Thermotransport of Gold in Solid Lithium Metal

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The thermotransport of Au in Li metal has been measured, using a steady state technique. The effective heat of transport, Q^{**}/g, of the Au impurity was found to be +4.1 kcal/mole, which is less than half the activation energy for isothermal diffusion of Au in Li. The diffusion mechanism cannot be determined unambiguously, but the results support the notion of interstitial transport.

In an effort to shed light upon the diffusion mechanisms in the lithium lattice, we have undertaken a study of the thermotransport of metallic impurities in lithium. Since the isothermal diffusion of such impurities in lithium has been extensively studied by OTT et al. [1], thermotransport experiments present a logic step forward. They are also a continuation of our own measurements of thermotransport and electrotransport in pure lithium [2]. This paper gives preliminary results on thermotransport of ^{195}Au in Li, employing a steady-state tracer technique.

The experimental set-up is somewhat similar to those of JAFFE and SHEWMON [3], BIERMANN, HEITKAMP and LUNDY [4], and WINTER and DRICKAMER [5]. A cylindrical sample (diameter 18.5 mm, length 2 mm), clamped between two copper blocks, and with initially homogeneous concentration of the impurity, is maintained under a temperature gradient of about 150°/cm. The experiments are conducted in a vacuum better than 5×10^{-6} Torr, and the copper blocks are heated/cooled by silicone oil/glycerol-ethanol kept at constant temperatures by two commercial oil baths.

After a sufficient time for practically attaining steady state, the sample is sectioned into about 15 slices. The distribution of the tracer impurity is then obtained by a procedure, similar to that used by MUNDY et al. [6]. The Li metal, of 3N5 grade, was obtained from the Foote Lithium Corporation. The ^{195}Au isotope was obtained from NEN Chemicals, Germany, and free of radioactive impurities. The homogeneous samples were made by evaporating [6] a thin active layer onto one side of the sample and then annealing during 4 days near the melting point of lithium. That the impurity was then actually uniformly distributed was checked by taking off and analyzing two thin slices, one on each side of the specimen. This also served to give us flat, smooth and clean surfaces in contact with the copper blocks.

The temperature is measured at two points of the sample, using stainless steel clad cromel-alumel thermocouples. One of these thermocouples penetrates about 0.1 mm into the center of the flat hot surface of the specimen. The other thermocouple (outer diameter 0.25 mm) enters from the curved surface, about 1.5 mm from the hot end, 2 mm deep into the sample. This latter thermocouple is simply nailed into the soft lithium metal to ensure good thermal contact. The experimental geometry has been chosen so that the radial drop in temperature in the specimen is negligibly small. A travelling microscope mounted above the vacuum cell is used to measure the length of the sample as well as the position of the thin thermocouple. This latter position reading can be checked during the sectioning of the specimen; one easily notices which slice bears an indentation from the thermocouple.

Knowing the temperature at two points of the specimen and the thickness of each slice, and assuming a linear temperature gradient (probably true for this sample geometry apart from a thin region at each flat surface) one can readily calculate the temperature in the middle of each slice. The logarithm of the specific activity of each slice is then plotted versus the inversed temperature. One such graph is shown in Fig. 1 where the straight line is a least-square-fit of the data points.

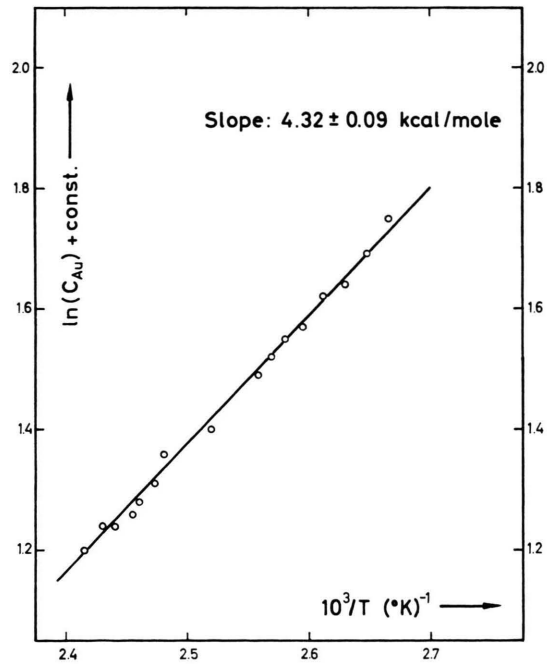

Fig. 1. The natural logarithm of the Au concentration as a function of the inverse absolute temperature.

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It can be shown (see e. g. ref. [7]) that, under the conditions of our experiment (steady-state, initially homogeneous specimen, linear temperature gradient), the points in a diagram such as Fig. 1 should (under the assumption of constant energy parameters of diffusion) indeed lie on a straight line, the slope of which should yield an effective heat of transport, Q^{**}/g, according to the formula

$$\partial(\ln c)/\partial(1/T) = (Q^{**}/g)/R\,. \qquad (1)$$

Here c is the impurity concentration, T the absolute temperature, R the gas constant. The effective correlation factor g entails the possible deviation from Nernst-Einstein ion conductivity.

The values of Q^{**}/g for each specimen are listed in Table 1 together with a wide estimate of their margins of error, which mainly depend on temperature fluctuations at the cold end. Table 1 also shows the mean temperatures for the different samples. The mean value of Q^{**}/g was found to be $+(4.1 \pm 0.9)$ kcal/mole.

Sample	Mean temperature °C	Q^{**}/g kcal/mole
4	127	3.9 ± 0.7
5	131	3.9 ± 0.7
6	122	4.3 ± 0.8
7	126	4.2 ± 1.2
Mean value and RMS deviation:		4.1 ± 0.9

Table 1. Results of thermotransport experiments, Au in Li.

To obtain then the physical heat of transport, Q^*, of the Au impurity in the Li lattice one has to take into consideration the fairly rapid motion of the Li lattice itself in the temperature gradient. This can be done by using the formula [7]:

$$(Q^*/g)_{\mathrm{Au}} = (Q^{**}/g)_{\mathrm{Au}} + (D_{\mathrm{Li}}/D_{\mathrm{Au}})\,(Q^*/g)_{\mathrm{Li}}\,. \qquad (2)$$

Here D_{Li} and D_{Au} are the diffusion coefficients of Li and Au in Li. $(Q^*/g)_{\mathrm{Li}}$ is the experimental heat of transport of pure Li, and equal to 11.2 kcal/mole [2]. The mean value of the factor $D_{\mathrm{Li}}/D_{\mathrm{Au}}$ is 0.08 in our temperature range [8, 9].

Calculating first Q^* for the assumption of a simple vacancy mechanism we arrive at an approximate value $Q^* = 3.9$ kcal/mole. From the now classical Wirtz-Brinkman-LeClaire treatment of thermotransport, one has that Q^* should be about equal to the difference between the energy of migration, E_{m}, and that of formation, E_{f}. Accordingly, for thermotransport of Au in Li, this would then mean that E_{m} exceeds E_{f} by a fairly large amount, a quite remarkable result, bearing in mind that the alkalis (especially Li) are very open structures. Direct measurements on both Na and Li find E_{f} for vacancies to be definitely greater than E_{m} [10, 11]. We therefore conclude that the simple vacancy mechanism alone cannot be responsible for the thermotransport of the Au-atoms.

In sodium results from self-diffusion [12] and from dilatometric measurements [10] have been tentatively interpreted in terms of a relaxed vacancy-type mechanism. According to a recent computer simulation of the diffusion process by TORRENS and GERL [13], there is no large relaxation around a vacancy in lithium. The same is implied by calculations on alkalis by SHYU et al. [14]. Therefore it seems that a vacancy-type defect mechanism cannot alone be operating in thermotransport.

The calculations of TORRENS and GERL [13] however suggest that interstitials could exist in similar concentrations as vacancies. FEDER [11] in his dilatometric determination of defect concentration in Li, arrives at a result, suggesting that, although vacancies are found to be the dominant defect in thermal expansion, interstitials may well also be present. That interstitials may be important in self-diffusion is also implied by activation volume measurements on Li [15]. Furthermore, other experiments [1, 16–18] (isothermal impurity diffusion in various systems) have been given interpretations in terms of interstitials.

One would accordingly like to suggest that an interstitial-like mechanism operates in the thermotransport of Au in Li. A simple interstitial is however not quantitatively compatible with our results, as from the Wirtz-Brinkman-LeClaire theory one has that Q^* should then be equal to the activation energy of diffusion (11.0 kcal/mole, ref. [9]). This is not so in our case. One explanation may be the postulate of some kind of "mixed" interstitial mechanism. Such an explanation is favoured by our own experiments on thermotransport in pure Li [2]. We found a large positive value for $(Q^*/g)_{\mathrm{Li}}$, and, surprisingly, an isotope effect in the "wrong" direction (^{6}Li was enriched at the hot part of the specimen). Another possibility is that the Nernst-Einstein factor g is responsible. If a split interstitial is operating, each diffusive step may entail a shorter displacement of energy, making g less than unity (see ref. [19]).

Summing up, these results can not be interpreted in terms of a simple kind of defect, but the evidence suggests that an interstitial type of mechanism may be the

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one mainly responsible for thermotransport of Au in Li. Further experimental and theoretical work in this field should be illuminating.

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Desorientierung von optisch ausgerichteten Na-Atomen durch Edelgas-Stöße

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Cross sections for noble-gas-induced sodium spin disorientation have been measured and calculated by applying the spin-orbit and spin-exchange-model of R. Herman.

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Die Relaxation der Spinpolarisation $\langle S_z \rangle$ durch Edelgasstöße ist für $S_{1/2}$-Grundzustände wesentlich schwächer als für P_j-Zustände ($j \neq 0$). Während die Desorientierungsquerschnitte der P-Zustände von der Größenordnung des gaskinetischen Querschnittes ($\sim 10^{-16}$ cm^2) sind, liegen die entsprechenden Werte für $S_{1/2}$-Grundzustände der Alkaliatome zwischen 10^{-20} cm^2 und 10^{-26} cm^2. Zur Erklärung dieser kleinen Wirkungsquerschnitte hat HERMAN zwei verschiedene Wechselwirkungen vorgeschlagen: Einmal den Spinaustausch zwischen dem Valenzelektron und dem Edelgas-Kernspin [1] und zum anderen eine Kopplung des Valenzelektronenspins mit einem stoßinduzierten Bahnmoment [2]. Im folgenden werden analog der Theorie von Herman Desorientierungsquerschnitte für Na-Edelgas-Stöße berechnet und mit experimentellen Werten verglichen.

Die *Spin-Bahn-Kopplung* liefert in erster störungstheoretischer Näherung einen vernachlässigbaren Beitrag zur Relaxation. Der Wechselwirkungsterm zweiter Ordnung kann geschrieben werden

$$H_{\mathrm{eff}} = \gamma(R)\, \boldsymbol{K} \cdot \boldsymbol{S}, \quad \boldsymbol{K}/\hbar = \boldsymbol{r} \times \boldsymbol{p},$$

wobei $\boldsymbol{S}$ der Spin des Valenzelektrons und $\boldsymbol{K}$ der Gesamtbahndrehimpuls des Stoßpaares bedeutet. Zur expliziten Berechnung der vom Kernabstand R abhängigen Faktoren $\gamma(R)$ betrachtet Herman sowohl Deformationen wie auch Überlappungen der beiden Stoßpartner. Obwohl bei den leichten Alkaliatomen Überlappungseffekte sicher eine größere Rolle spielen als bei Rb und Cs, werden sie hier vernachlässigt, da zu ihrer Berechnung genaue Wellenfunktionen notwendig sind.

Eine Abschätzung der Deformationen auf Grund weitreichender Coulomb-Kräfte führt zu

$$\gamma(R) \sim -(2/9)\,[\Delta E_{\mathrm{disp}}(R) \cdot E_{\mathrm{res}}(^2\mathrm{p})]\ (E+I)^{-2}$$

mit der Dispersionsenergie $\Delta E_{\mathrm{disp}} = -C_6/R^6$, der Feinstrukturaufspaltung $E_{\mathrm{res}}(^2\mathrm{p})$, der Edelgasionisationsenergie I, und der Alkali-Resonanzenergie E. Für Na-He-Stöße errechnet sich dieser Beitrag zu

$$\gamma(b_0) = 7{,}5 \cdot 10^{-9}.$$

Der kinetische Radius b_0 wurde durch Mittelung der beiden Lennard-Jones-Radien [3] erhalten, während die van der Waals-Konstanten C_6 und C_8 der Literatur [4] entnommen wurden.

Zur Berechnung der abstoßenden Nahkräfte wird zunächst die Wechselwirkungsenergie E' ohne Deformation für das Na-He-System im Abstand b_0 ermittelt:

$$E' = +0{,}012 \text{ at. E.}$$

Dabei wurde als He-Wellenfunktion die 1s-Wasserstoffunktion mit der effektiven Kernladung $Z = 27/16$ und für Na eine 3s-Wasserstoffunktion mit $Z = 1{,}846$ benutzt. Dies ergibt einen Wert für die Stärke der kurzreichweitigen Wechselwirkung bei Na-He von $\gamma(b_0) = 2{,}6 \cdot 10^{-5}$ und übertrifft also den weitreichenden Beitrag um vier Größenordnungen.

	σ_{SB}	σ_{SS}	$\sigma_{\mathrm{theor.}}$	σ_{exp}
He	$36 \cdot 10^{-26}$	$3{,}8 \cdot 10^{-23}$ (He^3)	$36 \cdot 10^{-26}$	$\sim 10 \cdot 10^{-26}$
Ne	$3{,}4 \cdot 10^{-24}$	$4{,}5 \cdot 10^{-22}$ (Ne^{21})	$4{,}5 \cdot 10^{-24}$	$(3{,}6 \pm 1{,}1) \cdot 10^{-24}$
Ar	$13 \cdot 10^{-23}$	—	$13 \cdot 10^{-23}$	$(9{,}6 \pm 4{,}3) \cdot 10^{-23}$
Kr	$4 \cdot 10^{-22}$	$1{,}2 \cdot 10^{-20}$ (Kr^{83})	$1{,}7 \cdot 10^{-21}$	$(1{,}5 \pm 0{,}3) \cdot 10^{-21}$
Xe	$9 \cdot 10^{-22}$	$5{,}9 \cdot 10^{-20}$ (Xe^{129})	$2{,}9 \cdot 10^{-20}$	$(6{,}6 \pm 1{,}1) \cdot 10^{-20}$

Tab. 1. Wirkungsquerschnitte in cm^2.

Mit der Streuphase Φ kann der Desorientierungsquerschnitt σ_{SB} nach der Stoßparameter-Methode abgeschätzt werden:

$$\sigma_{\mathrm{SB}} = \frac{4\pi}{3} \int_0^\infty \Phi^2(b_0)\ b\ \mathrm{d}b\,, \quad \Phi = (K/2) \int \gamma(t)\ \mathrm{d}t\,.$$

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