sity maxima in the energy loss spectrum. However, only the maximal positions which correspond to the most probable momentum exchanges are used in the present analysis; these remain unappreciably affected. In this sense Eq. (1) is valid for the total momentum, including the normal component [C. B. Duke (private communication)].

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PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Diffusion and Correlation Effects in Copper-Zinc Alloys*

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(Received 30 January 1970)

The self-diffusion coefficients of copper in copper-zinc alloys containing 0–4-at.% zinc have been measured at 894.4 and 946.7 °C. These results, together with the correlation factor for the diffusion of zinc in copper as determined from measurements of the isotope effect, are used to obtain the relative jump frequencies of the zinc atoms and the neighboring copper atoms by means of the theory of Howard and Manning. The isotope effect for the diffusion of both copper and zinc has been measured in α–Cu-Zn alloys containing 4- and 30-at.% Zn, and in ordered and disordered β–Cu-Zn. The results support Manning's theory of correlation effects in concentrated alloys for those cases where the theory should be applicable (30-at.% Zn and disordered β–Cu-Zn). The agreement is poorer for those cases where the theory is less applicable (4-at.% Zn and ordered β–Cu-Zn). The isotope effect for the diffusion of copper is the same in ordered and in disordered β–Cu-Zn. This supports our earlier conclusion that the Elcock-McCombie mechanism is not the dominant mechanism in ordered β–Cu-Zn when the state of the order is described by $S = 0.7$.

INTRODUCTION

The correlation factor f_i for the diffusion of an impurity in an otherwise pure metal can give detailed information on the relative magnitudes of the jump frequencies of the impurity and host atoms. Experimental values of f_i for diffusion in metals can be obtained from measurements of the isotope effect in diffusion[1,2] or from the effect of solute on the self-diffusion of the solvent in dilute alloys.[3] By combining the results of these two types of experiments, the ratios of various atomic jump frequencies about an impurity-vacancy pair can be obtained.[4] Such experiments and calculations were described for the diffusion of zinc in silver in a previous paper[5]; this paper presents similar results for the diffusion of zinc in copper.

Correlation effects in concentrated alloys are more complicated than in dilute alloys; Manning[6] treated them using a rather simplified model. This model is expected to give a more accurate description of correlation effects in concentrated alloys than in dilute alloys, because vacancy binding to the solute becomes more important in the latter. We have attempted to test the range of validity of Manning's theory of correlation effects in binary alloys by measuring the isotope effect for the diffusion of both copper and zinc in copper alloys containing 4- and 30-at.% zinc, and of copper in an alloy containing 50-at.% zinc in both the ordered and disordered states. The results on the alloys containing 50-at.% zinc together with our previous results on the isotope effect for the diffusion of zinc in the same alloy[7] allow us to draw qualitative conclusions about the mechanism of diffusion in β–Cu-Zn.

EXPERIMENTAL

The thin-layer geometry and lathe sectioning were used. The isotope ratios were determined by a half-life separation described in detail by the authors elsewhere.[5,8]

Materials

Single crystals of copper or of β brass were grown from 99.999% pure materials by the Bridgman method. The crystals containing 1–4- or 30-at.% zinc were grown by the strain-anneal method. Specimens 1 cm in diameter by 0.8 cm long were spark cut from the long single crystals, mechanically polished, etched, and given a preliminary anneal near the melting point. The preliminary anneal of the alloy crystals was done in capsules containing turnings of the same composition as the sample in order to eliminate the loss of zinc from the sample surfaces. Only crystals found to be good by metallographic and x-ray examination were used.

Carrier-free ^{67}Cu and high-specific-activity ^{65}Zn were purchased from Oak Ridge National Laboratory; ^{64}Cu and ^{69}Zn were produced by neutron irradiation of 99.999% pure copper foil and enriched ^{68}ZnO, respectively. No radioactive impurities could be detected in the plated tracers with a multichannel analyzer and a Ge(Li) detector. Counting of the ^{64}Cu, ^{67}Cu, and ^{69}Zn over a period of ten half-lives further substantiated the high radiochemical purity of the tracers.

Diffusion Measurements

The copper or zinc radioisotopes were deposited by electroplating. For the measurements of the effect of zinc additions on the self-diffusion of copper, each copper-zinc sample was plated with ^{67}Cu and sealed into a separate stainless-steel capsule by electron-beam welding to eliminate transport of zinc from one sample to another through the vapor phase. The five stainless-steel capsules plus a pure copper crystal plated with ^{65}Zn were sealed off in one quartz capsule and annealed simultaneously so that errors in the time and temperature of the diffusion anneal would not enter into the determination of the relative values of D. The temperature difference over the six samples was less than 1 °C. For all the other diffusion measurements, the plated samples were sealed off in small quartz capsules under a vacuum of better than 2×10^{-5} Torr and annealed for periods ranging from 4 to 40 h at temperatures measured to ± 1 °C, including calibration corrections. Time corrections for heating and cooling of the specimen were applied to each diffusion anneal. After diffusion, the cylindrical surfaces of the samples were turned down to avoid surface diffusion effects, and about 20 sections were cut on a lathe. The chips were brushed into tared bottles, and the section thicknesses were determined from the section weights and the density and diameter of the samples. Careful brushing kept the weight losses to less than 0.5%. The chips were dissolved in 1 ml of HNO_3 and counted in a well-type scintillation counter. Each section was counted to a minimum of 10^4 counts over background. After enough sections had been removed for the penetration plots, several additional sections were taken for analyses of the zinc content.

Isotope Effect Measurements

A mixture of ^{64}Cu ($t_{1/2} = 12.74$ h) and ^{67}Cu ($t_{1/2} = 62.21$ h), or of ^{65}Zn ($t_{1/2} = 245$ days) and ^{69}Zn ($t_{1/2} = 13.8$ h) was electroplated onto the sample surfaces. The same techniques were used for the diffusion anneals and sectioning as in the diffusion measurements; however, instead of counting each section once to 10^4 counts above background, each section was counted to 10^6 counts at least six times in the 72 h directly following the sectioning.

Total γ radiation A above a lower-level discriminator was counted. "Hot" sections were diluted to an activity of 5×10^5 counts/min: the volume to be counted was kept constant. This procedure was used to avoid changes in the gain of the photomultiplier tube, and to keep the uncertainty of the dead-time correction to less than 0.1%. The ratio of the activities of the two isotopes α and β (^{64}Cu and ^{67}Cu or ^{65}Zn and ^{69}Zn) was determined by fitting these counting data to the time elapsed from an arbitrary zero time:

$$A = A_\alpha e^{-\lambda_\alpha t} + A_\beta e^{-\lambda_\beta t} \; . \qquad (1)$$

Here A_α and A_β are the activities due to the isotopes α and β at time zero, and λ_α and λ_β are the decay constants which are calculated from the above half-lives. Corrections accurate to 0.1% were made for counter dead time, background, and counter drift. Null-effect experiments using the same counter, isotope pairs, and technique showed that the isotope ratio was independent of the counting rate.[5,8]

RESULTS

Effect of Zn on the Diffusion of Cu in Cu-Zn Alloys

The mathematical solution of the diffusion equation for the boundary conditions used in our experiments is

$$C = K e^{-X^2/4Dt} \; , \qquad (2)$$

where C is the specific activity in a section whose center is X cm from the original surface, t is the annealing time, and K is a constant. Figure 1 shows that the penetration plots for the diffusion of

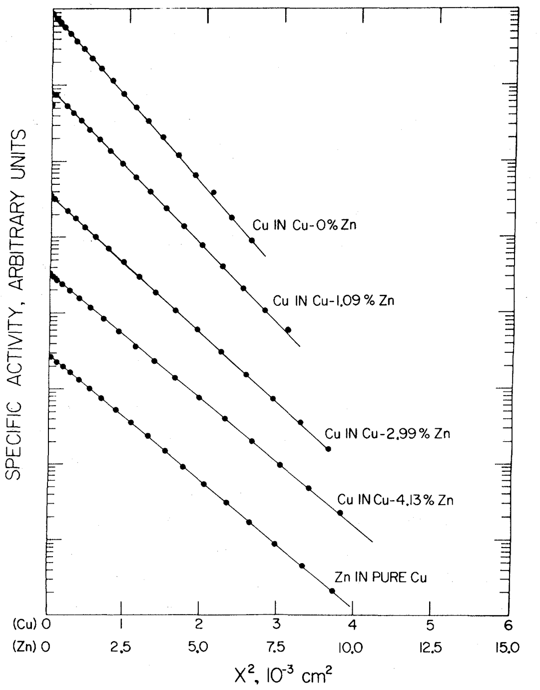

FIG. 1. Log specific activity versus penetration distance squared for the diffusion of ^{67}Cu in pure copper and copper-zinc alloys and for the diffusion of ^{65}Zn in pure copper at 946.7 °C.

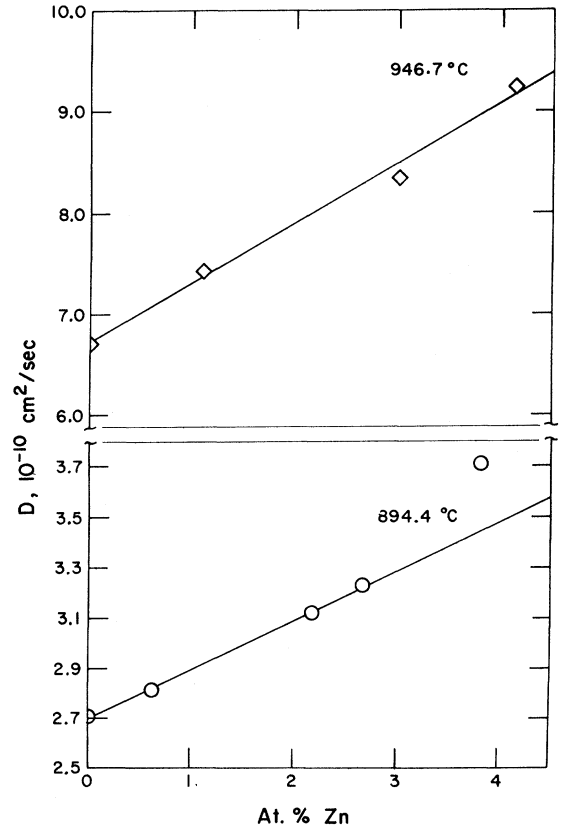

FIG. 2. Diffusion coefficients of ^{67}Cu in copper-zinc alloys versus zinc concentration for diffusion at 894.4 and 946.7 °C.

^{67}Cu in Cu-Zn alloys and ^{65}Zn in pure copper at 946.7 °C do obey Eq. (2). The values of D from this run and a similar run at 894.4 °C (Table I) vary linearly with zinc concentration (Fig. 2) as predicted by theory, except the value of D_{Cu} from the 4%-zinc alloy at 894.4 °C. Solute-solute interactions are apparently significant at this temperature and concentration, so this point was not considered when drawing the lines in Fig. 2. The temperatures of these experiments were close to those used in the measurements of the isotope effect for the diffusion of zinc in pure copper (894.5 and 946.4 °C).[7] The values of D_{Zn} and D_{Cu} in pure copper agree within 1% with our previously published values[7,8] as well as with those of other workers.[9,10]

TABLE I. Effect of zinc on self-diffusion in copper.

		894.4 °C	946.7 °C
Tracer	C_{Zn} (at. %)	$D(10^{-10}\ cm^2/sec)$	$D(10^{-10}\ cm^2/sec)$
^{65}Zn	0	9.66	22.7
^{67}Cu	0	2.71	6.70
	0.62	2.81	
	1.09		7.42
	2.17	3.12	
	2.68	3.23	
	2.99		8.33
	4.06	3.71	
	4.13		9.23

Isotope Effect for the Diffusion of Copper and Zinc in Cu-Zn Alloys

If Eq. (2) is written for the simultaneous diffusion of isotopes α and β, one obtains

$$\ln(C_\alpha/C_\beta) = \text{const} - (\ln C_\alpha)[(D_\alpha/D_\beta) - 1] \ . \qquad (3)$$

The plots of $\ln(C_\alpha/C_\beta)$ versus $\ln C_\alpha$ for the copper isotopes (Fig. 3) and zinc isotopes (Fig. 4) obey Eq. (3). The error bars in Figs. 3 and 4 are the standard errors of $\ln(C_\alpha/C_\beta)$ calculated from a linear least-squares fit to Eq. (1). The values of $[(D_\alpha/D_\beta) - 1]$ obtained from the slopes of these plots, and their standard errors, are listed in Table II together with our previous results on the zinc isotope effect in pure copper and in β-Cu-Zn[7] and the copper isotope effect in pure copper.[8] The penetration plots from the isotope effect experiments were also linear over a factor of 10^3 in

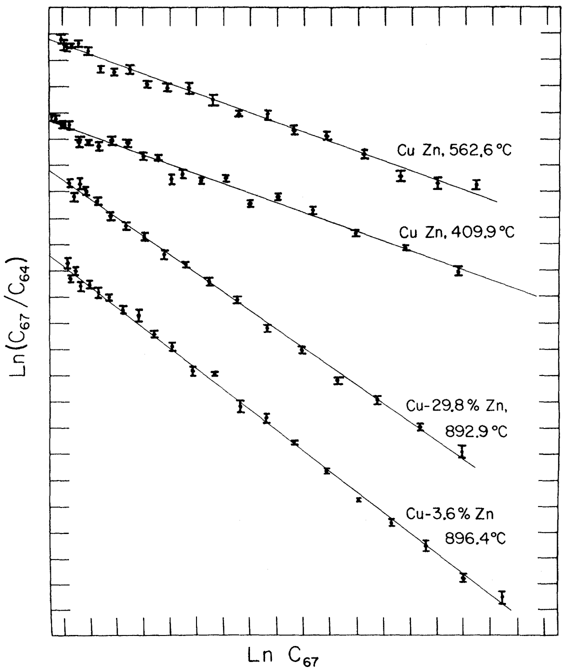

FIG. 3. $\ln(C_{67}/C_{64})$ versus $\ln C_{67}$ for the diffusion of copper in copper-zinc alloys. Each division on the ordinate is 0.01. Each division on the abscissa is 0.5.

specific activity and were as good as those in Fig. 1.

The isotope effect is related to the correlation factor by the equation[1,2,11]

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

where D and m are the diffusion coefficients and masses of two isotopes α and β of the same element, and ΔK is the fraction of the kinetic energy of the saddle-point configuration – associated with motion in the diffusion direction – that is possessed by the diffusing atom. The values of $f\Delta K$, calculated from the experimental values of $[(D_\alpha/D_\beta)-1]$ by means of Eq. (4), are also listed in Table II.

DISCUSSION

Effect of Zinc on the Diffusion of Copper in Cu-Zn Alloys

The effect of solute on the self-diffusion coefficient of the solvent in dilute alloys can provide information about the correlation factor f_i for impurity diffusion in the pure solvent. For impurity diffusion in the fcc lattice, f_i is given by[12]

$$f_i=(\omega_1+\tfrac{7}{2}F\omega_3)/(\omega_1+\omega_2+\tfrac{7}{2}F\omega_3)\ . \tag{5}$$

Here ω_1 is the rate of exchange of a vacancy neighboring an impurity atom with any of the four solvent atoms that are also neighbors of the impurity; ω_3 is the frequency of vacancy jumps that dissociate the impurity-vacancy pair; and ω_2 is the impurity-vacancy exchange rate. The term F is a function of the ratio ω_4/ω_0, where ω_4 is the frequency of the association jump (reverse of a ω_3 jump), and ω_0 is the frequency of solvent-vacancy exchanges in the pure solvent crystal.

The relation between f_i and the effect of solute on self-diffusion of the solvent, as derived by Lidiard,[3] is given by the equations

$$D_s(C)=D_s(0)(1+bC), \tag{6}$$

$$f_i=1-\frac{4f_0}{b+18}\left(\frac{D_i}{D_s(0)}\right)\ , \tag{7}$$

for diffusion in fcc alloys. Here $D_s(0)$ is the self-diffusion coefficient in the pure solvent; $D_s(C)$ is the diffusion coefficient of the solvent in a dilute binary alloy containing atomic fraction C of solute; D_i is the impurity diffusion coefficient in the pure solvent; f_0 is the correlation factor for self-diffusion in the pure solvent; and b is a constant of proportionality.

The correlation factor f_i can also be determined from measurements of the isotope effect for the diffusion of the impurity and of the solvent in the

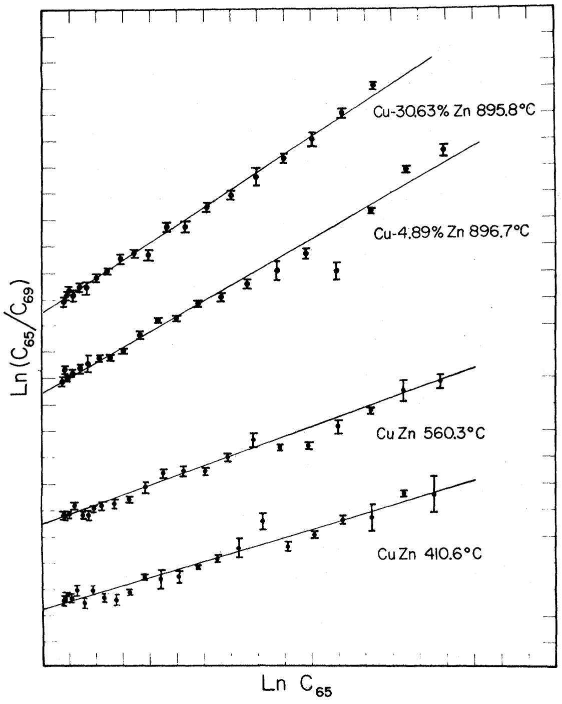

FIG. 4. $\ln(C_{65}/C_{69})$ versus $\ln C_{65}$ for the diffusion of zinc in copper-zinc alloys. Each division on the ordinate is 0.01. Each division on the abscissa is 0.5.

TABLE II. Isotope effect results.

Isotopes	C_{Zn} (at. %)	Temp. (°C)	D (cm^2/sec)	$(D_\alpha/D_\beta)-1^{\mathrm{a}}$	$f\Delta K$
^{64}Cu, ^{67}Cu	0	894–1061		$0.0155\pm0.000\,32$	0.684 ± 0.014 (Ref. 8)
	3.6	896.4	3.75×10^{-10}	$0.0158\pm0.000\,17$	0.699 ± 0.007
	29.8	892.9	4.31×10^{-9}	$0.0143\pm0.000\,20$	0.632 ± 0.009
	46.2	562.6	1.70×10^{-8}	$0.0074\pm0.000\,20$	0.325 ± 0.009
	46.8	409.9	1.77×10^{-10}	$0.0074\pm0.000\,23$	0.325 ± 0.010
^{65}Zn, ^{69}Zn	0	894.5	9.75×10^{-10}	0.0123 ± 0.0001	0.41 (Ref. 7)
	0	946.4	2.27×10^{-9}	0.0124 ± 0.0003	0.41 (Ref. 7)
	4.89	896.7	1.31×10^{-9}	$0.0118\pm0.000\,29$	0.389 ± 0.010
	30.6	895.8	1.67×10^{-8}	$0.0135\pm0.000\,25$	0.446 ± 0.008
	49.0	560.3	4.46×10^{-8}	0.0074 ± 0.0002	0.24 (Ref. 7)
	47.2	410.6	4.38×10^{-10}	0.0061 ± 0.0003	0.20 (Ref. 7)

[a] For Zn tracers, $(D_{65}/D_{69})-1$ is listed; for Cu tracers, $1-(D_{67}/D_{64})$ is listed.

pure solvent. The first gives $f_i\,\Delta K$, and the second gives ΔK, which is assumed to be the same for solute and solvent.

We have used both techniques to measure f_i for the diffusion of zinc in copper. We have obtained values of b and f_i (Lidiard) from the plots of Fig. 2, and of f_i (ISO) from our values of the isotope effect for the diffusion of zinc[7] and of copper[8] in copper (Table III).[13] The difference between f_i (Lidiard) and f_i (ISO), 25%, is much larger than the estimated maximum errors of 4% in f_i (Lidiard) and f_i (ISO). The difference is also much larger in the present case than it is for the diffusion of zinc in silver.[5]

In arriving at Eq. (7), Lidiard has assumed that all solvent jumps occur with a correlation factor f_0. Howard and Manning[4] have removed this assumption and found that for a given set of values of D_i, $D_s(0)$, and b there is a range of possible values of f_i, and that unique values of ω_4/ω_0, ω_3/ω_1, and ω_2/ω_1 correspond to each value of f_i. Using the values of b, $D_i/D_s(0)$, and f_i (ISO) in Table III, Manning[14] obtained results for zinc diffusion in copper, which are listed in Table IV.

The apparent temperature dependence of these jump frequencies should not be taken seriously since they are very sensitive to the value of f_i; increasing f_i (ISO) by 0.01 decreases ω_4/ω_0 by 5%, and ω_3/ω_1 and ω_2/ω_1 by 15% each. Thus we know the jump-frequency ratios only to 30%, even though we measure the relative diffusion coefficient of ^{65}Zn and ^{69}Zn to within 0.03%. Nevertheless, the jump-frequency ratios are of the expected magnitude. Since zinc diffuses faster than copper in copper, ω_2/ω_1 is expected to be greater than unity. Similarly, since zinc is an electropositive impurity in copper and hence is believed to attract vacancies, we expect ω_4/ω_0 to be greater than unity.

The present results are in fair agreement with LeClaire's calculations[15] of f_i and b based on the screened electrostatic interaction between vacancies and impurities. He obtained $b=8.2$ and $f_i=0.55$ for the diffusion of zinc in copper at 727 °C. Extending the calculation to include ω_4 jumps lowers f_i to 0.49, and improves the agreement between theory and experiment.

The same theory has been used by LeClaire to calculate the values of the jump-frequency ratios. Since the jump frequencies depend exponentially on the temperature,

$$\omega_i=\nu_i\,e^{-H_i/RT}\ , \tag{8}$$

we may write

$$\omega_j/\omega_0=(\nu_j/\nu_0)e^{-\Delta H_j/RT}\ , \tag{9}$$

where ΔH_j is the difference between the activation energies for ω_j and ω_0 jumps. LeClaire calculated values of ν_2/ν_0 and ΔH_j, and assumed that $\nu_1=\nu_3=\nu_4=\nu_0$. We have used his calculated values of ΔH_j and ν_2/ν_0 and our experimental values of the jump-frequency ratios for diffusion at 946.7 °C to obtain $\nu_1/\nu_0=0.8$, $\nu_3/\nu_0=0.6$, and $\nu_4/\nu_0=1.2$. These results are in fair agreement with the value of unity assumed by LeClaire.

TABLE III. Correlation factors for the diffusion of zinc in copper.

T (°C)	b	$D_i/D_s(0)$	f_i (Lidiard)	f_i (ISO)
894.4	7.23	3.56	0.56	0.47
946.7	8.78	3.39	0.60	0.47

TABLE IV. Jump frequency ratios of a vacancy near a zinc atom in copper.

T (°C)	ω_4/ω_0	ω_3/ω_1	ω_2/ω_1
894.4	1.2	0.5	2.5
946.7	1.5	0.9	3.6

Isotope Effects for α-Cu-Zn

The isotope effect for diffusion in α-Cu-Zn is discussed in terms of Manning's theory,[6] which treats correlation effects for diffusion in binary alloys as follows. He assumes that vacancy exchanges with tracer atoms A and B occur with jump frequencies ω_A and ω_B independently of the configuration of the surrounding atoms, and that all vacancy exchanges with nontracer atoms occur with an average frequency W given by

$$W = \omega_A N_A + \omega_B N_B \ , \tag{10}$$

where N_A and N_B are the molar fractions of A and B. Although this may be an acceptable model in random alloys with composition near 50-50, the assumptions become less realistic in dilute alloys where solute-vacancy interaction can become more important.

In this model, the correlation factor f_A for diffusion of A atoms in a random A-B alloy is[6]

$$f_A = \frac{(M_0+2)(N_A D_A + N_B D_B) - 2D_A}{(M_0+2)(N_A D_A + N_B D_B)} \ , \tag{11}$$

where M_0 is a constant equal to 7.15 for the fcc lattice and 5.33 for the bcc lattice. The equation for f_B is similar, with $-2D_A$ replaced by $-2D_B$.

A direct comparison between the correlation factors calculated from Eq. (11) and the isotope-effect results cannot be made because we do not know ΔK. However, the ratio f_A/f_B calculated from measured values of D_A and D_B can be compared to the ratio $(f\Delta K)_A/(f\Delta K)_B$ if one assumes that $\Delta K_A = \Delta K_B$, an assumption that should be valid within the framework of Manning's model. For the purposes of this comparison, the values of D_{Cu} were corrected to the temperatures and compositions used to measure D_{Zn} (see Table II). The compositional dependence of D_{Cu} from Table I and the temperature dependence of D_{Cu} reported by Hino *et al.*[9] for the 30%-zinc alloys were used for the correction. The corrections were small (12% or less) and are believed to be accurate to 2%.

The agreement between f_A/f_B calculated from Eq. (11) and $(f\Delta K)_A/(f\Delta K)_B$ (Table V) is good for the alloy with 30-at.% zinc but is outside the range of errors at the 4-at.% zinc concentration. This disagreement is expected in dilute alloys because the binding of the solute to vacancies becomes important and the assumptions inherent in Eq. (10) are not valid.

If the agreement between the experimental and theoretical ratios of the correlation factors implies that the values of f_{Zn} and f_{Cu} from Eq. (11) are correct, then $\Delta K_{\mathrm{Zn}} = \Delta K_{\mathrm{Cu}} = 0.76 \pm 0.03$ in a copper–30-at.% zinc alloy, i.e., alloying with zinc decreases ΔK.

$f\Delta K$ for the diffusion of copper and of zinc is the same within experimental error in pure copper as it is in the 4-at.% zinc alloy. This indicates that solute-solute interactions perturb the correlation factors less than they do the diffusion coefficient of the solute, as discussed above.

Isotope Effects for β – Cu-Zn

The β phase of the Cu-Zn system has a disordered bcc structure at high temperatures that becomes ordered with the CsCl structure at lower temperatures. If diffusion in the disordered alloy takes place by nearly random vacancy motion, and diffusion in the ordered alloy occurs by the highly correlated Elcock-McCombie mechanism,[16] the isotope effect should be appreciably larger for the disordered structure than for the ordered structure. Nevertheless, our previous measurements of the isotope effect for the diffusion of zinc in ordered and disordered β-Cu-Zn showed only a small difference in $f\Delta K$ between the two states of order. We concluded that the sequences of atomic jumps

TABLE V. Correlation factors in Cu-Zn alloys. The quoted error on $f_{\mathrm{Zn}}/f_{\mathrm{Cu}}$ is the range that results from errors of ±5% in D_{Zn} and D_{Cu}. The error limits on $(f\Delta K)_{\mathrm{Zn}}/(f\Delta K)_{\mathrm{Cu}}$ cover the range allowed by the probable errors listed in Table II.

T (°C)	C_{Zn} (at.%)	Corrected D(cm^2/sec)	$f_{\mathrm{Zn}}/f_{\mathrm{Cu}}$	$(f\Delta K)_{\mathrm{Zn}}/(f\Delta K)_{\mathrm{Cu}}$
896.7	4.89	$D_{\mathrm{Zn}} = 1.31 \times 10^{-9}$ $D_{\mathrm{Cu}} = 4.05 \times 10^{-10}$	0.456 ± 0.050	0.557 ± 0.020
895.8	30.6	$D_{\mathrm{Zn}} = 1.67 \times 10^{-8}$ $D_{\mathrm{Cu}} = 4.84 \times 10^{-9}$	0.650 ± 0.025	0.706 ± 0.023
560.3	49.0	$D_{\mathrm{Zn}} = 4.46 \times 10^{-8}$ $D_{\mathrm{Cu}} = 1.88 \times 10^{-8}$	0.732 ± 0.023	0.738 ± 0.035
410.6	47.2	$D_{\mathrm{Zn}} = 4.38 \times 10^{-10}$ $D_{\mathrm{Cu}} = 1.80 \times 10^{-10}$	0.721 ± 0.023	0.615 ± 0.050

in the ordered and disordered alloys are similar and that the Elcock-McCombie mechanism is not the dominant mechanism.

The present measurements of the isotope effect for the diffusion of copper in ordered and disordered β–Cu-Zn (Table II) are very similar to our results for the diffusion of zinc.[7] The moderately large value of 0.325 obtained for $f\Delta K$ in both states of order leads to the conclusion stated in the preceding paragraph. It should be noted that at the lowest temperature where D is large enough to allow a copper isotope-effect experiment to be done (~410 °C), the order in Cu-Zn is far from perfect ($S=0.7$). Thus, it is not surprising that Elcock-McCombie loops are not dominant at 410 °C because these loops are a very inefficient means of transport, and with $S=0.7$ these loops are not required, since approximately $\frac{3}{4}$ of the atoms have at least one "wrong" neighbor.

The results on the isotope effect for the diffusion of copper in β–Cu-Zn do allow us to say something about the diffusion mechanism that could not be said on the basis of the zinc measurements only. As in the preceding section, we can compare the ratio f_A/f_B based on the theory of diffusion by the vacancy mechanism in a random alloy to the measured ratio $(f\Delta K)_A/(f\Delta K)_B$. Again, the values of D_{Cu} were corrected to the temperatures and compositions used to measure D_{Zn}, using the data of Kuper *et al.*[17]

The agreement between these ratios (Table V) is excellent for the disordered state, but is outside the range of errors for the ordered structure. Again, it is not surprising to find disagreement between a result based on a model of a random alloy and an experimental result obtained on an ordered alloy. The agreement of the ratios for disordered β–Cu-Zn implies that diffusion in this material occurs by the vacancy mechanism. Ordering of the alloy causes the motion of the zinc atoms to become slightly more correlated at 410 °C than they are in the disordered state, but not as highly correlated as expected for the Elcock-McCombie mechanism.

If the values of f_{Zn} and f_{Cu} from Eq. (11) are correct, we obtain $\Delta K_{\mathrm{Zn}}=\Delta K_{\mathrm{Cu}}=0.39\pm0.01$ in disordered β–Cu-Zn. This value is low for diffusion by the vacancy mechanism even in a bcc metal (ΔK for pure sodium is 0.5).[18] However, if we extend the decrease in ΔK, observed between pure copper and the 30- to the 50-at.% Zn alloy, we obtain $\Delta K=0.40$ for β–Cu-Zn based on $\Delta K=0.5$ for the pure material. Thus, $\Delta K=0.39$ in disordered β–Cu-Zn does not seem unreasonable for diffusion by the vacancy mechanism.

SUMMARY

The correlation factor for the diffusion of zinc in copper as determined from measurements of the isotope effect has been compared with measurements of the effect of solute additions on self-diffusion. The values of f_i, b, and $D_i/D_s(0)$ are consistent with the theory of Howard and Manning. Fair agreement with the theories of Lidiard and LeClaire is also obtained.

Manning's theory of correlation effects for diffusion by the vacancy mechanism in concentrated alloys provides values of $f_{\mathrm{Zn}}/f_{\mathrm{Cu}}$ in good agreement with the experimental values of $(f\Delta K)_{\mathrm{Zn}}/(f\Delta K)_{\mathrm{Cu}}$ in those cases where the theory should be applicable (30-at.% Zn and disordered β–Cu-Zn). The agreement with experiment is poorer in those cases where the theory is less applicable (4-at.% Zn and ordered β–Cu-Zn).

The equality of the isotope effect for the diffusion of copper in ordered and disordered β–Cu-Zn supports our earlier conclusion that the Elcock-McCombie mechanism is not the dominant mechanism in ordered β–Cu-Zn when the state of the order is described by $S=0.7$.

ACKNOWLEDGMENTS

We thank Dr. J. Manning for calculating the jump-frequency ratios, L. Robinson, L. Nowicki, R. Kentra, and J. Elbe for their assistance with the experimental work, and A. Essling for the chemical analyses.

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*Work supported by the U.S. Atomic Energy Commission.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Effect of Interactions on the Kondo Resistivity of Dilute *Au*Fe Alloys*

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(Received 17 February 1970)

Measurements are presented of the resistivity of a number of *Au*Fe alloys with concentrations varying from 0.002- to 2- at.% Fe in the temperature range 0.45–40 °K. Very dilute *Au*Fe alloys have already been found to obey an equation due to Hamann. The more concentrated alloys studied here show departures from Hamann's equation due to interactions between the impurities, and these have been taken into account by assuming that they modify the Hamann equation by a factor $(1-\gamma'/T^2+\delta'/T^4)$. It is found that for concentrations greater than 0.01-at.% Fe, the spin resistivity no longer increases linearly with concentration; it is suggested that this is due to correlations between partially formed spin-compensated states. It is also found that the internal field distribution in *Au*Fe alloys can be approximated by a Gaussian. In the most concentrated alloys, the low-temperature resistivity varies linearly with temperature with a slope which is independent of concentration, in agreement with theoretical prediction.

I. INTRODUCTION

In a previous paper,[1] hereafter referred to as I, measurements were presented of the electrical resistivity of some *Au*Fe, *Cu*Fe, and *CuAu*Fe alloys between 0.45 and 300 °K. From these measurements, it was possible to determine Kondo temperatures and find temperature and concentration dependences of the resistivity, so that the theoretical predictions of various authors could be tested.[2] In this paper the resistivity of the *Au*Fe system is studied to higher concentrations, and the results are analyzed by taking into account the effect of interactions between impurities.

Most of the theoretical work on dilute magnetic alloys assumes that the alloys are sufficiently dilute to neglect interactions between the impurities. However, in practice, a long-range magnetic ordering occurs through the Ruderman-Kittel-Yosida (RKY) interaction and this suppresses the spin scattering and can give rise to a resistance maximum. The problem of interactions between impurities in a random alloy has been treated by Marshall[3] and by Klein and Brout[4] in terms of a probability distribution of internal fields. The impurities are assumed to be subjected to effective fields; the value of these fields can be described by a continuous probability distribution function $P(H)$. They showed that the $P(H)$ curve is symmetrical about $H=0$ with a finite probability $P(0)$ of having a zero field, which is inversely proportional to the concentration of impurities.

An early pre-Kondo attempt to account for the resistance maximum is due to Yosida,[5] who calculated the resistivity to second order in perturbation theory. At very high temperatures the resistivity is proportional to $J^2S(S+1)$, of which two-thirds comes from spin-flip scattering. At absolute zero the resistivity is proportional to J^2S^2, the spin-flip scattering freezing out and making no contribution.

More recently, Silverstein[6] put forward a theory in which he showed that the Kondo expression for the spin resistivity is modified by a factor due to the internal field distribution. In the low-concentration limit he made a moment expansion in even powers of H/T and showed that the concentration dependence of the temperature of the resistance maximum depended on the form used for the distribution of internal fields.

Abrikosov[7] calculated the resistivity due to transition-metal impurities by developing a special quantum-field-theory technique for the spin system. He extended his calculations to consider the effect of a unique internal field[8] and found that his original expression was modified by a factor due to the field, this factor having a form similar to that