Impurity Diffusion in Lithium

1. The Diffusion of Cd, Hg and Ga

2. Survey of the Diffusion of Metallic Impurities in Lithium

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The diffusion of $^{115\mathrm{m}}$Cd, ^{203}Hg and ^{72}Ga tracers in lithium metal has been studied, using a thin film deposition and sectioning method.

The experimental results can be expressed by the following Arrhenius relations:

$$D_{\mathrm{Cd}} = 0.62 \exp\{-(15.00 \pm 0.53)/RT\},$$
$$D_{\mathrm{Hg}} = 1.04 \exp\{-(14.18 \pm 0.47)/RT\},$$
$$D_{\mathrm{Ga}} = 0.21 \exp\{-(12.91 \pm 0.32)/RT\}.$$

These results, which do not agree with any established theory of impurity diffusion in a metallic lattice, are discussed together with data from previous experiments in terms of the systematics of the dependence of the diffusivity on the "ionizability" of an impurity atom in Li, and on the size of the impurity. In this way a qualitative explanation of the different diffusions rates can be obtained. The relatively large and electropositive impurities appear to diffuse mainly via a vacancy mechanism and the small and electronegative ones mainly as interstitials. The distinction substitutional-interstitial is less pronounced for very large impurities, which may also exhibit tendencies to be trapped at lattice defects.

Introduction

This investigation is part of a systematic study of atom transport processes in solid and liquid alkalis and other metals, pursued at this laboratory. Most of the experimental work has hitherto been done on lithium.

Among the defect mechanisms proposed to operate in diffusion processes in metals, the vacancy has proved to be the most successful, especially in close-packed metals.

Recent studies[1,2,3] have shown that under certain conditions the diffusivity of metal ions in a metal matrix may be interpreted in terms of interstitial solubility; there is indeed ample evidence that noble metal impurities diffuse as interstitials in alkali metals as well as in several polyvalent matrices.

Results from thermotransport measurements in lithium[4,5] have also been interpreted in terms of an interstitial-like transport mechanism for certain metallic impurities. That an interstitial diffusion mechanism could operate also in lithium self-diffusion is further implied by interdiffusion measurements on isotopically pure lithium matrices[6]. This diffusion mode is also supported by recent computer simulation studies[7], where it was found that interstitials could well exist together with vacancies.

In an X-ray dilatometric measurement on lithium[8] it was found that the vacancy was the dominant defect in thermal expansion. However the experimental results do not fully exclude coexisting interstitials, which may well be much more mobile.

The ideas of differential interstitial-substitutional diffusivity of impurities in lithium have been supported in connection with measurements of the diffusion of the fast impurity Cu[2] in Li and of the slowly diffusing impurities Sn, Pb, Sb, and Bi[3] in Li.

The present investigation was undertaken in order to study the applicability of these considerations to some impurities, which diffuse with about the same rate as that of self-diffusion in lithium, and to compare these with earlier discussed systematics of impurity diffusion in the lithium lattice.

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Experimental Procedure

The experimental technique was a version of the well known thin film plating and sectioning method, which with a metal evaporation and vapor deposition apparatus had been applied to the highly reactive and corrosive lithium metal. This method has been described thoroughly before [9].

The lithium metal was from Foote Lithium Corporation, and had a chemical purity of 3N8. For an analysis of the metal see Table 6. Two of the radioactive tracers, ^{115m}Cd and ^{203}Hg, were from New England Nuclear Corporation and received in the form of salts of high specific activity dissolved in HCl. The ^{72}Ga was produced by neutron irradiation of 5N pure Ga metal at AB Atomenergi, Sweden. The radioactive isotopes were checked by multichannel analysis and found to be free from radioactive impurities.

After the casting of the lithium samples, the diameter of the individual grain usually exceeded 10 mm. This was achieved by a slow and unidirectional cooling of the casting mold.

The radioactive counting was done with a well-type NaI(Tl) scintillation crystal and a RIDL solid state single channel analyzer. Special attention was given to corrections for the short half-life of ^{72}Ga (12.5 hours).

Experimental Results

The experimentally determined diffusion coefficients are given in Tables 1—3. The errors in D are between 1 and 3% and are due mainly to the scatter in the penetration profiles. These values are

T °C	$D \cdot 10^{10}$ cm²/sec
82.1	3.166
86.7	5.914
86.7	5.589
106.7	13.75
117.5	26.84
132.9	37.63
138.9	62.98
141.3	76.15
149.8	96.51
155.1	127.7
158.8	189.8
175.8	392.8

Table 1. Experimental Results for Diffusion of Cadmium in Lithium

T °C	$D \cdot 10^{10}$ cm²/sec
57.8	59.8
75.5	135.2
85.8	178.9
107.9	620.0
118.3	1143
128.3	2175
136.0	3046
146.0	4671
165.6	9641
173.6	11830

Table 2. Experimental Results for Diffusion of Mercury in Lithium

T °C	$D \cdot 10^{8}$ cm²/sec
116.5	1.208
141.6	3.255
154.8	5.106
163.4	6.971
173.4	10.40

Table 3. Experimental Results for Diffusion of Gallium in Lithium.

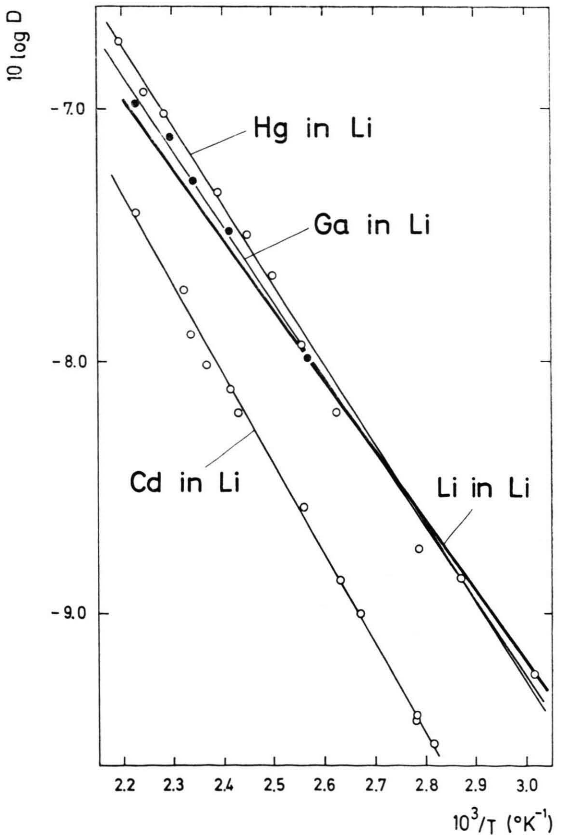

Fig. 1. Arrhenius plots for diffusion of Cd, Hg and Ga in lithium metal.

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plotted in Fig. 1. together with the line representing the self-diffusion data in normal lithium[6]. All the hitherto measured Arrhenius-lines for impurities diffusing in lithium are plotted in Fig. 2. The data have been analyzed by a least squares approximation procedure, and the values of the activation energies and frequency factors for the impurities studied in this investigation are listed in Table 4 together with the same data for the other impurities earlier measured.

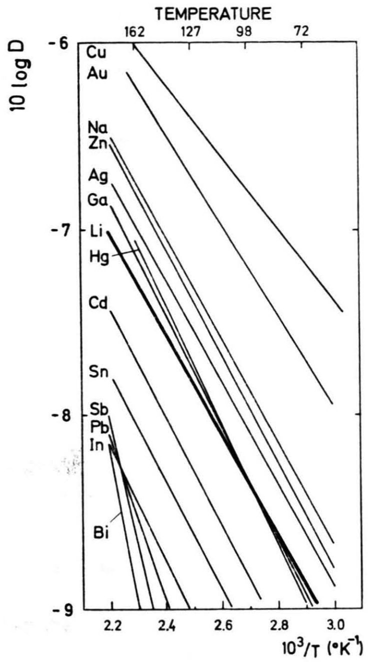

Fig. 2. Arrhenius plots of impurity diffusion in lithium metal.

Tracer	D_0 cm²/sec	Q kcal/mole	Ref.
$^{7}\mathrm{Li}_6$	0.120	12.634 ± 0.139	6
$^{6}\mathrm{Li}_7$	0.123	12.848 ± 0.222	6
$^{7}\mathrm{Li}_7$	0.14	12.87 ± 0.18	6
$^{6}\mathrm{Li}_6$	0.14	12.60 ± 0.25	6
Cu	0.047	9.22 ± 0.22	2
Au	0.21	10.99 ± 0.18	16
Ag	0.37	12.83 ± 0.25	15
Na	0.41	12.61 ± 0.15	33
Zn	0.57	12.98 ± 0.24	9
Ga	0.21	12.91 ± 0.32	
Hg	1.04	14.18 ± 0.47	
Cd	0.62	15.00 ± 0.53	
In	0.39	15.87 ± 0.36	34
Sn	0.26	15.00 ± 1.20	3
Pb	$1.6 \cdot 10^{2}$	25.21 ± 1.2	3
Sb	$1.6 \cdot 10^{10}$	41.5 ± 4.5	3
Bi	$5.3 \cdot 10^{13}$	47.3 ± 3.4	3

Table 4. Impurity Diffusion Data in Lithium.

Discussion

Theoretical and experimental work in the field of metals and alloys has generally arrived at the conclusion that metallic impurities in metal matrices usually dissolve substitutionally rather than interstitially. The substitutional mode of solution requires generally less energy than the interstitial, primarily because of electrostatic compatibility, reduced ion core overlap and less induced strain in the solvent lattice. These considerations in the form of simple geometrical rules, HÄGGS rules[10], suggests that a solute atom "fits" into the interstices of the solvent matrix if the ratio of the diameter of the solute atom to that of the solvent is less than 0.59. This diameter ratio corresponds to the largest sphere that will fit into the interstices of a close-packed lattice of spheres. This rule has explained the occurrence of carbon, nitrogen, hydrogen and boron in the interstitial sites of many metals. Interstitial solubility of metals in metals is, however, in most cases definitely contrary to Hägg's rules.

The most thoroughly studied type of diffusion has been that of substitutional atoms diffusing by exchange with vacancies (see e.g. Refs. [11,12]). If interstitials have participated in the diffusion process, their mobility has been high, as no vacancy formation energy was needed for diffusion. Thus, even if the concentration of interstitials is rather small their contribution to the diffusion may be considerable.

In recent years, fast and presumably interstitial diffusivity has been found for copper in some semiconductors[13,14], and for the noble metals and zinc in some polyvalent metals[1], lithium[2,15,16], sodium[17], and potassium[18]. This interstitial diffusion

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and solution mode, which has been impossible to account for by established diffusion models, has been explained by the assumption of a dissociative mode of solution of impurities in a host lattice. This dissociative diffusion mechanism has manifested itself by the evidence that the noble metals impurity diffusion rates exceed self-diffusion by several orders of magnitude[14]. This is in contrast to normal diffusion behaviour in close-packed metals, where impurity diffusion generally is within about one order of magnitude from self-diffusion.

In interstitial diffusion the ion core of a migrating species is considered[3] as playing a major role in determining the magnitude of its activation energy, whereas in substitutional diffusion the electronic interaction between the diffusing atom and a vacancy[19, 20, 21] is known to be of dominant importance.

In metals where interstitial solubility is found, generally relatively large interstitial positions exist in the lattice. In lithium metal the reformulation of Hägg's rule would allow a considerable number of impurities to dissolve interstitially. A geometrical consideration of the size of the available positions in the lattice shows that as the nearest neighbour distance is 3.03 Å, the tetrahedral interstitial site has a diameter of about 2.3 Å, and the face-centered site a diameter of about 1.6 Å. These values may be compared with the substitutional site, which has a diameter of about 4 Å. There is thus quite considerable space in the lithium lattice for impurity ions, both in substitutional and interstitial positions. It is even possible to accomodate some non-ionized metal atoms in the vacant interstitial sites with relatively small ion core overlap and excess induced strain in the lattice.

One thing which must be taken into account is the fact that the normally quoted Goldschmidt radii pertain to the atoms in their own lattices, and therefore these values might not necessarily be applicable to these atoms as solutes in other metal matrices.

Experimental work with these "interstitial-carrying" types of metals[1], has shown that interstitial solution is especially favored if the solvent is polyvalent or very electropositive and the solute poorly ionized or very electronegative. Thus the "size-rule" which has to be fulfilled as a necessary condition has to be combined with certain ionization conditions.

Interstitial solubility in metals, where certain size and ionization conditions are fulfilled, has now been verified by various experimental work, e.g. diffusion measurements[2], hardness tests[22], high pressure measurements of atomic mobilities[23, 24, 25], Mössbauer effect measurements[26], experiments with centrifugal force fields[27], and thermotransport of metallic tracers[28].

In the lithium metal lattice, the effective size of the impurity atom can be said to be qualitatively influenced by the relative value (ΔI) of the first ionization potential of the solvent (I_{Li}) and that of the solute (I_{imp})

$$\Delta I = I_{\text{imp}} - I_{\text{Li}} .$$

In lithium the first ionization potential is quite low, 124 kcal/mole. This indicates that there is a rather small amount of energy available to force solutes into higher states of ionization, and therefore one could expect the impurities to enter the lithium lattice either as unionized atoms or as singly ionized ions. See Table 5, where the first and second ionization potentials are listed for all impurities studied in the lithium matrix.

The problem with the solution and diffusion mode of metal atom impurities in the lithium lattice can to the first degree of approximation be reduced to a consideration of:

A) The ionizability of the impurity and the electrostatic screening of the ion by the core and conduction electrons (electronegativity).

B) The size of the ion or atom.

The diffusion data for the impurities studied hitherto in the lithium lattice may be discussed in the following way:

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Solute	ΔQ $\frac{\text{kcal}}{\text{mole}}$	r_a ÅU	r_i ÅU	I_1	I_2 kcal/mole	ΔI	EN	DM	Group	Period	Isotope	Ref.
Li	0	1.51	0.60	124	1740	0	1.0	V (I)	IA	2	^{6}Li	6
Cu	− 3.4	1.25	0.96	178	467	54	1.9	I	IB	4	^{64}Cu	2
Au	− 1.6	1.40	1.37	213	472	89	2.4	I	IB	6	^{195}Au	16
Ag	+ 0.2	1.40	1.26	175	494	51	1.9	I (V)	IB	5	^{110m}Ag	15
Na	0.0	1.90	0.95	119	1088	−5	0.9	V	IA	3	^{22}Na	33
Zn	+ 0.4	1.38	0.74	216	412	92	1.6	I	IIB	4	^{65}Zn	9
Ga	+ 0.3	1.41	0.81	138	472	14	1.6	V (I)	IIIA	4	^{72}Ga	
Hg	+ 1.5	1.57	1.10	241	432	117	1.9	I	IB	6	^{203}Hg	
Cd	+ 2.4	1.50	1.14	207	389	83	1.7	I (V)	IIB	5	^{115m}Cd	
In	+ 3.2	1.61	1.32	133	434	9	1.7	V	IIIA	5	^{114m}In	34
Sn	+ 2.4	1.58	1.22	169	336	45	1.8	V (I)	IVA	5	^{113}Sn	3
Pb	+12.6	1.69	1.40	171	346	47	1.8	V	IVA	6	^{210}Pb	3
Sb	+29	1.54	0.89	199	380	75	1.9	I	VA	5	^{124}Sb	3
Bi	+35	1.65	0.98	185	384	61	1.9	I	VA	6	^{207}Bi	3

Table 5. Impurities in Lithium: differences ($\Delta Q = Q_i - Q_{Li}$) in experimental activation energies, Goldschmidt metallic radii (r_a), univalent ionic radii (r_i), first ionization potential (I_1), second ionization potential (I_2), potential difference ($\Delta I = I_1 - I_{Li}$), Pauling electronegativities (EN), and inferred diffusion modes (DM). I = interstitial diffusion, V = vacancy diffusion, parentheses denoting possible intermediate cases.

1. Cadmium: The first ionization potential is 207 kcal/mole and the second is 389 kcal/mole. When Cd enters the lithium lattice, two cases have to be regarded; a) it could exist as a substitutional metal ion Cd^+, having an ion radius of 1.14 Å, which is smaller than Ag^+, or b) it could also occur as neutral Cd, with a radius of 1.50 Å, in which state it would be larger than Au and rather difficult to fit into an available interstitial site in the lattice. If it existed in the state of Cd^+, it could be expected to diffuse faster than the self-diffusion rate, probably like Na^+ or Ag^+. In the non-ionized state it would be expected to participate in diffusion as a fairly large interstitial, and because of its size exhibit quite a low diffusion rate. For diffusion of Cd in lithium a mechanism which combines interstitial and substitutional diffusive jumps could also exist. This was first suggested by MILLER[29] for diffusion of Cd in lead. In this mechanism the Cd ion moves from a substitutional site in the lattice to an adjacent interstitial site. A Li ion from the lattice jumps into the vacant place, leaving another vacancy behind, into which the Cd ion then moves from its interstitial position. This type of mechanism might be especially favoured if the impurity can be either ionized or non-ionized and if its mass is considerably higher than that of the solvent metal atoms, as this contributes a greater relative exchange frequency to the solvent atoms with the available vacant lattice site.

2. Mercury: The first ionization potential is 241 kcal/mole and the second 432 kcal/mole. The big difference between the first ionization potential for this impurity and that of lithium, makes an ionization improbable as it requires too much energy. Therefore Hg will probably enter the solvent lattice as a very big interstitial. There is however a considerable difference in the solubility and diffusivity between Hg and Cd, for Cd could be ionized and thus interact and be trapped by vacancies, while Hg can not be ionized at all. Thus it is possible for Hg to diffuse faster than Cd, despite the fact that as interstitials they have about the same radius. The assumption of a tightly squeezed interstitial seems also to be suggested by the fact that the Arrhenius plot for Hg crosses that of Li. The strain may give a particularly high pre-exponential term, caused by the heavy but, because of excess lattice strain, quite fast vibrating impurity atom[30].

3. Gallium: The first ionization potential is 138 kcal/mole and the second is 472 kcal/mole. The difference, ΔI, between this first ionization potential and that for Li is 14 kcal/mole, a relatively small amount of energy. This implies that it is quite probable for the gallium impurity to enter the lithium matrix as a singly ionized atom Ga^+, with a radius of only 0.81 Å, which is slightly larger than that for lithium, 0.60 Å. Because of electrostatic compatibility this impurity should dissolve and diffuse in the same way as the Li matrix atoms[6][*].

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[*] Apart from suggested non-classical effects in Li.

The other impurity atoms hitherto studied in the lithium lattice can according to the same treatment be discussed in the following way:

4. Copper[2]*:* The ionization potential is considerably larger than that of Li and therefore Cu probably enters the Li lattice mainly as an un-ionized atom. This together with the relatively small atomic size results in a high diffusion rate. The tendency for the diffusivities of the noble metal solutes to be expressed by the sequence

$$D_{\mathrm{Cu}} > D_{\mathrm{Au}} > D_{\mathrm{Ag}} \gg D_{\mathrm{self}}.$$

as found in Li is present in all the metals where the interstitial-like solubility and diffusivity is taking place.

5. Gold[16]*:* Presumably unionized and will squeeze into the interstitial positions with some difficulty, the strain field and position causing enhancement of the diffusivity. It has been shown that the discrepancy between the experimental cohesive energy and cohesion[31, 32] arising from the interactions between the s valence electrons and the positive ion cores is greatest for gold and smallest for silver in the pure noble metals, indicating that the correlation forces are stronger between silver ion cores. If this unequal interaction is carried over to lithium, then for equal amounts of dissolved gold and silver, a higher percentage of gold will be found in the interstitial sites.

6. Silver[15]*:* The first ionization potential of Ag is lower than that of Au and Cu, thus it seems possible for the Ag tracers to enter the solvent lattice both as un-ionized Ag atoms and as ions, Ag^+. It may be assumed that the substitutional positions are favored, if electronically feasible, since this introduces a smaller strain in the host matrix. Both Au and Ag probably dissolve substitutionally more than interstitially, but the latter mode contributes most to the diffusion. The reason why Ag diffuses slower may partly be that it is less electronegative or less screened and less favored by the correlation forces and thus less represented in the interstitial positions. Ag has moreover a more stable and thus less polarizable d-shell and thus one would expect Ag to act as a "harder point" than Au (FRIEDEL, in Ref.[1]).

7. Sodium[33]*:* The ionizability of Na is larger than that of Li. Thus it is certainly singly ionized as Na^+ and can fit substitutionally into the lattice. The radius of of the Na^+ ion is however considerably larger than that of Li^+. This might result in a closer binding of the Na^+ ion to the effective charge of a vacancy, since the core wave functions extend out further, as does the valence cloud. This together with the effect of lattice strain, seems to account for the enhanced diffusivity of Na, relative the self-diffusion.

8. Zinc[9]*:* This solute is considerably less ionizable than the solvent, and thus probably not ionized and must take an interstitial position in the lithium lattice. Zn is slightly smaller than Au as a neutral atom, and has a considerably smaller electronegativity so the observed decrease in diffusivity might be due to the smaller lattice strain enhancement of the diffusion together with less screening effects in the interaction with charges in the lattice. It is however conspicuous that Zn has a full d-shell in analogy with the noble metals and an atom size about equal to that of Au and Ag. Thus to some extent the relatively rapid diffusivity of Zn might be connected with correlation forces.

9. Indium[34]*:* The relatively easy ionizability of this solute, in combination with the rather large atom and ion size, makes it appear probable that In dissolves substitutionally and diffuses mainly via vacancies. Even if the lattice positions offer ample space, there will be a considerable barrier against motion. This will give a contribution to the activation energy for diffusion, above that of vacancy formation and decrease the diffusivity markedly.

10. Tin[3]*:* Presumably partial interstitial solubility and slow diffusivity of this impurity. Sn appears to be an intermediate case in this context.

11. Lead[3]*:* This solute diffuses presumably with a vacancy mechanism, which because of ionizability and size conditions requires more motion energy than for instance In. This also leads to a fairly slow diffusion rate.

12. Antimony[3]*:* Small ionizability and large size of the atoms leads to interstitial diffusion.

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13. Bismuth[3]*:* This solute atom would appear to diffuse as a very big, tight-fit interstitial in the same way as Sb.**

Element	Content
Li	99.98 %
Na	0.0034%
K	0.0032%
Cl	0.0031%
N_2	0.0020%
Ca	$<$ 0.001 %
Fe	$<$ 0.001 %
Ni	$<$ 0.001 %
Cr	$<$ 0.001 %
Al	$<$ 0.001 %
Si	$<$ 0.001 %
Co	$<$ 0.001 %
Cu	$<$ 0.001 %

Table 6.
Chemical Analysis
of Lithium.

Summary

The assumption that it is not probable for a metal impurity atom in the highly electropositive lithium matrix to be more than singly ionized offers an explanation of the diffusive behaviour of impurities in lithium.

Two competing mechanisms appear to operate, to the effect that the relatively large and easy-to-ionize impurities diffuse mainly via vacancies and the small and electronegative impurities as interstitials. The results also seem to indicate that a slight stress in an interstitial site in the solvent lattice as induced by the impurity atoms enhances and a large stress decreases the diffusion rate. Further a degree of trapping of charged impurities at intrinsic defects is suggested.

The interstitial impurity atoms should according to this interpretation be Cu, Au, Zn, Hg, Sb and Bi, while the substitutionals should be Na, In and Pb Intermediate cases should be Ag, Cd and Sn. The evidence concerning Ga, which exhibits similar characteristics as Li in Li-self-diffusion, is so far rather inconclusive. The statement that lithium self-diffusion may to some extent be due to interstitials appears fairly plausible in light of the present results.

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** The big impurities (Bi, Sb, Pb, In) all merge to the same diffusivity at the melting point, and the distinction between "interstitial" and "substitutional" appears to become less marked at high temperatures. These are parallels to the behaviour of large inert gas interstitials in ionic media[30], and the high activation energies may as these possibly be attributed to binding with lattice defects.