. Physik **44**, 221 (1943); and J. A. Brinkman, Phys. Rev. **93**, 345 (1954).

¹⁶This method was used in Ref. 9 to calculate the fraction of the migration energy carried across the barrier

by the jumping atom.

¹⁷H. B. Huntington, G. A. Shirn, and W. A. Wadja, Phys. Rev. **99**, 1085 (1955).

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Lattice Dynamics of Holmium[†]

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The dispersion relation for the normal modes of vibration of holmium metal at room temperature has been measured by means of slow-neutron inelastic scattering techniques. Phonon frequencies for wave vectors along the principal symmetry directions have been determined and, in addition, some experimental information about the phonon frequencies along the boundaries of the Brillouin zone are reported. The data have been fitted with a Born-von Kármán force model which includes interactions out to the eighth nearest neighbor. The interactions have been assumed to be general (tensor) out to the fourth nearest neighbor and axially symmetric beyond. The model has been used to calculate a frequency distribution function $g(\nu)$, the lattice specific heat, and the corresponding Debye temperature.

I. INTRODUCTION

As part of a program to obtain detailed information about the lattice dynamics of the heavy rare-earth metals, we have made neutron inelastic scattering measurements of the phonon-dispersion relation of holmium at room temperature. Data have been obtained for all six branches of the dispersion relation in the principal symmetry directions. The data obtained along the zone boundaries are less complete than those obtained for Tb, but they are sufficient to permit the evaluation of the force-constant parameters in an eighth-nearest-neighbor model such as was used for Tb.¹ Previous measurements on Ho by Leake *et al.*² are in good agreement with our results where there is an overlap of the two sets of data.

The model fitted to the measured dispersion relation has been used to calculate a frequency distribution function for Ho, and this in turn has been used to calculate a variety of thermodynamic properties. In particular, the lattice specific heat has been calculated and compared with measurements³ to permit the determination of the magnetic contribution to the total specific heat.

II. MEASUREMENTS AND RESULTS

The measurements were carried out at the Oak Ridge high-flux isotope reactor on a triple-axis neutron spectrometer. The majority of the data was obtained with the constant- Q method. For most of the measurements the analyzer was set to accept scattered neutrons with an energy E' corresponding to a frequency of 6 THz (~ 25 meV), although in order

to check the data, some measurements were carried out using scattered neutrons with frequencies of 7.2 and 10 THz. As monochromator and analyzer the (0002) Bragg reflections from two Be crystals were used.

Two samples were studied. Both were irregularly shaped disks grown by the strain-anneal method by Reed of the Oak Ridge National Laboratory Solid State Division. One crystal, about 30 mm in diameter and 3 mm thick, was oriented with the c axis about 45° from the normal to the disk, and measurements in the ab plane were made with this crystal. The second sample, 20 mm in diameter and 6 mm thick, was oriented with the c axis nearly parallel to the normal of the disk, and was used for the remainder of the measurements. For Ho, the lattice parameters at room temperature are $a = 3.577$ and $c = 5.616 \text{ \AA}$.

A selection of measured phonon frequencies in Ho at room temperature is given in Table I, where they are compared to the corresponding frequencies in Tb.¹ The complete results are shown in Figs. 1 and

TABLE I. A selection of measured normal-mode frequencies in Ho and Tb at room temperature (10^{12} cps).

| | Ho | | Tb | |
|--------------|-----------|-----------|--------------|---------------------|
| Γ_6^- | 1.94±0.03 | 1.82±0.03 | Γ_3^+ | 3.40±0.07 3.25±0.04 |
| A_3 | 1.34±0.03 | 1.30±0.02 | A_1 | 2.56±0.04 2.44±0.04 |
| M_4^- | 1.96±0.03 | 1.75±0.03 | M_4^+ | 1.65±0.03 1.59±0.04 |
| | | | M_3^+ | 3.04±0.03 2.90±0.03 |
| M_2^- | 3.08±0.05 | 3.05±0.04 | M_1^+ | 3.05±0.05 2.89±0.04 |
| K_6 | 2.46±0.05 | 2.32±0.04 | | |
| $L_1(A)$ | 1.85±0.07 | 1.78±0.06 | | |