Differential Diffusion of Impurities in Isotopic Lithium Matrices *

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The diffusion of ^{22}Na and ^{195}Au has been investigated in solid, isotopically pure ^{6}Li and ^{7}Li metal. The Na tracer has been found to diffuse by about 4% faster in ^{6}Li than in ^{7}Li. For Au the corresponding difference was 4% at the melting point, but as much as about 15% at $\frac{2}{3}\,T_{\rm m}$ (°K). A formalism is given for the interpretation of diffusion experiments where the matrix isotope mass is varied. The present results for Na in Li can be plausibly explained in terms of the vacancy mechanism. For Au diffusion in Li, the interpretation appears incompatible with a simple vacancy mechanism, and the anomalous departure from the inverse root mass relationship can be connected with recently detected quantum effects in ^{6}Li$-$^{7}Li mutual diffusion.

Introduction

Studies of isotope effects in atom transport have become a powerful tool in obtaining information about point defects and relaxations in condensed matter. In solid state diffusion the radioisotope technique has been brought to a high degree of precision [1–3].

Lithium has no radiotracers, and the mass spectrometric analysis of systems with small Li concentrations is rather difficult. On the other hand, lithium as *matrix* offers a new and practicable isotope diffusion technique, one where the mass of the solvent, rather than solute, is varied. Separated ^{7}Li and ^{6}Li can be obtained relatively inexpensively. The 15% difference in mass is greater than for any other exploitable metallic isotope mixture.

The first solid state project of this kind was an investigation of the diffusion of tracer ^{6}Li in the ^{7}Li matrix, and vice versa [4]. The main results, of relevance for the present paper, indicated that ^{6}Li in ^{7}Li diffuses faster than ^{7}Li in ^{6}Li, close to the melting point by some 20%, at (2/3) $T_{\rm m}$ by about 40%. The implication of these isotope inter-diffusion results is, that the self-diffusion of pure ^{6}Li is higher than that of ^{7}Li by much more than the classical inverse root mass value of $\sqrt{7/6} \cong 1.08$. The best explanation appeared to lie in quantum tunneling. As for the mechanism of self-diffusion in Li, evidence hitherto is not conclusive; arguments exist in favour of interstitials as well as of vacancies [4–6]. Of several studied impurities in Li, the noble metals in particular [7] appear to diffuse at a rate incompatible with vacancy based theories [8, 9] (see also subsequent discussion), and it has been argued [10, 11] that only easily ionizable and relatively large impurities (such as the alkali metals) in Li will tend to diffuse by a straightforward vacancy mechanism.

The present work was initiated in order to shed further light on the mechanisms of impurity diffusion in Li, and to test the usefulness of the isotopic matrix method. Two significantly differing impurities were chosen: Na, for which diffusion in Li is supposed [11, 12] to take place via vacancies, and Au, which probably [7, 11, 12] moves by an interstitial type mechanism.

Experimental Procedure and Results

The radioactive thin layer deposition and slicing technique of diffusion studies in Li has been described earlier [13–15]. In the present investigation, the distinctive

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feature was that at each temperature two lithium samples, of similar pre-treatment but of different isotopic compositions (7.5, respectively 95.0% ^{6}Li), were annealed together in the same temperature bath. Precautions were taken in the plating, heating, cooling and slicing routine to safeguard identical effective anneal time for both samples. The only significant error in differential diffusivity thus arose from counting and from depth determination. The diffusion coefficients were computed from the penetration profiles (see Fig. 1). The statistical accuracy of slope determination was within about 1%. The temperature determination was accurate within 0.2 °C. The ratio of the diffusion coefficients at each temperature had a reproducibility of about 4% at the lowest, better than 2% at the highest temperatures.

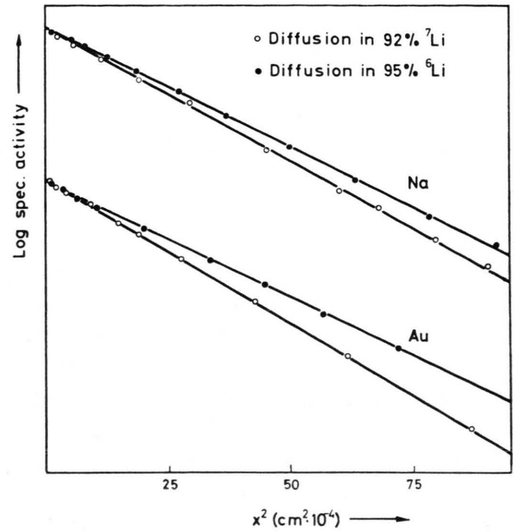
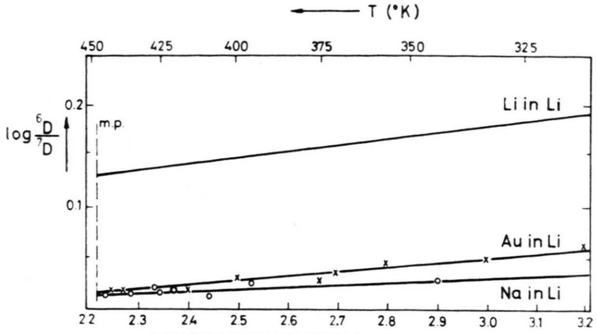


Fig. 1. Penetration profiles for Na and Au diffusion in isotopic ^{7}Li and ^{6}Li.

The measured differential diffusivities are shown in Fig. 2. In Fig. 3 the diffusive behaviour of ^{22}Na and ^{195}Au in Li is shown by an Arrhenius plot. In both figures, self-diffusion graphs are also drawn for comparison. These latter are model-dependently computed from isotope interdiffusion (see Tables 2 and 4 of Ref. [4]), and must be regarded as just a qualitative representation.

It can be seen from Figs. 2 and 3 that both impurities diffuse faster in ^{6}Li than in ^{7}Li. The differential diffusivity of Na in Li is, on an average, 4%, and suggests only a very slight temperature dependence, from 3% at T_m to 7% at $\frac{2}{3}\,T_m$, a tendency inside the margin of the experimental error. For Au one finds a similarly low value of $^6D/^7D$ close to the melting point, but at lower temperatures the differential diffusivity strikingly rises to about 15%. One can thus discern a significant difference in the behaviour of the two tracers.



	$^6D/^7D$	
	T=450 °K	T=350 °K
Li	1.35	1.57
Na	1.03±0.02	1.07±0.03
Au	1.04±0.02	1.14±0.03

Fig. 2. Differential diffusivities of Na and Au in Li, experimental results. The "Li in Li"-line is tentatively calculated from results on ^{6}Li—^{7}Li mutual diffusion [4].

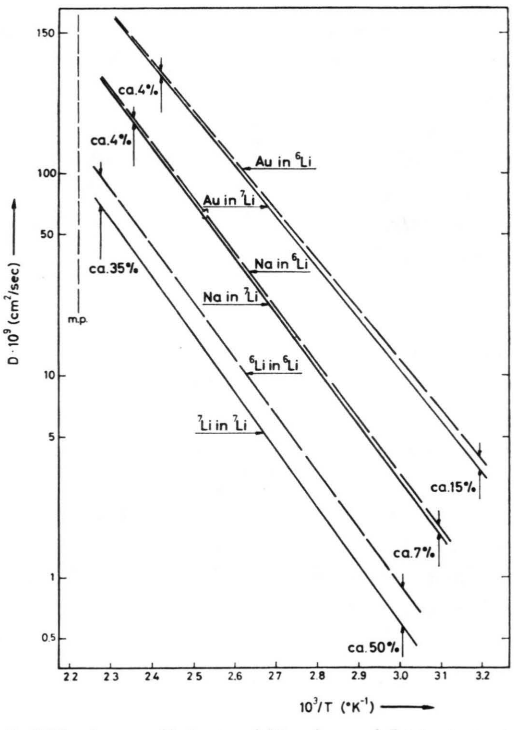


Fig. 3. Diffusion coefficients of Na, Au and Li in isotopic lithium metal. The $^6D_6$- and $^7D_7$-lines are tentatively calculated from results on ^{6}Li—^{7}Li mutual diffusion [4].

Differential Diffusivity, Varying Matrix Mass, Vacancy Model

For a tracer diffusing by a simple vacancy mechanism one can express the diffusion coefficient in regard of variable mass as

$$D = A\, w_{\mathrm{t}}\, f$$

with
$$f = (1 + B\, w_{\mathrm{t}}/w_0)^{-1}\,, \tag{1}$$

where A is a mass-independent term, w_{t} and w_0 are the frequencies of jumps into an adjacent vacancy of a tracer atom and a matrix atom, respectively, and the constant B in the correlation factor f approximately equals 0.37 for a bcc matrix.

We shall denote the differential diffusivity with variable matrix mass m by $a_{\mathrm{D}}^{\mathrm{m}}$, defined as

$$a_{\mathrm{D}}^{\mathrm{m}} = \mathrm{d} \ln D / \mathrm{d} \ln m \cong \frac{{}^1D_{\mathrm{M}} - {}^2D_{\mathrm{M}}}{D_{\mathrm{mean}}} \Big/ \frac{{}^1m - {}^2m}{m_{\mathrm{mean}}}\,, \tag{2}$$

where ${}^{1,2}D_{\mathrm{M}}$ are the diffusion coefficients of the tracer of mass M in the isotope matrices 1, resp. 2.

Logarithmic differentiation of Eq. (1) yields

$$a_{\mathrm{D}}^{\mathrm{m}} = \mathrm{d} \ln w_0 / \mathrm{d} \ln m + f \cdot \mathrm{d} \ln \left(\frac{w_{\mathrm{t}}}{w_0} \right) \Big/ \mathrm{d} \ln m\,. \tag{3}$$

Now, the cohesive forces and interatomic distances are practically the same for the two isotopic Li metals[16, 17], and no existing theoretical or other arguments suggest that the isotopic lattice vibration frequencies should not obey the classical inverse root mass law. The jump frequency w_0 contains such a frequency (ν_0'). According to the anomalies found in Ref. [4], however, there is also a non-classical mass dependent term accounting e. g. for the tunneling transmission probability. The quantum dependence can be expressed in exponential form[4], rigorous at least for the case of tunneling:

$$P(m) = \mathrm{const} \cdot \exp \left[- \left(\frac{m}{m_{\mathrm{mean}}} \right)^{1/2} \cdot \frac{\Delta Q}{R\,T} \right], \tag{4}$$

where ΔQ, varying only slowly with temperature[4], is indepedent of isotope mass. One might then write

$$\mathrm{d} \ln w_0 / \mathrm{d} \ln m = - \tfrac{1}{2} - \tfrac{1}{2}\, \Delta Q / R\,T\,, \tag{5}$$

where the first RHS term acounts for the classical mass relation.

A fully rigorous treatment of $\mathrm{d} \ln (w_{\mathrm{t}}/w_0) / \mathrm{d} \ln m$ should entail a consideration of the frequency spectrum at lattice and saddle point configurations (see Ref. [2]). A useful simplification is obtained[4] by treating the diffusing tracer atom, mass M, at the saddle point as oscillating in phase with, say, $(p-1)$ matrix atoms, and in antiphase with another number, q, of matrix atoms. The frequency of the oscillating reduced mass, simulating the saddle point mode, is

$$\nu_{\mathrm{t}} = \mathrm{const} \cdot \left[\frac{M + (p-1)\, m}{M + (p-1+q)\, m}\, q\, m \right]^{-1/2}. \tag{6}$$

Hence

$$w_{\mathrm{t}}/w_0 = \mathrm{const} \cdot \frac{1}{P(m)} \left[\frac{M + (p-1+q)\, m}{M + (p-1)\, m} \right]^{1/2} \tag{7}$$

and

$$\mathrm{d} \ln (w_{\mathrm{t}}/w_0) \tag{8}$$
$$= \left[\frac{1}{2} \frac{\Delta Q}{R\,T} + \frac{1}{2} \frac{q\, m\, M}{(M + p\, m - m)\,(M + p\, m - m + q\, m)} \right] \mathrm{d} \ln m\,.$$

The last term in brackets can be found to express the share of total kinetic energy at saddle point, associated with the migrating atom and not its vicinity. It corresponds in fact to $\tfrac{1}{2}$ times the energy distribution factor ΔK of the rigorous treatment[2].

Equation (3) can now be written as

$$a_{\mathrm{D}}^{\mathrm{m}} = - \frac{1}{2} \left[(1 - f\, \Delta K) + (1 - f)\ \frac{\Delta Q}{R\,T} \right]. \tag{9}$$

Neglecting for a while all non-classical effects, one may compare the wellknown expression for the isotope effect of varying tracer mass

$$\frac{\Delta D}{D} \Big/ \frac{\Delta \sqrt{M}}{\sqrt{M}} = - f \cdot \Delta K \tag{10 a}$$

with the recently derived one for varying matrix mass,

$$\frac{\Delta D}{D} \Big/ \frac{\Delta \sqrt{m}}{\sqrt{m}} = - 1 + f \cdot \Delta K\,. \tag{10 b}$$

Comparison of Results with Vacancy Model

a) Na in Li

Substituting the mass difference of the imperfectly isotopic matrices, 0.875, together with the mean mass of 6.5 and the results for Na in Li, into Eq. (2), one obtains an average value

$$a_{\mathrm{D}}^{\mathrm{m}} \cong -0.30\,.$$

Further, the substitution of $M = 22$, $m = 6.5$, $q = 6$ (see Ref. [4]), and $p = 1$ into Eq. (8) yields the value of about 0.64 for ΔK.

One may now check, whether the experiments yield a reasonable value of the correlation factor f, by writing Eq. (9) as

$$f = \frac{2 \cdot a_{\mathrm{D}}^{\mathrm{m}} + 1 + (\Delta Q / R\,T)}{\Delta K + (\Delta Q / R\,T)}\,, \tag{11}$$

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which here becomes

$$f \cong \frac{0.40 + (\Delta Q/R\,T)}{0.64 + (\Delta Q/R\,T)} \tag{12}$$

on an average.

Now, the assumption of a vacancy mechanism in self-diffusion required[4] that $\Delta Q \cong 5$ kcal/mole, which would make $\Delta Q/R\,T$ as great as about 7. The substitution into Eq. (12) would yield $f \cong 0.97$. Such a high value would indicate [see Eq. (1)] that Li atoms jump much more (about 12 times) frequently into vacancies than does solute Na. However, this seems improbable, as in fact Na is a faster diffuser than Li in lithium metal (see Fig. 3) roughly in agreement with the vacancy based theory by LE CLAIRE[8]. Three ways out of the dilemma may be suggested.

a) Both Na-impurity diffusion and self-diffusion take place by the vacancy mechanism, but the Na ion binds the defect so as to make the effective barrier to Li tunneling too high and too broad, inhibiting non-classical effects. Then $f \cong 0.62$, implying $w_{\mathrm{Na}}/w_{\mathrm{Li}} \cong 1.6$, which appears reasonable.

b) Na diffuses by vacancies, but matrix atoms do not. Here again quantum effects can be neglected and again $f \cong 0.62$.

c) Neither self-diffusion nor Na impurity diffusion is of the vacancy type, and so the above treatment of the isotope effect is invalid. This appears slightly far-fetched, as several arguments[11, 12] favor vacancies as the diffusion mechanism for Na in Li; but until certainty is reached this possibility should perhaps not be omitted.

If, however, any one of the other two conclusions is correct, then the present results imply that the Na impurity has a somewhat higher jump frequency into vacancies than has a Li matrix atom. The very slight, if real, temperature dependence of $a_{\mathrm{D}}^{\mathrm{m}}$ suggested by the experiments has the sign and order of magnitude compatible with the smaller barrier for motion of the impurity.

b) *Au in Li*

The results obtained for Au in Li are $a \cong -0.30$ at the highest, and $a \cong -1.0$ at the lowest temperatures. Equation (8) yields a low ΔK value for the heavy tracer, $\Delta K \cong 0.16$.

Hence, under the assumption of a vacancy mechanism, via Eq. (11):

$$f \cong \frac{0.40 + (\Delta Q/R\,T)}{0.16 + (\Delta Q/R\,T)} \quad (\text{at } 450\ ^\circ\mathrm{K}) \tag{13 a}$$

and

$$f \cong \frac{-1.0 + (\Delta Q/R\,T)}{0.16 + (\Delta Q/R\,T)} \quad (\text{at } 300\ ^\circ\mathrm{K}). \tag{13 b}$$

Au is a very fast diffuser in Li, which even more than in the case of Na makes it seem improbable that the Li quantum effects enter via a vacancy mechanism of self-diffusion. However, if the quantum terms are neglected, then Eqs. (13) yield a correlation greater than unity at the higher, negative at the lower temperature, i. e. unacceptable results. One may then conclude that whatever the nature of self-diffusion, Au in Li most probably does not diffuse by a straightforward vacancy mechanism. However, the possibility of a simple interstitial mechanism for Au also seems precluded, as at the low temperature the classical mass effect of about 8% is definitely exceeded, which can hardly be attributed to an independently moving heavy tracer.

The mobility of the tracer therefore appears coupled with that of the matrix atoms. One speculative example is the case of an interstitial gold atom adjacent to a vacancy. LECLAIRE's "homovalent" theory[8] predicts that as a substitutional impurity in Li, Au would repel vacancies; an interstitial Au ion, however, might instead act as a positive charge and be attracted to the vacancy, which would cause it occasionally to occupy the vacant substitutional site. A displacement would only take place if the vacancy instead exchanged with a matrix atom, the mobility of Li then being rate-determining for Au diffusion. The presently observed results are compatible with such a mechanism, as long as the jump frequency of Au at the highest temperatures is comparable with that of Li and at lower temperatures considerably exceeds that of Li.

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