PHYSICAL REVIEW B VOLUME 9, NUMBER 4 15 FEBRUARY 1974

Isotope effect for self-diffusion*

J. J. Burton†

Argonne National Laboratory, Argonne, Illinois 60439

(Received 1 August 1973)

We have calculated the correction factor ΔK to the isotope effect for self-diffusion by computing the normal vibrational frequencies of the defective lattice and applying absolute rate theory. We find for single-vacancy diffusion in face-centered-cubic solids $\Delta K_1 \approx 0.96$, and for divacancy diffusion in argon $\Delta K_2 \approx 0.90$. ΔK_1 for single-vacancy diffusion in body-centered-cubic metals is calculated to be ≈ 0.72 in sodium and ≈ 0.89 in iron. The mass dependence of the isotope effect is also examined. The results of our calculations are compared with experiment.

I. INTRODUCTION

The mass dependence of the self-diffusion coefficient is generally expressed as[1]

$$f\Delta K = \frac{D_\alpha / D_\beta - 1}{(m_\beta / m_\alpha)^{1/2} - 1}, \tag{1}$$

where D_α and D_β are experimental diffusion coefficients of two tracers of the same solute of masses m_α and m_β in the same solvent. f is the correlation factor which is a characteristic of the diffusion mechanism and can be calculated from first principles.[2,3] ΔK is a correction term which arises from the cooperative nature of the jump process.[4–6]

An experimental determination of $f\Delta K$ provides a most important clue to the diffusion mechanism. For instance, a value of 0.78 for $f\Delta K$ for self-diffusion in a face-centered-cubic (fcc) solid strongly indicates a single-vacancy mechanism.[7] However, a knowledge of $f\Delta K$ does not uniquely determine the mechanism, as ΔK is generally unknown. A prior knowledge of ΔK is particularly necessary when the experimental results for $f\Delta K$ depend on temperature and one wishes to fit the data so as to obtain information about the various mechanisms which contribute to diffusion.[8] Therefore, theoretical estimates of ΔK are very useful.

Two closely related theories are widely used to describe self-diffusion in solids: absolute rate theory[9] and dynamical theory.[10,11] Feit[6] has shown that, though the physical interpretations of rate theory and dynamical theory are dissimilar, the two theories lead to identical formal expressions for the diffusion jump frequency. We shall, in this paper, use the rate-theory formalism to calculate ΔK. Estimates of ΔK have been made previously.[12–15] However, ΔK has not been calculated exactly by rate theory; this requires computation of the normal vibrational modes of the defective lattice.

II. THEORY

According to the absolute-rate-theory formulation, the jump frequency is given by[16]

$$\Gamma = \frac{\langle \frac{1}{2}\dot{u}^2 \rangle^{1/2}}{\lambda} \, \frac{Z^s(3N-1)}{Z(3N)}, \tag{2}$$

where Z is the complete quantum-mechanical partition function for the full $3N$ dimensional system of N atoms, Z^s is the partition function for the N atoms with motion constrained to the $(3N-1)$-dimensional hypersurface orthogonal to the path of motion through the saddle point, λ is the de Broglie wavelength of the diffusion atom, $h/(mKT)^{1/2}$, and $\dot{u}$ is the velocity of the diffusing atom in the jump direction. Equation (2) has been used by Franklin[16] to calculate the frequency factor for copper single-vacancy self-diffusion; he obtained good agreement with experiment when anharmonic effects were considered. Assuming that the harmonic approximation is sufficient for calculation of the partition functions, Eq. (2) reduces to a familiar form at high temperature obtained by Vineyard[9]

$$\Gamma = \left(\prod_{i=1}^{3N} \nu_i \Big/ \prod_{i=1}^{3N-1} \nu_i' \right) e^{-\Delta U / kT}, \tag{3}$$

where ν_i are the $3N$ normal vibrational frequencies at equilibrium, ν_i' are the $(3N-1)$ normal frequencies with the system constrained to the $(3N-1)$-dimensional hypersurface orthogonal to the path of motion through the saddle point, and ΔU is the energy difference between the saddle point and the equilibrium position.

Equation (3) for Γ is very convenient for calculating ΔK. Let us call $\Gamma(m_\alpha)$ the value of Γ for a tracer with mass m_α and $\nu(m_\alpha)$ the eigenfrequencies for this mass. (Note that, in general, all of the eigenfrequencies and eigenvectors are mass dependent.) Then

$$\Delta K = \frac{\Gamma(m_\alpha)/\Gamma(m_\beta) - 1}{(m_\beta / m_\alpha)^{1/2} - 1} \tag{4a}$$

$$= \left[\left(\prod_{i=1}^{3N} \nu_i(m_\alpha)/\nu_i(m_\beta) \Big/ \prod_{i=1}^{3N-1} \nu_i'(m_\alpha)/\nu_i'(m_\beta) \right) - 1 \right] \times [(m_\beta / m_\alpha)^{1/2} - 1]^{-1}. \tag{4b}$$

The difficulty in evaluating ΔK is the determination of the eigenfrequencies, ν, in Eq. (4b). Approximate expressions for ΔK have been developed[12-14,17] which avoid calculation of the frequencies. There is no way to assess the accuracy of various approximations for ΔK without direct evaluation of Eq. (4b).

It is not possible to exactly evaluate the normal-mode vibration frequencies in Eq. (4b); however they can be approximated quite accurately. Consider a region containing N atoms imbedded in a rigid crystal. If the N atoms are allowed to vibrate as $3N$ coupled oscillators while the remainder of the crystal is rigid, $3N$ normal vibrational frequencies are obtained. Now move one atom to a diffusion saddle point, and again $3N$ normal frequencies are obtained; one of these, associated with motion through the saddle point, is imaginary and the other $3N-1$, required for the computation of Γ, are positive. These eigenfrequencies for the N-coupled-atom system give an approximation to Γ. As N gets large, the value of Γ becomes more reliable. This approach has been applied previously to the calculation of vacancy-formation entropies, and the method and convergence problems have been thoroughly discussed.[18,19]

III. MODELS

We have used the procedures described above to calculate ΔK for diffusion in argon, copper, sodium, and body-centered-cubic (bcc) iron. The interactions of argon atoms were described by a Lennard-Jones potential. Those of the copper, sodium, and iron atoms were described by a Morse potential. The relaxed positions of the atoms adjacent to the defect were obtained by Burton[20] for argon and by Wynblatt[21] for copper, sodium, and iron. In the defect configuration calculations,[20,21] the relaxations of at least 26 atoms near the defect were considered explicitly.

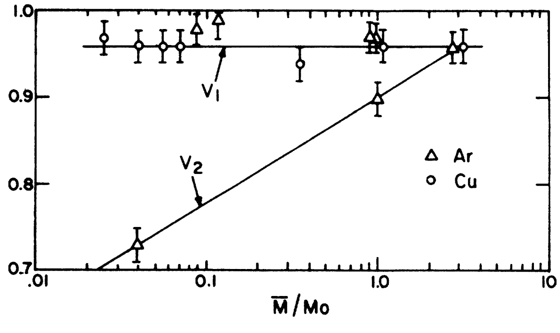

FIG. 1. Calculated ΔK for self-diffusion in argon and copper plotted against $\bar{M}/M_0$, where M_0 is the mass of the lattice atom and $\bar{M}$ is the average mass of the tracer pair. V_1 and V_2 indicate single-vacancy and divacancy mechanisms.

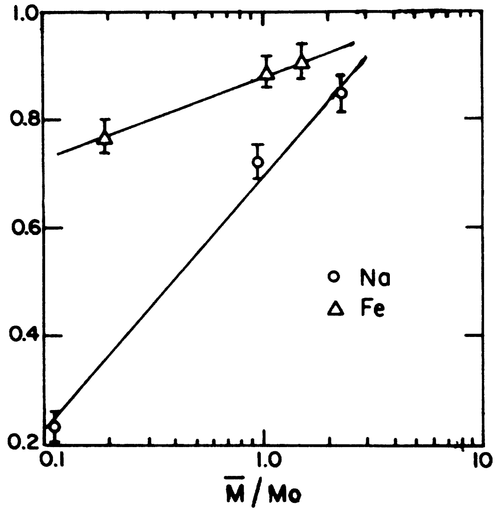

FIG. 2. Calculated ΔK for self-diffusion in iron and sodium by a single-vacancy mechanism.

IV. RESULTS

The calculated values of ΔK are shown in Fig. 1 for the fcc solids, argon and copper, and in Fig. 2 for the bcc solids, sodium and iron. We plot ΔK as a function of $\bar{M}/M_0$, where $\bar{M}$ is the average atomic mass of the isotope pair in Eq. (4) and M_0 is the atomic mass of the host lattice atoms. $\bar{M}/M_0 \approx 1$ corresponds to the normal cases of self-diffusion where all of the available isotopes have similar masses. We show the mass dependence in the figures primarily because of recent discussion of the possible mass dependence of the isotope effect. The uncertainties in ΔK shown in the figures reflect the uncertainty in our calculations of the eigenfrequencies in Eq. (4b); a random error of ±0.001% in the eigenfrequencies gives an uncertainty in ΔK of ±0.01.

In the course of this work, we calculated vibrational eigenfrequencies for both a lattice with an equilibrium defect and with the diffusing atom at the saddle point. These are used to obtain a number of quantities of interest in self-diffusion. Table I gives the effective frequency in Eq. (3)

$$\nu^* = \prod_{i=1}^{3N} \nu_i \Big/ \prod_{i=1}^{3N-1} \nu_i' \qquad (5)$$

ν^* calculated exactly is three to four times larger than predicted by the Einstein approximation. We also list the number of localized modes of the lattice with the atom in the saddle point, as well as the force constant, $k_{\mathrm{s.p.}}$, for the saddle-point decomposition mode. This force constant and ν^* in Eq. (5) were normalized by the frequency $\nu_{\max}$ and the force constant, $k_{\max}$, for the highest-frequency lattice normal modes in order to facilitate comparison of the various materials. We also give

TABLE I. Results of normal-mode calculations on the self-diffusion saddle point. ν^* is the frequency [Eq. (5)], ν_{max} is the maximum lattice frequency, $k_{\mathrm{s.p.}}$ is force constant for the decomposition mode of the saddle point, and k_{max} is the maximum lattice-mode force constant.

Structure	Material	Defect	$(\nu^*/\nu_{\mathrm{max}})$ exact	Number of saddle-point localized modes	$k_{\mathrm{s.p.}}/k_{\mathrm{max}}$	Number of nearest neighbors to diffusing atom in saddle point	Distance of nearest neighbors to diffusing atom in saddle point divided by lattice nearest-neighbor distance
fcc	Cu	V_1	0.36	1	−0.09	4	0.84
	Ar	V_1	0.21	3	−0.07	4	0.92
	Ar	V_2	0.85	1	−0.03	2	0.92
bcc	Na	V_1	0.11	0	−0.005	6	0.97
	Fe	V_1	0.13	0	−0.12	6	0.97

some data in the table regarding the structure of the saddle point.

V. DISCUSSION

Several results are apparent from Figs. 1 and 2 and Table I:

(i) ΔK for the single-vacancy mechanism is nearly unity for all fcc solids and is independent of mass.

(ii) ΔK for the single-vacancy mechanism in bcc solids is material dependent and decreases for low mass isotopes.

(iii) There are very few band-gap vibrational modes associated with the saddle-point configuration in fcc solids and none in bcc.

(iv) The force constant for the decomposition mode of the saddle point is small compared to largest normal-mode force constants. This means that the lifetime of the saddle point is large compared to high-frequency lattice vibrational times, and that the saddle-point configuration can be "thermalized" within its lifetime.

Our values of ΔK can be understood as follows: ΔK can be regarded as proportional to the fraction of the total kinetic energy of the saddle-point decomposition mode associated with the diffusing atom in the saddle point.[4,5] In the extreme case where the jumping atom is completely decoupled from the lattice and the important jump mode is completely localized on the jumping atom, all of the kinetic energy is carried by the jumping atom and $\Delta K \approx 1$. In the other extreme case, where the jumping atom is very well coupled to the lattice, the diffusive jump is highly cooperative involving the simultaneous motion of a very large number of atoms, and the jump rate is independent of the mass of the jumping atom giving $\Delta K \approx 0$.

In the case of the single vacancy in fcc materials, the saddle-point atom is very close to its nearest neighbors (Table I) and the nearest-neighbor force constants are very large compared to usual lattice force constants. Therefore the saddle-point atom is effectively decoupled from the lattice, there are localized modes, and $\Delta K \approx 1$. In the bcc systems, the saddle-point atom is not so close to its neighbors, the diffusing atom is well coupled to the lattice, there are no local modes, and ΔK is reduced.

Our results for the mass dependence of ΔK are difficult to understand. Apparently, less energy is carried by lighter diffusing atoms than by heavy diffusing atoms but we have no simple physical explanation of this result. A similar phenomena has been observed for impurity diffusion in lithium.[22]

Our results for ΔK are compared in Table II with those calculated by other investigators.[12-14] The data in the table indicate theoretical agreement that $\Delta K \approx 0.96$ for the single-vacancy self-diffusion mechanism in any fcc solid. However, for the single-vacancy self-diffusion mechanism in bcc solids, we can only say that ΔK is greater than 0.65 and varies widely from system to system.

These results are in agreement with the limited reliable experimental data available on ΔK, which are also collected in Table II. The problem with most experimental data on the isotope effect is that $f\Delta K$ is measured for only one temperature. Hence, unless the result can be assigned unequivocally to one particular mechanism, as in Pd,[7] it is not possible to reach reliable conclusions on the value of ΔK. If $f\Delta K$ is measured over a wide temperature range, it is possible to fit the experimental data and obtain estimates of diffusion parameters for the (possibly several) operative mechanisms. This has been done by Feit[24] with Mundy's data[25] for self-diffusion in sodium and by Burton[8] with Rothman's data[26] for silver, and the results for ΔK for the single-vacancy mechanism are in the table. The calculated results are in good agreement with experiment.

TABLE II. Values of ΔK.

	Structure	Mechanism	Material or model	ΔK	Reference
Theory					
	fcc	V_1	Ar	0.96 ± 0.02	This work
			Cu	0.96 ± 0.02	This work
			Cu	0.92	14
			Born-Mayer potential	0.98	13
			Ho potential (Ref. 23)	0.98	13
		V_2	Ar	0.90 ± 0.02	This work
	bcc	V_1	Na	0.72 ± 0.02	This work
			Fe	0.88 ± 0.02	This work
			Born-Mayer potential	0.65	13
			Ho potential (Ref. 23)	0.97	13
Experiment					
	fcc	V_1	Ag	≥ 0.90	8, 26
			Pd	1.02 ± 0.04	7
	bcc	V_1	Na	0.65–0.74	24, 25

VI. CONCLUSIONS

We have calculated the correction to the isotope effect, ΔK, for several model systems. We find

(i) For single-vacancy self-diffusion in fcc solids

$$\Delta K = 0.96 \pm 0.02 \ .$$

(ii) For the single-vacancy self-diffusion in bcc iron and sodium

$$1.00 \geq \Delta K \geq 0.65 \ .$$

These results are in good agreement with experiment. We also find

(iii) ΔK can depend on the mass of the diffusing isotopes. In particular in bcc solids and for divancancy diffusion in argon, ΔK is smaller for light isotopes than for heavy isotopes. This result appears to agree with a recent study of impurity diffusion in Li.[22] We also find:

(iv) ΔK for divacancy diffusion in argon is ≈0.90

(v) Absolute rate theory can give values of $\Delta K < 0.5$. (Note light masses diffusing in Na, Fig. 2.)

ACKNOWLEDGMENTS

The author would like to express his appreciation to P. Wynblatt for providing the coordinates for copper, iron, and sodium and to J. N. Mundy for his helpful discussion of the work.

---

*Work performed under the auspices of the U.S. Energy Commission.

†Permanent address: Esso Research and Engineering Co., P. O. Box 45, Linden, N. J. 07036.

[1] N. L. Peterson, Solid State Phys. 22, 409 (1968).

[2] K. Compaan and Y. Haven, Trans. Faraday Soc. 54, 1498 (1958).

[3] R. E. Howard, Phys. Rev. 144, 650 (1966).

[4] J. G. Mullen, Phys. Rev. 121, 1649 (1961).

[5] A. D. LeClaire, Philos. Mag. 14, 2171 (1966).

[6] M. D. Feit, Phys. Rev. B 5, 2145 (1972).

[7] N. L. Peterson, Phys. Rev. A 136, A568 (1964).

[8] J. J. Burton and F. Froozan, Philos. Mag. 27, 473 (1973).

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

[10] S. A. Rice, Phys. Rev. 112, 804 (1958).

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

[12] J. J. Burton, Phys. Rev. B 2, 5010 (1970).

[13] H. B. Huntington, M. D. Feit, and D. Lortz, Cryst. Lattice Defects 1, 193 (1972).

[14] R. C. Brown, J. Worster, N. H. March, R. C. Perrin, and R. Bullough, Z. Naturf. A 26, 77 (1971).

[15] B. N. N. Achar, Phys. Rev. B 2, 3848 (1970).

[16] W. Franklin, Phys. Rev. 180, 682 (1969).

[17] H. R. Glyde, Phys. Rev. 180, 722 (1969).

[18] J. J. Burton, J. Phys. Chem. Solids 33, 589 (1972).

[19] J. J. Burton, Phys. Rev. B 5, 2948 (1972).

[20] J. J. Burton, Phys. Rev. 182, 885 (1969).

[21] P. Wynblatt, J. Phys. Chem. Solids 29, 215 (1968).

[22] J. N. Mundy and W. D. McFall, Phys. Rev. B 7, 4363 (1973).

[23] P. S. Ho, Phys. Rev. 169, 523 (1968).

[24] M. Feit, Philos. Mag. 25, 769 (1972).

[25] J. N. Mundy, Phys. Rev. B 3, 2431 (1971).

[26] S. J. Rothman, N. L. Peterson, and J. T. Robinson, Phys. Status Solidi 39, 635 (1970).