PHYSICAL REVIEW VOLUME 121, NUMBER 6 MARCH 15, 1961

Isotope Effect in Intermetallic Diffusion[*][†]

JAMES G. MULLEN[‡]
Physics Department, University of Illinois, Urbana, Illinois

(Received November 7, 1960)

Ten measurements of the isotope effect for diffusion of Fe^{55} and Fe^{59} in pure single crystals of silver and copper have been made over approximately a 300°C temperature interval below the melting point. The measured isotope effect was found to be about $\frac{2}{3}$, significantly less than the value of unity expected from conventional reaction rate theory.

It is shown from Vineyard's extension of reaction rate theory that the measured isotope effect is to a good approximation a product of the Bardeen-Herring correlation factor and the fraction of the total translational kinetic energy associated with the diffusing tracer in a tracer-vacancy exchange. It is shown that the ring, interstitialcy, crowdion, and relaxion mechanisms are not responsible for diffusion in the systems studied.

The three-frequency theory of correlation for vacancy diffusion in fcc lattices is extended to show that the relative frequency factors are completely specified by a knowledge of the correlation factor and the diffusion coefficients. An expression for the difference in the Arrhenius Q and the activation energy due to the temperature dependence of the correlation factor is derived. This theory is shown to be inconsistent with the observed isotope effect if many-body effects are neglected. It is shown that a "long-range" repulsive interaction between the vacancy and impurity would be necessary if the measured isotope effect is to be explained purely in terms of correlation.

I. INTRODUCTION

EYRING'S[1] general theory of reaction rates has been applied by Zener[2] and Wert[3] to the problem of diffusion in the solid state. By considering the diffusion process to be represented by an atom moving over a potential barrier, Wert shows that the average jump frequency, Γ, varies as $m^{-\frac{1}{2}}$, where m is the mass of the diffusing atom. In addition to assuming a one-body model, the theory presumes that a state exists at the top of the barrier with a sufficient lifetime that thermodynamic properties can be defined for the activated complex, and that the irreversible nature of the diffusion process enters through some unspecified mechanism whereby an atom which crosses a diffusion barrier loses most of its energy before it can cross the barrier in the opposite direction.

Prigogine and Bak[4,5] have recently proposed a theory of diffusion which shows how irreversibility may result from the nonharmonic interactions between the crystalline normal modes and a moving particle. A model is used that presumes that a particle moves in a one-dimensional parabolic well and is annihilated when its energy reaches a certain critical value. The theory predicts that the diffusivity is proportional to m^{-2}, in contrast to the $m^{-\frac{1}{2}}$ dependence predicted by reaction rate theory. Prigogine and Bak point out that altering the assumption of an unperturbed harmonic potential may change the dependence of D on m, although it will probably be larger than $m^{-\frac{1}{2}}$.

In neither of the above two theories is the motion of the barrier atoms taken into account. This effect has been incorporated explicitly in reaction rate theory by Vineyard.[6] Vineyard's theory differs from that of Zener and Wert in that the motion of the host atoms is explicitly taken into account by considering the diffusion process as the motion of a representative point over a potential barrier in the N-dimensional configuration space of the crystal containing $N/3$ atoms. In this theory, as in conventional reaction rate theory, the assumption of an equilibrium state at the top of the barrier is still incorporated, and the question of irreversibility is not treated explicitly. Vineyard's analysis indicates that the solute-vacancy exchange frequency is proportional to $(m^*)^{-\frac{1}{2}}$, where m^* is an effective mass whose value is bounded by the smallest and largest mass of the entire system.

Rice *et al.*[7–10] have also examined the many-body aspects of the diffusion process. This treatment differs from that of Vineyard in that the assumption of an equilibrium state at the top of the barrier is removed. However, thus far it has not been possible to use this model to calculate the dependence of the jump frequencies on the many-body effects for any realistic case.

The measured mass dependence of the diffusivity will also be affected by the diffusion mechanism in the following two ways: (1) in cases where several atoms move simultaneously, m^*, and hence the jump frequency, will be altered; (2) correlation effects, such as occur in vacancy diffusion, will modify the rates of isotopic diffusion in a solid, since the correlation factor depends on

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[*] This work was supported in part by the U. S. Atomic Energy Commission.

[†] Based on a thesis submitted to the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics.

[‡] Present Address: Solid State Science Division, Argonne National Laboratory, Argonne, Illinois.

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[8] S. A. Rice and N. H. Nachtrieb, J. Chem. Phys. **31**, 139 (1959).

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TABLE I. Previous measurements of the isotope effect.

Reference	Tracer or solute	Host material	E_B
11	Ni (stable isotopes)	Cu	0.96±0.3[a]
12	Fe^{55}, Fe^{59}	Ag	4.3 ±1.0
13	Cd^{115m}, Cd^{109}	Ag, Cu	0.0 ±0.1
14	Na^{22}, Na^{24}	NaCl	~1
15	Li^6, Li^7	Si	0.94±0.25
16	H^1, H^2	Pd	0.85±0.3[a]
17	Li^6, Li^7	W	0.88±0.25

[a] The error in these cases is the present author's estimate.

the solute-vacancy exchange rate which is in turn a function of the isotopic mass.

To date, there have been very few measurements of the effect of isotopic mass on diffusion. Table I gives a list of the measurements which have been reported in the literature.[11–17] Most of these measurements are not sufficiently precise to permit many of the theoretical questions to be answered. The isotope effect E_B in Table I, is defined by

$$E_B=\frac{1-D_B/D_A}{1-(m_A/m_B)^{\frac{1}{2}}}. \tag{1}$$

The present investigation is an attempt to determine precisely the isotope effect for diffusion in a substitutional solid system. The isotopes chosen for this experiment were Fe^{55} and Fe^{59}, and the crystalline matrices, silver and copper. The two isotopes were diffused simultaneously into the silver and copper crystals in order to eliminate the errors in the measurement of temperature and penetration depth. Since both isotopes diffuse under identical conditions, the temperature and penetration depth errors, which are dominant in the measurement of the diffusion coefficient, are negligibly small in the measurement of the isotope effect.

The iron isotopes were selected as tracers in this experiment for the following reasons: (1) These isotopes are easily obtained with very high purity; (2) they have a large, 7%, mass difference; (3) they have very different decay schemes which permitted the use of the novel differential counting technique described later; (4) the study of diffusion of these two isotopes permitted a careful re-examination of the anomalously large isotope effect reported by Lazarus and Okkerse.[12]

The iron isotopes were diffused into the host crystal from a very thin (10 to 30 A) plane layer originally on the surface. The concentration of iron c, after diffusing a time t, is given as a function of tracer penetration into the crystal x by the equation

$$c=\frac{c_0}{(\pi Dt)^{\frac{1}{2}}}\exp(-x^2/4Dt), \tag{2}$$

where D is the diffusion coefficient, and c_0 the initial concentration of iron at the surface. Since both isotopes are diffused simultaneously, the relative concentration of the two isotopes as a function of position will differ, if D_{55} is not the same as D_{59}. From Eq. (2) the relative concentration as a function of penetration is given by

$$\ln\frac{c_{55}}{c_{59}}=\text{constant}+\left(1-\frac{D_{59}}{D_{55}}\right)\frac{x^2}{4D_{59}t}. \tag{3}$$

In this experiment, the diffusion of the Fe^{59} isotope was first measured to determine the factor $1/4D_{59}t$. Then, by measuring the ratio of the two isotopic activities as a function of x^2, it was possible to evaluate the term $1-D_{59}/D_{55}$, which, by Eq. (1), is proportional to the isotope effect E_{59}.

II. EXPERIMENTAL PROCEDURES

A. Determination of Fe^{59} Diffusivity

The silver and copper single crystals used in this investigation were grown in vacuum from 99.99% pure Handy and Harmon silver and 99.998% pure American Smelting and Refining Company copper. Crystals were grown, about 0.75 inch in diameter and 3 to 4 inches in length, in specially machined AUC grade graphite crucibles. The single crystals were cast into bakelite cylinders with plaster of Paris and sectioned into smaller cylinders of about ½-inch length with a water-cooled cutoff wheel. The specimens were alternately etched and polished with progressively finer emery paper until a mirror surface of 4/0 smoothness was obtained. The polished crystals were annealed in a vacuum furnace at 100°C below the melting point for at least 24 hours. Only specimens which did not recrystallize on anneal were used in the experiment.

Both the Fe^{55} and Fe^{59} isotopes were received from Oak Ridge National Laboratory in the form of chlorides. Both isotopes were combined in the plating bath, which consisted of a saturated ammonium oxalate solution whose *p*H was reduced to four by the addition of oxalic acid. About 3 to 10 atom layers of radioactive iron were plated on each of the specimens. This moderately heavy plating, in addition to the use of hand-polished quartz flats placed against the ends of the specimens during diffusion, eliminated the effect of evaporation of the iron isotope from the surface of the specimens that was observed by Mackliet[18,19] and Lazarus.[12] The plated specimen with attached quartz flats was placed in a Vycor or quartz tube which was closed at one end, and

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maintained in an atmosphere of pure argon during the "necking-down" procedure. The specimen was finally sealed off in a vacuum of less than 10^{-5} mm Hg.

The encapsulated specimens were placed in diffusion furnaces for periods of 3 hours to 1.5 months depending on the temperature. The time of anneal was usually chosen so that the concentration of iron tracer at a penetration of 0.01 inch would be approximately 1/50 the surface concentration after the diffusion anneal. The temperature of each specimen was measured during the course of the diffusion anneal with a chromel-alumel thermocouple, which was calibrated at the time of the experiment against a standard Pt-Pt 10% Rh thermocouple. The furnace temperatures were maintained by resistance-bridge and Tag Celectray controllers to within about ±1°C. After the diffusion anneal was completed, the specimens were quickly removed from the furnace and quenched in cold water.

The diffused specimens were mounted on a precision lathe with an adjustable chuck, which was oriented so that the plane face of the specimen was perpendicular to the axis of rotation. To eliminate the iron tracer which had diffused from the sides of the specimen, a layer of 0.03-inch to 0.05-inch thickness was removed from the sides of the cylindrical specimen. After turning, sections were taken from the face of the specimen, which were typically 0.0007 to 0.001 inch thick. The chips were collected by surrounding the specimen and sectioning tool with a paste-board enclosure.

The chips from each slice were placed in stainless-steel counting planchets and weighed on a Mettler semimicro balance which gave readings to 0.01 mg. To check that no chips were lost in handling, the specimen was weighed before and after sectioning. The difference in weight usually checked with the sum of the weight of the slices to within 0.1 to 0.3%. The thickness of each slice was determined from the diameter of the specimen before sectioning and the weight and density of that slice, rather than using a dial gauge reading.

The diffusivity of Fe^{59} was determined by counting the 1.1-Mev γ ray from Fe^{59} which can readily be distinguished from the 5.9-kev x rays of Fe^{55}. The Fe^{59} activity was determined by using a scintillation spectrometer, with a single-channel pulse-height analyzer and lead shielded, $1\frac{1}{2}$-inch diam by $1\frac{1}{2}$-inch thick NaI(Tl) crystal as a detector.

B. Determination of the Relative Diffusivity of Fe^{55} and Fe^{59}

Because the 5.9-kev x ray from Fe^{55} is almost completely absorbed by the copper and silver chips, it was necessary to remove the iron tracer chemically from each slice of the solvent material, and then electroplate the iron onto flat copper planchets in order to determine the relative diffusion rates. The iron tracer was separated from the host material by dissolving the chips from each section in nitric acid, adding 3 mg of iron carrier, and precipitating the iron as a hydroxide. It was necessary to make the solution strongly basic to avoid precipitation of the copper and silver ions. The iron hydroxide was centrifuged, and the decant containing the silver, or copper, was discarded. Residual silver was removed by dissolving the iron hydroxide in hydrochloric acid. In order to eliminate residual copper, the iron hydroxide was dissolved in HCl, diluted, and the iron reprecipitated as a hydroxide. The repurified iron hydroxide was redissolved in HCl and combined with a saturated ammonium oxalate solution in a simple electroplating cell, using a Pt anode. In the chemical separation, the tracer iron atoms were never transferred from the centrifuge tubes in which the chips were originally placed, until the oxalate solution containing the Fe tracers was added to the electroplating cell. The plating was carried out at 7 volts for $\frac{1}{2}$ hour then at 5 volts for approximately one to two hours. During the plating, oxalic acid was added to prevent the *p*H from becoming sufficiently high to precipitate the iron as a hydroxide. The plating was not continued longer than the minimum time necessary for completion, as excessive plating led to a decomposition of the oxalate ion and the subsequent deposit of a carbon film. Properly plated specimens exhibited a luster similar to platinum.

After the plating was completed, the cells were dismantled and the planchets washed in water and alcohol and wiped dry. Activity deposited on the edge of the planchets was taken off with fine emery paper. The stems of the planchets were then cut off and the resulting specimen glued onto a flat planchet holder.

The relative ratio of the two isotopes for each slice of the sectioned specimen was measured with a single halogen-quenched, argon-filled, GM detector. A 200 CB Amperex tube was used because it did not give spurious counting effects and was sensitive to both beta and x rays. To distinguish between the 5.9-kev x ray of Fe^{55} and the beta radiation from Fe^{59}, a 0.036-inch thick beryllium absorber and a 0.0002-inch thick gold absorber were used. These absorbers were mounted on a slide which was enclosed in a standard lead shield. The slide passed between the specimen being counted and the GM detector, making it possible to interchange the two absorbers in a reproducible manner without moving the specimen or counter tube. When the gold absorber was placed between the specimen and absorber, the Fe^{55} x rays were highly absorbed. When the beryllium absorber was placed between the specimen and detector, the Fe^{59} betas were highly absorbed.

Consider a specimen which has both isotopes Fe^{55} and Fe^{59}. If the counting rate for this sample is N_{Be} when the Be absorber is placed between the sample and the GM tube, and N_{Au} when the Au absorber is in this position, then both N_{Be} and N_{Au} will consist of two components, i.e.,

$$N_{\mathrm{Be}}=N_{55}+\epsilon^{59}N_{59}, \quad \text{and} \quad N_{\mathrm{Au}}=N_{59}+\epsilon^{55}N_{55},$$

where N_{55} is the fraction of Fe^{55} radiation which is counted through the Be absorber, N_{59} the fraction of Fe^{59} radiation which is counted through the Au absorber, ϵ^{59} the counting rate of a pure Fe^{59} source through the Be absorber as compared with the rate through the Au absorber, and ϵ^{55} the counting rate of a pure Fe^{55} source through the Au absorber as compared with the rate through the Be absorber. The solution of these two equations for N_{55}/N_{59} is

$$N_{55}/N_{59}=(N_{\mathrm{Be}}-\epsilon^{59}N_{\mathrm{Au}})/(N_{\mathrm{Au}}-\epsilon^{55}N_{\mathrm{Be}}). \qquad (4)$$

Since the sensitivity of the GM tube is not the same for both isotopes, and the fraction of Fe^{55} radiation which is transmitted by the Be absorber is not the same as the fraction of Fe^{59} radiation transmitted by the Au absorber, the ratio, N_{55}/N_{59}, determined by Eq. (4), is not equal, but only proportional to the relative concentration of the two isotopes. This multiplicative constant does not alter the form of Eq. (3), however, and hence a plot of $\ln(N_{55}/N_{59})$ vs $x^2/4D_{59}t$ gives the same slope, $1-D_{59}/D_{55}$.

To measure the transmission coefficients, ϵ^{55} and ϵ^{59}, it was necessary to prepare a pure Fe^{55} source and a pure Fe^{59} source. These were made with the identical geometry and with the same electroplating technique as the specimens used in measuring the ratio, N_{55}/N_{59}. The values of the transmission coefficients were determined to be $\epsilon^{55}=0.025$ and 0.020 and $\epsilon^{59}=0.047$ and 0.048 for the two counting systems used. Both ϵ^{55} and ϵ^{59} were measured repeatedly with at least two pure Fe^{55} and Fe^{59} sources, to an experimental uncertainty of at most 5%.

In the early stages of the experiment a Robot camera was used to take pictures of the scalers at 17-minute intervals, while the specimens were being counted. By calculating the standard error from the total number of counts, and independently from the deviation from the mean of the number of counts in each interval, it was possible to show that no spurious counting effects were occurring in either the scaler or detector. After the magnitude of the effect was clearly established, self-consistency of the data was taken as an adequate check on the counting.

To maintain a constant high voltage on the GM tube, a harmonic-free Sola transformer was used to regulate the line voltage to the high voltage supply and scalers.

C. Treatment of Data and Examination of Errors

The error in measurement of the temperature is typically 1°C and at most 2°C. A 1°C error in T corresponds to a 2.5% error in D, for iron diffusing in silver and copper. The error in the measurement of x, the penetration distance, is estimated to be of the order of 1%. This contributes a 2% error in x^2, and hence a 2% error in D. From all causes, the uncertainty in the measurement of $D(T)$ is typically 3 to 5%.

The diffusion profiles for Fe^{59} diffusing in silver indicate a curvature at low temperatures. This curvature progressively increases as the diffusion anneal temperature decreases and is believed to be caused by the extreme insolubility of iron in silver at these temperatures. In these cases D was estimated from the asymptotic slope of the diffusion profile. Here the error may be as great as 10 or 20%, although the self-consistency with the higher temperature data seems to indicate a much smaller error.

The diffusion parameters D_0 and Q in the Arrhenius relation, $D=D_0\exp(-Q/RT)$, were determined by a least-squares fit of the data, assuming that the weighting factors for all of the D's were equal. In the case of copper, Mackliet's data were included with the present data, except for the lowest temperature point, where the shape of Mackliet's diffusion profile indicated that a considerable amount of iron had probably evaporated from the surface of the specimen. If this point is discarded, the curvature in the Arrhenius plot for iron diffusing in copper, noted by Mackliet, appears to be negligible within the experimental errors.

Since x^2 is in error by 2%, and $1/4D_{59}t$ by 3%, the systematic error in the isotope effect due to errors in $x^2/4D_{59}t$ is about 4%.

The most serious error in the determination of E_{59} is the statistical error due to the fact that there was a practical limit to the number of counts which could be taken for any given specimen. Typically, 50 000 to 300 000 counts were taken for each specimen measured through each absorber.

The background error was also important for specimens with low activity. Background was measured for both absorbers for each measurement of E_{59}. It was found to vary by about 0.3 count per minute, and this was taken as the background error rather than the smaller statistical error indicated by the total number of counts.

The standard error due to the limited number of counts and background fluctuations were combined to

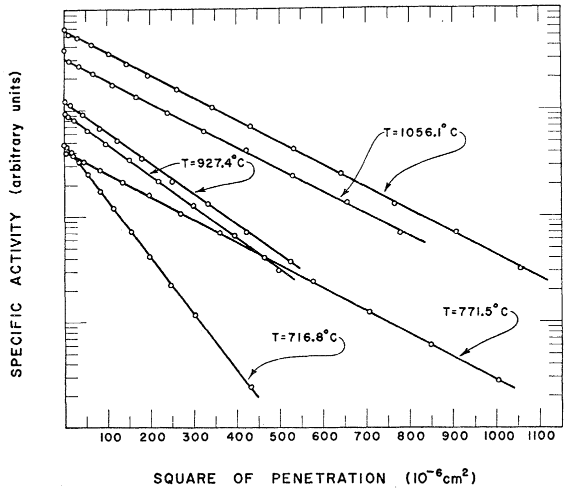

FIG. 1. Diffusion profiles for Fe^{59} diffusing in copper.

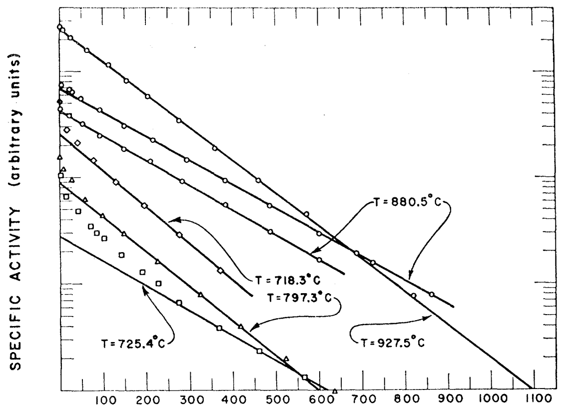

FIG. 2. Diffusion profiles for Fe^{59} diffusing in silver.

determine the standard error and weighting factor for each point.

The slope of the $\ln(N_{55}/N_{59})$ vs $x^2/4D_{59}t$ curve was determined by a least-squares analysis of the data, using the above-mentioned weighting factors for each point. The resulting statistical error, which was typically 10% for E_{59}, and the 4% error in $x^2/4D_{59}t$, are believed to be the only significant errors in the experiment. However, because of the importance of an accurate evaluation of the errors in this experiment, other possible sources of error will be examined in the subsequent discussion.

Four corrections were made to the raw data. They were (1) dead time correction, (2) background correction, (3) correction for finite transmission coefficients, and (4) correction for the decay of Fe^{55} and Fe^{59}. Except for the background correction all of the other corrections were determined to sufficient accuracy that they did not make a significant contribution to the error in the measured isotope effect. Because of conflicting values cited in the literature, the half-life of Fe^{59} was remeasured and found to be 45.1 days with a maximum error of 1%. This is in excellent agreement with the value quoted by Schuman and Camilli.[20]

It was also shown that the long-term high-voltage drift of 3 volts at the operating voltage led to a negligible error in the measured isotope effect. No significant contamination of the Fe^{55} and Fe^{59} sources was indicated in the Oak Ridge specifications. Also, the measured half-life and gamma spectra did not reveal any other radioactive impurities. To check against any possible radioactive contamination in the chemistry and electroplating, a dummy specimen was always prepared as a control. The dummy, which received the same chemistry and electroplating treatment as the other specimens, in no case indicated radioactive contamination.

To show that no significant errors resulted from absorption of the Fe^{55} x ray due to the 3 mg of iron carrier which was added in the radiochemical separation, the following calibration experiment was performed. Using equal amounts of Fe^{55} and varying the amount of iron carrier from 1 mg to 6 mg, six specimens were plated. When these were then counted, it was found that there was no x-ray absorption for any of the specimens within the limits of accuracy of the experiment. It was also shown that the plating was quantitative, so that any small absorption coefficient for the x rays was the same for all specimens, and hence did not contribute to the error in N_{55}/N_{59}.

In another calibration experiment, five specimens were prepared from a stock solution with the same ratio of Fe^{55} to Fe^{59} activity, but different net activities. The ratio, N_{55}/N_{59} was found to reproduce to within an average deviation from the mean of 0.2%, which established the accuracy of the counting.

In a final calibration experiment, the relative ratio of Fe^{55} to Fe^{59} was arranged in the proportion 1:2:3:6. These relative ratios reproduced to within the pipetting error, which was taken as a final check on the accuracy of the procedures used.

III. EXPERIMENTAL RESULTS

Six measurements of D were made for Fe^{59} diffusion in copper, and six measurements of D for Fe^{59} diffusion in silver. The plots of ln (concentration) vs square of (distance from origin) are shown in Figs. 1 and 2. It

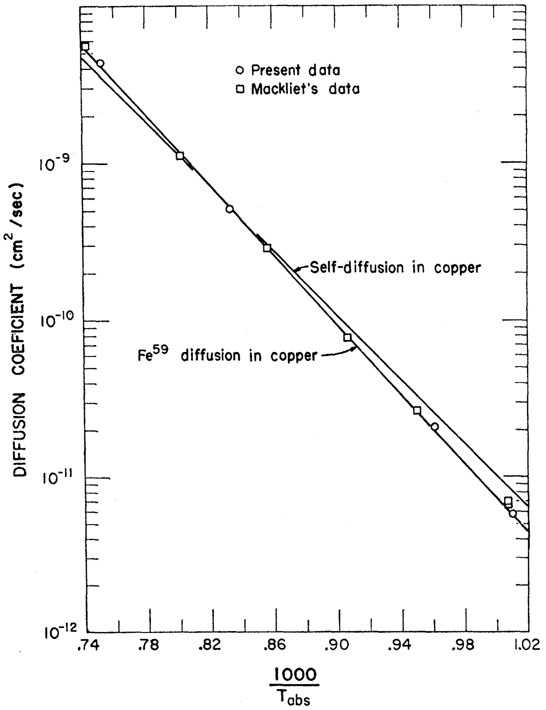

FIG. 3. Fe^{59} diffusion in copper. The Arrhenius parameters for self-diffusion were taken to be $D_0=0.20$ cm²/sec and $Q=47.1$ kcal/mole.

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[20] R. P. Schuman and A. Camilli, Phys. Rev. 84, 158 (1951).

TABLE II. Diffusion of Fe^{55} and Fe^{59} in copper and silver.

Host material	Temperature (°C)	$1/4D_{59}t$ (10^3 cm^{-2})	D_{59} (cm^2/sec)	$1-D_{59}/D_{55}$	E_{59}
Cu	1056.1	4.86	4.38×10^{-9}	0.0256 ± 0.0018	0.742 ± 0.052
Cu	1056.1	4.77	4.46×10^{-9}	0.0235 ± 0.0012	0.681 ± 0.036
Cu	927.4	6.71	5.16×10^{-10}	...	...
Cu	927.4	6.78	5.11×10^{-10}	0.0234 ± 0.0015	0.679 ± 0.043
Cu	767.3	4.97	2.10×10^{-11}	0.0224 ± 0.0010	0.650 ± 0.028
Cu	716.8	12.35	5.76×10^{-12}	0.0203 ± 0.0018	0.590 ± 0.053
Ag	927.5	7.17	2.82×10^{-9}	0.0259 ± 0.0023	0.751 ± 0.068
Ag	880.5	5.20	1.24×10^{-9}	0.0168 ± 0.0030[a]	0.487 ± 0.087[a]
Ag	880.5	5.30	1.21×10^{-9}	0.0168 ± 0.0024	0.487 ± 0.070
Ag	797.3	7.37	2.25×10^{-10}	0.0212 ± 0.0020	0.615 ± 0.060
Ag	725.4	5.53	4.40×10^{-11}	0.0261 ± 0.0027	0.757 ± 0.078
Ag	718.3	7.99	3.74×10^{-11}	...	...

[a] Because of the small number of points, the error was estimated in this case instead of using the least-square value.

should be noted that in no case do these diffusion profiles indicate that activity left the surface of the specimens during the diffusion anneal.

The least-squares values of the parameters in the Arrhenius relation are $D_0(\mathrm{Cu})=1.01\pm0.23$ cm^2/sec, $Q(\mathrm{Cu})=50.95\pm0.46$ kcal/mole, $D_0(\mathrm{Ag})=2.42\pm0.23$ cm^2/sec, $Q(\mathrm{Ag})=49.04\pm0.21$ kcal/mole.

The actual error in the case of silver is possibly two to three times the value indicated, since the low-temperature diffusion coefficients for silver are almost certainly less accurately determined than the self-consistency of the data would indicate. Arrhenius plots of the data are given in Figs. 3 and 4.

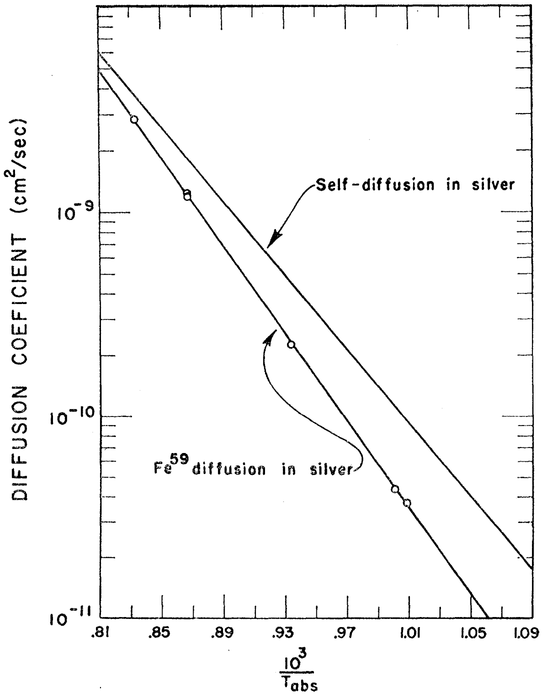

FIG. 4. Fe^{59} diffusion in silver. The Arrhenius parameters for self-diffusion were taken to be $D_0=0.40$ cm^2/sec and $Q=44.1$ kcal/mole.

Recently, Tomono and Ikushima[21] reported a gross disagreement with the diffusion data for iron in copper given by Mackliet. Except for one point, the present diffusion data are in complete agreement with those of Mackliet. The discrepancy between the results of Tomono and Ikushima and that of Mackliet and the present investigation may result from inadequate attention to inhibition of oxidation of the iron tracer in the former experiment, as evidenced by the extremely small penetration depths observed, or to poor control in counting the weak x ray from the Fe^{55} tracer. Ikushima *et al.*[22] plan to repeat the experiment using Fe^{59} as a tracer.

Ten measurements of the isotope effect were made. The plots of $\ln(N_{55}/N_{59})$ vs $x^2/4D_{59}t$, for diffusion in copper and silver are shown in Figs. 5 and 6.

The measured values of D_{59} and E_{59} are given in Table II. Except for the two lowest temperature silver points, the least-squares standard error is an accurate estimate of the actual error in the isotope effect, E_{59}. It does, however, neglect the possible 4% error due to inaccuracies in $x^2/4D_{59}t$.

It may be noted that the values of the isotope effect measured in the present experiment are of the order of 0.7, far below the value reported by Lazarus and Okkerse[12] for Fe^{55} and Fe^{59} in silver. Apparently the earlier experiment gave a spurious result. Part of the discrepancy may have resulted from evaporation of tracer during the diffusion anneal, since the diffusion profiles showed curvature of the type that is associated with tracer leaving the surface. This would have increased the apparent isotope effect, since Fe^{55} would leave the surface more rapidly than Fe^{59}. Later attempts by the writer to duplicate the earlier result using the same techniques proved unsuccessful, and indicated that fairly large errors were inherent in the methods used for isotope separation and counting. This experience prompted the development of the new techniques used in the present investigation.

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[21] Y. Tomono and A. Ikushima, J. Phys. Soc. Japan **13**, 762 (1958).

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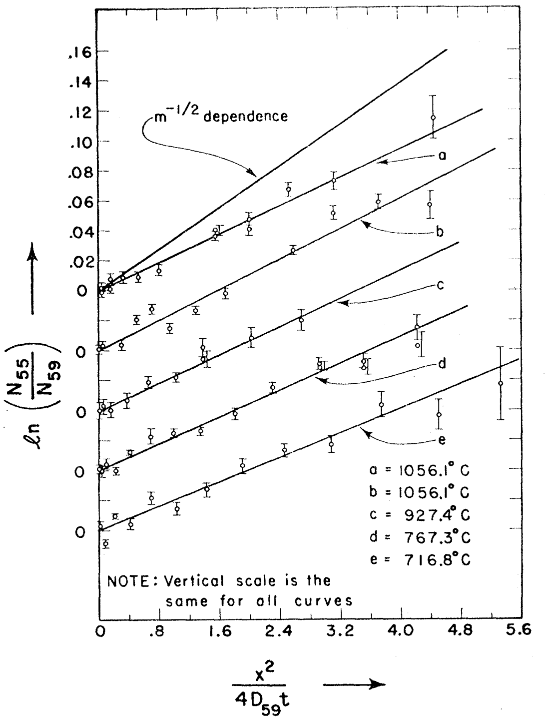

FIG. 5. Relative rates of diffusion of Fe^{55} and Fe^{59} in copper.

IV. DISCUSSION

A. Implications of the Data on the Theory of Prigogine and Bak

According to the theory proposed by Prigogine and Bak, $D\propto m^{-2}$. Hence, it follows from Eq. (1) that $E_{59}\approx 4$ by their theory. Since the observed value of E_{59} is only about $\frac{2}{3}$, a factor of 6 smaller than that predicted by the Prigogine and Bak theory, a serious descrepancy exists between the theory and experiment. As mentioned earlier, the model which they use to calculate the diffusivity, while explicitly taking into account irreversibility, may be too unrealistic a description of the diffusion process. Rice[9] has pointed out that if the collective motion of the shell atoms is taken into account, there will be a reduction of the isotope effect predicted by this model. The inclusion of this effect, however, can hardly account for the factor of 6 discrepancy between the theory and experiment.

B. Connection between Many-Body Effects, Correlation Effects, and the Isotope Effect

Schoen[13] and Tharmaligam and Lidiard[23] have shown that when diffusion occurs by a correlated mechanism, such as the vacancy or interstitialcy mechanism, the isotope effect is, in general, smaller than for a noncorrelated mechanism. For crystals with the proper rotational symmetry, such as the fcc lattice, the correlation factor for vacancy diffusion is shown to be

$$f_B=(1-D_B/D_A)/(1-\rho), \tag{5}$$

where f_B is the correlation factor for the isotope B, D_B is the diffusion coefficient for isotope B, D_A the diffusion coefficient for isotope A, and ρ is the ratio of the solute vacancy exchange rate for isotope B compared to isotope A.

From Vineyard's extension of reaction rate theory, the factor ρ can be expressed in terms of the masses of the two isotopes, m_A and m_B, and the fraction of the translational kinetic energy which the solute atom has compared to the total translational kinetic energy associated with the motion of a representative point crossing the barrier in the N-dimensional configuration space of the crystal, ΔK. In the N-dimensional configuration space the potential energy of the entire crystal is represented as $\phi(m_1^{\frac{1}{2}}x_1\cdots m_N^{\frac{1}{2}}x_N)$, where $x_1\cdots x_N$ corresponds to the N degrees of freedom associated with the $N/3$ atoms, and m_j is the mass corresponding to the coordinate x_j. We can consider vacancy diffusion as represented by the motion of a point in this configuration space moving over a barrier in the potential function ϕ. A hypersurface S is defined such that it passes through the saddle point of the barrier and is every-

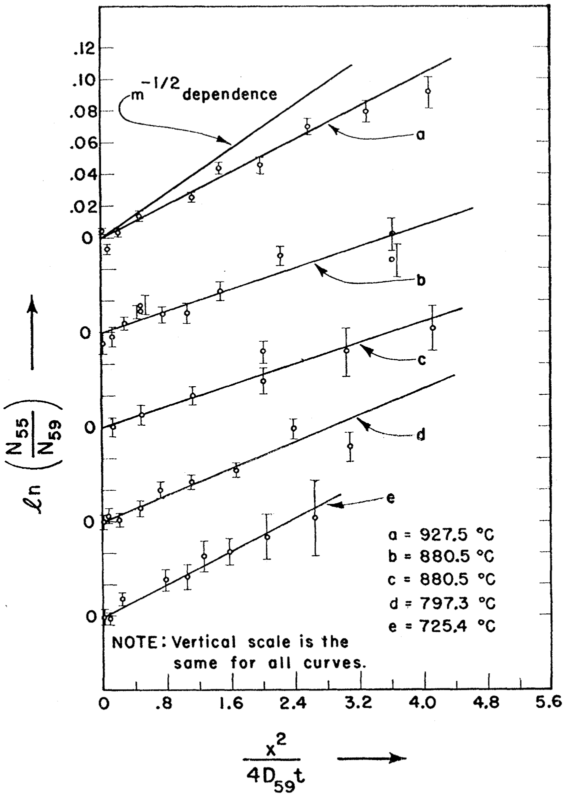

FIG. 6. Relative rates of diffusion of Fe^{55} and Fe^{59} in silver.

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[23] K. Tharmalingam and A. B. Lidiard, Phil. Mag. 44, 899 (1959).

where perpendicular to the lines of constant ϕ. The kinetic energy associated with motion of the representative point at the saddle point can be considered to be composed of two parts; the first may be thought of as a vibrational kinetic energy corresponding to motion "parallel" to the hypersurface S, and the second a translational kinetic energy corresponding to motion "perpendicular" to S. Calling the velocity in this latter direction $\dot{\zeta}$, the total translational kinetic energy, T, is given by $\sum_1{}^N\frac{1}{2}m_j(c_j\dot{\zeta})^2$, where c_j is the direction cosine of the angle between $\dot{\zeta}$ and x_j. Making use of the relation $\sum c_j{}^2=1$ and orienting the axes so that two of the c's are eliminated, it follows that for a solute of mass m_1 at the saddle point in a host crystal, whose atoms are of mass m_2, that T is given by

$$T=\tfrac{1}{2}[c_1{}^2m_1+(1-c_1{}^2)m_2]\dot{\zeta}^2\equiv\tfrac{1}{2}m^*\dot{\zeta}^2, \tag{6}$$

where m^* is an effective mass associated with the motion perpendicular to S, and c_1 is the cosine of the angle between the normal to S and the axis 1, which is associated with the direction of motion of m_1 at the barrier. The first term of the right-hand expression represents the translational kinetic energy of the solute m_1 and the second term represents the translational kinetic energy of the solvent atoms. The factor ΔK is the ratio $(c_1{}^2m_1)/m^*$. If we now consider two solute isotopes, A and B, we can write for the fraction of the translational kinetic energy carried by the solute atoms B, $\Delta K_B=(c_1{}^2m_B)/m_B{}^*$. Also, from Eq. (6) we have $m_B{}^*=c_1{}^2m_B+(1-c_1{}^2)m_2$, and $m_A{}^*=c_1{}^2m_A+(1-c_1{}^2)m_2$. From these three equations it follows that

$$\Delta K_B=(1-m_A{}^*/m_B{}^*)/(1-m_A/m_B). \tag{7}$$

This equation in principle gives the desired information, since $\rho=(m_A{}^*/m_B{}^*)^{\frac{1}{2}}$ and the above relation gives $\rho(\Delta K_B,m_A,m_B)$. This leads to a rather complicated connection between the quantities f_B, ΔK_B, and the measured isotope effect E_B. A simplification occurs, however, if the masses m_A and m_B are of comparable magnitude, as is true in the present investigation. In this event, from Eq. (7) we can write to a good approximation that

$$\Delta K_B=(1-\rho)/[1-(m_A/m_B)^{\frac{1}{2}}].$$

Using this expression we can eliminate $(1-\rho)$ from Eq. (5) with the result,

$$E_B=f_B\Delta K_A. \tag{8}$$

Hence, within the framework of reaction rate theory, as extended by Vineyard, it has been shown that the measured isotope effect is to a good approximation equal to the product of the correlation factor and the fraction of the translational kinetic energy which is possessed by the solute as it crosses the saddle point. Since the measured isotope effect in the present investigation is about $\frac{2}{3}$, it follows that the correlation factor is at least $\frac{2}{3}$, and that the solute atom possesses at least $\frac{2}{3}$ of the total kinetic energy associated with the solute jump.

It would be valuable to measure the isotope effect for self-diffusion, where the correlation factor is known, and ΔK_B could be directly determined.

C. Mechanisms which are Incompatible with the Experimental Data

In Vineyard's[6] discussion it is shown that when a group of atoms move simultaneously, as in the ring mechanism, the mass dependence of the jump frequency is to first order inversely proportional to the square root of the sum of the masses of the group which makes the jump, provided the jump process is equivalent to the motion of a representative point over a single potential barrier in configuration space. For Fe^{55} and Fe^{59} this means that to first order

$$\frac{\Gamma_{55}}{\Gamma_{59}}=\left(\frac{m_{59}+(n-1)m_2}{m_{55}+(n-1)m_2}\right)^{\frac{1}{2}},$$

where $n-1$ are the number of host atoms which jump and m_2 is the mass of each host atom. It is of interest to note that for all values of $n=2$ or higher the predicted isotope effect would be smaller than 0.5 for copper and 0.35 for silver. Since the measured isotope effect is larger than these values in all cases, all mechanisms are excluded which involved the simultaneous jumping of one or more host atoms. This restriction presumably precludes all forms of the ring mechanism, the interstitialcy mechanism, the crowdion mechanism,[24] and the relaxion mechanism.[25]

D. Extensions of Weak-Binding Theory of Correlation

In impurity diffusion the Bardeen-Herring correlation factor depends on the crystalline geometry and the jump frequency of atoms in the region of the impurity. Lidiard[26,27] has proposed a model of impurity diffusion for the fcc lattice which depends on three jump frequencies ν_1, ν_2, and ν_3, where ν_1 is the jump frequency of the solute atom into a vacancy, ν_2 is the jump frequency of each of the four solvent atoms which are nearest neighbors of the solute and the vacancy, and ν_3 the jump frequency of each of the seven atoms which are nearest neighbors of the vacancy but not of the solute. In the limit of very short range interaction between the vacancy and impurity all other frequencies may be taken as ν_0. Manning[28] has used this model to calculate f_i with the result

$$f_i=1/(\alpha+1),\quad \text{where}\quad \alpha=\nu_1/(\nu_2+3.5F\nu_3), \tag{9}$$

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[24] H. R. Paneth, Phys. Rev. **80**, 708 (1950).

[25] N. H. Nachtrieb and G. S. Handler, Acta Met. **2**, 797 (1954).

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

[27] A. D. Leclaire and A. B. Lidiard, Phil. Mag. **1**, 518 (1956).

[28] J. R. Manning, Phys. Rev. **116**, 819 (1959).

F being the fraction of the vacancies which "effectively" do not return to the site where the dissociative jump occurred. In the limit of a nearest neighbor interaction, F is a constant which can be explicitly calculated; i.e., $3.5F=2.575$. For long-range interactions between the vacancy and impurity, F will depend on many jump frequencies. The analysis used by Manning does require that proper crystalline symmetry conditions be met. Also, any relaxation around the vacancy must be such that the rotational symmetry about the solute-vacancy exchange direction is not altered.

In the following analysis it will be shown that one of the frequencies can be eliminated from Eq. (9) for the weak binding limit and an expression for the difference between the activation energy and the Arrhenius Q due to the temperature dependence of the correlation factor will be derived. Manning[29] has shown by a numerical calculation that it is not unreasonable to expect this correction to be large. The following analysis is somewhat more general than Manning's in that the equations derived do not contain any assumptions about the pre-exponential factors for ν_2 and ν_3 jumps, which Manning took to be the same as for a ν_0 jump.

If D_i is defined as the diffusion coefficient for an impurity, and D_s the coefficient of self-diffusion of the host atoms, then

$$D_i/D_s=\nu_1 p_i f_i/\nu_0 p_s f_s, \tag{10}$$

where p_i is the probability that an impurity will have a vacancy for its nearest neighbor, p_s is the probability that a given host atom will have a vacancy as a nearest neighbor in self-diffusion, and f_s the self-diffusion correlation factor. Now p_i/p_s is equal to t_i/t_s, where t_i is the average time required for the vacancy to dissociate from an impurity atom, and t_s the average time required for the dissociation of a vacancy from a given host atom in self-diffusion. These times are inversely proportional to the dissociation jump frequencies, however, so that

$$p_i/p_s=t_i/t_s=\nu_0/\nu_3. \tag{11}$$

Combining Eqs. (10) and (11) gives

$$\nu_1/\nu_3=D_i f_s/D_s f_i. \tag{12}$$

If Eq. (12) is used to eliminate ν_1 in Eq. (9), we obtain

$$f_i=1-\frac{f_s D_i/D_s}{\nu_2/\nu_3+3.5F}, \quad \text{or} \quad \nu_2/\nu_3=\frac{f_s D_i}{D_s(1-f_i)}-2.575. \tag{13}$$

It is seen from Eqs. (12) and (13), that in those cases of vacancy diffusion where $f_i=E_B$ the relative frequencies, ν_1/ν_3 and ν_2/ν_3, are explicitly determined in this model.

It is found experimentally that diffusion coefficients obey the Arrhenius relation $D=D_0\exp(-Q/RT)$. The activation energy for an atomic jump is defined by $H=-d\ln\Gamma/d(1/RT)$, and is equal to the energy of motion of a tracer plus the energy of formation of a vacancy next to the tracer. It is common for f to be considered equal to 1, or constant as in the case of self-diffusion, in which case H is identical with Q. A temperature dependence of f will alter this relation, however, so that $H=Q+(1/f)df/d(1/RT)$. The difference between H and Q can be calculated explicitly for impurity diffusion in the weak-binding limit. The result follows directly from Eq. (13). It is

$$H-Q=\frac{1-f_i}{f_i}\left[Q_i-Q_s+\frac{E_{32}}{1+2.575\nu_3/\nu_2}\right], \tag{14}$$

where E_{32} represents the difference in the energy of motion for a ν_3 jump and a ν_2 jump. It is clear that this factor will, in general, be different from zero. It will be most important when the difference in impurity and self-diffusion Q's is large.

E. Comparison between the Three-Frequency Correlation Factor and the Measured Isotope Effect

As noted, the isotope effect is not, in general, a measure of the correlation factor, but represents the product of the correlation factor and the fraction of the translational kinetic energy possessed by the solute atom at the top of the barrier. In the limit that the solute possesses all of the kinetic energy associated with the jump, $\Delta K_B=1$, and $E_B=f_i$. Hence, it is of interest to try to make a comparison of the correlation

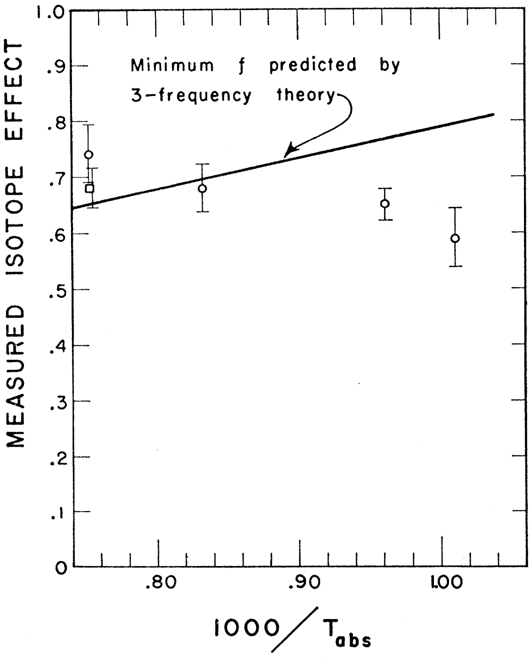

FIG. 7. Temperature dependence of the isotope effect for Fe^{55} and Fe^{59} diffusion in copper.

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[29] J. R. Manning, Phys. Rev. Letters 1, 365 (1958).

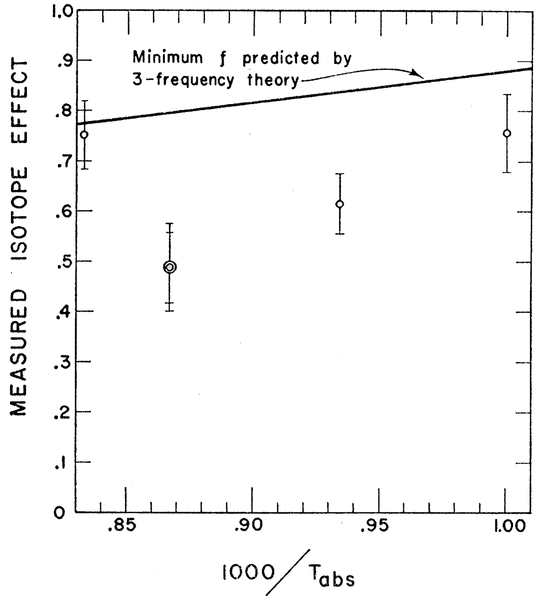

FIG. 8. Temperature dependence of the isotope effect for Fe^{55} and Fe^{59} diffusion in silver.

factor and the isotope effect. To make this comparison, the weak-binding model developed in the previous section will be used.

Using Eq. (13) and the self-diffusion data[30,31] shown in Figs. 3 and 4, it is found that no value of the parameter ν_2/ν_3 can be chosen which gives agreement between E_{59} and f_i. The best agreement is obtained by taking $\nu_2/\nu_3=0$. A comparison between experiment and theory for this case is shown in Figs. 7 and 8. Clearly, even with this extreme assumption, the disagreement between theory and experiment is outside of the experimental error.

It is of further interest to note that the slope of the E_{59} vs $1/RT$ curve for the case of copper does not agree with the value given in Eq. (14), except in the limit that f_i approaches unity. It is not possible to choose E_{32} and ν_3/ν_2 in a self-consistent manner, such that the last bracketed term is negative and of the same magnitude as the positive quantity Q_i-Q_s, provided the relative pre-exponential factors for ν_2 and ν_3 jumps do not differ by more than one order of magnitude.

There are two possible explanations for this discrepancy between f_i and E_{59}. The first is that the many-body effects may be the main cause of the observed isotope effect, in which case a correspondence between f_i and E_{59} would not be expected. Another possibility is that more than three frequencies are altered from the self-diffusion jump frequencies, which would mean that the solute-vacancy interaction distance is greater than a nearest neighbor distance. That this interaction must be of a repulsive character, in order to allow an identification of f_i with E_{59}, can be shown from the following argument. Define the frequency that a vacancy makes the reverse of a ν_3 jump to be ν_4. This will modify Eq. (11) in such a way that

$$f_i=1-\frac{f_sD_i/D_s(\nu_0/\nu_4)}{\nu_2/\nu_3+3.5F(\nu_4)}. \tag{15}$$

The dependence of F on ν_4 is quite complicated in general. It can be estimated, by considering the fraction of vacancies which effectively do return to the site where a dissociative jump occurs, i.e., $F'=1-F$. Consider F_n' to be the contribution to F' due to vacancies returning on the nth jump after a dissociative jump. Now $F_n'=\beta_1\nu_4/(\nu_4+11\nu_0)+\beta_2\nu_4/(2\nu_4+10\nu_0)+\beta_3\nu_4/(4\nu_4+8\nu_0)$, where the β's are, in general, a function of ν_4. For the main term F_1', however, the β's are constants which can be determined from the geometry of the crystal. The form of F_n' and particularly F_1', make it reasonable to approximate F' by the linear relation $F'=\beta\nu_4/\nu_0$. A reasonable choice of β is 0.26, which requires F' to be correct in the limits $\nu_4/\nu_0\rightarrow 0$ and $\nu_4/\nu_0\rightarrow 1$. Hence $F'\approx 1\text{-}0.26\ \nu_4/\nu_0$, in this linear approximation. It should be noted that this approximation is very poor as ν_4/ν_0 becomes large, but it is an adequate estimate in the range $0<\nu_4/\nu_0<2$, for present purposes, since it will overestimate the over-all sensitivity of F on ν_4/ν_0 in this range. Using this linear approximation for F in Eq. (15), it is seen that the factor in the numerator, ν_0/ν_4, controls the dependence of f_i on ν_4. Hence ν_4 must be less than ν_0 if the measured isotope effect is to be explained purely in terms of correlation. The condition that $\nu_4<\nu_0$ indicates a repulsion between iron atoms and vacancies. Such a repulsion is qualitatively in agreement with the predictions of Lazarus,[32] considering the effects of electron screening on solute diffusion.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Professor David Lazarus for his advice and criticism during the preparation of this thesis and for making valuable comments on the present manuscript. Also, the author is indebted to Dr. Boudewijn Okkerse for his contribution in the early stages of this experiment, and wishes to thank Dr. John Manning, Dr. Geritt Tichelaar, and Mr. Douglas Fitchen for stimulating discussions and aid in some of the experimental work. Dr. John Manning and Dr. Fausto Fumi have made helpful comments on the thesis material which are gratefully acknowledged.

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