[13] S. K. Ma and K. A. Brueckner, Phys. Rev. **165**, 18 (1968).
[14] D. J. W. Geldart and R. Taylor, Can. J. Phys. **48**, 155 (1970).
[15] T. G. Strand and R. A. Bonham, J. Chem. Phys. **40**, 1686 (1964).
[16] B. Y. Tong and L. J. Sham, Phys. Rev. **144**, 1 (1966).

PHYSICAL REVIEW B VOLUME 7, NUMBER 10 15 MAY 1973

Comparison of the Isotope Effect for Diffusion of Sodium and Silver in Lithium*

J. N. Mundy and W. D. McFall
Argonne National Laboratory, Argonne, Illinois 60439

(Received 20 November 1972)

Separate measurements were made at 150 °C of the simultaneous diffusion of sodium isotopes (^{22}Na and ^{24}Na) and silver isotopes (^{105}Ag and ^{110m}Ag) in lithium. The strength of the isotope effect $f\Delta K$ for sodium is 0.19 ± 0.01 and for silver 0.26 ± 0.01. These values do not correlate well with recent calculations of ΔK determined for impurity diffusion on the basis of the dynamical theory of diffusion. Measurement of the diffusion of silver in lithium is 45% greater than earlier data, and a possible explanation for this discrepancy is given.

I. INTRODUCTION

Many measurements of the isotope effect in diffusion have been made in the past ten years because of the information they provide on the basic mechanism of diffusion in crystals. The interpretation of these measurements has not always been unambiguous, and clarification has been sought using two distinct theories. However, both the reaction-rate theory[1-3] and the dynamical theory[4-6] result in an equation for the isotope effect of the same general form. The equation is given by

$$\frac{D_\alpha}{D_\beta} - 1 = f\Delta K\left[\left(\frac{m_\beta}{m_\alpha}\right)^{1/2} - 1\right] , \qquad (1)$$

where D_α, m_α, D_β, and m_β refer to the diffusion coefficient and mass of α and β isotope, respectively. f is the correlation factor and ΔK is interpreted in reaction-rate theory as that fraction of the total translational kinetic energy associated with the decomposition of the saddle-point configuration possessed by the migrating atom.

For self-diffusion in cubic metals, f is a geometric factor dependent only on the crystal structure and the atomic-jump process. Measurements of D_α/D_β yield the product $f\Delta K$; thus, if ΔK is close to unity, the experimental results yield an unambiguous value of f, which serves to identify the diffusion mechanism. Measurements of the isotope effect in metals with a close-packed structure[7-15] have shown that diffusion occurs primarily by means of vacancies. Measurements of the isotope effect in body-centered-cubic (bcc) metals[14-18] have yielded such low values of the isotope effect that it was impossible to identify, unambiguously, the mechanism of diffusion. However, experimental evidence does indicate, from measurements of the macroscopic change of length and the x-ray lattice parameter as a function temperature, that in lithium[19] and also in sodium[20] above room temperature, vacancies are the predominant defect. The measurements of the enhancement of sodium self-diffusion by additions of potassium[21] also suggest a vacancy mechanism of diffusion.

The low values of the isotope effect were found in self-diffusion experiments in which f is a geometric factor, and so a theoretical justification was sought for a low value of ΔK. Calculations of ΔK based on both reaction-rate theory[22,23] and dynamical theory[5] gave values of ΔK within 20% of unity. This similarity was unexpected because in the calculation of ΔK the differences in the theories should show most clearly.[22] In seeking to determine the relative merits of each theory, Achar[24] has developed, from the dynamical theory, the effect of resonance and local modes on ΔK. The theory is based on the fact that an impurity with mass much greater than that of the lattice atoms will give rise to resonance modes, whereas impurities of mass similar to the lattice atoms will give rise to localized modes. The effect of these modes on ΔK has shown that ΔK has a marked dependence on the mass factor M'/M, where M' is the impurity mass and M is the mass of a host atom. The extent to which ΔK will change is, of course, governed experimentally by the relative magnitudes of M' and M. Achar has calculated values of ΔK for three host lattices: lithium, sodium, and aluminum.

The effect of impurity mass on the value of ΔK has also been determined from the dynamical theory in a recent paper by Feit.[25] In Feit's approach, the resonance modes are not treated explicity, and the variation of ΔK is determined relative to ΔK_0. Feit used experimental values of ΔK_0 and suggested that the greatest differences in $\Delta K/\Delta K_0$ would be seen where ΔK_0 is low, as in sodium.

To ascertain the value of the dynamical theory in the analysis of isotope-effect data, we chose to measure the isotope effect for impurities of widely differing mass, namely, silver and sodium. As a host lattice, lithium was chosen because Achar's theory predicts the largest change in ΔK for this lattice. The calculated values of $\Delta K/\Delta K_0$ are 0.72 for sodium and 0.145 for silver. The values calculated for Feit's theory depend on the value chosen for ΔK_0. If one assumes a value for ΔK_0 similar to that found for sodium self-diffusion ($\Delta K_0 = 0.5$), the values of $\Delta K/\Delta K_0$ are 0.22 for sodium and 0.06 for silver. Thus, the choice of silver and sodium diffusion in lithium should serve not only to test the validity of the theories but also compare their relative merits.

II. IMPURITY DIFFUSION IN LITHIUM

Measurements of the isotope effect in diffusion obtain values only of $f\Delta K$ and not of ΔK. In the case of self-diffusion f is a geometric factor, but for impurity diffusion f will be a complex function of the jump frequencies of impurity and solvent atoms. It is clear that if one wishes to compare values of ΔK for different impurity isotopes diffusing in a host lattice, then, of necessity, impurities with approximately the same value of f must be chosen. As it is not possible to determine f independent of ΔK, the best method to ensure that f is approximately the same is to choose impurities which have similar values of the preexponential factor D_0 and similar activation energy Q. A number of host lattices with impurity diffusion fit this pattern. Lithium was chosen as the host lattice because the large changes in ΔK predicted by the theories should minimize any small variations that may exist in the values of f for each impurity.

Impurity diffusion in lithium has been measured for 13 impurities.[26-33] Three impurities, sodium, zinc, and silver, appear to fit the above requirements of similar values of D_0 and Q. It is difficult to separate the values within the experimental error. All of these impurities have suitable isotopes for measurements of the isotope effect, and the techniques for the separation of the isotope pairs ^{22}Na/^{24}Na,[17] ^{65}Zn/^{69}Zn,[11] and ^{105}Ag/^{110m}Ag[7] have been well established at Argonne National Laboratory. The present work examines the sodium and silver isotope pairs diffusing in lithium.

Previous interpretations of impurity diffusion in lithium have been summarized by Ott.[33] The particular impurities of sodium, zinc, and silver are of interest in this work. Sodium is interpreted as diffusing by a vacancy mechanism. Silver is interpreted as dissolving mainly substitutionally, but the largest contribution to diffusion was thought to be by means of interstitials. Zinc was also thought to diffuse interstitially. If these interpretations were correct, the choice of the two impurities of zinc and silver would be poor for a test of the theories of Achar and Feit, which are based on a vacancy mechanism of diffusion. Our choice of these impurities was based on a firm conviction that they diffused by means of a vacancy mechanism.

Part of the basis for the interpretation of interstitial diffusion in the Zn-Li and Ag-Li systems is the argument first used by Dyson *et al.*[34] to explain the fast diffusion of noble metals in lead. In these systems, the octahedral site between the ion cores of lead is sufficiently large to accommodate, with little or no distortion, the atomic size of the noble-metal atoms. This criterion appears to be applicable to the diffusion of noble metals in other metals with a close-packed structure. However, the more open structure of bcc metals does not necessarily result in larger interstitial "holes." As noted by Dariel *et al.*[35] and Barr,[36] effects other than ion size must play an important role in the determination of whether noble metals are "fast" diffusers in a host lattice.

The difficulty of establishing a criterion on the basis of ion size, electronegativity, and valence prompted a close look at the experimental properties of those systems in which fast diffusion was clearly established. An interstitial mechanism of diffusion has been used to interpret the extremely fast diffusion of noble metals in lead, tin, thallium, indium, cerium, praseodymium, and lanthanum.[34,35,37-44] The experimental features common to all fast impurity diffusion are as follows.

(a) The ratio of the impurity diffusion coefficient D_I to the self-diffusion coefficient D_s at the melting temperature is greater than 10^2.

(b) The ratio of the activation energy for impurity diffusion Q_I to the activation energy for self-diffusion Q_s is much less than unity.

(c) The values of the preexponential D_0 for the noble-metal impurities are, in the majority of cases, at least an order of magnitude less than the values of D_0 for self-diffusion.

An additional feature that has been observed for all the noble metals in lead is their low solubility.[37,45,46] Examples are listed in Table I for both fcc[34,37,45,46] and bcc systems[47,48] for which data are available for all the above features. For comparison, two alkali-metal systems, potassium in sodium and sodium in potassium,[51] have been included as examples of substitutional diffusion. It is clear from the table that the silver in lithium and the zinc in lithium systems do not show the features that one can expect for fast diffusion, but rather follow much more closely those features to be expected for substitutional diffusion. The sodium in lithium system is not shown in the table because the solubility information is unknown. The other three features are in close agreement with

TABLE I. Comparison of "fast" and "slow" impurity diffusion.

System	Structure	$(D_I/D_S)_{T_m}$	Q_I/Q_S	$(D_0)_I/(D_0)_S$	Ref.	Maximum solubility (at. %)	Ref.	Remarks
Cu in Pb	fcc	2×10^4	0.32	2×10^{-2}	34	$\sim2\times10^{-2}$	45	fast
Ag in Pb	fcc	5×10^2	0.58	1×10^{-1}	34	$\sim1\times10^{-2}$	46	fast
Au in Pb	fcc	4×10^3	0.38	9×10^{-3}	37	$\sim2\times10^{-3}$	37	fast
Au in Na	bcc	1×10^2	0.22	2×10^{-3}	47	$\sim2\times10^{-3}$	47	fast
Au in K	bcc	8×10	0.33	4×10^{-3}	48	$\sim1\times10^{-2}$	48	fast
K in Na	bcc	6.1	0.84	5×10^{-1}	51	3.1	49	slow
Na in K	bcc	5.6	0.76	2×10^{-1}	51	4.1	49	slow
Ag in Li	bcc	2.5	1.00	3	27	9.0	50	slow
Zn in Li	bcc	3.3	1.01	5	30	4.5	50	slow

those found for silver and zinc diffusion in lithium.

III. EXPERIMENTAL METHODS

The method used to obtain diffusion profiles was to observe the diffusion of a thin surface layer of radioactive impurity by sectioning. Most of the experimental details have been described in earlier papers.[17,30] However, some important differences are evident in the techniques, and these will be discussed. In particular, the differences in the preparation of the thin surface layer of sodium or silver on lithium will be examined in detail. The method used for preparing thin surface layers of sodium is not equally applicable to all other impurities and may have resulted in some unreliable data for impurity diffusion in lithium.

A. Materials

The lithium, with a purity of 99.98% was obtained from the Foote Mineral Co. The radioactive isotopes ^{22}Na and ^{110m}Ag were obtained in the chloride and nitrate form, respectively, from the International Chemical and Nuclear Corp. The ^{24}Na isotope was prepared by irradiation of high-purity NaCl in the Argonne CP-5 reactor, and ^{105}Ag was prepared by the reaction $^{105}\mathrm{Rh}(\alpha, 2n)\,^{105}\mathrm{Ag}$ and subsequent chemical separation. A Ge(Li) spectrometer was used to check all the isotopes, and they were found to be free of other radioactive impurities.

B. Surface-Layer Preparation

The active sodium metal was prepared in a tantalum evaporator boat under a helium atmosphere by ion exchange of molten lithium with active NaCl. The evaporator system was evacuated to a pressure of 2×10^{-6} Torr, the surface of the lithium sample was cleaned by a razor cut, and then the active sodium was evaporated. The temperature of the evaporator boat is adjusted empirically to ensure a reasonable efficiency of active sodium evaporation in a period of a few minutes. In the case of the sodium isotopes, the temperature was between 500 and 550 °C, so that both active sodium and inactive lithium were evaporated at the same time. The lower vapor pressure of NaCl should ensure that the radioactive atoms were deposited in metal form on the surface of the lithium. In the earlier investigations on sodium diffusion, this expectation was confirmed by using neutron-irradiated NaCl. When the NaCl was used soon after irradiation, the radioactive decay curve had two components: ^{24}Na (half-life 24 h) and ^{38}Cl (half-life 38.5 min), but the decay curve obtained from material evaporated in the above manner showed no chlorine component. The degree to which a radioactive isotope is evaporated in the metal or salt form will be a function of the evaporation temperature and the relative vapor pressures of the metal and its salt.

The problem of radioactive-salt evaporation was discovered when the ion-exchange method was applied to the silver isotopes. Diffusion profiles obtained from experiments with ^{110}AgCl showed small, but definite curvature when followed over a drop of three orders of magnitude in the specific activity. These curved profiles yielded values for the diffusion that were in approximate agreement with earlier measurements.[27] The curved profiles could have resulted from the higher evaporation temperature. This temperature was not measured, but the radiant heat from the boat did not disturb the surface of the lithium samples in any observable manner. The curved profiles would appear to result from the evaporation of AgCl. The exchange of silver ions in AgCl with lithium ions in the surface layer could be the rate-controlling step. The effect of a slower kinetic process in the surface layer could result in the observed concentration profiles and, in turn, result in low values of the measured diffusion coefficient. It should be emphasized that the curvature is not large and may not be observable unless the penetration is followed for a drop in the specific activity of more than two orders of magnitude. If the problem found in the present work on silver diffusion in lithium results because the impurity metal has a lower vapor pressure than its salt, then the data obtained on the diffusion of gold, tin, copper, and antimony may not be correct.[28,31,32] The present work suggests that the ion-exchange method is suitable for alkali-metal salts but is unsuitable for many other metal salts.

C. Silver Electropolating

To prevent problems of silver-salt evaporation, the silver was plated onto a platinum evaporator boat prior to evaporation. Plating efficiency was dependent on the silver-ion concentration in the plating solution. At the temperature of the diffusion anneal (150 °C), the solubility of silver in lithium is approximately 9%. However, to correctly measure a tracer-diffusion coefficient, the additions of inactive silver to the plating solution must be kept to a minimum. This objective was achieved by forming a small cup in the platinum evaporator boat and using this cup as both a cathode and electrolyte container. The concentration of silver nitrate was approximately 2 g/liter and sodium cyanide was added to bring the *pH* to 11.5. Using an open voltage of 4 V and a current density of 5–10 mA/cm^2, plating efficiencies of 70–80% were achieved.

D. Diffusion Measurements

When using radioactive tracers, which are not carrier-free, for measurements of impurity diffusion coefficients, care must be taken to ensure that the impurity levels necessary for measurement do not exceed the solubility limit. The higher count rates required for accurate determination of isotope effects in diffusion necessitate higher impurity levels than those for simple diffusion measurements. Solubility is seldom a problem when the radioactive tracer can be obtained carrier-free, as is the case for ^{22}Na and ^{105}Ag. The isotopes ^{24}Na and ^{110}Ag were made from neutron irradiations and contained, after preparation, a ratio of approximately $1:10^6$ active to inactive atoms.

Diffusion measurements were made at 150 °C for both sodium and silver in lithium using impurity-metal concentrations appropriate to those to be used in the isotope-effect measurements. Straight penetration profiles were found over three orders-of-magnitude drop in the specific activity, which indicated no measurable solubility problems.

Determination of the section thickness of lithium proved to be prone to error. Two methods were used for each experiment, and a comparison of the average thicknesses obtained by each method was used as a measure of the reliability of either method. The first method was to weight and section the lithium under a dry-air atmosphere. Unfortunately, if the atmosphere is too dry, the lithium welds to the razor and weight losses ensue. This can be prevented with an atmosphere of 10–50 ppm H_2O, but the film of oxide and hydroxide formed causes the slice to gain weight. These gains are particularly significant in lithium because of the low density and atomic weight of the element relative to that of lithium compounds.

The other method used was to allow the lithium to oxidize and dissolve in either dilute hydrochloric acid (sodium experiments) or dilute nitric acid (silver experiments). These acids were chosen because of the high solubility of the remaining salts in the acid. After the completion of the radioactive counting of all sections, the solutions were dried, and the resultant salt was weighed.

The average thickness obtained for each of eight experiments differed by over 1% from one method to the other, although none were consistently greater or smaller than the other. The comparison showed that it was not possible to measure the lithium sections to better than 1 or 2%.

E. Isotope-Effect Measurements

The counting procedures used to differentiate between the isotopes in each section have been described in earlier papers.[7,11,16] The ratio of the concentration of ^{22}Na to ^{24}Na was determined by a half-life separation.[11,16] Two completely separate measurements were made using different samples of lithium and separate diffusion anneals; both anneals were at 150 °C. The series of sections from each measurement were counted on separate counting systems.

The ratio of the concentration of ^{105}Ag to ^{110}Ag was determined by an energy separation method described in detail by Rothman, Peterson, and Robinson.[7] As the method followed carefully the previous work[7] on silver self-diffusion, only the additional precautions will be described. As with the sodium in lithium experiments, two separate experiments were performed with silver isotope diffusion into lithium, both anneals again at 150 °C. Each experiment was counted three times on one particular counting system, and then once on the system used for the second experiment. The latter was to confirm that the resultant isotope effect was not a function of small differences in the discriminator level settings. In one experiment, the ratio of activities $^{105}\mathrm{Ag}/^{110m}\mathrm{Ag}$ was approximately 1.3 and in the other approximately 2.0. The higher ratio should lessen the over-all error in the isotope-effect measurement, although, in practice, no improvement was observable.

The lithium sections for the sodium impurity experiments were oxidized and then dissolved in 2 ml of 3*N* HCl. This technique was not satisfactory for the silver impurity experiments because the AgCl precipitates out of solution, and the ratio of the ^{105}Ag/^{110m}Ag count rates becomes a function of time. Dissolution of the lithium in 2 ml of 9*N* nitric acid ensured the formation of the soluble compound silver nitrate. Previous experience with small concentrations of silver nitrate in solution showed that the ratio of the count rates could change with time. This phenomenon may result from the ability of silver ions to exchange with sodium ions in the walls of the glass counting bottles and thus change the counting geometry. To prevent recurrence of this phenomenon, the 2 ml of nitric acid used to dissolve the lithium oxide contained approximately 100 μg of silver nitrate. Measurements of standard bottles and the null effect also followed exactly the method used by Rothman, Peterson, and Robinson.

IV. EXPERIMENTAL RESULTS

A. Diffusion Measurements

The solution of the diffusion equation for the experimental conditions used in this work is

$$c_x = c_0 e^{-x^2/4Dt} , \tag{2}$$

where c_x is the specific activity of the tracer a distance x from the surface, and t is the time of anneal. The penetration profiles obtained in this work were linear over three orders of magnitude in concentration (see Fig. 1).

For the sodium diffusion in lithium three experiments were made, all at (150 ± 0.1) °C. The profiles for the two isotope-effect diffusion runs are shown in Fig. 1. The values of the diffusion coefficient obtained by computer fit from a least-squares fit of the data were (1.22 ± 0.01), (1.13 ± 0.01), and (1.12 ± 0.01)×10^{-7} cm^{2}sec^{-1}. The latter two measurements were from the isotope-effect experiments. The errors quoted are the sum of the errors in the measurement of the slope of the penetration profile and the anneal time and do not contain errors due to uncertainties in the weight of the lithium sections. Thus, the over-all error is probably on the order of 5%. This magnitude of error appears to be confirmed when compared with the average deviation of experimental points from the Arrhenius lines found for impurity diffusion in lithium.[26–33] The mean value of the three measured diffusion coefficients is 8% lower than the value calculated from the Arrhenius line of earlier measurements,[26] but this difference could be accounted for by different weighing procedures.

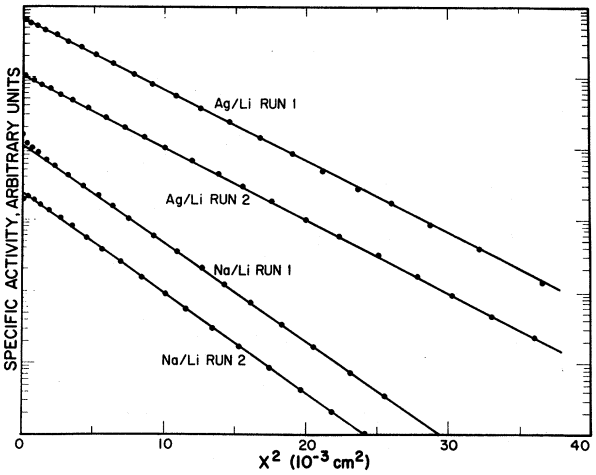

FIG. 1. Concentration profiles for the isotope-effect runs for diffusion of both sodium and silver in lithium.

For the silver diffusion in lithium, five measurements were made. The values obtained are listed in Table II, and the penetration profiles for the two isotope-effect runs are shown in Fig. 1. The mean value of D at 150.0 °C is 45% higher than that calculated from the Arrhenius line of earlier measurements.[27] This is a considerably greater difference than could be expected experimentally. As noted in Sec. III, evaporation of a silver salt instead of a silver metal could result in the apparent measurement of a lower diffusion coefficient. As the present work relies on the similarity of the impurity diffusion coefficients of silver and sodium in lithium, measurements of silver impurity diffusion were also made at 100 and 50 °C. In Fig. 2, the present silver impurity diffusion data are compared with the earlier sodium impurity diffusion[26] and the lithium self-diffusion data.[52] A least-squares fit of the silver impurity data to the Arrhenius relation $D = D_0 e^{-Q/RT}$ gave $D_0 = 0.54 \pm 0.05$ cm^{2}sec^{-1} and $Q = 12.83 \pm 0.10$ kcal/mole. A close similarity exists between the diffusion characteristics of the two impurities and, within the experimental errors inherent in the present methods, the Arrhenius lines are indistinguishable.

B. Isotope-Effect Measurements

Simultaneous diffusion of ^{24}Na and ^{22}Na into lithium and ^{110m}Ag and ^{105}Ag into lithium was measured. The ratio of the specific activities of the two isotopes (c_α/c_β) as a function of penetration c_α has been shown[53] to be

$$\ln\left(\frac{c_\alpha}{c_\beta}\right) = (\text{const.}) - \ln c_\alpha \left(\frac{D_\alpha}{D_\beta}\right) - 1 \quad . \tag{3}$$

The experimental plots of $\ln(c_\alpha/c_\beta)$ versus $\ln c_\alpha$ are shown for sodium diffusion in Fig. 3 and for silver diffusion in Fig. 4.

In the sodium isotope-effect experiment, each section for each run was counted at least ten times over a 4-day interval. The ratio of activities

TABLE II. Diffusivity of silver into lithium as a function of temperature.

Diffusion coefficient (cm^2/sec)	Temperature (°C)
$(1.20 \pm 0.01) \times 10^{-7}$	150.0
$(1.29 \pm 0.01) \times 10^{-7}$	150.0^a
$(1.28 \pm 0.01) \times 10^{-7}$	150.0^a
$(1.64 \pm 0.10) \times 10^{-8}$	100.0^b
$(1.11 \pm 0.02) \times 10^{-9}$	50.0

[a] Isotope-effect experiments.
[b] Curved penetration profile.

$^{22}Na/^{24}Na$ was determined by fitting the counting data to the time t elapsed since an arbitrary time zero:

$$A = A_{22} e^{-\lambda_{22} t} + A_{24} e^{-\lambda_{24} t} \quad , \qquad (4)$$

where A_{22} and A_{24} are the activities of ^{22}Na and ^{24}Na at time zero, and λ_{22} and λ_{24} are their decay constants. The error bars in Fig. 3 are the standard deviations obtained from the computer fit of the counting data to Eq. (4).

The slopes of $\ln(c_{22}/c_{24})$ versus $\ln c_{22}$ obtained for each run were 0.0085 ± 0.0004 and 0.0084 ± 0.0004. The mass factor $(24/22)^{1/2} - 1$ equals 0.04445 and the mean value of $(f\Delta K)_{Na/Li}$ equals 0.19 ± 0.01.

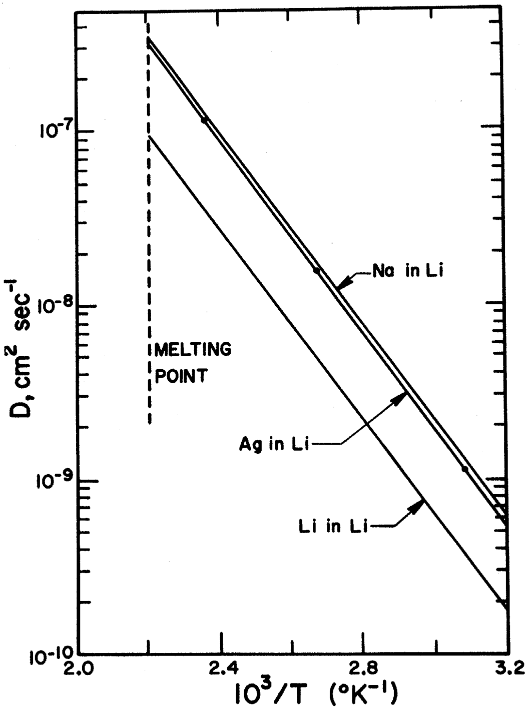

FIG. 2. Comparison of impurity diffusion of sodium and silver in lithium compared with lithium self-diffusion as a function of temperature.

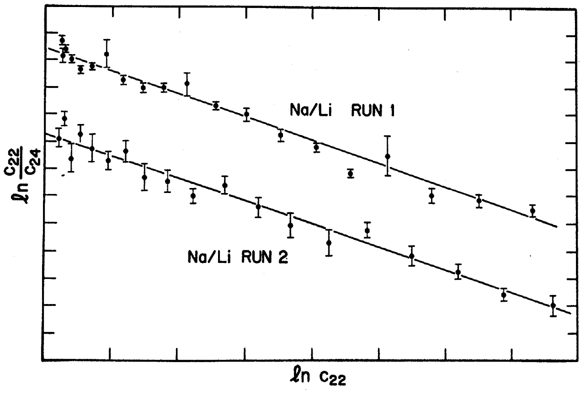

FIG. 3. Diffusion of ^{22}Na and ^{24}Na in lithium at 150 °C. Each division on the ordinate is 0.01. Each division on the abscissa is 1.0.

The silver isotope-effect diffusion data were counted three times on one counting system. Each set of data was processed separately for each of the two runs, and each point obtained for $\ln(c_{110}/c_{105})$ is plotted versus $\ln c_{110}$ in Fig. 4. A fourth count of all sections was made on the alternate counting system. No difference was found in the $\ln(c_{110}/c_{105})$ versus $\ln c_{110}$ slope. The null effect was counted four times on each counter. Only one set of data for the null effect is shown in Fig. 4, so that the error bars on the individual points can be shown. In the majority of cases, the spread in the values obtained for the individual sections is similar to the

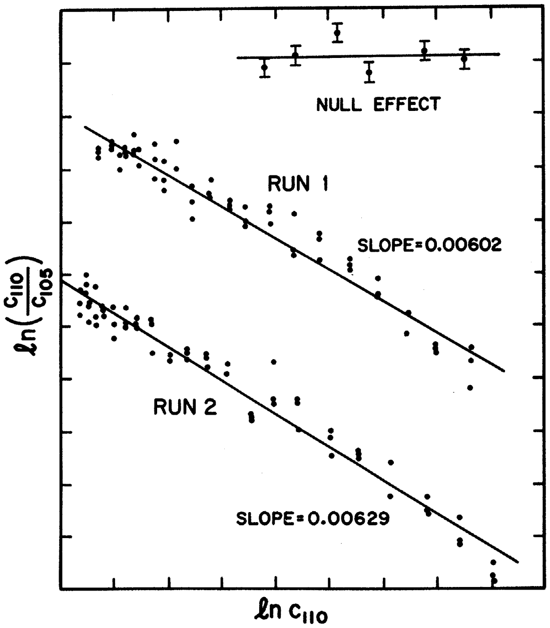

FIG. 4. Diffusion of ^{110m}Ag and ^{105}Ag in lithium at 150 °C. Each division on the ordinate is 0.01. Each division on the abscissa is 1.0.

error bars shown for the null-effect bottles. The few points that scatter outside these limits are probably the result of some small movement of the contents of that particular bottles.

The slopes of $\ln(c_{110}/c_{105})$ versus $\ln c_{110}$ were obtained by a least-squares fit to the combined data of the three sets of counts. The two slopes obtained were 0.0060 ± 0.0003 and 0.0063 ± 0.0003. The mean slope of the null effect was 0.0001 ± 0.0001. The mass factor $(110/105)^{1/2}-1$ equals 0.02343 and the mean value of $(f\Delta K)_{\mathrm{Ag/Li}}$ equals 0.26 ± 0.01.

V. DISCUSSION

Values of $f\Delta K$ for both sodium $[(f\Delta K)_{\mathrm{Na}}]$ and silver $[(f\Delta K)_{\mathrm{Ag}}]$ diffusion into lithium were obtained. The value of f is unknown but can be given in a simplified form as

$$f=\frac{5.33w_3}{2w_2+5.33w_3} , \tag{5}$$

where w_2 is the vacancy jump frequency for exchange with the impurity and w_3 is the vacancy jump frequency from a site neighboring on the impurity to a site not neighboring on the impurity.[54] The values of the diffusion coefficient for sodium and for silver diffusion in lithium are about $3\frac{1}{2}$ times greater than the self-diffusion coefficient of lithium. If half this difference were to be accounted for by a change in the w_2/w_3 frequency ratio, then f would decrease from 0.727 to 0.6. If one can assume 0.6 as a value of f for both impurities, then $(\Delta K)_{\mathrm{Na}}=0.32$ and $(\Delta K)_{\mathrm{Ag}}=0.43$.

The theory of Achar gives $(\Delta K)_{\mathrm{Na}}=0.72$ and $(\Delta K)_{\mathrm{Ag}}=0.14$. Feit's theory indicates that, for vacancy diffusion, the factor ΔK should have an upper limit of 0.5 in a bcc lattice. Both previous[16–18] and present experimental observations of the isotope effect would appear to fit this prediction. However, the theory further predicts that, in a host matrix of light atoms, substitutional impurities would exhibit values of ΔK significantly lower than those found for self-diffusion. Calculation of ΔK for sodium and silver yields $(\Delta K)_{\mathrm{Na}}=0.22$ and $(\Delta K)_{\mathrm{Ag}}=0.06$.

Thus the theories fail to predict the magnitudes of ΔK, and also fail to indicate that one might expect to find $(\Delta K)_{\mathrm{Ag}}$ greater than $(\Delta K)_{\mathrm{Na}}$. The ratio of the measured isotope effects

$$(f\Delta K)_{\mathrm{Ag}}/(f\Delta K)_{\mathrm{Na}}=1.37\pm 0.13 .$$

This suggests that unless f_{Ag} is at least 20% greater than f_{Na}, the value of $(\Delta K)_{\mathrm{Ag}}$ is measurably higher than $(\Delta K)_{\mathrm{Na}}$ and not four or five times smaller, as both theoretical treatments predict.

These results lead one to question either the basic assumptions made in the theories of Achar[24] and Feit[25] or the assumption that both impurities are diffusing substitutionally in lithium. Recent NMR measurements[55] in dilute alloys of lithium give some evidence that all silver-solute atoms occupy interstitial rather than substitutional positions in lithium. The possibility that silver occupies both interstitial and substitutional sites has also been considered.[33] In this model of dissociation diffusion, the silver ions in interstitial sites are considered to be in lower concentration but considerably more mobile than the silver in substitutional sites. However, the evidence presented in Table I strongly indicates substitutional impurity diffusion for silver in lithium, and the dissociative mechanism would suggest possible curvature in the Arrhenius line, which was not found experimentally (Fig. 2).

VI. CONCLUSIONS

The present results should not be interpreted as questioning the basic dynamical theory of diffusion but rather the assumptions used in the application of this theory to the mass dependence of the isotope effect for impurity diffusion. It is possible that the normal modes do not play a fundamental physical role in determining the mass effect or that the assumption that the reaction coordinate is the same for both impurity and self-diffusion is invalid.

ACKNOWLEDGMENTS

The authors wish to thank N. L. Peterson for his interest and encouragement and B. N. N. Achar, J. W. Miller, and S. J. Rothman for helpful discussions. We also wish to thank E. Molinelli for help with the experimental work.

---

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

[1] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

[2] J. G. Mullen, Phys. Rev. **121**, 1649 (1961).

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

[4] C. P. Flynn, Phys. Rev. **171**, 682 (1968).

[5] B. N. N. Achar, Phys. Rev. B **2**, 3848 (1970).

[6] M. D. Feit, Phys. Rev. B **3**, 1223 (1971).

[7] S. J. Rothman, N. L. Peterson, and J. T. Robinson, Phys. Status Solidi **39**, 635 (1970).

[8] P. Reimens and D. Bartdorff, Phys. Status Solidi B **50**, 305 (1972).

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

[10] N. L. Peterson, Phys. Rev. **136**, A568 (1964).

[11] N. L. Peterson and S. J. Rothman, Phys. Rev. **163**, 645 (1967).

[12] A. P. Batra, Phys. Rev. **159**, 487 (1967).

[13] T. Heumann and R. Imm, J. Phys. Chem. Solids **29**, 1613 (1968).

[14] C. M. Walter and N. L. Peterson, Phys. Rev. **178**, 922 (1969).

[15] D. Graham, J. Appl. Phys. **40**, 2386 (1969).

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

[17] J. N. Mundy, Phys. Rev. B **3**, 2431 (1971).
[18] V. Irmer and M. Feller-Kniepmeier, J. Appl. Phys. **43**, 953 (1972).
[19] R. Feder, Phys. Rev. B **2**, 828 (1970).
[20] R. Feder and H. Charbnau, Phys. Rev. **149**, 464 (1966).
[21] J. N. Mundy and W. D. McFall, Phys. Rev. B **5**, 2835 (1972).
[22] H. B. Huntington, M. D. Feit, and D. Lortz, Cryst. Lattice Defects **1**, 193 (1970).
[23] R. C. Brown, J. Worster, N. H. March, R. C. Perrin, and R. Bullough, Philos. Mag. **23**, 555 (1971).
[24] B. N. N. Achar (unpublished).
[25] M. D. Feit, Phys. Rev. B **5**, 2145 (1972).
[26] J. N. Mundy, A. Ott, and L. Löwenberg, Z. Naturforsch. **22a**, 2113 (1967).
[27] A. Ott and A. Nordén-Ott, Z. Naturforsch. **23a**, 473 (1968).
[28] A. Ott, Z. Naturforsch. **23a**, 1683 (1968).
[29] A. Ott, Z. Naturforsch. **23a**, 2126 (1968).
[30] J. N. Mundy, A. Ott, A. Lodding, and L. Löwenberg, Phys. Status Solidi **35**, 359 (1969).
[31] A. Ott, J. Appl. Phys. **40**, 2395 (1969).
[32] A. Ott, A. Lodding, and D. Lazarus, Phys. Rev. **188**, 1088 (1969).
[33] A. Ott, Z. Naturforsch. **25a**, 1477 (1970).
[34] B. F. Dyson, T. R. Anthony, and D. Turnbull, J. Appl. Phys. **37**, 2370 (1966).
[35] M. P. Dariel, G. Erez, and G. M. J. Schmidt, J. Appl. Phys. **40**, 2746 (1969).
[36] L. W. Barr, *Diffusion Processes* (Gordon and Breach, London, 1971), p. 185.
[37] G. V. Kidson, Philos. Mag. **13**, 247 (1966).
[38] B. F. Dyson, J. Appl. Phys. **37**, 2375 (1966).
[39] B. F. Dyson, T. R. Anthony, and D. Turnbull, J. Appl. Phys. **38**, 3408 (1967).
[40] T. R. Anthony, B. F. Dyson, and D. Turnbull, J. Appl. Phys. **39**, 1391 (1968).
[41] T. R. Anthony and D. Turnbull, Phys. Rev. **151**, 495 (1966).
[42] M. P. Dariel, D. Dayan, and D. Calais, Phys. Status Solidi A **10**, 113 (1972).
[43] M. P. Dariel, J. Appl. Phys. **42**, 2251 (1971).
[44] M. P. Dariel, G. Erez, and G. M. J. Schmidt, Philos. Mag. **19**, 1053 (1969).
[45] H. Gleiter, Acta Metall. **18**, 117 (1970).
[46] J. W. Miller, Phys. Rev. B **2**, 1624 (1970).
[47] L. W. Barr, J. N. Mundy, and F. A. Smith, Philos. Mag. **16**, 1139 (1967).
[48] F. A. Smith and L. W. Barr, Philos. Mag. **21**, 633 (1970).
[49] D. K. C. MacDonald, W. B. Pearson, and L. M. Towle, Can. J. Phys. **34**, 389 (1956).
[50] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).
[51] L. W. Barr, J. N. Mundy, and F. A. Smith, Philos. Mag. **20**, 389 (1969).
[52] A. Lodding, J. N. Mundy, and A. Ott, Phys. Status Solidi **38**, 559 (1970).
[53] L. W. Barr and A. D. LeClaire, Proc. Br. Ceram. Soc. **1**, 109 (1964).
[54] J. R. Manning, *Diffussion Kinetics for Atoms in Crystals* (Van Nostrand, Princeton, N. J., 1968), p. 117.
[55] J. M. Titman and B. M. Moores, J. Phys. F **2**, 592 (1972).

PHYSICAL REVIEW B VOLUME 7, NUMBER 10 15 MAY 1973

Bethe–Peierls Approximation in the Electronic Theory of Disordered Materials

F. Brouers, M. Cyrot, and F. Cyrot-Lackman
Laboratoire de Physique des Solides,[*] Faculté des Sciences, 91, Orsay, France

(Received 15 August 1972)

The effect of local environment on the total and partial densities of states of a disordered substitutional binary alloy is calculated within a Bethe–Peierls-type approximation. Compared to a molecular-field approximation, this method yields more precise results on the shape and structure of the alloy density of states.

In these last five years great effort has been devoted to the understanding of electronic properties of disordered systems. A major development of the theory has been the introduction of the coherent-potential approximation (CPA).[1,2] The CPA was derived at first in the framework of the multiple scattering theory. It corresponds to the determination of an effective medium such that the average scattering from a single atom is equal to zero. Recently a number of attempts have been made[3-6] to improve this single-site approximation by considering pairs, triplets, etc., embedded in a medium which does not scatter pairs, triplets, etc., on average. In practice the implementation of these theories seems to be a difficult analytical and numerical task.[7] On the other hand, it has been emphasized[2] that the CPA resembles the molecular-field theory of magnetism. The effective potential is determined self-consistently as the effective field is determined self-consistently in a Curie-Weiss or Bragg-Williams theory. The natural improvement of the molecular-field theory was proposed a long time ago by Bethe.[8] The idea is to take account of the local environment of each site, to calculate exactly the effect of the first shell of the nearest neighbors, and to use a self-consistent field to describe the effect of other atoms on the first shell. This theory yields qualitative improvement and new features.

In this paper, we report a calculation of a substitutional-binary-alloy density of states along this line. This seems to be particularly appropriate when short-range order has to be taken into account.