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Anisotropic Isotope Effect for Diffusion of Zinc and Cadmium in Zinc*†

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The sectioning technique and the half-life method of isotope discrimination were used to study the relative rates of diffusion of Zn^{65} and Zn^{69m}, and of Cd^{109} and Cd^{115} in high-purity zinc single crystals. The isotope effect, $E_{\beta}^{\alpha}=(1-D^{\alpha}/D^{\beta})/[1-(m^{\beta}/m^{\alpha})^{1/2}]$, was measured; D^{α}/D^{β} and m^{α}/m^{β} are the ratios of the diffusion coefficients and of the masses of the two isotopes α and β, respectively. The average of the values of E_{69}^{65} at 411.6 and 382.8°C for diffusion of zinc isotopes in zinc, parallel to the hexagonal axis, is 0.669 ± 0.024, whereas the corresponding value perpendicular to the hexagonal axis is 0.687 ± 0.022. These results are consistent with diffusion by vacancy (basal and nonbasal) mechanisms and appear to rule out the interstitial, ring, interstitialcy, and crowdion as the dominant mechanism. The observed isotope effect, both for parallel and perpendicular diffusions, is thus about 13% less than the value predicted on the basis of the inverse-square-root mass dependence of the atomic jump frequency, i.e., the correlation factor for self-diffusion. This deviation is apparently due to many-body aspects of diffusion, and on these considerations it is concluded that a small fraction (about 13%) of the translational kinetic energy of the activated state is possessed by atoms other than the jumping atom. At 410.1°C, the values of E_{115}^{109} for diffusion of cadmium isotopes in zinc, parallel and perpendicular to the hexagonal axis, are 0.507 ± 0.034 and 0.317 ± 0.032, respectively. These values indicate an attractive interaction between the cadmium impurity and the vacancy, the interaction being larger when both of them are in the same basal plane. Under the assumption that the many-body consideration is essentially the same as for self-diffusion, and by making some reasonable simplifying approximations as to how the presence of the impurity influences the vacancy jump, the enhancement of cadmium diffusion over zinc diffusion is examined. It is found that the rapid interchange of the cadmium impurity with the vacancy and the greater density of the vacancies next to the cadmium impurity are both responsible for the enhancement in the diffusivity of cadmium in zinc.

I. INTRODUCTION

THE atomistic approach to the problem of diffusion, based on a variety of postulated mechanisms, has in general yielded a deep insight into the exact processes involved. Basic to the understanding and the interpretation of the diffusion data, therefore, is the atomic mechanism of diffusion which must be assumed or established. The diffusion coefficient D in an isotropic material can be written as

$$D=\tfrac{1}{6}\omega a^{2}f\,, \tag{1.1}$$

where ω is the atomic jump frequency, a the root-mean-square jump distance, and f the Bardeen-Herring[1] correlation factor. The possible values of f lie between zero and unity for mechanisms where the jump of the diffusing atom is correlated with the direction of its preceding jump (as in the vacancy and interstitialcy mechanisms) and it equals unity for the cases where its motion is completely random (as in the interstitial and ring mechanisms). Since the work of Bardeen and Herring,[1] there have been many calculations of the correlation factor for different lattice structures, both isotropic[2,3] and anisotropic,[4-6] particularly for the vacancy-diffusion mechanism. All these calculations express the results as functions of various vacancy or interstitial jump fre-

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[1] J. Bardeen and C. Herring, in *Atom Movements* (American Society for Metals, Cleveland, Ohio, 1951), p. 87.

[2] A. B. Lidiard, Phil. Mag. **46**, 1218 (1955); A. D. LeClaire and A. B. Lidiard, *ibid.* **1**, 518 (1956); K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 786 (1956); **54**, 1498 (1958); J. R. Manning, Phys. Rev. **128**, 2169 (1962).

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[5] H. B. Huntington and P. B. Ghate, Phys. Rev. Letters **8**, 421 (1962).

[6] J. G. Mullen, Phys. Rev. Letters **9**, 383 (1962).

quencies assumed in the model. Only in the case of self-diffusion, however, have the correlation factors been evaluated exactly. Information regarding the mechanisms of diffusion can thus be obtained from an experimental determination of the correlation factor, particularly the one (or ones) pertaining to self-diffusion.

An approach to determine experimentally the correlation factor and hence the mechanisms of diffusion, particularly in metals, was first suggested by Schoen.[7] He pointed out that the correlation factor, both for self-diffusion and impurity diffusion, can be obtained by studying the relative rates of diffusion of two isotopes of the diffusing element. As a matter of fact, at present, the variation of diffusivity with isotopic mass seems to provide the best means of measuring the impurity correlation factors. During the last few years, measurements on the isotope effect in diffusion[8–11] in face-centered cubic (fcc) and body-centered cubic (bcc) materials have been reported in the literature.

The mass dependence in the diffusion coefficient enters mainly through the jump frequency of the diffusing atom and to a small extent through the frequencies pertaining to the jumps of the defect in the neighborhood of the solute. Applying Eyring's reaction-rate theory,[12] Wert[13] and Zener[14] treated the problem of atom jump frequency in interstitial diffusion on a one-body model by means of classical statistical mechanics. Wert[13] showed that the average jump frequency ω is given by

$$\omega = n\nu \exp(-\Delta G/kT)\,, \qquad (1.2)$$

where n is the number of equivalent paths of diffusion from a given site, ν the frequency of small oscillations of the diffusing atom in the direction of the saddle point, ΔG the free energy required to carry the defect from an initial equilibrium position to a saddle point, k the Boltzmann constant, and T the absolute temperature. The mass dependence of the average jump frequency ω enters through the vibrational frequency ν of the diffusing atom which varies as $(m)^{-1/2}$, m being the mass of the jumping atom. Lidiard[15] pointed out that these results are also applicable to diffusion by the vacancy and the interstitialcy mechanisms.

Even though only one atom jumps in the elementary process, the problem of diffusion is essentially a many-body one since the jumping atom is surrounded by other atoms with which it interacts. Vineyard[16] re-examined the diffusion process on the basis of the classical rate theory, emphasizing its many-body character. The vacancy jump was treated as a normal-mode problem in the mass-weighted configurational space of the crystal. The jump frequency, according to this theory, is the ratio of the product of N normal frequencies ν_j of the entire system at the starting point of the transition (with the diffusing atom at its original site and the vacancy at its adjoining site) to the product of $(N-1)$ normal frequencies ν_j' of the system constrained in the saddle-point configuration. It is found that the jump frequency varies as $(m^*)^{-1/2}$, where m^* is an effective mass which is bounded by the smallest and the largest atomic masses in the entire system. In the configuration with the diffusing atom at the saddle point, one of the N normal frequencies, say ν_1', is imaginary and corresponds to an unstable mode. The excitation of this mode results in the migration of the diffusing atom at the saddle point to a new lattice site. This frequency as well as other normal frequencies of the system are, in general, modified on using a tracer of different mass. It is shown that the mass dependence of the effective jump frequency results, however, entirely from the mass dependence of the mode ν_1'.

If several atoms are cooperatively involved in jumping to new sites, the jump frequency is dependent upon both the solvent atoms that jump and the diffusing atom. For example, in the ring mechanism, where a symmetrical ring of n atoms rotates collectively, it is shown[16] that the jump frequency ω varies approximately as $[m+(n-1)m']^{-1/2}$, m' being the average mass of the solvent atoms.

Rice *et al.*[17] have given an alternative approach to the many-body aspect of diffusion in terms of a dynamical theory based on the actual vibrational modes of the atoms. It avoids the requirement that the activated complex be in thermal equilibrium with the lattice. It is assumed in the theory that the elastic waves occasionally superimpose to give proper displacements to the migrating atom and the atoms surrounding the saddle point to permit the jump. It seems difficult to draw any quantitative conclusions about the mass dependence of the jump frequency.

Measurements of the isotope effect for diffusion of zinc and cadmium in single crystals of zinc are reported here. The choice of zinc as the host metal was made, since no work of this nature in an anisotropic medium

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[15] A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 275.

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

[17] S. A. Rice, Phys. Rev. **112**, 804 (1958); S. A. Rice and N. H. Nachtrieb, J. Chem. Phys. **31**, 139 (1959); A. W. Lawson, S. A. Rice, and R. D. Corneluissen, *ibid.* **32**, 447 (1960); S. A. Rice and H. L. Frisch, *ibid.* **32**, 1026 (1960).

has thus far been reported in the literature, and self-[18] and impurity-diffusion[19–21] data in zinc are already available.

II. THEORY

A. Isotope Effect

The magnitude of the isotope effect $E_\beta{}^\alpha$ was defined by Schoen[7] as

$$E_\beta{}^\alpha=[1-D^\alpha/D^\beta]/[1-(m^\beta/m^\alpha)^{1/2}], \quad (2.1)$$

where D^α/D^β and m^α/m^β are the ratios of the diffusion coefficients and of the masses of the two isotopes α and β, respectively.

If the only mass-dependence of the diffusion coefficient lies in the factor $(m)^{-1/2}$, then $E_\beta{}^\alpha$ can only have the value unity. This is indeed the case for interstitial diffusion.[8] However, in mechanisms involving correlation, for example the vacancy mechanism, a deviation from the inverse-square-root mass dependence exists.[9–11] This is due to the increased probability of reversing the solute-vacancy jump for the lighter atom which results in lowering its diffusion coefficient and hence in lowering the magnitude of the isotope effect.

B. Correlation Factors for Vacancy Diffusion in Zinc

For diffusion by vacancy mechanisms in a hexagonal lattice, such as that of zinc, two different jump lengths are involved, depending upon the initial orientation of the vacancy relative to the tracer. The diffusing atom moves through a distance λ_A for the nonbasal jump and λ_B for the basal jump; the lattice parameters a and c are, respectively, λ_B and $2(\lambda_A{}^2-\frac{1}{3}\lambda_B{}^2)^{1/2}$. Huntington and Ghate[5] have calculated the pertinent correlation factors for an impurity which is associated with a neighboring vacancy. With the vacancy and the impurity on adjacent sites in the same basal plane, they defined four different frequencies for the exchange of the vacancy (i) with the impurity, as ω_B; (ii) with either of the two solvent atoms in the same basal plane which are also nearest neighbors of both the vacancy and the impurity, as ω_b; (iii) with either of the two solvent atoms in the adjoining basal planes which are also the nearest neighbors of both the vacancy and the impurity, as ω_a; and (iv) with any of the seven solvent atoms (three in the same basal plane and four in the adjoining basal planes) that are nearest neighbors of the vacancy but not of the impurity, as ω_c. Figure 1 illustrates these jump frequencies and also those mentioned below.

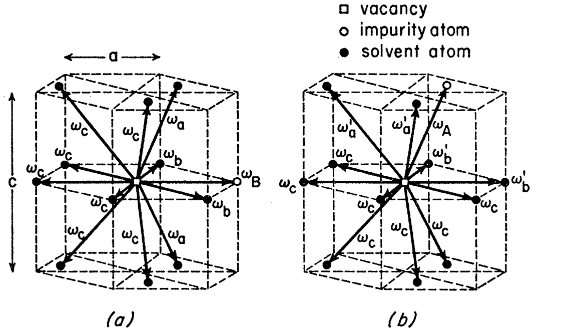

FIG. 1. Frequencies of vacancy-impurity and vacancy-solvent exchanges defined by Huntington and Ghate (Ref. 4) for diffusion in a hexagonal lattice; the vacancy and the impurity atom are on adjacent sites (a) in the same basal plane and (b) in the adjoining basal planes.

Four more frequencies are defined for the vacancy when the impurity happens to be its nearest neighbor in an adjoining basal plane: (i) ω_A refers to its exchange with the impurity; (ii) ω_b' to its exchange with either of the two solvent atoms in the same basal plane as the vacancy which are also nearest neighbors of the impurity; (iii) ω_a' to its exchange with either of the two solvent atoms in the same basal plane as the impurity which are also the nearest neighbors of the impurity; and (iv) ω_c' to its exchange with any of the seven solvent atoms (four in the same basal plane as the vacancy and three in the adjoining basal plane) that are nearest neighbors of the vacancy and not of the impurity.

The model for impurity diffusion in a hexagonal lattice thus employs eight different frequency parameters. Expressions obtained by Huntington[5] and Ghate[5,22] for the impurity correlation factors are reproduced below:

$$f_{A,z}=\frac{2\omega_a'+7F\omega_c'}{2\omega_a'+2\omega_A+7F\omega_c'}, \quad (2.2)$$

$$\lambda_B(f_{B,x}-1)(2\omega_a+\omega_b+7F\omega_c+2\omega_B) \\ =\sqrt{3}\lambda_{A,b}(f_{A,b}-1)\omega_a-2\lambda_B\omega_B, \quad (2.3)$$

$$\sqrt{3}\lambda_B(f_{B,x}-1)\omega_a'-2\lambda_{A,b}\omega_A=\lambda_{A,b}(f_{A,b}-1) \\ [2\omega_a'+3\omega_b'+7F\omega_c'+2\omega_A-\omega_a\omega_a' \\ \times(2\omega_a+3\omega_b+7F\omega_c+\omega_B)^{-1}]. \quad (2.4)$$

The nonbasal jumps contribute to diffusion both parallel and perpendicular to the hexagonal axis, the corresponding impurity correlation factors being $f_{A,z}$ and $f_{A,b}$, respectively; $f_{B,x}$ is the correlation factor for diffusion which results from the basal jumps; $\lambda_{A,b}$ is the projection of λ_A on the basal plane; F is the numerical factor which equals the effective fraction of the dissociated vacancies that do not return once they part company with the diffusing atom. The value of $F(=0.736)$, taken from the calculation[3] of the correlation factor in the fcc lattice, seems reasonable since the coordination

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[18] G. A. Shirn, E. S. Wajda, and H. B. Huntington, Acta Met. **1**, 513 (1953).

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[20] P. B. Ghate, Phys. Rev. **131**, 174 (1963).

[21] A. P. Batra and H. B. Huntington, Phys. Rev. **145**, 542 (1966); **154**, 569 (1967); A. J. Mortlock and P. M. Ewens, *ibid.* **156**, 814 (1967).

[22] P. B. Ghate, Phys. Rev. **133**, A1167 (1964).

number for both the fcc and hexagonal close-packed (hcp) lattices is the same.

Since $\omega_a\omega_a'(2\omega_a+3\omega_b+7F\omega_c+\omega_B)^{-1}$ is small compared with $(2\omega_a'+3\omega_b'+7F\omega_c'+2\omega_A)$ [the former is about 1% of the latter for self-diffusion], Eq. (2.4) can be approximated by

$$\sqrt{3}\lambda_B(f_{B,x}-1)\omega_a'-2\lambda_{A,b}\omega_A =\lambda_{A,b}(f_{A,b}-1)(2\omega_a'+3\omega_b'+7F\omega_c'+2\omega_A). \quad (2.5)$$

C. Vacancy Correlation Factors and the Isotope Effect

When the mass of the tracer atom is changed, the normal frequency of the ν_1' mode, which if excited leads to the passage of the diffusing atom from the saddle point to the new lattice site, is altered. This subsequently affects the jump rates of all atoms sharing the motion in this mode. In general, therefore, the frequencies of exchange of the impurity and the neighboring solvent atoms with the vacancy are altered by a change in the mass of the tracer atom. The fractional change in the diffusion coefficient resulting from isotopic substitution has been investigated by Schoen,[7] by Tharmalingam and Lidiard,[23] and by LeClaire.[24]

1. Diffusion Parallel to the Hexagonal Axis

Only nonbasal vacancy jumps contribute to diffusion parallel to the hexagonal axis. Let B' be the binding free energy between the impurity and the adjacent vacancy in the next basal plane. From the atomistic point of view, the diffusion coefficient[4] $D_{\parallel}$ can be expressed as

$$D_{\parallel}=(c^2/16)\omega_A f_{A,z}p\exp(B'/kT), \quad (2.6)$$

where $f_{A,z}$ is given by Eq. (2.2) and p is the probability that a solvent atom has a vacancy at an adjacent site, either in the basal plane or along the c axis, in an impurity-free region. For self-diffusion, this expression reduces to

$$D_{\parallel,s}=\frac{c^2}{16}\omega_{A,s}f_{A,z:s}p, \quad (2.7)$$

where the subscript s refers to the quantities pertaining to self-diffusion. Letting

$$\omega_a'+7F\omega_c'=u, \quad (2.8)$$

it can be shown[24] that for two isotopes α and β of the same diffusing element

$$\begin{aligned}D_{\parallel}{}^{\alpha}/D_{\parallel}{}^{\beta}-1&=\omega_A{}^{\alpha}f_{A,z}{}^{\alpha}/\omega_A{}^{\beta}f_{A,z}{}^{\beta}-1\\ &=(\omega_A{}^{\alpha}/\omega_A{}^{\beta}-1)[f_{A,z}{}^{\alpha}+(1-f_{A,z}{}^{\alpha})\\ &\quad\times(u^{\alpha}/u^{\beta}-1)(\omega_A{}^{\alpha}/\omega_A{}^{\beta}-1)^{-1}]. \quad (2.9)\end{aligned}$$

If the only frequency affected by isotopic substitution is that of marked atom-vacancy exchange, then $u^{\alpha}=u^{\beta}$, and

$$D_{\parallel}{}^{\alpha}/D_{\parallel}{}^{\beta}-1=f_{A,z}{}^{\alpha}(\omega_A{}^{\alpha}/\omega_A{}^{\beta}-1). \quad (2.10)$$

If $\omega\propto m^{-1/2}$ as predicted by one-body rate theory, then the isotope effect $E_{\parallel}$ from Eq. (2.1) equals

$$E_{\parallel}=(D_{\parallel}{}^{\alpha}/D_{\parallel}{}^{\beta}-1)/[(m^{\beta}/m^{\alpha})^{1/2}-1]=f_{A,z}{}^{\alpha}. \quad (2.11)$$

This expression was first given by Schoen[7] and later derived rigorously by Tharmalingam and Lidiard.[23]

2. Diffusion Perpendicular to the Hexagonal Axis

Both basal and nonbasal vacancy jumps contribute to diffusion perpendicular to the hexagonal axis. Let B be the binding free energy between the impurity and the adjacent vacancy in the same basal plane. The diffusion coefficient[4] $D_{\perp}$ is

$$D_{\perp}=\frac{a^2}{8}\omega_B f_{B,x}p\exp\left(\frac{B}{kT}\right)+\frac{a^2}{24}\omega_A f_{A,b}p\exp\left(\frac{B'}{kT}\right); \quad (2.12)$$

$f_{B,x}$ and $f_{A,b}$ can be obtained from Eqs. (2.3) and (2.5). For self-diffusion, $D_{\perp,s}$ is

$$D_{\perp,s}=\frac{a^2}{8}\omega_{B,s}f_{B,x:s}p+\frac{a^2}{24}\omega_{A,s}f_{A,b:s}p. \quad (2.13)$$

In one-body rate theory, the corresponding isotope effect $E_{\perp}$ is

$$E_{\perp}=(D_{\perp}{}^{\alpha}/D_{\perp}{}^{\beta}-1)/[\omega^{\alpha}(\omega_A{}^{\alpha},\omega_B{}^{\alpha})/\omega^{\beta}(\omega_A{}^{\beta},\omega_B{}^{\beta})-1]. \quad (2.14)$$

Since $(\omega^{\alpha}-\omega^{\beta})$ is small for a small change in the mass of the diffusing atom,

$$\begin{aligned}E_{\perp}&=\frac{1}{D_{\perp}}\left(\omega_A\frac{\partial D_{\perp}}{\partial\omega_A}+\omega_B\frac{\partial D_{\perp}}{\partial\omega_B}\right)\\ &=\frac{1}{D_{\perp}}\left[\frac{a^2}{8}\omega_B\left(f_{B,x}+\omega_A\frac{\partial f_{B,x}}{\partial\omega_A}+\omega_B\frac{\partial f_{B,x}}{\partial\omega_B}\right)p\exp(B/kT)\right.\\ &\quad\left.+\frac{a^2}{24}\omega_A\left(f_{A,b}+\omega_A\frac{\partial f_{A,b}}{\partial\omega_A}+\omega_B\frac{\partial f_{A,b}}{\partial\omega_B}\right)p\exp(B'/kT)\right]. \quad (2.15)\end{aligned}$$

From Eqs. (2.3) and (2.5), we find

$$\frac{\partial f_{A,b}}{\partial\omega_A}=2rf_{A,b}(f_{A,b}-1)\times[\sqrt{3}r\omega_a(f_{A,b}-1)-2\omega_B]G^{-1}, \quad (2.16)$$

$$\frac{\partial f_{A,b}}{\partial\omega_B}=2\sqrt{3}\omega_a'f_{B,x}(f_{A,b}-1)(f_{B,x}-1)G^{-1}, \quad (2.17)$$

$$\frac{\partial f_{B,x}}{\partial\omega_A}=2\sqrt{3}r^2\omega_a f_{A,b}(f_{A,b}-1)(f_{B,x}-1)G^{-1}, \quad (2.18)$$

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[23] K. Tharmalingam and A. B. Lidiard, Phil. Mag. **4**, 899 (1959).
[24] A. D. LeClaire, Phil. Mag. **14**, 1271 (1966).

and

$$\frac{\partial f_{B,x}}{\partial \omega_B}=2f_{B,x}(f_{B,x}-1)\times[\sqrt{3}\omega_a'(f_{B,x}-1)-2r\omega_A]G^{-1}, \quad (2.19)$$

where

$$r=\lambda_{A,b}/\lambda_B \quad (2.20)$$

and

$$G=2\sqrt{3}[r^2\omega_a\omega_A(f_{A,b}-1)+\omega_a'\omega_B(f_{B,x}-1)]-4r\omega_A\omega_B. \quad (2.21)$$

Further, it is evident that

$$\omega_a/\omega_a'=\exp[-(B-B')/kT]. \quad (2.22)$$

Using Eqs. (2.16) to (2.22), Eq. (2.15) reduces to

$$E_\perp=\frac{1}{D_\perp}\left[\frac{a^2}{8}\omega_B f_{B,x}{}^2 p\exp(B/kT)+\frac{a^2}{24}\omega_A f_{A,b}{}^2 p\exp(B'/kT)\right]. \quad (2.23)$$

Thus the isotope effect for diffusion perpendicular to the hexagonal axis is the average of the two correlation factors $f_{B,x}$ and $f_{A,b}$ weighted by the contribution to the total diffusion from basal and nonbasal jumps, respectively.

3. Diffusion in an Arbitrary Direction

The diffusion coefficient $D(\theta)$ in a direction making an angle θ with the hexagonal axis can be written as

$$D(\theta)=D_\parallel\cos^2\theta+D_\perp\sin^2\theta \quad (2.24)$$

$$=\left(\frac{c^2}{16}\cos^2\theta f_{A,z}+\frac{a^2}{24}\sin^2\theta f_{A,b}\right)\omega_A p\exp\left(\frac{B'}{kT}\right)+\frac{a^2}{8}\sin^2\theta f_{B,x}\omega_B p\exp\left(\frac{B}{kT}\right). \quad (2.25)$$

It can easily be shown that the isotope effect $E(\theta)$ is given by

$$E(\theta)=\frac{1}{D(\theta)}\left[\left(\frac{c^2}{16}\cos^2\theta f_{A,z}{}^2+\frac{a^2}{24}\sin^2\theta f_{A,b}{}^2\right)\omega_A p\times\exp\left(\frac{B'}{kT}\right)+\frac{a^2}{8}\sin^2\theta f_{B,x}{}^2\omega_B p\exp\left(\frac{B}{kT}\right)\right]. \quad (2.26)$$

4. Many-Body Effects

Treating the vacancy jump as a normal coordinate problem in the ordinary configurational space of the crystal, LeClaire[24] has recently discussed and reaffirmed the validity of the relation

$$(\omega^\alpha/\omega^\beta-1)/[(m^\beta/m^\alpha)^{1/2}-1]=\Delta K, \quad (2.27)$$

where ΔK represents the fraction of the total kinetic energy in the normal mode of frequency ν_1' that the diffusing atom possesses. This result was first derived by Mullen[9] by extending the analysis of Vineyard[16] using the relation between the displacements along the normal coordinates in the mass-weighted configuration space and the atomic displacements in the ordinary configuration space. The coupling coefficients between the two displacements were taken to be independent of the mass of the diffusing atom which, as LeClaire[24] has pointed out, is questionable.

It is seen from Eqs. (2.1), (2.10), and (2.27) that the isotope effect $E_\beta{}^\alpha$ is

$$E_\beta{}^\alpha=f^\alpha\Delta K. \quad (2.28)$$

The effect of a change in the jump frequencies of the solvent atoms participating in the diffusional jump ($\Delta K<1$), as a result of a change in the mass of the diffusing atom, on the isotope effect has also been considered by LeClaire.[24] It is assumed that the isotopic substitution is more likely to change particularly the jump frequencies of the solvent atoms ($\omega_a,\omega_a',\omega_b,\omega_b'$) which are nearest neighbors of both the vacancy and the diffusing atom whereas its effect on the dissociative jump frequencies (ω_c,ω_c') is probably negligible. If the diffusion occurs by a single monovacancy mechanism in contrast to two monovacancy mechanisms, as is the case for diffusion parallel to the hexagonal axis, it is shown that

$$E_\beta{}^\alpha\simeq f^\alpha\Delta K\left[1+\frac{1}{N}\left(\frac{1}{f^\alpha}-1\right)\left(\frac{1}{\Delta K}-1\right)\times\left(1+\frac{7}{2}F\frac{\omega_c'}{\omega_a'}\right)^{-1}\right], \quad (2.29)$$

where N is the number of nonmigrating barrier atoms which participate in the diffusional jump. For self-diffusion, $E_\beta{}^\alpha$ differs from $f^\alpha\times\Delta K$ by about 0.5%.

III. EXPERIMENTAL

The procedure employed for sample preparation was similar to that described elsewhere.[19] Single crystals, about $\frac{1}{2}$ in. in diameter, were grown by the Bridgman method from 99.999% pure zinc obtained from the American Smelting and Refining Company. After one end of a $\frac{1}{2}$-in.-long specimen cut from the crystalline rod was polished and etched, it was annealed in vacuum at 380°C for at least 30 h to remove any lattice strain remaining from the polishing process.

Radioisotopes Zn^{65} and Zn^{69m} were obtained in the chemical form $ZnCl_2$ from Isoserve, Inc. The radiochemical purity for both isotopes was claimed to be greater than 99%. Radioisotopes Cd^{109} and Cd^{115} in the chemical form Cd $(NO_3)_2$ were obtained, respectively, from New England Nuclear Corporation, and Nuclear Science and Engineering Corporation, the respective radiochemical purity claimed being greater than 99.9% and 98%. The appropriate pair of tracers was deposited on the polished face of the specimen (layer thickness $\approx 0.1\ \mu$) by electroplating[25] with a platinum anode from a high-specific-activity solution containing the two radioisotopes of the same element.

Two plated diffusion specimens, one of parallel and the other of perpendicular orientation, were sealed in an evacuated Pyrex container. A Pyrex flat was placed between their active faces to help reduce the evaporation of the radioisotopes from the surface. The sealed specimens were then placed in a Nichrome-wound furnace for the diffusion anneal. The temperature was controlled to within ±0.2°C and was measured by a Chromel-Alumel thermocouple which was placed immediately adjacent to the diffusion capsule at a height corresponding to the active faces of the specimens. This monitoring thermocouple was calibrated immediately after the anneal against a platinum–platinum-rhodium thermocouple standardized by the U. S. National Bureau of Standards. The temperature gradient in the furnace was sufficiently small that any temperature difference seen by the opposing active faces of the two crystals would produce a negligible effect in the diffusion coefficients. Warm-up corrections were applied in computing the time of the diffusion anneal.

The diffused specimen was mounted on a precision lathe and a circumferential layer $[>6(Dt)^{1/2}]$ was removed to eliminate effects of surface diffusion. About 15 to 20 sections were then turned off from the sample and the lathe turnings from each cut were carefully collected and transferred to preweighed glass counting vials. The sections were weighed on a Mettler balance with a precision of 0.02 mg, and each of them was then dissolved by adding to it 4 ml of 30% HCl.

The counting assembly consisted of a Baird-Atomic all-solid-state spectrometer (model 530), well scintillation detector (model 810C), and a readout printer. The spectrometer consisted of a fast and stable single-channel analyzer, amplifier, scaler, timer, and high-voltage power supply with a stability of 0.03% per day. The detector was $1\frac{3}{4}$-in.-diam×2-in.-thick NaI(Tl) well crystal integrally assembled with a photomultiplier tube. This was completely surrounded by a lead shield, approximately $2\frac{1}{2}$ in. in thickness, for the purpose of reducing the background counting rate. The photomultiplier had a mu metal shield to reduce magnetic field effects.

The counting was done in an air-conditioned laboratory and the counter was kept in continuous operation for the entire experiment. These factors help assure the stabilization of the many temperature-dependent components. The instrument was checked frequently with standard sources to ensure its stability.

Assay of specimens prepared with variable activities but constant isotopic ratio verified that the counting technique gave a ratio independent of the counting rate.

The counting vials fitted snugly into the well, thereby making it possible to recount them with reproducible geometry. In a preliminary experiment, 20 counting vials were picked at random and were examined for reproducibility by putting the same amount of radioactive solution in each of them. The counting rates from these vials overlapped within the counting statistics.

A. Counting Zinc Isotopes

Zn^{65} decays with a half-life of 245 days,[26] emitting γ rays of energy 0.511 and 1.11 MeV; Zn^{69m} decays with a half-life of 13.79 h[27] and with the emission of γ rays of energy 0.438 MeV to the 55-min ground level of Zn^{69}, from which only a β spectrum is emitted. Because of widely dissimilar half-lives of the two isotopes, the half-life method of isotope discrimination was employed to determine their relative concentration. The counting was started at least 10 h after the end of the diffusion anneal, during which Zn^{69m}–Zn^{69} equilibrium was established.

The activity of the sections was measured three times for each specimen at an interval of about 14 h by counting integrally the γ rays emitted by both isotopes. In case of three specimens, the bias discriminator was set at 320 keV and for the fourth at 160 keV. The first five or six sections were "hot" and a known fraction of each of these sections was, therefore, counted to reduce the large coincidence losses which would have been encountered otherwise. This, of course, did not affect the isotopic ratio and the pipetting could be performed accurately enough to obtain a good value of the specific activity of Zn^{69m}. The counting time for each specimen was about 2 h.

About 2 weeks were allowed to elapse in order to allow the activity of Zn^{69m} to decay to negligible proportions (by a factor of 10^5). Recounting was done twice for each section at an interval of about 15 days to obtain Zn^{65} activity. The counting usually required about five hours. At least 300 000 counts were collected for most of the sections and for each of the isotopes, giving a statistical uncertainty of 0.18%.

The counting rates were corrected for the dead-time losses. The dead-time was found to depend on the setting of the discriminator level as well as the spectrum being measured; that is, on the relative abundance of the two isotopes in the mixture. Therefore, it was found essential to measure the dead time of the counting assembly before and after each sample was counted, using the

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[25] *Modern Electroplating*, edited by F. A. Lowenheim (John Wiley & Sons, Inc., New York, 1963).

[26] *Nuclear Data Sheets*, compiled by K. Way *et al.* (National Academy of Sciences–National Research Council, Washington, D. C., 1963).

[27] S. J. Rothman (private communication).

sections being measured. For example, the dead-time for integral counting from 320 keV was found to be 2.00 ± 0.16 μsec, and from 160 keV, (1.69 ± 0.17) μsec for the pure Zn^{65} isotope. With higher proportions of Zn^{69m}, higher values for the dead time were obtained. During the very first counting, it was measured to be 2.7 μsec and 2.1 μsec, respectively, for the two different discriminator levels.

To obtain the Zn^{69m} activity, each count of Zn^{65} was combined with the corresponding count of Zn^{65} plus Zn^{69m}. Using the equation

$$N=N^{65}\exp(-\lambda^{65}t)+N^{69}\exp(-\lambda^{69}t)\,, \tag{3.1}$$

where N is the measured activity at time t and λ^{65} and λ^{69} are the decay constants for Zn^{65} and Zn^{69m}, respectively, the isotopic contributions N^{65} and N^{69} were calculated.

The data were also corrected for background and the decay of Zn^{69m} during the counting time. For the last group of sections, the latter correction was about 6%. All the sections were normalized to the starting time of counting.

B. Counting Cadmium Isotopes

Cd^{109} decays with a half-life of 470 days[26] to 41-sec Ag^{109m}. The emitted radiation consists of 22-keV x rays and 88-keV γ rays. The 2.33-day half-life Cd^{115} isotope[26] decays to 4.5-h In^{115m} isotope. Besides x rays and β rays, a number of γ rays (lowest energy: 0.335 MeV) are emitted during the decay of Cd^{115}. The isotope Cd^{115} was obtained by neutron bombardment $[Cd^{114}(n,\gamma)Cd^{115}]$ of Cd^{114} and in the process, a small quantity of 43-day half-life Cd^{115m} isotope (about 1 to 2%) was also produced.

The half-life method of isotope discrimination was used to determine the concentrations of Cd^{109} and Cd^{115}. The counting was started about two days after the end of the diffusion anneal during which the radioactive equilibrium was established to within 0.1%.

In counting Cd^{115} plus Cd^{115m} activity in each section, base-line discrimination was employed to suppress all radiation of energy less than 250 keV; γ rays of energy greater than 250 keV were counted. The counting time for each sample was about 6 h. In this energy range, there was no contribution from Cd^{109}. About a month was allowed to elapse in order to let the activity of Cd^{115} decrease by a factor of 10^5. By counting these sections once again, the residual activity due to Cd^{115m} was determined and then subtracted from the Cd^{115} plus Cd^{115m} counts to obtain the Cd^{115} activity.

The Cd^{109} plus Cd^{115m} activity in each section was determined by counting differentially γ rays in the energy range 50–120 keV. The counting time for each sample was about 12 h. By finding the relative activity in various energy ranges from a pure Cd^{115m} source, small corrections were applied to the measured Cd^{109} plus Cd^{115m} counts to obtain Cd^{109} activity.

About 100 000 counts from each slice and for each isotope were taken giving a statistical uncertainty of 0.32%.

The counting rates were corrected for dead-time losses, background, and the decay of Cd^{115} during the time of counting.

IV. RESULTS

Since the two radioisotopes of the same diffusing element were co-deposited in the form of a thin layer on the end face of the crystal, the concentration N^α of the tracer atoms of the isotope α at a perpendicular distance x from the active layer is given by[28]

$$N^\alpha=[N_0{}^\alpha/(\pi D^\alpha t)^{1/2}]\exp(-x^2/4D^\alpha t)\,, \tag{4.1}$$

where t is the time of the diffusion anneal, D^α the diffusion coefficient, and $N_0{}^\alpha$ the concentration of the tracer α originally present in the radioactive layer. The diffusion coefficient can thus be determined from the slope of the straight line resulting from the plot of $\ln N^\alpha$ versus x^2. The diffusion coefficients parallel and perpendicular to the hexagonal axis, $D_{\parallel}$ and $D_{\perp}$, can then be calculated from Eq. (2.24) by measuring $D(\theta)$ for two different orientations.

Considering both isotopes α and β and using Eq. (4.1), one finds

$$\begin{aligned}\ln(N^\beta/N^\alpha)&=\text{constant}-(D^\alpha/D^\beta-1)(x^2/4D^\alpha t)\\&=(\text{constant})'+(D^\alpha/D^\beta-1)\ln N^\alpha.\end{aligned} \tag{4.2}$$

If $\ln(N^\beta/N^\alpha)$ is plotted versus $\ln N^\alpha$ for different penetration depths and a straight line is drawn through the resulting points, the slope of the line will give $(D^\alpha/D^\beta-1)$.

A. Diffusion of Zinc Isotopes

The isotope effect in the self-diffusion of zinc was measured in four single crystals, two of which were of parallel orientations (angle between the specimen axis and hexagonal axis being 12°) and the other two of perpendicular orientations (angle between the specimen and the hexagonal axes being 86°). Two samples, one of parallel and the other of perpendicular orientation, were annealed at 411.6°C and the other two at 382.8°C.

The plots of ln (specific activity) versus (penetration distance from the origin)^2 are shown in Fig. 2. In all the diffusion profiles, there was no indication of evaporation from the sample surface; there was, however, an evidence of negligibly small amount of excess activity left on the surface of the specimen during the diffusion anneal, since the first point usually lies slightly above the line drawn through the points far removed from the sample surface. The diffusion coefficients were also measured in four more single crystals. Their values and the corresponding annealing temperatures are listed in

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[28] J. Crank, *Mathematics of Diffusion* (Clarendon Press, Oxford, England, 1956).

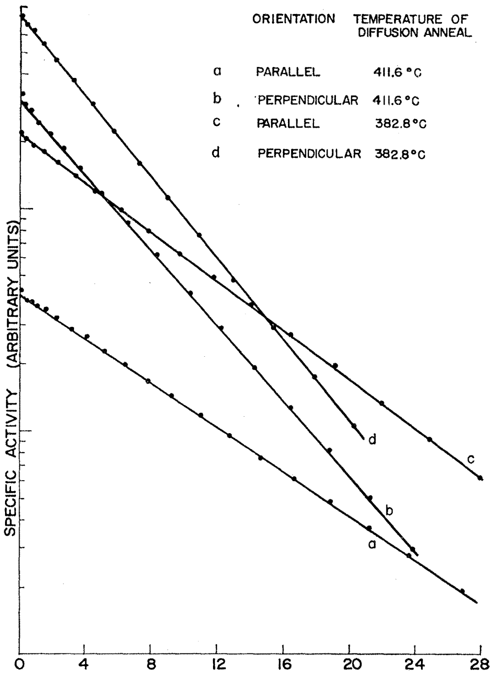

FIG. 2. Penetration profiles for diffusion of Zn^{65} in zinc.

TABLE I. Diffusion of Zn^{65} and Cd^{109} in zinc.

Solute	Diffusion temperature (°C)	$D_{\parallel}$ (cm²/sec)	$D_{\perp}$ (cm²/sec)
Zn^{65}	411.6	1.33×10^{-8}	7.90×10^{-9}
	404.8	1.13×10^{-8}	6.91×10^{-9}
	382.8	6.10×10^{-9}	3.69×10^{-9}
	352.2	2.89×10^{-9}	1.90×10^{-9}
Cd^{109}	410.1	3.12×10^{-8}	3.39×10^{-9}
	343.7	6.11×10^{-9}	6.71×10^{-9}

Table I. The present data and the earlier measurements[18] on the self-diffusion in zinc are shown in Fig. 3. The present results for diffusion parallel to the hexagonal axis are about 10% lower than those from earlier measurements. It seems, however, that the activation energy for parallel diffusion can be trusted. For diffusion perpendicular to the hexagonal axis, the value of diffusion coefficient is lower by as much as 20% at 410°C and 7% at 355°C. These values seem to indicate that the activation energy for perpendicular diffusion is less than that reported earlier.

Figures 4 and 5 show the computer-fitted plots of $\ln(N^{65}/N^{69})$ versus $\ln N^{69}$ for diffusion of zinc in two of the four single crystals. A and B refer to the two orientations, parallel and perpendicular, respectively. The first number refers to the first or second count of Zn^{65} and the second to the first or second or third count of Zn^{69m}. The scale for $\ln(N^{65}/N^{69})$ is the same for all the curves; only the zero position has been shifted for each of them. The fractional change in the diffusion coefficient, $(1-D^{69}/D^{65})$, and the isotope effect, $E_{69}{}^{65}$, together with their least-squares standard deviations are listed in Table II for each of the four specimens.

B. Diffusion of Cadmium Isotopes

The isotope effect for the diffusion of cadmium in single crystals of zinc was measured at 410.1 and 343.7°C.

The concentration-depth curves are shown in Fig. 6.

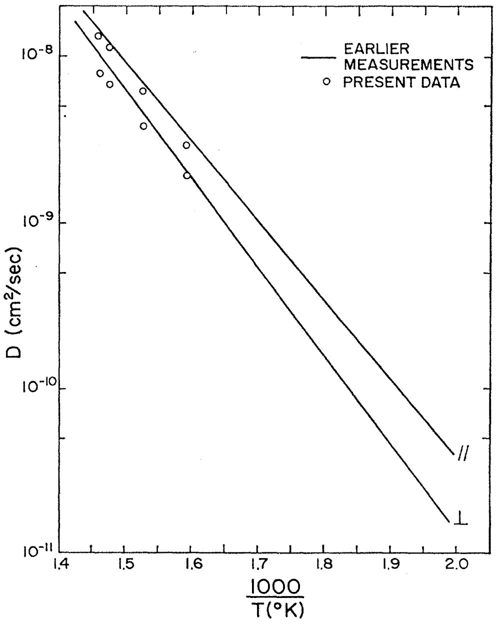

FIG. 3. LnD versus $1000/T$ plotted for self-diffusion in zinc.

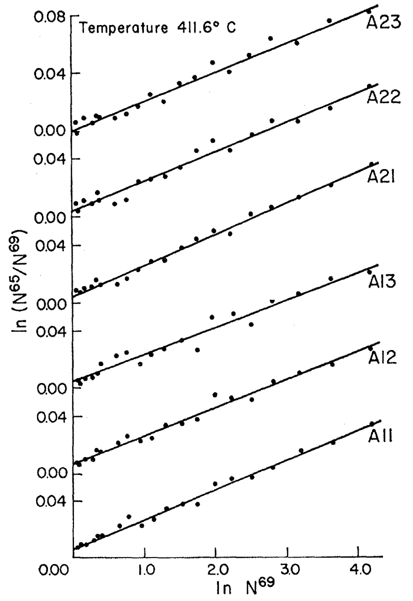

FIG. 4. Diffusion of Zn^{65} and Zn^{69m} in zinc; orientation: parallel.

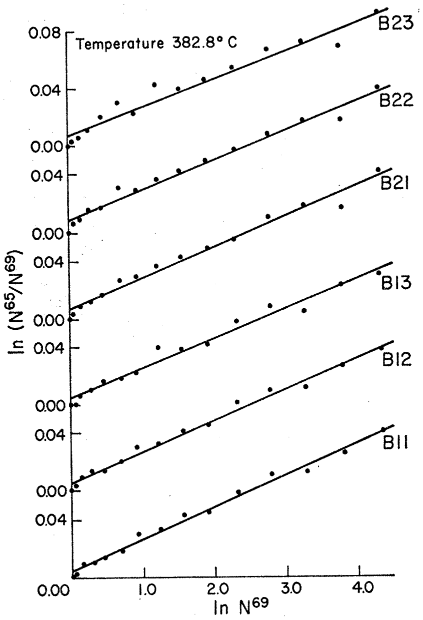

FIG. 5. Diffusion of Zn^{65} and Zn^{69m} in zinc; orientation: perpendicular.

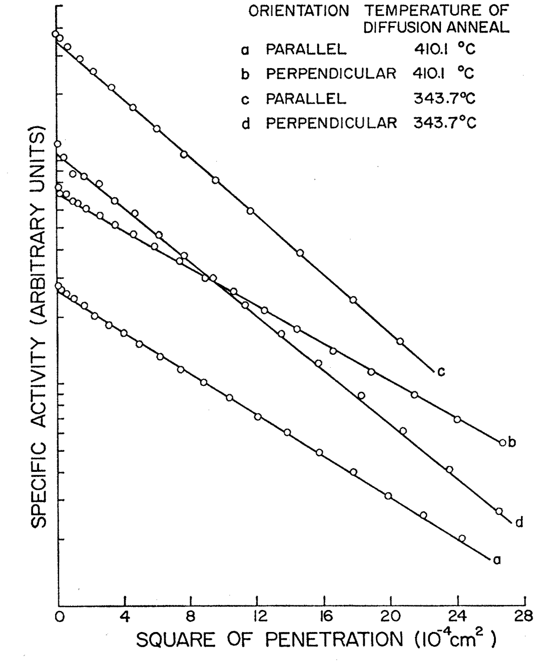

FIG. 6. Penetration profiles for diffusion of Cd^{109} in zinc.

Some activity was left on the specimen surface during the diffusion anneal, particularly at the low temperature. This is probably due to the fact that cadmium has a low solubility in zinc. The values of the diffusion coefficients are given in Table I. These are in very good agreement (within 3%) with the earlier measurements[20] on anisotropic diffusion of cadmium in zinc.

The linear curves obtained by plotting $\ln(N^{109}/N^{115})$ versus $\ln N^{115}$ for cadmium-diffusion are shown in Fig. 7. A least-squares fit to the data allowed the fractional change in the diffusion coefficient, $(1-D^{115}/D^{109})$, to be measured directly. The results of the individual samples are summarized in Table III.

TABLE II. Diffusion of Zn^{65} and Zn^{69m} in zinc.

Temperature (°C)	Orientation	Zn^{65} Count	Zn^{69m} Count	$(1-D^{69}/D^{65})$	$E_{69}{}^{65}$
411.6	Parallel	1	1	0.0208±0.0006	0.705±0.019
		1	2	0.0198±0.0006	0.673±0.021
		1	3	0.0190±0.0008	0.646±0.029
		2	1	0.0214±0.0005	0.728±0.016
		2	2	0.0207±0.0008	0.703±0.027
		2	3	0.0203±0.0008	0.689±0.029
		Average[a]		0.0203±0.0007	0.691±0.023
411.6	Perpendicular	1	1	0.0198±0.0003	0.672±0.010
		1	2	0.0207±0.0005	0.702±0.017
		1	3	0.0186±0.0005	0.632±0.015
		2	1	0.0197±0.0003	0.669±0.012
		2	2	0.0206±0.0005	0.699±0.016
		2	3	0.0185±0.0005	0.628±0.017
		Average		0.0196±0.0004	0.667±0.015
382.8	Parallel	1	1	0.0200±0.0005	0.680±0.016
		1	2	0.0186±0.0006	0.634±0.019
		1	3	0.0178±0.0007	0.606±0.023
		2	1	0.0203±0.0007	0.689±0.024
		2	2	0.0191±0.0009	0.648±0.030
		2	3	0.0182±0.0012	0.619±0.041
		Average		0.0190±0.0008	0.646±0.025
382.8	Perpendicular	1	1	0.0221±0.0006	0.750±0.022
		1	2	0.0216+0.0006	0.733±0.021
		1	3	0.0204±0.0009	0.694±0.031
		2	1	0.0211±0.0009	0.717±0.031
		2	2	0.0205±0.0009	0.695±0.031
		2	3	0.0191±0.0012	0.651+0.042
		Average		0.0208±0.0009	0.707±0.029

[a] Average $E_{\parallel,a}$ and $E_{\perp,a}$ are 0.669±0.024 and 0.687±0.022, respectively.

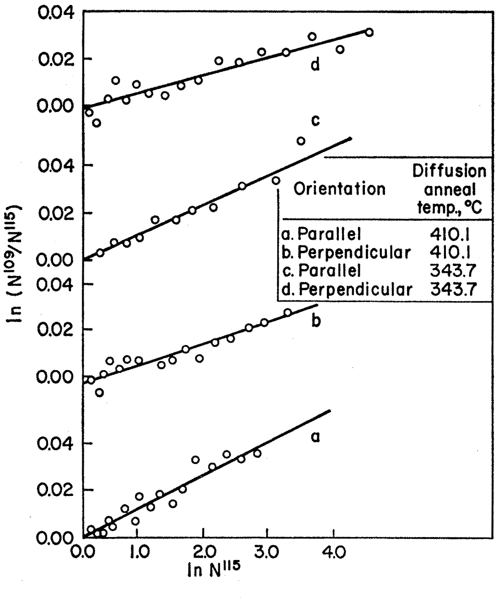

FIG. 7. Diffusion of Cd^{109} and Cd^{115} in zinc.

TABLE III. Diffusion of Cd^{109} and Cd^{115} in zinc.

Diffusion temperature (°C)	Orientation	$(1-D^{115}/D^{109})$	$E_{115}{}^{109}$
410.1	Parallel	0.0134 ± 0.0009	0.507 ± 0.034
410.1	Perpendicular	0.0084 ± 0.0008	0.317 ± 0.032
343.7	Parallel	0.0119 ± 0.0006	0.449 ± 0.023
343.7	Perpendicular	0.0072 ± 0.0009	0.273 ± 0.034

C. Errors in the Diffusion Coefficient

The temperature of the diffusion anneal could be specified to within ±0.4°C. This would introduce an error of ±1% in D at 400°C. The error in the penetration depth which is a cumulative result of errors in the measurements of the area of the sample face, mass of the section, uncertain thickness of the first cut, and misalignment of the sample during sectioning is estimated to be ±1.5%. It is seen from Eq. (4.1) that this would contribute an error of ±3% in D. The error introduced in D due to warm-up correction, air-quenching of the sample after the diffusion anneal, and counting is probably no more than ±0.5%. Considering all these errors together, it is believed that the uncertainty in the measurement of $D(T)$ from random causes is typically ±4%.

D. Errors in the Isotope Effect

It is evident from Eq. (4.2) that the determination of $(D^\alpha/D^\beta-1)$ and hence the isotope effect involves only the weighing and counting of each section cut from the sample. Since both isotopes were diffused simultaneously in the same crystal, all errors resulting from variation of specimen history, time and temperature of diffusion anneal were eliminated. The error in weighing each section is estimated to be less than 0.5%, which would correspond to even a smaller error in the isotope effect. The statistical errors as a result of a finite number of counts is 0.18% for diffusion of zinc isotopes and 0.32% for diffusion of cadmium isotopes. For a counting rate of 10^6 counts/min, the error resulting from the uncertainty in the dead time of the counting assembly is estimated to be less than 0.5%. For slices of lower activity, this error is still smaller and is much less for N^β/N^α.

The maximum correction for the decay of short half-life radioisotope during counting was about 10%. A 1% error in its half-life would result in a maximum error of 0.1% in the ratio N^β/N^α.

The standard deviation in the slope $(D^\alpha/D^\beta-1)$, as a result of scatter in the data, is typically 3.5% for diffusion of zinc isotopes and 10% for diffusion of cadmium isotopes. This seems to exceed the errors we assign to the measurements. There may, therefore, be some other causes for error which produce scatter in the data as we go from one section to another. The possible causes, in case of cadmium diffusion, could be absorption of low-energy γ rays in the counting of Cd^{109} and the correction applied to the data because of the presence of a small quantity of Cd^{115m} in the isotopic mixture of radio-cadmium.

The presence of very small amounts of radioactive impurities which diffuse at a rate different from that of the tracer seems to be a likely source of systematic error. In fact, for diffusion of zinc isotopes, a decrease in the isotope effect is generally observed for common Zn^{65} counts and successively different Zn^{69m} counts. The Zn^{69m} activity was observed to decay by a factor of 4 to 5 during this time. This seems to indicate that a fast diffusing impurity was counted with Zn^{69m}. This source of error appears to be quite significant and might have decreased the average value of the isotope effect by as much as 4%.

V. DISCUSSION

A. Diffusion of Zinc Isotopes

1. *Self-Diffusion Data*

From the earlier measurements[18] on the self-diffusion in zinc, where the activation energies for diffusion parallel and perpendicular to the hexagonal axis were found to be 21.8 and 24.3 kcal/mole, respectively, it was concluded that a nonbasal vacancy plus a basal vacancy (or a basal 3-ring) diffusion mechanism could explain the experimental data. The analysis consisted in comparing the experimentally observed diffusion anisotropy with that calculated for different diffusion mechanisms. It should be pointed out that a unique specification of diffusion mechanisms is possible only to within sets of mechanisms which have different jump vectors.

Figure 3, which includes the present work and the earlier measurements[18] as well, indicates disagreement near the high-temperature end of the Arrhenius plot of D versus $1/T$. The plots of $D_{\parallel}$ and $D_{\perp}$ are probably less inclined to each other, and the corresponding activation energies seem closer to the one for diffusion parallel to the hexagonal axis. Since the penetration data for the present work show almost no scatter over the entire diffusion length, it seems reasonable to conclude that there is probably much smaller dependence of the diffusion anisotropy on temperature. Under these circumstances, some of the mechanisms disproved earlier (nonbasal vacancy with either interstitialcy or 4-ring, etc.) would also be able to explain the data, and the task of resolving experimentally the diffusion mechanisms from the self-diffusion data would become difficult. More measurements, however, are needed to confirm this. It may be mentioned that the impurity-diffusion data in zinc has always been satisfactorily interpreted and explained in terms of basal and nonbasal vacancy mechanisms.

The correlation factors for self-diffusion, assuming a vacancy mechanism, depend upon the ratio of the basal and nonbasal jump frequencies. The present data indicate this ratio, $\omega_{B,s}/\omega_{A,s}$, to be about 0.73. The correlation factors, $f_{A,z:s}$, $f_{A,b:s}$, and $f_{B,x:s}$, turn out to be

0.761, 0.753, and 0.805, respectively; the corresponding values[22] from earlier measurements[18] are 0.777, 0.775, and 0.784, respectively, at 393.4°C.

2. *Isotope-Effect Data*

It is evident from Table II, which lists the average of six independent values of $(1-D^{69}/D^{65})$ and $E_{69}{}^{65}$, that the observed isotope effect for both parallel and perpendicular diffusions is the same within the experimental errors.

If a single mechanism is responsible for diffusion, then from Eq. (2.10)

$$1-D^{\alpha}/D^{\beta}=f^{\alpha}(1-\omega^{\alpha}/\omega^{\beta})\,. \tag{5.1}$$

It is assumed here that the isotopic substitution alters only the jump frequency of the tracer atom. Since f is known for various mechanisms of diffusion, the value of $(1-D^{69}/D^{65})$ for each one of them can be calculated from Eq. (5.1), assuming inverse-square-root mass dependence for the jump frequency. These values are listed in Table IV.

It is possible to infer the diffusion mechanisms by comparing the experimental values of $(1-D^{69}/D^{65})$ with the corresponding values calculated theoretically. It can be seen from Tables II and IV, that exchange, interstitialcy, 3-ring, and 4-ring mechanisms predict values which are too low, and interstitial mechanism one which is too high for $(1-D^{69}/D^{65})$ to be compatible with the experimental results. Any of these mechanisms cannot, therefore, be responsible for self-diffusion in zinc. The mechanisms where many atoms jump simultaneously (crowdion, relaxion) are also ruled out because they predict even smaller values for $(1-D^{69}/D^{65})$. The observed values, however, are slightly lower than, but come closest to, the values calculated for the vacancy (basal and nonbasal) mechanisms. The explanation of this discrepancy is almost certainly based on the many-body aspects of diffusion which lowers the value of $(1-D^{69}/D^{65})$. It is, therefore, concluded that the experimental results are consistent with diffusion by the basal and nonbasal vacancy mechanisms and appear to rule out substantial contribution from other mechanisms.

It may be pointed out in passing that the theoretical approach of Prigogine and Bak,[29] which predicts m^{-2} dependence for the jump frequency and which has been repudiated by all of the few measurements reported in the literature so far, is in drastic disagreement with the present work as well.

TABLE IV. Theoretical values of $(1-D^{69}/D^{65})$ for diffusion of zinc in zinc.

Diffusion mechanism	$(1-\omega^{69}/\omega^{65})$	f	$(1-D^{69}/D^{65})$
Interstitial	0.0294	1	0.0294
Vacancy (basal and nonbasal)	0.0294	0.78[a]	0.0229
Vacancy—basal	0.0294	0.76[b]	0.0223
—nonbasal	0.0294	0.79[b]	0.0232
Exchange	0.0150	1	0.0150
Interstitialcy	0.0150	~0.8	~0.0120
3-ring (basal and nonbasal)	0.0101	1	0.0101
4-ring	0.0076	1	0.0076

[a] Reference 22.
[b] Present work.

LeClaire[24] has recently made a primary contribution in the understanding of the isotope effect in diffusion and we apply his ideas in the interpretation of the data. Equation (2.28) indicates that when the surrounding host atoms participate in the motion during the diffusional jump of the migrating atom ($\Delta K<1$), the isotope effect should be less than that predicted on one-body model. ΔK has been interpreted as the fraction of the kinetic energy associated with the ν_1' mode which the diffusing atom possesses. The atoms around a vacancy are relaxed and drawn inwards. During the vacancy-tracer exchange, the neighboring atoms continuously rearrange themselves and after the exchange is completed, they take up new relaxed positions around the site vacated by the diffusing atom. In order to accomplish this, kinetic energy is supplied by the ν_1' mode, excitation of which leads to the passage of the diffusing atom to the new lattice site and the movement of the neighboring host atoms to their new relaxed positions. Therefore, in the vacancy mechanism, the total kinetic energy of the ν_1' mode is shared between the diffusing atom and the neighboring host atoms, particularly the barrier atoms, and $\Delta K<1$.

On a one-body model, the isotope effect parallel to the hexagonal axis should equal $f_{A,z}$ as shown in Eq. (2.11) and that perpendicular to the hexagonal axis for self-diffusion (call it $f_{\text{basal}:s}$) can be calculated from Eq. (2.23) with $B=B'=0$. The values of $f_{A,z:s}$ and $f_{\text{basal}:s}$ from the present work are 0.76 and 0.79, respectively, the corresponding values for ΔK from Eq. (2.28) and the average values of the observed isotope effect are 0.88 ± 0.03 and 0.87 ± 0.03, respectively; $f_{A,z:s}$ and $f_{\text{basal}:s}$, on the basis of the earlier measurements[18] on the self-diffusion, both equal 0.78[22] and ΔK turns out to be 0.86 ± 0.03 and 0.88 ± 0.03, respectively. The correction term in the isotope effect due to a change in the associative jump frequency on isotopic substitution from Eq. (2.28) is negligible. From the numbers for ΔK mentioned above it seems, therefore, that there is no anisotropy in ΔK. However, it may be mentioned that in a hexagonal structure with close-packing ($c/a=1.63$), one would expect same ΔK for diffusion both parallel and perpendicular to the hexagonal axis since both vacancy jumps (basal and nonbasal) have similar environments. However, in a zinc lattice ($c/a=1.86$) for a basal jump with no relaxation around a vacancy, four atoms form a kite-like figure around the saddle point and the jump direction is orthogonal to the plane of the barrier atoms; for a nonbasal vacancy jump, the four atoms are situated at the corners of a rectangle and the jump direction

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[29] I. Prigogine and T. A. Bak, J. Chem. Phys. 31, 1368 (1959).

makes an angle of about 6° with the normal to the plane containing the barrier atoms. The dissimilarity in the environments of the two jumps might result in a small anisotropy in ΔK, since both basal and nonbasal vacancy jumps contribute to the perpendicular diffusion, whereas only the nonbasal jumps are responsible for parallel diffusion.

Recently an empirical relation has been found to exist between ΔK and the formation volume of the defect[11,24]; no experimental data on the latter are available to confirm it for zinc.

B. Diffusion of Cadmium Isotopes

1. *Isotope-Effect Data*

In Table V, the theoretical values for $(1-D^{115}/D^{109})$ calculated from Eq. (5.1) are given for various diffusion mechanisms. These values, as in other impurity isotope-effect studies, are single valued for uncorrelated mechanisms (interstitial, ring). For correlated mechanisms (vacancy, interstitialcy), only an upper limit can be set for these values since the correlation factor can take on any value between zero and unity. Comparison of the experimental values for $(1-D^{115}/D^{109})$ listed in Table III with the corresponding values for various diffusion mechanisms given in Table V, makes it evident that an unambiguous identification of mechanisms for diffusion cannot be made. It appears, therefore, that the isotope-effect studies for cadmium diffusion are rather inconclusive in so far as their inferences about the operating mechanisms are concerned. However, the present studies of isotope effect in self-diffusion and the convincing interpretation of the impurity-diffusion[19–21] data lend confidence to the assumption that the basal and nonbasal vacancy mechanisms are operating and are responsible for diffusion of cadmium in zinc. The cadmium isotope-effect data are not in conflict with this assumption.

2. *Cadmium Impurity-Vacancy Binding Energy*

The binding energy of a vacancy to an impurity atom is defined as the difference between the energy of formation of the vacancy in the pure solvent and that same energy when the solvent atom removed is a nearest neighbor to the impurity atom. There are two important contributions to the binding energy, namely, the change in the strain energy around the impurity and the electrostatic interaction between the vacancy and the impurity. In this work on diffusion of cadmium in zinc, the size of the cadmium atom is larger than that of the host atom[30] and the strain introduced due to this mismatch can be relieved if a vacancy happens to be at a site adjacent to the cadmium atom. Thus the vacancy is likely to be bound to the cadmium atom which is bound substitutionally in zinc matrix. It is possible to calculate the contribution due to the electrostatic bonding of the vacancy to the impurity if the potential around the impurity atom is known.

TABLE V. Theoretical values of $(1-D^{115}/D^{109})$ for diffusion of cadmium in zinc.

Diffusion mechanism	$(1-\omega^{115}/\omega^{109})$	f	$(1-D^{115}/D^{109})$
Interstitial	0.0264	1	0.0264
Vacancy (basal and nonbasal)	0.0264	0 to 1	$\leqslant 0.0264$
Exchange	0.0133	1	0.0133
Interstitialcy	0.0133	0 to 1	$\leqslant 0.0133$
3-ring (basal and nonbasal)	0.0089	1	0.0089
4-ring	0.0067	1	0.0067

From the isotope-effect measurements for diffusion of cadmium in zinc, we have approximately estimated the binding energy of the cadmium atom to a vacancy in the zinc matrix. We shall first examine the data for diffusion parallel to the hexagonal axis which involves only the nonbasal vacancy jumps.

We shall make the following simplifying approximations for the jump frequencies that enter the Eq. (2.2) for $f_{A,z}$ in the presence of a cadmium atom next to the vacancy, these being in adjacent basal planes: (1) The exchange rate of the vacancy with the zinc atom when both are the nearest neighbors of the cadmium atom is unaffected by the presence of the cadmium impurity, that is, $\omega_a'=\omega_{A,s}$. (2) The dissociative frequency ω_c' is altered and is written as

$$\omega_c'=\omega_{A,s}\exp[-(1-\gamma')B'/kT], \qquad (5.2)$$

where γ' is a number whose possible value lies between zero and unity. In case of an attractive interaction between the vacancy and the impurity atom, the exchange of the vacancy with a solvent atom becomes less frequent if in doing so it effects a separation between the vacancy and the impurity atom. In other words, the barrier over which the vacancy climbs to effect an interchange with the solvent atom is increased by $(1-\gamma')B'$ for a dissociative jump ω_c'. (3) F, the factor that accounts for the dissociated vacancies which effectively do not return to the impurity atom after they once leave it, is probably also changed. When the vacancy leaves the first coordination shell, the probability for the reverse jump is relatively greater because of the decrease in the barrier height by about $\gamma'B'$. Thus the correction factor now becomes

$$F_A'=1-(1-F)\exp(\gamma'B'/kT). \qquad (5.3)$$

With these approximations, $f_{A,z}$ from Eq. (2.2) becomes

$$f_{A,z}=\frac{1+3.5F_A'\exp[-(1-\gamma')B'/kT]}{1+\omega_A/\omega_{A,s}+3.5F_A'\exp[-(1-\gamma')B'/kT]}. \qquad (5.4)$$

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[30] L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals* (Cornell University Press, Ithaca, New York, 1960).

It follows from Eq. (5.4) that

$$\omega_A/\omega_{A,s}=\{1+3.5F_A'\exp[-(1-\gamma')B'/kT]\}\times(1-f_{A,z})/f_{A,z}. \quad (5.5)$$

Also from Eqs. (2.6) and (2.7), we have

$$\omega_A/\omega_{A,s}=D_{\text{II}}f_{A,z:s}e^{-B'/kT}/D_{\text{II},s}f_{A,z}. \quad (5.6)$$

$f_{A,z:s}$ is known, and on the assumption that the many-body consideration is essentially the same as for self-diffusion, $f_{A,z}$ for cadmium diffusion can be calculated from Eq. (2.29) using the experimental values for the isotope effect from Table III. One can then solve graphically the Eqs. (5.5) and (5.6) for B' and $\omega_A/\omega_{A,s}$. It seems reasonable to take $\gamma'=1/2$. The values for B' and $\omega_A/\omega_{A,s}$ turn out to be 0.024 eV and 2.09, respectively, at 410.1°C. The corresponding values at 343.7°C are 0.018 eV and 2.84, respectively.

In the analysis for the binding energy from the isotope effect perpendicular to the hexagonal axis, both basal and nonbasal vacancy jumps are involved. The correlation factors $f_{A,b}$ and $f_{B,x}$ can be obtained from Eqs. (2.3) and (2.5). In the evaluation of these for the cadmium impurity we make simplifying approximations similar and in addition to those made before, that is,

$$\begin{aligned}\omega_b'&=\omega_b=\omega_{B,s},\\ \omega_a'&=\omega_a=\omega_{A,s},\\ \omega_c&=\omega_{B,s}\exp[-(1-\gamma)B/kT],\\ \omega_c'&=\omega_{A,s}\exp[-(1-\gamma')B'/kT],\\ F_A'&=1-(1-F)\exp(\gamma'B'/kT),\\ F_B'&=1-(1-F)\exp(\gamma B/kT).\end{aligned} \quad (5.7)$$

We once again assume $\gamma=\gamma'=\frac{1}{2}$.

Under these approximations, the expressions for $f_{B,x}$ and $f_{A,b}$ for cadmium impurity turn out to be

$$f_{B,x}=1+\frac{2\phi\omega_B/\omega_{A,s}+2\omega_A/\omega_{A,s}}{3-\eta\phi} \quad (5.8)$$

and

$$f_{A,b}=1+\frac{2\eta\omega_A/\omega_{A,s}+6\omega_B/\omega_{A,s}}{3-\eta\phi}, \quad (5.9)$$

where

$$\eta=2+\frac{\omega_{B,s}}{\omega_{A,s}}+7F_B'e^{-B/2kT}+2\frac{\omega_B}{\omega_{A,s}}, \quad (5.10)$$

$$\phi=3+2\frac{\omega_{B,s}}{\omega_{A,s}}+7F_A'e^{-B'/2kT}+2\frac{\omega_A}{\omega_{A,s}}. \quad (5.11)$$

Further combining Eqs. (2.12) and (2.13), one obtains

$$D_\perp/D_{\perp,s}=\frac{3f_{B,x}\dfrac{\omega_B}{\omega_{A,s}}e^{B/kT}+f_{A,b}\dfrac{\omega_A}{\omega_{A,s}}e^{B'/kT}}{3f_{B,x:s}\dfrac{\omega_{B,s}}{\omega_{A,s}}+f_{A,b:s}}.$$

Equation (2.23), which gives the effective correlation factor for perpendicular diffusion, together with Eqs. (2.28), (5.8), and (5.9) can be solved for $\omega_B/\omega_{B,s}$ as a function of the binding energy B between the vacancy and the cadmium atom, both being in the same basal plane. B' and $\omega_A/\omega_{A,s}$ have already been calculated and $\omega_{B,s}/\omega_{A,s}=0.73$ from the present self-diffusion data. Equation (5.12) also contains two unknowns, B and $\omega_B/\omega_{B,s}$. It is thus possible to obtain graphically these two quantities. At 410.1°C, B and $\omega_B/\omega_{B,s}$ turn out to be 0.085 eV and 3.71, respectively. The corresponding values at 343.7°C are 0.082 eV and 4.40.

The numerical values for the binding energy indicate an attractive interaction between the vacancy and the cadmium impurity, the interaction being larger when both of them are in the same basal plane. Thus the enhancement in the diffusivity of cadmium in zinc over that of zinc in zinc is partly due to the rapid interchange of the cadmium impurity with the vacancy and partly because of greater density of vacancies next to the cadmium impurity.

It was hoped that these studies might reveal some information about the Friedel oscillations[31] in the potential around the impurity. From the standpoint of these oscillations in a divalent metal, an impurity (positive with respect to the metal) would repel a negative point charge when they are nearest neighbors in the lattice.[32] If the vacancy in zinc behaved as a point charge, we would expect a repulsive interaction between it and the cadmium impurity on an adjacent site. But the vacancy cannot be considered as a point charge. From our analysis, we get an appreciable attractive interaction between the vacancy and the cadmium impurity. Our assumptions are based on a non-Friedel type of potential. Nevertheless, we would be unable to explain the observed enhancement in the perpendicular diffusion of cadmium in zinc at a temperature below 350°C even in the extreme case when $\omega^{cd}\to\infty$, assuming the same density of vacancies next to the cadmium impurity as in the pure matrix; a repulsive interaction will make the situation even worse.

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[31] J. Friedel, Phil. Mag. **43**, 153 (1952).

[32] A. Blandin and J. L. Déplanté, *Metallic Solid Solutions* (W. A. Benjamin, Inc., New York, 1963), p. IV-1.