PHYSICAL REVIEW B VOLUME 8, NUMBER 12 15 DECEMBER 1973

Isotope Effect for Copper Diffusion into Lithium*

J. N. Mundy and W. D. McFall
Argonne National Laboratory, Argonne, Illinois 60439
(Received 23 July 1973)

The diffusion coefficients of copper into lithium have been measured over a temperature range of 90 to 147 °C. A single exponential fit of the data gives $D = (0.3 \pm 0.2)\, e^{(-10\,000 \pm 600)/kT}$. The solubility of copper in lithium was found to be less than 5×10^{-3} at. %. The value of the isotope effect $f\Delta K$ at 147 °C was 0.11 ± 0.03. The results are interpreted in terms of a dissociative mechanism of diffusion.

I. INTRODUCTION

An increasing number of examples of fast impurity diffusion[1–17] have been reported in the past seven years. Many of these examples were interpreted as due to diffusion by an interstitial mechanism. An analysis by Anthony *et al.*[18] suggested that interstitial dissolution and diffusion would be favored for (a) a polyvalent solvent, (b) a small solute-ion size, and (c) a low solute valence. A recent paper by Owens and Turnbull[19] has shown that although sodium diffusing in lead should fit the above criterion for interstitial diffusion, the measured low diffusivity suggests that the sodium diffuses by a vacancy mechanism. Dariel *et al.*[2] and Barr[3] have also noted that effects other than ion size and valence must play an important role in the determination of whether certain impurities are "fast" diffusers in a host lattice.

Although it is difficult to establish criteria for impurity diffusion by an interstitial mechanism, it is relatively easy to observe the features that are common to all the "fast" diffusers. Independent of whether the host lattice has a close packed or open structure or is multivalent, two features are observed: (a) The values of the activation energy for impurity diffusion, Q_I, are significantly lower than the activation energy for self-diffusion in the host lattice, Q_H. (b) The values of the pre-exponential factor for impurity diffusion, $(D_0)_I$, are significantly lower than the pre-exponential factor for self-diffusion in the host lattice, $(D_0)_H$.

The vast majority of the measurements of "fast" diffusion have been observed with noble metals as impurities. In Table I, we have listed values of the ratios Q_I/Q_H and $(D_0)_I/(D_0)_H$ that have been found for noble-metal diffusion in various host lattices. The interstitial mechanism has been used to explain the diffusion process in these systems. We have, therefore, not included values for host lattices such as Al, α-Fe, γ-Fe, Pt, and the noble metals because in these lattices the ratio of Q_I/Q_H is within 10% of unity. In such cases, where the ratio of Q_I/Q_H is not significantly different from unity, impurity diffusion has been explained in terms of a vacancy mechanism of diffusion.[30,31]

The systems in Table I span a large range of values in the ratios of Q_I/Q_H and $(D_0)_I/(D_0)_H$. For the interstitial mechanism, this spread of values could be explained in terms of the difference between the various noble-metal–host-metal interionic distances.[32] The spread could also be accounted for by the dissociative mechanism proposed by Frank and Turnbull.[33] The dissociative mechanism involves an equilibrium between the concentration of substitutional solute atoms C_s and interstitial solute atoms C_i. If D_s and D_i are the respective diffusion coefficients of the substitutional and interstitial solute atoms, then the solute diffusivity is given by

$$D_I = \frac{C_i}{C_i + C_s} D_i + \frac{C_s}{C_i + C_s} D_s \ . \qquad (1)$$

Equation (1) would suggest that measurements of the impurity diffusion coefficient over a wide range of temperature could lead to curvature in the Arrhenius plot. This curvature has not been observed in the Arrhenius plots of the "fast" diffusers, which would indicate that, for diffusion by a dissociative mechanism, the first term of Eq. (1) is predominant. Evidence obtained from centrifuge studies (Au-Na,[3] Au-K,[3] and Au-In[34]), indicates that the noble metal dissolves to a large extent in interstitial sites in the host lattice. These examples are from the first part of Table I, and, if a dissociative mechanism is the operative process, one might expect to find an increasing contribution to diffusion from the substitutional solvent atom for higher values of Q_I/Q_H.

Measurements of the diffusion of copper into lithium[28] have been interpreted to be the result of an interstitial mechanism. The values of Q_I/Q_H and $(D_0)_I/(D_0)_H$ fit well into the latter part of Table I. [The $(D_0)_I/(D_0)_H$ ratio has been determined here using the corrected value of $(D_0)_I$ for the Cu-Li system noted by Ott in a later paper.[35]] The relatively high value of Q_I/Q_H would suggest that, for a dissociative mechanism, the Arrhenius plot could show some curvature. Although the data

TABLE I. "Fast" noble-metal impurity diffusion.

Impurity	Host	Structure	Q_I/Q_H	$(D_0)_I/(D_0)_H$	Ref.
Au	Tl (*c* axis)	hcp	0.12	5×10^{-5}	7, 20
Au	Na	bcc	0.22	2×10^{-3}	14, 21
Au	K	bcc	0.23	4×10^{-3}	15, 22
Au	Tl (*a* axis)	hcp	0.23	1×10^{-3}	7, 20
Au	Tl	bcc	0.30	7×10^{-4}	7, 20
Cu	Pb	fcc	0.31	8×10^{-3}	1, 23
Cu	Sn (*a* axis)	tetr.	0.31	2×10^{-4}	6, 24
Au	In	fct	0.36	3×10^{-3}	8, 25
Au	Pb	fcc	0.39	9×10^{-3}	4, 23
Au	La	fcc	0.40	1×10^{-2}	11
Au	Ce	fcc	0.41	7×10^{-3}	9, 26
Au	Sn (*c* axis)	tetr.	0.43	7×10^{-4}	5, 24
Ag	Sn (*c* axis)	tetr.	0.48	8×10^{-4}	5, 24
Ag	Tl (*c* axis)	hcp	0.49	7×10^{-2}	7, 20
Ag	Tl (*a* axis)	hcp	0.52	1×10^{-1}	7, 20
Ag	Pb	fcc	0.56	5×10^{-2}	1, 23
Ag	Ce	fcc	0.58	4×10^{-2}	9, 26
Ag	Tl	bcc	0.60	6×10^{-2}	7, 20
Ag	In	fct	0.61	4×10^{-2}	8, 25
Cu	Pr	bcc	0.61	6×10^{-1}	10, 27
Au	Pr	bcc	0.68	4×10^{-1}	2, 27
Ag	In (*a* axis)	fct	0.68	1×10^{-1}	8, 25
Au	Sn (*a* axis)	bcc	0.70	1×10^{-2}	5, 24
Ag	Pr	bcc	0.73	4×10^{-1}	2, 27
Cu	Li	bcc	0.73	4×10^{-1}	28, 29
Ag	Sn (*a* axis)	tetr.	0.79	2×10^{-2}	5, 24

were linear within experimental error, it may be that over the measured temperature range the values of D_I are insensitive to the varying contributions of substitutional and interstitial solute atoms. A more sensitive way to look at diffusion mechanisms is by measurement of the isotope effect in diffusion.[36]

The equation for the isotope effect can be written in the following general form:

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

where D_α, m_α, and D_β, m_β refer to the diffusion coefficients and masses of the α and β isotopes; f is the correlation factor; and ΔK is the fraction of the total translational kinetic energy associated with the decomposition of the saddle-point configuration possessed by the migrating atom. When the diffusion process is the result of more than one mechanism, Eq. (2) can be rewritten as

$$D_\alpha/D_\beta - 1 = \sum_i p_i f_i \Delta K_i \delta m_i \quad , \tag{3}$$

where the subscript i refers to the ith mechanism, and p_i is the fraction of diffusion that occurs by that ith mechanism. The mass term has been written as δm_i, since this will be a function of the masses of all atoms involved in the jump process. If the measured value of $D_\alpha/D_\beta - 1$ is composed of components of substitional and interstitial diffusion, then, to determine values of p_i, it is necessary to have a knowledge of f_i, ΔK_i, and δm_i for each mechanism. For both the simple substitutional and the simple interstitial mechanisms, only one atom is relocated at the conclusion of the jump, and δm_i is given by

$$\delta m_i = (m_\beta/m_\alpha)^{1/2} - 1 \quad . \tag{4}$$

The simple interstitial mechanism is an independent random walk of a single particle; therefore, f is unity. Although the value of ΔK is less certain, it has been shown to be unity in some interstitial systems[37,38] and is expected to be close to unity according to theory[39] and computer simulations.[40,41]

The value of f_i for substitutional diffusion is a complex function of the jump frequencies of solute and solvent atoms. Measurements of copper diffusion in lithium[28] and lithium self-diffusion[29] allow an estimate to be made of the value of f_i. The value of ΔK for substitutional diffusion is also uncertain, but recent measurements of the isotope effect of both sodium and silver diffusion in lithium allow ΔK to be estimated.[42]

The present experiments measure the diffusion of copper into lithium over the temperature range 90–147 °C and also the effect of isotopic mass in this system at a temperature of 147 °C. The experiments have been performed in an attempt to observe the two parts of the dissociative mechanism and to obtain some measure of the proportion of interstitial and substitutional diffusion.

II. EXPERIMENTAL METHODS

The method used to obtain the diffusion profiles was to observe by sectioning, the diffusion of a thin surface layer of ^{64}Cu. Most of the experimental details have been described in earlier papers.[43,44] The important differences in techniques will be noted. The problems arising from the low solubility of copper in lithium will be discussed.

A. Materials

The lithium with a purity of 99.98% was obtained from the Foote Mineral Co. For the single-isotope diffusion experiments ^{64}Cu was prepared by the irradiation of copper foil of 99.999% purity in the Argonne CP-5 reactor. Higher count rates are required to measure the isotope effect in diffusion than are needed for single-isotope diffusion experiments. To overcome the problem of the low solubility of copper in lithium, the ^{64}Cu had to be obtained with a higher specific activity than could be attained with the CP-5 reactor (flux $\sim 6\times10^{13}$ $n/\mathrm{cm}^2\,\mathrm{sec}$). The isotopes of ^{64}Cu and ^{67}Cu with high specific activity were purchased from Oak Ridge National Laboratory. These isotopes are obtained from fast-neutron irradiation of ZnO enriched in ^{64}Zn and ^{67}Zn, respectively, and are subsequently chemically separated. All isotopes used were examined with a multichannel analyzer, and no radioactive impurities were observed. The measured values of the half lives (^{64}Cu was 12.71 ± 0.05 h and ^{67}Cu was 62.5 ± 0.3 h) agreed well with the values found by Rothman and Peterson.[45]

B. Diffusion Measurements

The surface of the lithium sample was cleaned by a razor cut in an evaporator system evacuated to a pressure of 2×10^{-6} Torr. The active copper metal was evaporated from a tantalum boat on to the clean lithium surface. The ^{67}Cu and ^{64}Cu isotopes prepared at Oak Ridge National Laboratory were supplied in the chloride form. To avoid the problems associated with the evaporation of salt rather than metal,[42] the copper was electroplated on to the tantalum boat from the copper chloride solution. The technique closely followed that used for electroplating silver on to tantalum.[42]

The problem of determining the section thickness of lithium has been discussed by Mundy and McFall.[42] For the present measurements, we determined the section thickness by the weight of the lithium slices weighed as metal under a dry-air atmosphere.

The counting procedures used to differentiate between the ^{67}Cu and ^{64}Cu isotopes in each section followed closely those used by Rothman and Peterson.[45] The lithium sections were allowed to oxidize and then were dissolved in 2 mliter of dilute HCl. Each section was counted nine times over a 3-day interval, each time to 10^6 counts. The ratios of ^{64}Cu/^{67}Cu were determined by fitting the counting data to the time t elapsed since an arbitrary time zero

$$A = A_{64}e^{-\lambda_{64}t} + A_{67}e^{-\lambda_{67}t} \quad , \tag{5}$$

where A_{64} and A_{67} are the specific activities of ^{64}Cu and ^{67}Cu at time zero, and λ_{64} and λ_{67} are their decay constants. The count rates were corrected for counters background and dead time to an accuracy of 0.1%. The first nine sections were diluted to an initial count rate of 5×10^5 counts per min. A null-effect experiment showed zero dependence of the isotopic ratio on counting rate.

III. EXPERIMENTAL RESULTS

Deposition of a thin layer of radiotracer and subsequent annealing usually result in a Gaussian dependence of the concentration, i.e.,

$$c(x) = c(0)e^{-x^2/4Dt} \quad . \tag{6}$$

Here $c(x)$ is the concentration of tracer as a function of depth x, $c(0)$ is the concentration at the surface of the sample, and t is the annealing time. A plot of $\ln c$ vs x^2 should lead to a straight line, but in the present work all the diffusion anneals determined on the basis of Eq. (6) resulted in curved penetration profiles. Examples of two curved profiles are shown in Fig. 1. The initial point on the upper curve was an order of magnitude higher than the second point and is not shown

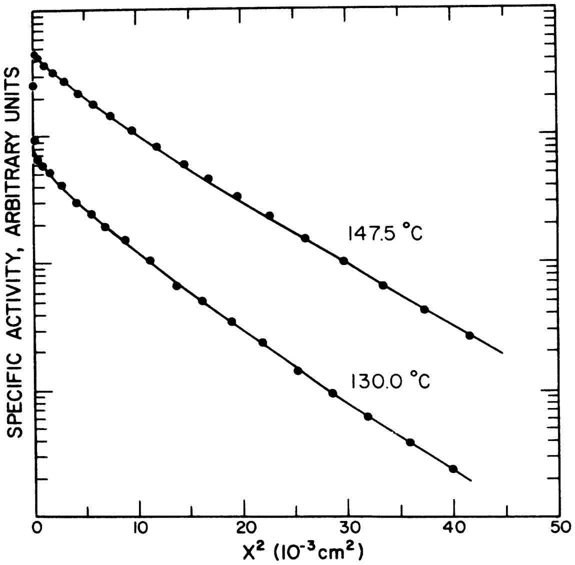

FIG. 1. Concentration profiles of copper diffusion in lithium. The lines give the profile obtained from the low-solubility solution of Malkovitch.

in the figure. The high initial point was a second feature characteristic of all penetration profiles. A high initial point has been found often in the penetration profiles determined for radiotracer diffusion into alkali metals.[42,46] It is unusual, however, to find the initial point greater than a factor of 2 above the second point.

Curved penetration profiles can result from the formation of an impurity-solvent compound at the surface, followed by dissociation and diffusion. Although silver and gold are known to form compounds with lithium,[47] copper-lithium compounds are unknown, and, therefore, it is unlikely that compound formation is the cause of the curved profiles.

The form of the profiles shown in Fig. 1 could result from a low solubility of copper in lithium. A low solubility of noble metals in lithium might be expected because of the high electronegativity factor.[46] Although the solubility of copper in lithium is not known, the solubilities of silver (9 at.%) and gold (1 at.%) in lithium are relatively high.[48,49] Solubility problems were not discussed in the earlier work on copper diffusion in lithium.[28] Penetration profiles were not given, and, therefore, it is difficult to ascertain if solubility problems were encountered. As can be seen from Fig. 1, curvature might not be observable if the profiles were followed over a small drop in the levels of specific activity.

Barr *et al.*[50] investigated the effect of low solubility on the penetration profiles for gold diffusion in sodium. We conducted a similar investigation on one of the copper/lithium samples and the diffusion profile obtained showed the same characteristic features as those found for the gold/sodium system.

For the isotope-effect measurements, we expected to overcome the solubility problem using isotopes purchased from Oak Ridge National Laboratory. We anticipated that copper isotopes prepared by fast-neutron irradiation of ZnO, with subsequent chemical separation, would be carrier free. Unfortunately, the simultaneous diffusion anneal of copper isotopes ^{67}Cu and ^{64}Cu at a temperature of 147 °C also resulted in a curved penetration profile. If the copper isotopes were carrier free, the solubility of copper in lithium would be extremely low. However, it was found that the ZnO used for preparation of the isotopes contained small amounts of copper impurity. At the time of the diffusion anneal, the specific activity of both isotopes was probably between 400 and 800 mC/mg Cu.

The data for the five diffusion anneals were computed by two methods. The first was a least-squares fit of the data to Eq. (6), and the second was a least-squares fit of the data to the equation given by Malkovitch[51]

$$c(x,t)=\frac{2\alpha}{\sqrt{\pi}}\int_{x/2(Dt)^{1/2}}^{\infty} e^{-y^2}\operatorname{erf} y\left(\frac{\tau}{t-\tau}\right)^{1/2} dy\ . \tag{7}$$

Here t is the anneal time, and τ is the time for the impurity to dissolve into the host matrix,

$$\tau=\pi S_0^2/4D\alpha^2\ , \tag{8}$$

where S_0 is the total quantity of solute placed initially on the surface and α is the terminal solubility. The diffusion coefficients obtained by both methods are given in Table II. The lines drawn in Fig. 1 were obtained from the Malkovitch solution. A value of χ^2 is given for each computed value of the diffusion coefficient. The solution for the low solubility of Malkovitch significantly improves, in most cases, the value of χ^2. The low-solubility solution obtains values of τ from which an estimate can be made of the terminal solubility of copper in lithium. The results of these calculations are given in Table II, column 6. The values could be in error by 50% as they depend on our knowledge of the specific activity. The values appear to show a maximum solubility of 5×10^{-3} at.% in the temperature region 100–130 °C.

The diffusion coefficients obtained from both the Gaussian and low-solubility solution are shown in Fig. 2. The errors shown for the low-solubility solution include the errors in the fit of the data to Eq. (7), the error in the anneal time, and the error in the determination of the thicknesses of the lithium sections from their weight.[42] The error bars are rather large, and it is not clear whether the Arrhenius plots show curvature. A least-squares fit of the values of D, obtained using Eq.

TABLE II. Diffusion of ^{64}Cu into lithium as a function of temperature.

T (°C)	Gaussian solution D(cm^2 sec^{-1})	χ^2	Low-solubility solution D(cm^2 sec^{-1})	χ^2	α(at.%)
147.5	1.17×10^{-6}	51.4	1.46×10^{-6}	3.1	1.0×10^{-3}
137.0	8.36×10^{-7}	411.1	1.14×10^{-6}	392.4	1.9×10^{-3}
130.0	5.87×10^{-7}	2905.2	7.42×10^{-7}	161.0	4.2×10^{-3}
106.0	3.01×10^{-7}	10.4	3.98×10^{-7}	6.8	5.0×10^{-3}
90.0	1.82×10^{-7}	4833.6	2.26×10^{-7}	85.4	1.5×10^{-3}

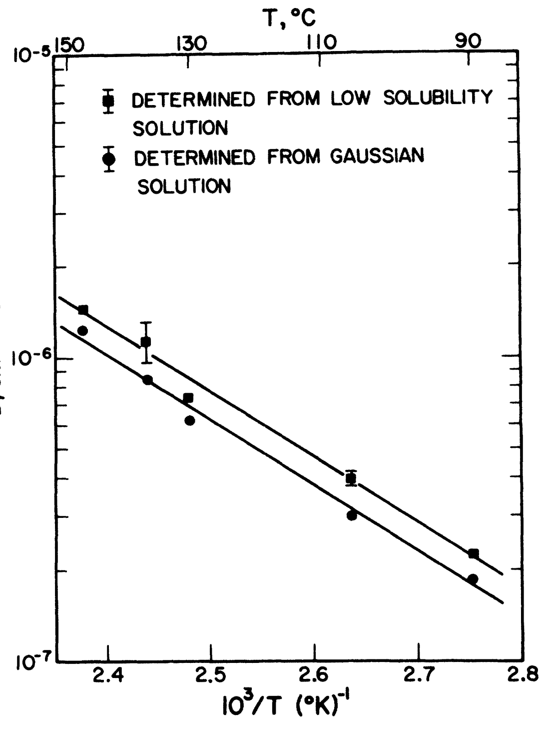

FIG. 2. Comparison of the diffusion coefficients of copper in lithium as a function of temperature determined by (a) a low-solubility solution and (b) a Gaussian solution.

(7), to a single exponential gives the equation

$$D=(0.3\pm 0.2)\exp\left(\frac{-10\,000\pm 600}{kT}\right) . \qquad (9)$$

A two-exponential fit of the same data gives the equation

$$D=(4.9\pm 0.5)\exp\left(-\frac{13\,000\pm 600}{kT}\right)$$

$$+(0.01\pm 0.001)\exp\left(-\frac{8\,000\pm 600}{kT}\right) . \qquad (10)$$

The activation energy in the first term is similar to that found for self-diffusion in lithium, which might be expected if the copper diffused by a vacancy mechanism.

The 147.5 °C anneal was used to observe the simultaneous diffusion of ^{64}Cu and ^{67}Cu isotopes into lithium. The ratio of the specific activities of the two isotopes (c_α/c_β) as a function of the specific activity of one of the isotopes (c_α) has been shown[52] to be

$$\ln(c_\alpha/c_\beta)=\text{const.}-\ln c_\alpha(D_\alpha/D_\beta-1) . \qquad (11)$$

Equation (11) is valid for concentration profiles that follow a Gaussian distribution. The experimental plot of $\ln(C_{67}/C_{64})$ vs $\ln C_{67}$ is shown in Fig. 3; the results of the null-effect experiment are plotted on the same figure.

The slope of $\ln(C_{67}/C_{64})$ vs $\ln C_{67}$ is 0.0025 ± 0.0007. Thus the effect of mass on the diffusion rate of copper into lithium is small. For such a small value, the effect of using Eq. (10) instead of an equation based on the low-solubility solution is likely to be small and within the error of the measurement. The mass factor $(67/64)^{1/2}-1$ equals 0.02317, and $(f\Delta K)_{\mathrm{Cu/Li}}$ equals 0.11 ± 0.03.

IV. DISCUSSION

The present work shows that, for the copper-lithium system $Q_I/Q_H=0.79$, copper is relatively insoluble in lithium, and the isotope effect for diffusion is small. We will discuss this information in terms of one and two mechanisms of diffusion.

A. Single-Vacancy Mechanism

Measurements of the macroscopic change in length and the x-ray lattice parameter as a function of temperature indicate that, in lithium[53] in the temperature range 30–180 °C, the predominant defects are single vacancies. The activation energy for self-diffusion in lithium[29] (12.6 kcal/mole) is considerably higher than the measured value for the activation energy of copper diffusion in lithium (9.8 kcal/mole). Copper diffusion by means of a vacancy mechanism would require an unexpectedly large impurity-vacancy binding energy.

The isotope effect measures the product of $f\Delta K$. The factor ΔK is not known, but recent measurements of $f\Delta K$ for sodium and silver diffusion in lithium[42] suggest that $(\Delta K)_{\mathrm{Cu/Li}}<0.5$. The ratio of D_I/D_H suggests a very low value for f, and one might expect therefore that a vacancy mechanism would yield a value of $f\Delta K$ equal to zero within experimental error. The measured value of 0.11 ± 0.03 gives further evidence that the impurity dif-

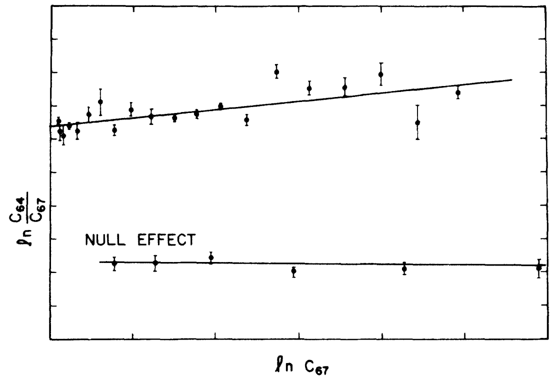

FIG. 3. Diffusion of ^{67}Cu and ^{64}Cu in lithium at 147 °C. Each division on the ordinate is 0.01. Each division on the abscissa is 1.0.

fusion does not take place by means of a single-vacancy mechanism.

B. Single-Interstitial Mechanism

Centrifuge studies[3,34] of the three systems, Au-Na, Au-K, and Au-In have indicated that the noble metal is dissolved to a large extent on interstitial sites in the host lattice. The solubility of the noble metal in these systems is known to be extremely small.[21,22,54] No direct link exists between interstitial dissolution and low solubility, but the present results show that copper has a low solubility in lithium and interstitial dissolution might not be unexpected.

The simple interstitial mechanism is the random walk of a single particle, and for such a mechanism $f = 1$. The value of ΔK is less certain, but is known to be close to unity for some interstitial systems.[37,38] The present measurements are in complete disagreement with a value of $f\Delta K$ close to unity. The present measurements could be expected to bear a closer relationship to the recent measurements on the diffusion of silver in lead[55] than on the previous measurements of interstitial systems.[37,38] The measured values of $f\Delta K$ for the silver diffusion in lead were approximately 0.25. The possible causes for such a low isotope effect were discussed in detail by Miller *et al.*[55] and will not be repeated here. Since the host lattices have different structures, the two systems are not completely comparable. The measured value of $f\Delta K = 0.11$ is, however, much lower than that for the Ag/Pb system, which suggests that the mechanism is different in each system or the single mechanism is not an adequate description for either system.

C. Dissociative Mechanism

The small amount of curvature observed in the Arrhenius plot could be explained in terms of two mechanisms that lead to an expression of the form of Eq. (10). The errors on the individual diffusion coefficients and the relatively small range of temperature make it difficult to be certain that a separation of data into two components is meaningful. Equation (10) would suggest that at 147 °C the two processes contribute approximately equal amounts to the over-all diffusion rate.

To interpret the isotope-effect result in terms of two mechanisms, we make use of Eq. (3). We assume a value of $f\Delta K = 0.05$ for the vacancy mechanism and an equal proportion of diffusion occurring by both mechanisms. On the basis of these assumptions, $f\Delta K$ for the "interstitial" mechanism is 0.17. A value of $f\Delta K$ somewhat reduced from the 0.25 value found for the Ag-Pb system might not be unexpected for the more open structure of the body-centered-cubic lattice of lithium.

V. CONCLUSIONS

Although an unambiguous interpretation of the results is not possible, the dissociative mechanism would appear to be more appropriate than the single diffusion mechanisms we have considered. More meaningful results would require a larger range of temperature measurements of the diffusion coefficient and a reduction of the errors of measurement. It would also be valuable to measure the isotope effect for diffusion at different temperatures. Unfortunately, the low solubility of copper in lithium makes these improvements both difficult and costly.

ACKNOWLEDGMENTS

The authors wish to thank N. L. Peterson, J. W. Miller, and S. J. Rothman for helpful discussions. The authors are particularly grateful to J. W. Miller for his considerable assistance in processing our data for the low-solubility solution.

---

[*] Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] B. F. Dyson, T. R. Anthony, and D. Turnbull, J. Appl. Phys. **37**, 2370 (1966).

[2] M. P. Dariel, G. Erez, and G. M. J. Schmidt, J. Appl. Phys. **40**, 2746 (1969).

[3] L. W. Barr, *Diffusion Processes* (Gordon and Breach, London, 1971), p. 185.

[4] G. V. Kidson, Philos. Mag. **13**, 247 (1966).

[5] B. F. Dyson, J. Appl. Phys. **37**, 2375 (1966).

[6] B. F. Dyson, T. R. Anthony, and D. Turnbull, J. Appl. Phys. **38**, 3408 (1967).

[7] T. R. Anthony, B. F. Dyson, and D. Turnbull, J. Appl. Phys. **39**, 1391 (1968).

[8] T. R. Anthony and D. Turnbull, Phys. Rev. **151**, 495 (1966).

[9] M. P. Dariel, D. Dayan, and D. Calais, Phys. Status Solidi A **10**, 113 (1972).

[10] M. P. Dariel, J. Appl. Phys. **42**, 2251 (1971).

[11] M. P. Dariel, G. Erez, and G. M. J. Schmidt, Philos. Mag. **19**, 1053 (1969).

[12] H. Gleiter, Acta Metall. **18**, 117 (1970).

[13] J. W. Miller, Phys. Rev. B **2**, 1624 (1970).

[14] L. W. Barr, J. N. Mundy, and F. A. Smith, Philos. Mag. **20**, 389 (1969).

[15] F. A. Smith and L. W. Barr, Philos. Mag. **21**, 633 (1970).

[16] G. M. Hood and R. J. Schultz, Philos. Mag. **26**, 329 (1972).

[17] C. T. Candland and H. B. Vanfleet, Phys. Rev. B **7**, 575 (1973).

[18] T. R. Anthony, J. W. Miller, and D. Turnbull, Scr. Metall. **3**, 183 (1969).

[19] C. W. Owens and D. Turnbull, J. Appl. Phys. **43**, 3933 (1972).

[20] G. A. Shirn, Acta Metall. **3**, 87 (1955).

[21] J. N. Mundy, L. W. Barr, and F. A. Smith, Philos. Mag. **14**, 785 (1966).

[22] J. N. Mundy, L. W. Barr, and F. A. Smith, Philos. Mag.

15, 411 (1967).

[23] J. W. Miller, Phys. Rev. **181**, 1095 (1969).

[24] C. Coston and N. H. Nachtrieb, J. Phys. Chem. **68**, 2219 (1964).

[25] J. E. Dickey, Acta Metall. **7**, 350 (1959).

[26] M. P. Dariel, D. Dayan, and A. Languille, Phys. Rev. B **4**, 4348 (1971).

[27] M. P. Dariel, G. Erez, and G. M. J. Schmidt, Philos. Mag. **19**, 1045 (1969).

[28] A. Ott, J. Appl. Phys. **40**, 2395 (1969).

[29] A. Ott, J. N. Mundy, L. Löwenberg, and A. Lodding, Z. Naturforsch. A **23**, 771 (1968).

[30] N. L. Peterson and S. J. Rothman, Phys. Rev. B **1**, 3264 (1970).

[31] N. L. Peterson, *Solid State Physics* (Academic, New York, 1968), Vol. 22, p. 409.

[32] T. R. Anthony, *Diffusion Processes* (Gordon and Breach, London, 1971), p. 935.

[33] F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956).

[34] T. R. Anthony, Acta Metall. **18**, 877 (1970).

[35] A. Ott, Z. Naturforsch. A **25**, 1477 (1970).

[36] N. L. Peterson, *Solid State Physics* (Academic, New York, 1968), Vol. 22, p. 409.

[37] E. M. Pell, Phys. Rev. **119**, 1014 (1960).

[38] A. J. Bosman, P. E. Brommer, and G. W. Rathenau, J. Phys. Radium **20**, 241 (1959).

[39] A. D. LeClaire, Philos. Mag. **14**, 1271 (1966).

[40] H. B. Huntington, M. D. Feit, and D. Lortz, Cryst. Lattice Defects **1**, 193 (1970).

[41] R. C. Brown, J. Worster, N. H. March, R. C. Perrin, and R. Bullough, Philos. Mag. **23**, 555 (1971).

[42] J. N. Mundy and W. D. McFall, Phys. Rev. B **7**, 4363 (1973).

[43] J. N. Mundy, Phys. Rev. B **3**, 2431 (1971).

[44] J. N. Mundy, A. Ott, A. Lodding, and L. Löwenberg, Phys. Status Solidi **35**, 359 (1969).

[45] S. J. Rothman, and N. L. Peterson, Phys. Status Solidi **35**, 305 (1969).

[46] L. W. Barr, J. N. Mundy, and F. A. Smith, Philos. Mag. **16**, 1139 (1967).

[47] B. W. Mott, *The Alkali Metals* (The Chemical Society, London, 1967), p. 92.

[48] M. Hansen, *Constitution of Binary Alloys*, 2nd ed. (McGraw-Hill, New York, 1958), p. 29.

[49] R. P. Elliott, *Constitution of Binary Alloys*, 1st Suppl. (McGraw-Hill, New York, 1965), p. 29.

[50] L. W. Barr, J. N. Mundy, and F. A. Smith, Philos. Mag. **20**, 389 (1969).

[51] R. Malkovitch, Fiz. Met. Metalloved. **15**, 880 (1963).

[52] L. W. Barr and A. D. LeClaire, Proc. Br. Ceram. Soc. **1**, 109 (1964).

[53] R. Feder, Phys. Rev. B **2**, 828 (1970).

[54] F. A. Shunk, *Constitution of Binary Alloys*, 2nd Suppl. (McGraw-Hill, New York, 1969), p. 72.

[55] J. W. Miller, S. J. Rothman, J. N. Mundy, L. C. Robinson, and R. E. Loess, Phys. Rev. B 8, 2411 (1973).