Diffusion of Silver in Solid Lithium Metal

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(Z. Naturforsch. **23 a**, 473—474 [1968] ; received 23 January 1968)

The diffusion of Ag^{110m} in lithium has been measured, using a thin film plating and sectioning method, between 67° and 160 °C. The data fit the Arrhenius relation

$$D = D_0 \cdot \exp(-Q/R\,T),$$

where
$D_0 = 0.37 \pm 0.13$ cm² sec⁻¹ and $Q = 12.83 \pm 0.25$ kcal·mol⁻¹.

There are reasons to believe that diffusion takes place by a highly relaxed or cooperative mechanism. The difference in activation energy between Ag tracer diffusion in Li and Li self-diffusion is very small.

A systematic study of diffusion phenomena in solid and liquid alkali metals is being persued at this laboratory. In solid lithium, Lodding and Thernquist have studied atomic mobilities applying thermal[1,2] and electric[3] gradients. This paper deals with an investigation of isothermal diffusion of tracer impurity in Li.

Tracer diffusion in alkali metal has gained particular interest in recent years. Self-diffusion data have been obtained for Na by several investigators, with a good degree of mutual agreement[4–6]. In the latest of these investigations, by Mundy and co-workers, self-diffusion in K[7] and alkali impurity diffusion in Na and K[8] was also measured. In lithium, four mutually rather contradictory sets of self-diffusion data, obtained by different methods[5,9–11], are available. We are presently concluding a new investigation of lithium self-diffusion, using the method of this paper[12]. Other impurity data for Li are listed together with the present result in Table 1.

	D_0 cm² sec⁻¹	Q kcal·mol⁻¹
Li in Li *	0.12 ± 0.05	12.62 ± 0.21
Na in Li	0.41 ± 0.09	12.61 ± 0.15
Zn in Li *	0.72 ± 0.30	13.19 ± 0.30
Ag in Li	0.37 ± 0.13	12.83 ± 0.25

* Preliminary results, see refs. [12] and [14].

Table 1. Impurity diffusion data in lithium.

The experimental method, see reference[6,14], was a version of the classical thin film method. We observed the diffusion out of a thin radioactive layer plated onto a cylinder of lithium metal. The solvent metal came from Foote Lithium Corp. and had a purity of 3N8. The Ag^{110m} isotope was from New England Nuclear Corporation and was free from radioactive impurities.

For the geometry employed, the solution of Fick's 2nd law is

$$c = c_0 \frac{1}{\sqrt{\pi D t}} \cdot \exp\left(-\frac{x^2}{4 D t}\right), \tag{1}$$

where c is the specific activity in the slice at a distance x from the surface,
c_0 is the activity at the first slice, and
t is the annealing time.

When plotting the specific activity versus square of distance, we obtained linear penetration profiles. On some of the plots the initial point lay a little above the linear profile, probably because of oxide or nitride blocking of the tracer. The linearity of the plot is an indication that there is no disturbance from grain boundaries or dislocations.

The experimental values of the diffusion coefficient, D, are given in Table 2 and plotted in Fig. 1. The errors in D are individually quoted, because the major error arose from the scatter in the penetration profiles, which varied from run to run.

T in °C	$D \cdot 10^9$ in cm² sec⁻¹
67.0	(2.09 ± 0.09)
77.6	(3.41 ± 0.09)
93.8	(9.58 ± 0.15)
122.9	(30.6 ± 0.7)
132.6	(47.8 ± 1.2)
149.2	(82.8 ± 0.6)
160.3	(120 ± 7)

Table 2. Experimental results.

From the slope of the line in the $\ln D$ versus $1/T$ diagram (Fig. 1) we obtained the activation energy Q, and from the intercept on the $1/T$ axis we got the D_0 term in the Arrhenius equation for D:

$$D = D_0 \cdot \exp(-Q/R\,T). \tag{2}$$

These are listed in Table 2, together with the other known values of diffusion parameters in lithium.

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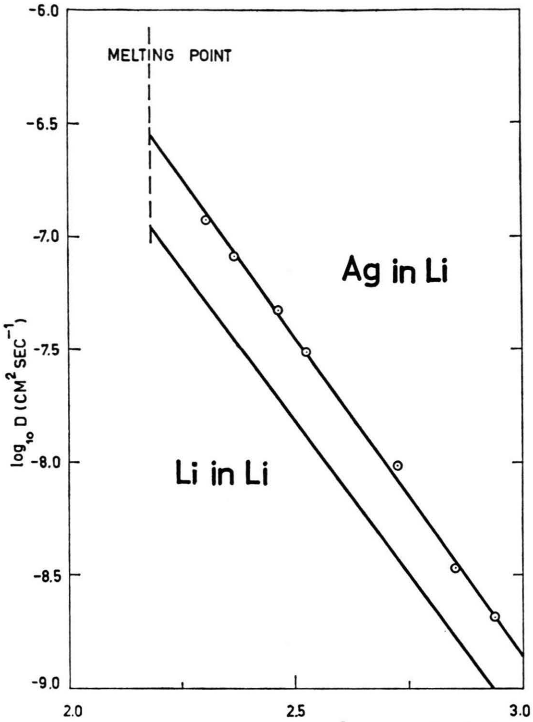

Fig. 1. Arrhenius plot of Ag^{110m} diffusion in Li. The Li self-diffusion line is computed from preliminary values of ref. [12].

Theoretical treatments [8, 15–18] have been applied to impurity diffusion in metals, in the case of fcc systems with rather good success. Partly because of lack of experimental data, in bcc metals it has not been possible so far to achieve any comparable succes.

All theory has been mainly concerned with differences in activation energies. The sign and magnitude of the difference, defined by $\delta Q = Q_i - Q_s$, (the suffix i referring to the impurity, s to the solvent) has been put in connection with energy differences calculated from the nearly-free electron model or with elastic strain interactions due to atom size differences. In lithium Q_s could up to now hardly be considered as known sufficiently accurately to furnish a meaningful reference, as the experimental values ranged from 11 to 13.5 kcal/mole. However, as our own recent self-diffusion measurements on Li [12] were performed using the method of the present paper, they appear relatively well suited for comparison, thus the activation energies of Ag in Li, as well as those of other impurities in lithium, seem about the same as that of self-diffusion. This is remarkable, especially in comparison with homovalent impurity diffusion data in Na [8], where considerable δQ values were obtained. The present results offer an especially striking contrast, when compared to the behaviour of Au in Na [19], where the diffusivity is reported to be by at least two orders of magnitude greater than that of other impurities in Na. This latter difference in behaviour can, however, possibly be understood by the consideration of the respective atom size ratios.

Evidence from self-diffusion and other measurements in alkali metals favours the assumption of a relaxed vacancy mechanism [6, 20]. In Li a particularly great relaxation seems to occur [10]; activation volume measurements (using NMR) have indicated that a vacancy or corresponding defect in Li occupied only about 28% of the atomic volume, as compared to 41% in Na. It appears reasonable to think, that diffusion in Li takes place by a cooperative mechanism, each diffusive step involving the adjustment of a considerable number of adjacent atoms.

This research has been supported by the Swedish Council for Applied Research and the Adlerbertska forskningsfonden. We wish to acknowledge discussions with Docent A. Lodding and Dr. J. N. Mundy and also the assistance of ing. H. Olsson, fil. lic. L. Löwenberg and fil. kand. H. Olsén at various stages of the experimental work.

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