β unspecified, the first showing the anomalous behavior in transverse H, the second in longitudinal H. These experiments emphasize the large anisotropy (both in crystalline orientation and field direction) associated with this effect.

In the course of measuring the field variation of X, the corresponding variation in the surface resistance, R, was observed. Under certain circumstances $R(H)$ also shows an anomalous decrease with increasing H. A more detailed account of the complex behavior of $R(H)$ and $X(H)$ will be given at a later date.

Although no decrease in λ with increasing H was reported by Pippard, it is not certain whether this anomalous effect is altogether absent at 9.4 kMc/sec. An unfavorable choice of crystalline orientation and of magnetic field direction might have obscured detection of this behavior, particularly if at the higher frequency the effect is considerably smaller. For these reasons a detailed comparison between the experiments at 1000 Mc/sec and 9400 Mc/sec is difficult at the present time.

Efforts to explain the anomalous behavior of $X(H)$ on the basis of a size effect for the normal electron assembly (as observed in the dc magnetoresistance of thin wires of normal metals[9]) have so far been unsuccessful.

The author wishes to express her gratitude to Dr. A.B. Pippard for direction during the initial stages of this work and for many valuable suggestions.

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*This research was supported in part by the National Science Foundation grants to the low-temperature laboratory of the Institute for the Study of Metals.

†Standard Oil of Indiana Predoctoral Fellow (1955-6); Bell Telephone Predoctoral Fellow (1956-7). This work is based in part on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Chicago.

[1] A.B. Pippard, Proc. Roy. Soc. (London) A203, 210 (1950).

[2] A.B. Pippard, Proc. Roy. Soc. (London) A191, 370 (1947); A203, 98 (1950).

[3] E. Laurmann and D. Shoenberg, Proc. Roy. Soc. (London) A198, 560 (1949).

[4] The angles α and β in turn specify the crystallographic orientation of the tetrad axis and the dyad axis (100) relative to the wire axis, following the convention of E. Fawcett, Proc. Roy. Soc. (London) A232, 519 (1955).

[5] A.B. Pippard, Proc. Roy. Soc. (London) A191, 399 (1947).

[6] J. Bardeen, Phys. Rev. 94, 554 (1954).

[7] Kindly supplied by Dr. W.A. Tiller, Westinghouse Research Laboratory.

[8] Kindly supplied by Dr. A. Strauss, Chicago Midway Laboratories

[9] D.K.C. MacDonald, Handbuch der Physik (Springer-Verlag, Berlin, 1956), Vol. 14, p. 186.

CORRELATION AND THE ISOTOPE EFFECT FOR DIFFUSION IN CRYSTALLINE SOLIDS*

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(Received July 7, 1958)

Bardeen and Herring[1] showed that for the diffusion of the atoms of a pure crystalline solid via the random walk of lattice vacancies, the directions of consecutive jumps of each atom are correlated. The effect of such correlation on the diffusion coefficient D for this case and for other examples of diffusion in cubic cyrstals has been analyzed by Bardeen and Herring[1] and several other authors.[2-7]

We should like to suggest that the dependence of D on the isotopic mass of the diffusant is a function of the correlation between the directions of consecutive jumps of a diffusing atom. LeClaire and Lidiard[5] have shown that while this correlation is zero for interstitial diffusion, it is different from zero for diffusion by the interstice[8] mechanism as well as by the vacancy mechanism. Isotope effect measurements should therefore be useful in deciding among possible diffusion mechanisms in particular cases.

Lidiard[3] has shown that for diffusion by the vacancy mechanism of a solute atom B in infinitely dilute solution in a fcc crystal of A atoms,

$$D \cong \frac{a^2}{6}\,\frac{w_2(w_1+7k_1/2)}{w_1+w_2+7k_1/2}\,p, \qquad (1)$$

where a is the jump distance; w_2, w_1, and k_1 are the probabilities per second that a vacancy on a site next to B make an exchange with B, with any particular one of the four A atoms which are nearest neighbors of both B and vacancy, and with any particular one of the other seven A atoms adjacent to the vacancy, respectively; and p is the fraction of time during which there is a vacancy on a site adjacent to B. We may use Eq. (1) to evaluate the ratio of the diffusion coefficients for two isotopes of an element of masses m_α and m_β diffusing in the A crystal. We shall assume that w_2 depends on the isotopic mass of B, but that w_1, k_1, and p do not. From analyses by Wert[9] and by Lidiard[7] of the atomic jump frequency Γ, it is found that

$$\Gamma(m_\beta)/\Gamma(m_\alpha) \cong (m_\alpha/m_\beta)^{1/2}. \qquad (2)$$

For diffusion by the vacancy mechanism, $\Gamma=w_2 p$; hence

$$w_2(m_\beta)/w_2(m_\alpha)\cong(m_\alpha/m_\beta)^{1/2}. \qquad (3)$$

Let us now apply Eqs. (1) and (3) to the evaluation of the isotope effect for four cases. We define the strength of the isotope effect by

$$E=\frac{[D(m_\beta)/D(m_\alpha)]-1}{(m_\alpha/m_\beta)^{1/2}-1}, \qquad (4)$$

where $m_\alpha > m_\beta$.

(a) "Slow" solute atom diffusion: $w_1(m_\beta)/(w_1 + 7k_1/2)=s \ll 1$. Consecutive jumps of B are only weakly correlated, and $E\cong 1-s$.

(b) "Fast" solute atom diffusion: $w_2(m_\beta)/(w_1 + 7k_1/2)=s \gg 1$. Consecutive jumps of B are strongly correlated, and $E\cong 1/s$.

(c) Self-diffusion in a pure crystal. The lattice (except for the tracer atoms) is treated as consisting of atoms of a single isotopic species of mass m_0, with $w_1(m_0)=k_1(m_0)$. If $[w_1(m_0)](m_0)^{1/2} \cong [w_2(m_\alpha)](m_\alpha)^{1/2}\cong[w_2(m_\beta)](m_\beta)^{1/2}$, then

$$E\cong\frac{1}{1+(2/9)(m_0/m_\beta)^{1/2}}. \qquad (5)$$

(d) Self-diffusion in a solid solution. For treating the diffusion of two isotopes of a constituent B of a random solid solution of A and B atoms, we make the following assumptions: the probability per second that a vacancy make an exchange with a particular neighboring atom X is given by w_1 if X is an A atom and by w_2 if X is a B atom; all A atoms are of a single isotopic species; all B atoms (except for the tracers) are of a single isotopic species of mass m_0. We find

$$E\cong\frac{1}{1+(2/9)(m_0/m_\beta)^{1/2}[N+(1/s')(1-N)]}, \qquad (6)$$

where $s'=w_2(m_0)/w_1$, and N is the atom fraction of B atoms.

For interstitial diffusion, diffusion by ring mechanisms, and diffusion by the vacancy of interstice mechanisms with only weak correlation,

$$D(m_\beta)/D(m_\alpha)\cong\Gamma(m_\beta)/\Gamma(m_\alpha); \qquad (7)$$

hence $E\cong1$. E has been found to be approximately one for the diffusion of H in Pd,[10,11] Ni in Cu,[12] and Na in NaCl and KCl.[13] It appears that measured values of E smaller than one have not been reported.

For an investigation of the isotope effect in cases where correlation might be expected to have a determining influence, the diffusion of Cd in Ag and in Cu was chosen. At the temperatures (~715°C) selected for diffusion, $D(\mathrm{Cd})/D(\mathrm{Ag})\cong3.6$ in Ag,[14] and $D(\mathrm{Cd})/D(\mathrm{Cu})\cong 8.2$ in Cu.[15] Measurements were made of D for Cd^{109} and Cd^{115m} tracers in a single crystal of pure Ag and in one of pure Cu. In each case, both radioisotopes were electroplated on the same crystal, and after diffusion, sectioning of the diffusion zone, and weighing of the sectioned samples, the isotope activities were counted separately with a single-channel pulse-height analyzer. The experimental procedure will be described in detail in a forthcoming paper.

As shown in Table I, E was found to be approximately zero both in Ag and in Cu. It is suggested that these results are consistent with diffusion of Cd atoms by the vacancy mechanism, with $w_2 \gg w_1 + 7k_1/2$. It may be shown that the results are also consistent with interstice, but not interstitial, diffusion of Cd.

Table I. Isotope effect E for diffusion of Cd^{109} and Cd^{115m} in Ag and Cu. The probable errors for E are based on the uncertainty in each D value, as determined from a straight line fitted to the observed diffusion profile by least squares

Diffusion crystal	E
Ag (first count of Cd^{109})	-0.04 ± 0.07
Ag (second count of Cd^{109})	$+0.05 \pm 0.07$
Cu	-0.05 ± 0.05

From Eq. (1), it may be seen that if $w_2 \gg w_1 + 7k_1/2$, then – as noted by Lidiard[3] – $D=(a^2/6)\times(w_1+7k_1/2)p$. In this case, D should depend not on the mass of the tracer atoms, but on the mass of the solvent atoms.

The author would like to thank Professor John Bardeen for several illuminating discussions. Special thanks are due to Dr. S. Singer, Dr. J. D. Fox, Mr. R. N. Peacock, and Mr. H. R. Lewis, Jr., who introduced the author to experimental techniques which made these isotope effect measurements possible and who gave much valuable advice. The author is also grateful to Mr. G. DePasquali for assistance with radiochemical

separations, and to Mr. E. Goeler, who prepared the Illiac least squares program used for analyzing the data.

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*Supported in part by the U. S. Atomic Energy Commission.

†Now at Convair Scientific Research Laboratory, San Diego, California.

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

[2] Hoffman, Turnbull, and Hart, Acta Metallurgica 3, 417 (1955).

[3] A. B. Lidiard, Phil. Mag. 46, 1218 (1955).

[4] K. Compaan and Y. Haven, Trans. Faraday Soc. 52, 786 (1956); Proceedings of the Third International Conference on Reactivity of Solids, Madrid, April, 1956 (unpublished).

[5] A. D. LeClaire and A. B. Lidiard, Phil. Mag. 1, 518 (1956).

[6] C. W. McCombie and A. B. Lidiard, Phys. Rev. 101, 1210 (1956).

[7] A. B. Lidiard, Encyclopedia of Physics (Springer-Verlag, Berlin, 1957), Vol. XX, chapter on "Ionic Conductivity."

[8] E. Koch and C. Wagner, Z. physik. Chem. B38, 295 (1937); F. Seitz, Acta Cryst. 3, 355 (1950).

[9] C. Wert, Phys. Rev. 79, 601 (1950).

[10] W. Jost and A. Widmann, Z. physik. Chem. B29, 247 (1935).

[11] We have been informed by Dr. O. N. Salmon, of General Electric Knolls Atomic Power Laboratory, that in measurements of the temperature dependence of H^1 and H^3 diffusion in Pd and in stainless steel, slight deviations from Eq. (11) were observed. These experiments are described in two reports of Knolls Atomic Power Laboratory: D. Randall and O. N. Salmon, Knolls Atomic Power Laboratory Report KAPL 904, 1953; (unpublished) O. N. Salmon and D. Randall, Knolls Atomic Power Laboratory Report KAPL 984, 1954, (unpublished). We thank Dr. Winfield W. Tyler for informing us of this work.

[12] W. A. Johnson, Trans. Am. Inst. Mining Met. Engrs. 166, 114 (1946).

[13] M. Chemla, Ann. phys. 1, 959 (1956).

[14] C. T. Tomizuka and L. M. Slifkin, Phys. Rev. 96, 610 (1954).

[15] Kuper, Letaw, Slifkin, Sonder, and Tomizuka, Phys. Rev. 96, 1224 (1954).

SIMPLE APPROXIMATION FOR THE NONUNIQUE FIRST FORBIDDEN TRANSITION*

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(Received July 28, 1958)

It is well known that the energy spectra of many nonunique first forbidden β transitions have roughly statistical shapes. That is, the energy shape correction factor, C, is constant. This can be understood by expanding the transition probability in powers of the nuclear radius ρ.[1] The leading terms are associated with the Coulomb factor $\xi \equiv \alpha Z/2\rho \approx Z/A^{\frac{1}{3}}$ and they give constant C.[2] The approximation of keeping only the leading terms in powers of ρ (i.e., in descending powers of ξ) we call the "ξ-approximation." (This approximation has been expressed by $\xi \gg W_0$, where W_0 is the maximum β-ray energy.[2]) In this letter we shall examine the accuracy of the ξ-approximation and show its consequences for other observables such as the longitudinal polarization and β-γ correlations.

Let us assume that the (local) V and A interactions[3,4] and the two-component theory of the neutrino, $C_V = C_V'$ and $C_A = C_A'$,[5] characterize the β decay. In the ξ-approximation the shape correction factor is energy independent:

$$C = |V|^2 + |Y|^2, \tag{1}$$

where

$$V = \xi' v_0 + \xi w_0 , \tag{2}$$

and

$$Y = \xi' y_0 - 2\xi(u_0 + x_0)(1+\gamma_1)^{-1} . \tag{3}$$

Here the subsidiary parameters have the following significance[2]:

$$\begin{aligned} &\eta = -C_V \int \vec{r} R(-2), \eta w_0 = C_A \int \vec{\sigma}\cdot\vec{r} R(1), \\ &\xi' \eta v_0 = C_A \int i\gamma_5 \, R(-1), \eta u_0 = C_A \int i\vec{\sigma}\times\vec{r} R(1), \\ &\xi' \eta y_0 = -C_V \int i\vec{\alpha} R(-1), \eta x_0 = -C_V \int \vec{r} R(1). \end{aligned} \tag{4}$$

The energy-independent quantity $R(\kappa)$ entering in the matrix element involves the ratio of the actual electron wave function to the point charge function evaluated at the nuclear surface (and thus R depends on the electron angular momentum quantum number κ shown). We do not need to know the details of R, if we do not evaluate the nuclear matrix elements themselves. In this way, finite nuclear size effects are taken into account, in the ξ-approximation.

The parameters $u_0, \ldots, y_0$ are defined so they may be of order unity (except, of course, that some may vanish due to selection rules). For this purpose, a parameter, ξ', is introduced to relate the relativistic to the nonrelativistic matrix elements. It has been theoretically predicted that

$$\xi' = \xi\lambda, \text{ with } \lambda = 1,^6 \text{ or } 2.^7 \tag{5}$$