estimation of ξ are, however, large enough that considerable contributions from multiple scattering or other effects might still be present.

The good agreement obtained in predicting the discontinuity in slope of $C_e(n)$ gives one some confidence in believing that the mechanism of virtual recoil is indeed responsible for this effect. If this is to be the case, then the experimental results can be considered as providing a credible figure for the rigid-band parameter $d\ln C_e/dn$. The value of 0.04 found in this way is rather different from the figure of around -0.4 generally found from band-structure calculations, although these appear to be very sensitive to the form of Slater exchange chosen.[16] While computations of the energy bands of Ag are still thin on the ground, the various discussions[17] of silver's sister metal Cu are unanimous in predicting for this parameter a number that is negative and of order of magnitude unity. Thus, while the present theory seems capable of accounting for the discontinuity in slope of $C_e(n)$, it remains beyond our reach to predict the absolute value of the electronic specific heat in these alloys. If the band-structure calculations are correct, one must look for some further mechanism that will contribute to $C_e(n)$ an amount linear in n but which lies outside the scope of one-electron band-structure calculations.

Extension of this theory to alloys such as *Ag*Sn, in which the scattering potential is much stronger than in *Ag*Cd, does not seem justifiable, since the Born approximation leading to Eq. (9) would not be valid. Difficulties are also encountered when the mass of the solvent is markedly different from that of the solute, whose displacement must then be expressed in terms of localized impurity modes. While work is in progress to extend the theory in this latter direction it is not expected that the mechanism of virtual recoil alone will be adequate to explain such observations as that of the specific heat of Ag, for example, which on addition of small amounts of Au shows[18] an initial *decrease* in C_e.

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Isotope Effect in Self-Diffusion in Iron*

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The isotope effect in self-diffusion was measured in the δ, γ, and α phases of Fe using a new isotope pair, Fe^{52}-Fe^{59}. The isotope-effect data, together with measurements taken on the effect of Co solute additions on Fe self-diffusion, were used to deduce the most likely mechanisms for self-diffusion in all three phases. The data are consistent with a vacancy mechanism in fcc γ-Fe. In bcc α- and δ-Fe, the data are consistent with a vacancy or interstitialcy mechanism. The mechanism seems to be the same in δ- and in α-Fe.

INTRODUCTION

A STUDY of the isotope effect in diffusion can often be helpful in defining the diffusion mechanism through the relationship[1–3]

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

where D_α, m_α and D_β, m_β refer to the diffusion coefficient and mass of the α and β isotope, respectively. The term E is the strength of the isotope effect, f is the correlation factor, and ΔK is defined as the fraction of the kinetic energy in the saddle-point configuration that resides in the migrating atom.[4] The quantity ΔK is, therefore, a measure of the coupling of the jumping atom with the rest of the crystal and corrects for the deviation of the atomic vibrational frequency[5] from the $m^{-1/2}$ dependence.

For self-diffusion in cubic metals, f is a geometrical factor and is only dependent on the diffusion mechanism and crystal structure. If ΔK is close to unity, then an isotope-effect experiment yields an unambiguous value of f, which identifies the diffusion mechanism.

Isotope-effect measurements are perhaps the most powerful, but not the only, method of determining correlation factors. Based on a vacancy model in the fcc structure, Lidiard[6] has developed a statistical theory of the effects of solutes on solvent self-diffusion in dilute alloys. Assuming the solute to be a weak perturbation,

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Lidiard has derived the equation

$$f_i = 1 - \frac{4f_0}{b+18}\left(\frac{D_i}{D_s(0)}\right). \tag{2}$$

Here f_i is the correlation factor for the solute, f_0 is the correlation factor for the solvent in pure solvent, D_i is the impurity-diffusion coefficient of the solute in pure solvent, $D_s(0)$ is the self-diffusion coefficient of the solvent in pure solvent, and b is evaluated by the expression

$$D_s(c) = D_s(0)(1+bc). \tag{3}$$

Here $D_s(c)$ is the diffusion coefficient of the solvent in an alloy containing a concentration c of solute. Equation (2) has been modified by Gibbs[7] for the bcc structure and results in a change from 18 for fcc crystals to 14 for bcc crystals.

Howard and Manning[8] have extended the theory of the effect of solutes on solvent self-diffusion in dilute fcc alloys. The main feature is that Lidiard's simplifying assumption that all solvent jumps occur with a correlation factor f_0 has been removed from their theory. The Howard-Manning theory yields a range of allowable values of f_i that is consistent with experimental data for $D_i/D_s(0)$ and b, with the range becoming narrow for slow diffusing solutes. For a number of solutes in Ag,[8] the calculated f_i, using the theory of Lidiard, always falls within the range of the Howard-Manning theory.

A distinctive feature of both theories is that f_i for slow diffusing solutes should lie in the range $f_0 < f_i < 1$ if diffusion is via vacancies. An experiment using a slow diffusing solute therefore becomes a test for consistency with a vacancy mechanism.

Although a vacancy mechanism predominates for self-diffusion in fcc metals ($\Delta K \sim 1$ and $f=0.78$), the situation is not as clear in bcc metals. Isotope-effect measurements in Na [9] give a value of $E=0.37\pm0.02$, suggesting that either the diffusion mechanism is not by a vacancy, but rather by a divacancy or interstitialcy; or diffusion is by vacancies with a small ΔK. A small ΔK implies a significant coupling of the neighboring atoms to the jumping atom. Other experiments in Na have been unable to differentiate unambiguously between these possible mechanisms. In addition to the unusually low value of the isotope effect in bcc Na, a number of bcc metals show anomalous diffusion behavior. Clearly, further experimental studies on diffusion mechanisms in bcc metals is very desirable.

Iron was chosen for this study for many reasons, principally because a good isotope pair, Fe^{52} ($\tau_{1/2}=8.3$ h)-Fe^{59} ($\tau_{1/2}=45.1$ days), could be developed for use in isotope-effect experiments. Iron has a known slow diffusing solute, Co, with sufficient solubility in all phases so that experiments can be performed on the effect of Co solute on Fe self-diffusion. Also, Fe of high purity can be obtained, handled easily, and studied in both the bcc and fcc phases, and the temperature dependence of self-diffusion follows an Arrhenius relation.

EXPERIMENTAL

Isotope-Effect Experiments

The two radioactive iron isotopes Fe^{52} and Fe^{59} were diffused simultaneously from a thin-layer geometry. The concentration of each tracer, as a function of distance, can be described by

$$C = C_{(x=0)} \exp(-x^2/4Dt), \tag{4}$$

where C indicates specific activities, x is the distance from the plane surface, and t is the time of anneal. When both tracers are considered, two equations of the above form can be combined to give

$$\ln\frac{C_\beta}{C_\alpha} = \text{const} + \ln C_\beta\left(1 - \frac{D_\beta}{D_\alpha}\right). \tag{5}$$

Equation (5) shows that the accuracy of $(1-D_\beta/D_\alpha)$ is determined by the accuracy of C_β/C_α. This ratio must be measured very carefully because $\ln(C_\beta/C_\alpha)$ changes only by about 0.1 across the diffusion zone.

The diffusion samples were machined from high-purity iron (99.95+% pure) provided by the American Iron and Steel Institute. The Fe^{59} tracer was purchased from Nuclear Science and Engineering Corp. and the Fe^{52} was made by an $(\alpha,2n)$ reaction on Cr^{50} in a metallic, natural Cr target. The maximum cross section for this reaction is about 20 mb at 38 MeV,[10] and about 2 mC were obtained from a 400-mA h exposure. The Fe^{52} was radiochemically purified by using two solvent extraction steps.

The Fe^{52} isotope has a slightly troublesome feature: It does not decay directly to a stable isotope.[11] The isotope decays by electron capture and β^+ emission to Mn^{52}, which has two isomeric states. One is the excited Mn^{52m} ($\tau_{1/2}\simeq 21$ min) through which more than 99% of the decay to stable Cr^{52} occurs. Because the Mn^{52m} comes into secular equilibrium with Fe^{52} within approximately 3 h, it has no effect on our counting scheme for Fe^{52} and Fe^{59}. The remaining (about 0.06% as obtained from several determinations) goes through 5.7-day half-life Mn^{52}. This 5.7-day Mn^{52} has been properly corrected for, where necessary.

The two isotopes were mixed so that an Fe^{52}/Fe^{59} ratio of about 6:1 was achieved at the start of counting and the mixture was electroplated onto the Fe samples from an ammonium oxylate plating bath.

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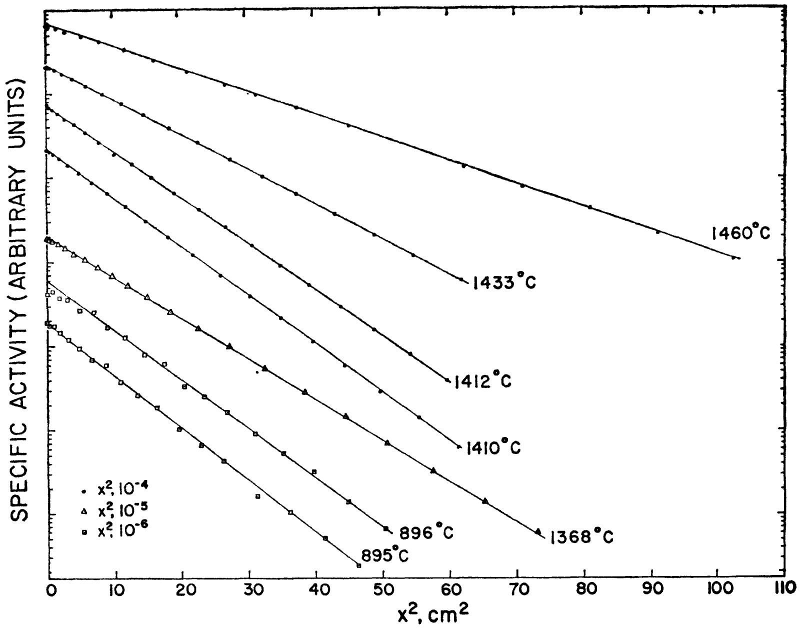

FIG. 1. Penetration plots for Fe self-diffusion.

Encapsulation for the δ- and γ-phase runs was done by placing the samples in Armco Fe cans and electron-beam welding the cans in a vacuum. The γ-run samples were face to face, with a very small gap between them, and surrounded by an Armco Fe collar to reduce evaporation effects. Encapsulation in Ta was attempted, but proved unsuccessful due to gross reaction between the can and the samples, even when a tungsten foil was placed between the sample and the can. Samples encapsulated in Ta showed a pickup of about 2 wt% Ta through what appeared to be vapor transport. Samples run in the α phase were placed in Fe or Ta cups and encapsulated in quartz in a vacuum.

Diffusion anneals in the δ and γ phases were done in a Pt-Rh tube furnace. A flow of argon through the furnace protected the exterior of the Fe can. The temperature was monitored with Pt/Pt-Rh thermocouples that were periodically checked for drift at the Cu or Ag melting point. The furnace was controlled to ±2°C and the total temperature uncertainty was probably less than ±5°C. All annealing times were corrected for heating and cooling.

TABLE I. Self-diffusion and isotope effect in Fe.

Temp. (°C)	D (cm²/sec)	$1-D_{59}/D_{52}$	E	ΔK [a]
1460	1.19×10^{-7}	0.0201±0.0004	0.328±0.007	0.451±0.009
1460	1.16×10^{-7}	0.0206±0.0004	0.337±0.007	0.464±0.009
1433	8.20×10^{-8}	0.0208±0.0003	0.340±0.005	0.468±0.007
1433	7.95×10^{-8}	0.0206±0.0003	0.337±0.005	0.464±0.007
1412 [b]	6.06×10^{-8}	0.0203±0.0003	0.332±0.005	0.457±0.007
1412 [b]	5.68×10^{-8}	0.0209±0.0003	0.342±0.005	0.470±0.007
1410 [c]	6.13×10^{-8}	0.0207±0.0003	0.338±0.005	0.465±0.007
1410 [c]	5.72×10^{-8}	0.0208±0.0002	0.340±0.004	0.468±0.005
1368	4.28×10^{-10}	0.0325±0.0008	0.531±0.013	0.679±0.017
1368	4.70×10^{-10}	0.0324±0.0008	0.529±0.013	0.676±0.017
896 [b]	3.33×10^{-11}	0.0281±0.0015	0.459±0.025	0.631±0.034
896 [b]	3.31×10^{-11}	0.0234±0.0013	0.382±0.021	0.525±0.029
895 [b]	2.94×10^{-11}	0.0307±0.0030	0.502±0.049	0.691±0.067
895 [b]	2.58×10^{-11}	0.0264±0.0009	0.431±0.015	0.593±0.021

[a] Assuming vacancy. [b] Corrected for Co. [c] Corrected for Mn.

Diffusion anneals in the α phase were done in an air furnace that was controlled to ±1°C and had a maximum temperature uncertainty of about ±1°C.

Sectioning for δ and γ runs was done on a precision lathe after the outside diameter had been reduced to eliminate edge effects. About 20 sections were taken over an activity drop of 10^3. The sections were collected and weighed to ±1%. The sum of the weights of the sections agreed with the weight change of the sample to ±1%. The values of x were calculated by using the weight of the section, the diameter of the sample, and the density of Fe.

The α-run sectioning was done by a precision parallel grinder using emery papers. The papers were counted directly and the section weight was taken as the sample weight change after each section was ground.

Lathe sections were dissolved in HCl and diluted where necessary so that no sections counted above 10^6 counts/min. Total γ radiation above a lower-level discriminator was counted with a well-type scintillation counter. Each section was counted to 10^6 total counts at least six times over a period of about three days. The activity contribution of each isotope was determined by fitting these counting data to the elapsed time t using the relationship

$$C_{\mathrm{tot}}=C_{52}\exp(-\lambda_{52}t)+C_{59}\exp(-\lambda_{59}t)\,, \qquad (6)$$

where C_{52} and C_{59} are the specific activities of Fe^{52} and

Fe^{59} at zero time, and λ_{52} and λ_{59} are the decay constants. The Fe^{52}-Fe^{59} isotope pair lent itself nicely to this half-life separation scheme because of the relatively large difference in decay constants [i.e., $\lambda_{52}=(1.392 \pm 0.003)\times 10^{-3}$ min^{-1} from several determinations, and $\lambda_{59}=(1.07\pm 0.01)\times 10^{-5}$ min^{-1} from the literature[9]]. Corrections good to 0.1% were made for dead time, background, and counter drift.

Additional details on experimental procedures for isotope effects that have been applied in this study are given by Peterson[12] and by Rothman and Peterson.[13]

Effect of Co on Fe Self-Diffusion in Fe-Co Alloys

Fe-Co alloys containing 0.75, 1.50, 2.25, and 3.0 at.% Co were made by induction melting Ferrovac E and 99.99% pure Co in high purity, recrystallized alumina crucibles in an argon atmosphere. The ingots were homogenized at 1450°C for 6 h and machined into samples. The Fe^{59} was electroplated onto the alloys and an unalloyed Ferrovac E sample from an ammonium oxylate plating bath. The Co^{60}, prepared by neutron irradiation of a thin Co foil, was vapor deposited onto a Ferrovac E sample.

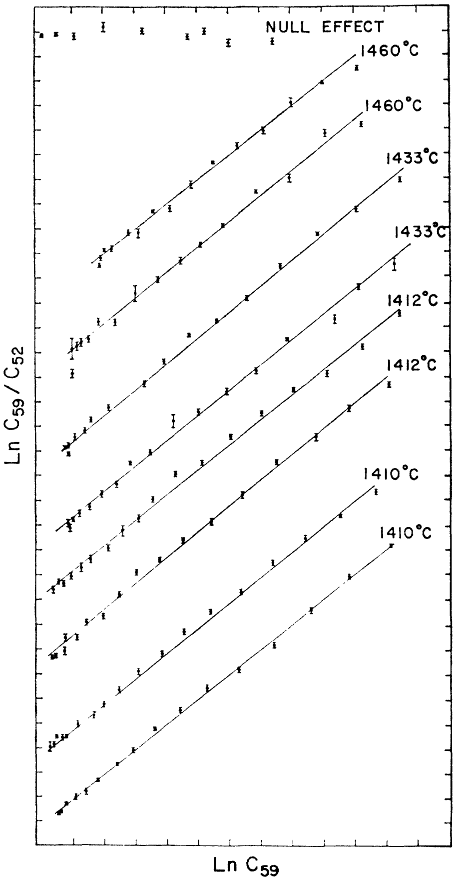

FIG. 2. The $\ln(C_{59}/C_{52})$ versus $\ln C_{59}$ for self-diffusion in δ-Fe. Each division on the ordinate is 0.01 and each division on the abscissa is 0.5. The $\ln C_{59}$ decreases from left to right. The $\ln(C_{59}/C_{52})$ is negative and decreases from bottom to top.

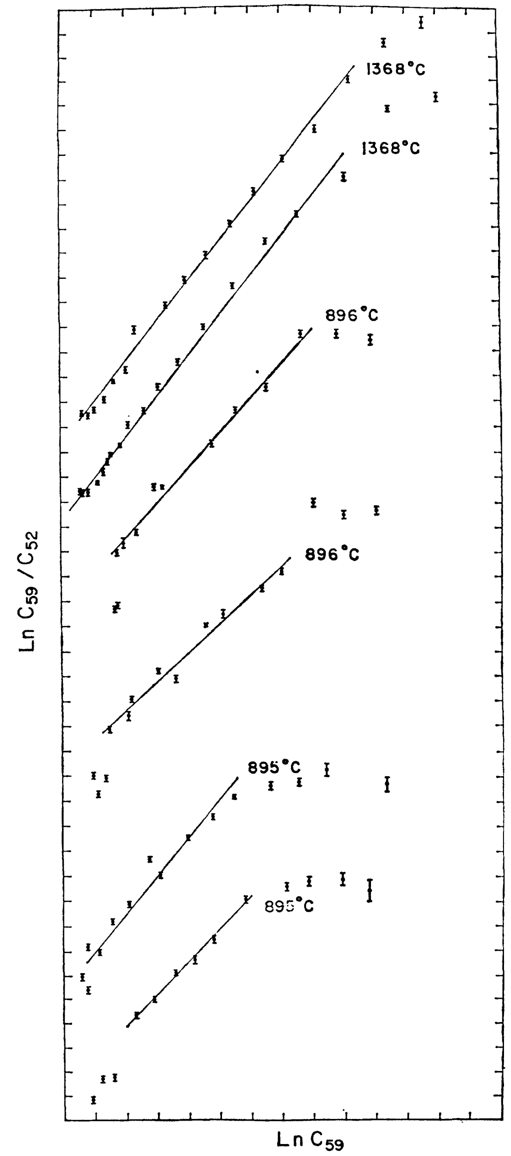

FIG. 3. The $\ln(C_{59}/C_{52})$ versus $\ln C_{59}$ for self-diffusion in γ- and α-Fe. Each division on the ordinate is 0.01 and each division on the abscissa is 0.5. The $\ln C_{59}$ decreases from left to right. The $\ln(C_{59}/C_{52})$ is negative and decreases from bottom to top.

The six samples for a given run were electron-beam welded into six individual compartments of a special Armco Fe container. The special design of the container was required to reduce to a minimum any variation in D from sample to sample due to errors in the time or temperature of the diffusion anneal. These samples were annealed in the same furnace, using the same thermocouples as used for the δ and γ isotope-effect experiments. The temperature uncertainty for these runs

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[12] N. L. Peterson, Phys. Rev. **132**, 2471 (1963).

[13] S. J. Rothman and N. L. Peterson, Phys. Rev. **154**, 552 (1967).

was about ±2°C, and the temperature difference between samples was probably less than a few tenths of a degree centigrade. Corrections for heating and cooling were necessary in the δ phase.

All sectioning and weighing was done according to the procedures used on the δ and γ isotope-effect runs. The lathe turnings were counted directly without dissolution for at least 10^4 counts above background. Corrections to 1% were made for dead time and background. The stubs of the diffusion samples were analyzed for Co content after sectioning.

RESULTS

Fe Self-Diffusion

Two measurements of the Fe self-diffusion coefficient were made at each of four temperatures in the δ phase, one temperature in the γ phase, and two temperatures in the α phase.

The results are given in Table I and agree with existing data[14,15] to 10%, with the exception of one low value at 895°C. This low value is consistent with the observation of some activity holdup in the sample. Representative penetration plots are shown in Fig. 1.

Because the principal goal of this research was to study the diffusion mechanism in Fe and not to obtain self-diffusion coefficients *per se*, the temperature range investigated in each phase was narrow and no attempt was made to obtain activation energies.

Isotope Effect in Fe Self-Diffusion

The isotope-effect results are summarized in Table I and shown in Figs. 2 and 3. The error bars represent the standard deviation of the fit of the data to Eq. (6). The quantity $1-D_{59}/D_{52}$ was determined from a least-squares calculation of $\ln(C_{59}/C_{52})$ versus $\ln C_{59}$. The errors given in Table I for $1-D_{59}/D_{52}$ are the standard deviations obtained from the least-squares calculation.

Runs at temperatures of 1412, 896, and 895°C were done with Fe^{59} that was contaminated with Co^{60}. The data have been corrected by calculating the activity of Co^{60} in each section and subtracting from the calculated activity contribution due to Fe^{59} in that section. This is reasonable because Co^{60} ($\tau_{1/2}=5.24$ yr) should act like Fe^{59} ($\tau_{1/2}=45.1$ days) in the half-life separation scheme. The new Fe^{52}/Fe^{59} ratio is then calculated less the Co^{60} contribution. The Co^{60} activity in each section was calculated using the concentration of Co^{60} in Fe^{59} and the ratio between the Co impurity diffusion coefficient in Fe and the Fe self-diffusion coefficient (accurately known from the effect of Co solute on Fe-self-diffusion experiments). The concentration of Co^{60} in the 1412°C run was $(6\pm2)\%$, as determined from the multichannel analysis of the Fe^{59} solution. This uncertainty can have a reasonably large effect on the slope of $\ln(C_{59}/C_{52})$ versus $\ln C_{59}$. If 6% Co^{60} is assumed, then $1-D_{59}/D_{52}$ goes from an uncorrected value of 0.0265 to 0.0203; if 5% Co^{60} is assumed, the value goes from 0.0265 to 0.0214. Because a 6% Co^{60} correction gave good agreement with the uncontaminated runs in the δ phase, the Co^{60} contamination levels in the α-phase runs were adjusted assuming 6% Co^{60} in the 1412°C run. The concentrations were 2.1 and 1.7% Co^{60} at 895 and 896°C, respectively. A reasonable correction for Co^{60} is possible because D_{Co}/D_{Fe} is accurately known and is close to unity. If D_{Co}/D_{Fe} were differed greatly from unity, the correction would be extremely doubtful.

As previously mentioned, Fe^{52} has a radioactive daughter Mn^{52}, and if the concentration of Mn^{52} is approximately 0.2%, it must be corrected. The samples run at a temperature of 1410°C contained about 0.8% Mn^{52} in the Fe^{52}, and a correction was necessary. The procedure consisted of running an isotope-effect experiment without Fe^{59} so that the Mn^{52}/Fe^{52} ratio in each section could be determined. Because Mn^{52} ($\tau_{1/2}=5.7$ days) acts like Fe^{59} in the half-life separation scheme, the Mn^{52}/Fe^{52} ratios obtained in the above experiment could be applied to a normal Fe^{52}-Fe^{59} experiment to obtain corrected Fe^{59}/Fe^{52} ratios. This method corrected the value of $1-D_{59}/D_{52}$ obtained at the temperature of 1410°C, from 0.0202 to 0.0207. All other runs had less than 0.1% Mn^{52} and corrections were unnecessary. The variation in Mn^{52} content between runs was a function of the chemical purification of Fe^{52}.

The points labeled "null effect" in Fig. 2 show that the isotope effect is not affected by the counting rate. To obtain these points, aliquots covering the usual activity range were taken from a Fe^{52}-Fe^{59} mixture and counted, as described earlier for the isotope-effect experiments.

Our best average values of E in Eq. (1) for δ-, γ-, and α-Fe are as follows:

$$E_\delta=0.337\pm0.007\,,$$

$$E_\gamma=0.530\pm0.014\,,$$

and

$$E_\alpha=0.43\pm0.05\,.$$

If a vacancy mechanism is assumed, the following ΔK's are obtained:

$$\Delta K_\delta=0.464\pm0.009\,,$$

$$\Delta K_\gamma=0.678\pm0.019\,,$$

and

$$\Delta K_\alpha=0.59\pm0.07\,.$$

Because of experimental limitations (i.e., the short half-life of Fe^{52} and the small D in α-Fe), the results obtained in the α phase are of much lower quality than those found in the δ and γ phases. Figure 3 shows the large curvature in all the $\ln(C_{59}/C_{52})$ versus $\ln C_{59}$ plots for α runs. The least-squares fit of these data was done by discarding some of the first and last points in each

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[14] D. W. James and G. M. Leak, Phil. Mag. 14, 701 (1966).

[15] Th. Heumann and R. Imm, J. Phys. Chem. Solids 29, 1613 (1968).

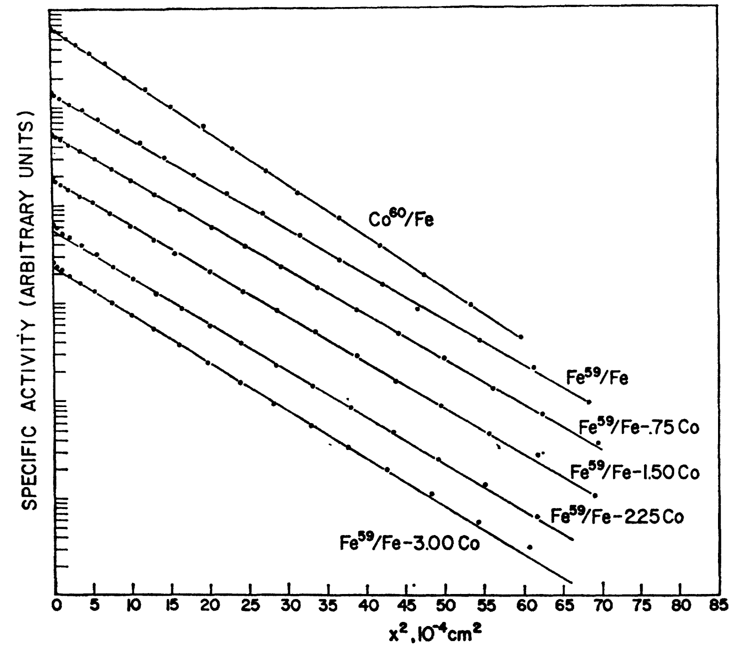

FIG. 4. Penetration plots for diffusion of Co^{60} and Fe^{59} in unalloyed Fe and Fe-Co alloys at 1428°C.

plot. The points that were used for the least-squares fit are evident from the plotted lines. The leveling out of the points near the upper end of each plot was probably due to diffusion down short-circuiting paths and has been found in other isotope-effect studies even when no tailing was evident in the penetration plot.[16] The low points at the beginning of these plots are probably due to surface effects and may be a result of either activity evaporation or holdup.

The last two points for the two samples run at a temperature of 1368°C were not included in the least-squares values of $1-D_{59}/D_{52}$. Again, the leveling out of these points was probably due to diffusion down grain boundaries or dislocations.

Effect of Co on Fe Self-Diffusion in Fe-Co Alloys

Penetration plots for Fe-Co alloys run at a temperature of 1428°C are shown in Fig. 4. The diffusion coefficients obtained from this run and for Fe-Co alloys run at temperatures of 1368 and 895°C are plotted versus Co concentration in Fig. 5 and are given in Table II. By using the experimental values for b and $D_i/D_s(0)$, the following values of f_i in δ-, γ-, and α-Fe were calculated according to the Lidiard theory (bcc form of the Lidiard theory, as derived by Gibbs, was

TABLE II. Effect of Co on Fe self-diffusion.

Alloy composition (at.% Co) Nominal	Actual	1428°C (D, 10^{-8} cm²/sec)	1368°C (D, 10^{-10} cm²/sec)	895°C (D, 10^{-11} cm²/sec)
0	0	7.29	5.24	3.11
0.75	0.77	7.43	5.27	3.06
1.50	1.50	7.38	5.16	3.45
2.25	2.21	7.30	...	3.10
3.0	2.95	7.18	...	2.97
		$D_{Co}=6.42$ $b=-0.6\pm0.5$ $f_i=0.81\pm0.01$	$D_{Co}=3.54$ $b=-1.1\pm1.0$ $f_i=0.88\pm0.01$	$D_{Co}=2.29$ $b=-1.1\pm0.8$ $f_i=0.83\pm0.01$

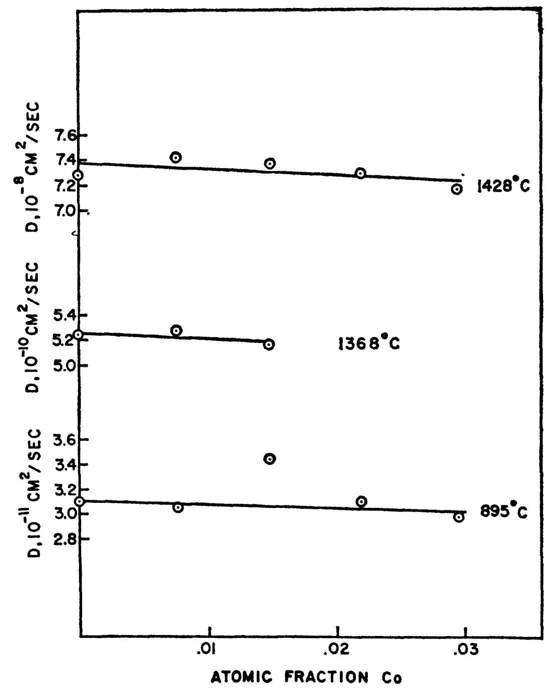

FIG. 5. Diffusion coefficient of Fe^{59} in Fe and Fe-Co alloys as a function of Co concentration at 895, 1368, and 1428°C.

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[16] N. L. Peterson and S. J. Rothman, Phys. Rev. 177, 1329 (1969).

used for α- and δ-Fe):

$$f_{i(\delta)}=0.81\pm0.01,$$

$$f_{i(\gamma)}=0.88\pm0.01,$$

and

$$f_{i(\alpha)}=0.83\pm0.01.$$

The uncertainties in f_i were obtained by substituting the standard deviations calculated for b and the estimated error in $D_i/D_s(0)$ into Eq. (3).

Manning[17] has calculated the allowed range of f_i in the γ phase using the Howard-Manning theory[8] and the data in Table II. He obtained $0.83<f_i<1.00$, which includes the value 0.88 that was obtained by using the Lidiard theory.

Because of the unusually high value of D for the 1.50% Co sample run at a temperature of 895°C, it was not included in the least-squares determination of b for the α run. Why this D was so high is not completely clear, but the penetration plot for the sample shows a much larger evaporation effect than in the other samples. Unfortunately, the 2.25 and 3.0 at.% Co alloys in the γ run were not usable, so b at 1368°C was calculated from only three data points.

DISCUSSION

In the bcc δ phase the value of $E=0.337$ is consistent with several mechanisms including the vacancy, divacancy, interstitialcy, interstitial, and direct exchange. The four-atom ring is eliminated. Several interdiffusion studies in dilute bcc Fe-alloy systems (i.e., Fe-Al,[18] Fe-Cr,[19] and Fe-V[20]) have shown Kirkendall shifts, thus eliminating the direct exchange. A ΔK of only 0.34 is required for the mechanism to be consistent with an interstitial, but measurements of the isotope effect for interstitial diffusion in many different materials have shown ΔK close to unity.[21] The low value of $E=f\Delta K$ is, therefore, most consistent with the vacancy, divacancy, and interstitialcy mechanisms. Our results on the effect of Co additions on Fe self-diffusion, giving an $f_i=0.81$, are consistent with a vacancy mechanism (i.e., $0.727<f_i<1$). The results on the Fe-Co alloy studies, however, show that the Fe self-diffusion coefficient is nearly constant with Co additions (i.e., $b\approx0$) and might be interpreted as being consistent with an interstitialcy mechanism. It is difficult to predict what f_i should be for a divacancy mechanism.

The results on the isotope effect in α-Fe give a value of $E=0.43$. This is appreciably higher than the value of E in δ-Fe, but because of the experimental uncertainties in the α phase care must be exercised in attaching undue significance to the difference. The Fe-Co alloy studies in α-Fe resulted in $f_i=0.83$, suggesting that diffusion occurs via the same mechanism in bcc α and δ phases, and also suggesting that any difference in E between α and δ may be due to a difference in ΔK. Because of the small temperature ranges of stability of δ and paramagnetic α, accurate values of D_0 and Q for self-diffusion in the two phases have been difficult to measure. Most of the data in α- and δ-Fe can be satisfactorily fitted to one diffusion equation [i.e., $D=(2.01\ \text{cm}^2/\text{sec})\,e^{-(57\,500\ \text{cal})/RT}$],[14] which suggests that the same mechanism is operating in both phases (i.e., no breaks or curvature in the Arrhenius plot over a range of D of 10^4).

If divacancies provide a sizeable contribution to diffusion, the relative effect of their contribution will increase with increasing temperature. Hence, divacancy diffusion is inconsistent with our observation of nearly identical values for f_i in α- and δ-Fe. Further theoretical work is required before an equation for f_i for divancies can be obtained that might or might not eliminate them as a mechanism.

A rough correlation between $\Delta V/V$ for diffusion and ΔK has been found in systems where both have been measured. These two quantities are indications of the relaxation about a defect (i.e., a low ΔK is associated with a small $\Delta V/V$, if a large relaxation occurs). Hanneman *et al.*[20] have measured $\Delta V/V$ in bcc α-Fe containing dilute concentrations of vanadium and found a value of 0.45. This is consistent with our measurement of $\Delta K=0.464$ in bcc δ-Fe and might be interpreted as evidence for a highly relaxed vacancy. No data on $\Delta V/V$ for Fe self-diffusion are available.

The isotope-effect results obtained in fcc γ-Fe give $E=0.530$ with a resulting value of $\Delta K=0.678$ for a vacancy. Divancies, direct exchange, and four-atom-ring mechanisms are eliminated. The interstitialcy mechanisms seem rather unlikely in this close-packed structure. The ΔK is considerably lower than those measured for other fcc structures, but agrees with the Heumann-Imm[15] value of 0.74±0.08. This low value of ΔK seems consistent with the Hanneman *et al.*[20] measurement of $\Delta V/V=0.75$ in γ-Fe containing low concentrations of V. The values of f_i obtained from the Fe-Co alloy studies using the theories of Lidiard and of Howard and Manning are consistent with diffusion by the vacancy mechanism in γ-Fe (i.e., $0.78<f_i<1$).

The facts that $D_i/D_s(0)<1$ and $f_i>0.78$ suggest that Co impurity atoms repel vacancies in all phases of iron. Manning's calculations[17] of the allowed range of f_i give $w_4/w_0<1$ for $f_i>0.84$ in γ-Fe; hence, Co atoms also repel vacancies at the second nearest-neighbor position in γ-Fe.

Recent preliminary calculations by Welch[22] indicate that the energy of motion of a vacancy in bcc Na is negative. Because of this negative energy, Welch has

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[17] J. R. Manning (private communication).

[18] K. Sato, Trans. Japan Inst. Metals 4, 121 (1963).

[19] H. W. Paxton and E. J. Pasierb, Trans. AIME 218, 794 (1965).

[20] R. E. Hanneman, R. E. Ogilvie, and H. C. Gatos, Trans. AIME 233, 691 (1965).

[21] L. W. Barr and A. D. LeClaire, Proc. Brit. Ceram. Soc. 1, 109 (1964).

[22] D. O. Welch (private communication).

suggested that the stable configuration for an atom adjacent to a vacancy would be the atom in the saddle-point position with a split vacancy on either side. The energy of motion of a vacancy in Na, as implied from the self-diffusion measurements of Mundy *et al.*[9] and the Simmons-Balluffi-type experiment of Feder and Charbnau,[23] is very low; hence, unlike the fcc structure, the difference in energy between a bcc Na atom in the saddle-point configuration and the same atom on a lattice site next to a vacancy is small. This adds some credence to the calculation of Welch. Since the experimental values of $f\Delta K$ are about the same for Na and bcc Fe, a comparison of these two elements is not totally unreasonable.

The jumping of an atom associated with a split vacancy must involve the cooperative motion of another atom so that the mass factor in Eq. (1) would be reduced. To a first approximation, the correlation factor for a split vacancy should be very similar to that for a normal vacancy, so $f\approx 0.7$ combined with the reduced mass factor yields a value of ΔK near unity (i.e., $\Delta K=0.9$ for δ-Fe). In independent studies of defects, such as the Simmons-Balluffi experiments, the split-vacancy mechanism would be difficult to verify because it should behave like a vacancy. Possibly the presence of split vacancies can be detected through studies of the effect of solutes on self-diffusion, but this requires an extension of the theories of Lidiard and of Howard and Manning. This concept is merely a calculated possibility; the inclusion does, however, provide an interesting alternative mechanism for diffusion in bcc metals.

Our calculations of f and ΔK involved three simplifying assumptions. First, an assumption was made that the correlation factor for Fe^{59} is the same as for the host atoms. Second, for Eq. (1) to be strictly applicable, $\Delta K=1$ was assumed. Third, quantum effects were ignored. The three resulting corrections have been calculated using LeClaire's equations.[4] They are all about 2%, tend to cancel one another, and have no significant affect upon our values of ΔK.

SUMMARY

Self-diffusion in bcc Fe probably takes place by either vacancies or interstitialcies. The data obtained from isotope-effect experiments and the effect of Co on Fe self-diffusion in both α- and δ-Fe are most consistent with a vacancy mechanism. Interstitialcies are also a strong possibility, but the theory of the effect of solutes on self-diffusion has not been extended beyond vacancies, so that there is considerable uncertainty in predicting what the diffusional behavior should be like if interstitialcies dominate. Divacancies appear to be somewhat unlikely, but cannot be eliminated.

Isotope-effect measurements and studies on the effect of Co on Fe self-diffusion indicate that self-diffusion in fcc γ-Fe is most likely via vacancies. The relatively low value of ΔK indicates that the atoms around a vacancy relax more in γ-Fe than in other fcc metals.

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[23] R. Feder and H. P. Charbnau, Bull. Am. Phys. Soc. 11, 49 (1966).