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Self-Diffusion in Potassium[†]

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The self-diffusion of ^{42}K in potassium has been measured over the temperature range $-52.2 \pm +61.8\,^\circ$C. The temperature dependence of the diffusion coefficient can be described by $D = 0.16 \pm 0.01\, e^{-(9360 \pm 50)/RT}$. However the deviations of the individual points from this Arrhenius line suggest that diffusion could be occurring by two mechanisms.

INTRODUCTION

Metals with a bcc structure have been subdivided into two groups on the basis of their diffusional behavior.[1] The first or "normal" group contains Li, Na, K, Fe, Nb, Mo, Ta, and W. These metals have diffusion coefficients that obey the Arrhenius relation

$$D = D_0 e^{-Q/RT} . \tag{1}$$

The preexponential factors for these metals lie between 0.1 and 10 cm^2 sec^{-1}, and the activation energies Q obey the melting-point rule $Q = 32 T_m$ (T_m is the melting point). The second or "anomalous" group contain β-Zr, β-Ti, β-Hf, V, Cr, γ-U, and ϵ-Pu. These metals have diffusion coefficients that follow curved Arrhenius plots or have values of D_0 and Q not in accordance with the above empirical rules.

Recent measurements of self-diffusion in sodium[2] have shown that when the experiments extended over a wide range of temperature, the diffusion coefficients followed a curved Arrhenius plot. The data could be fitted to a two-exponential equation of the form

$$D = D_{01} e^{-Q_1/RT} + D_{02} e^{-Q_2/RT} . \tag{2}$$

The values of D_{01} and Q_1 obtained are in accordance with the empirical rules for "normal" diffusion.

A close examination of the data on diffusion in bcc metals[2] indicates that not only does sodium not fit into the so-called "normal" group but that the concept of "normal" and "anomalous" bcc diffusers may be misleading. Measurements of the self-diffusion coefficient of potassium over a wide range of temperature were made to determine if the Arrhenius plot is truly linear. If the diffusion behavior of potassium is similar to that of sodium, one has further evidence for disregarding the two-group concept of bcc metals.

EXPERIMENTAL METHOD

The measurements were made in the same man-

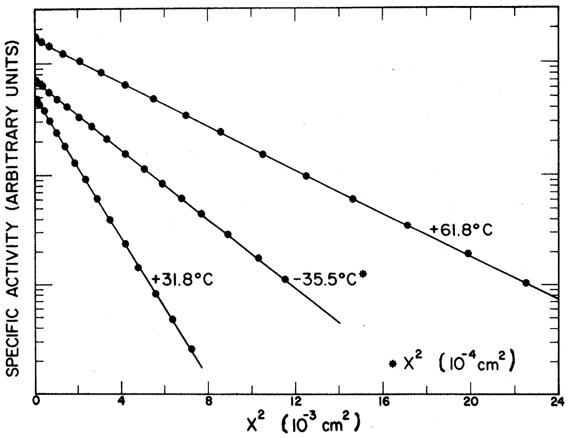

FIG. 1. Concentration profiles for diffusion of ^{42}K into potassium.

TABLE I. Diffusion of ^{42}K in potassium as a function of temperature.

Temperature (°C)	D (cm^{2}sec^{-1})
61.8	$1.27 \pm 0.01 \times 10^{-7}$
47.2	$6.58 \pm 0.10 \times 10^{-8}$
46.8	$6.64 \pm 0.07 \times 10^{-8}$
31.7	$2.97 \pm 0.02 \times 10^{-8}$
15.0	$1.15 \pm 0.01 \times 10^{-8}$
0	$4.82 \pm 0.10 \times 10^{-9}$
−17.2	$1.51 \pm 0.03 \times 10^{-9}$
−26.6	$7.73 \pm 0.07 \times 10^{-10}$
−35.5	$4.07 \pm 0.02 \times 10^{-10}$
−35.9	$3.77 \pm 0.05 \times 10^{-10}$
−43.3	$1.92 \pm 0.03 \times 10^{-10}$
−52.2	$8.57 \pm 0.20 \times 10^{-11}$
−52.2	$9.02 \pm 0.20 \times 10^{-11}$

ner as the previous measurements on self-diffusion in potassium.[3] The potassium (3N7) was supplied by United Mineral and Chemical Corp. and had a melting point of 63.5 ± 0.1 °C. High-specific-activity ^{42}KCl (~ 6 mCi/mg) was obtained from International Chemical and Nuclear Corp. Half-life and γ-ray spectroscopic measurements on the ^{42}KCl revealed no sign of radioactive impurity. Measurements were made from − 52.2 to + 61.8 °C. This greatly extended range of measurement was made possible by the higher specific activity of ^{42}KCl, which allowed longer diffusion anneals, and by the ability to cut thinner sections.[2]

Examples of the penetration profiles are shown in Fig. 1. All the profiles were linear over two orders of magnitude drop in activity. Oxidation of the surface of the samples has been lessened in this work, but the initial point of the profile remains high and was rejected in the calculation of the slope. Values of the diffusion coefficient are given in Table I and plotted as a function of temperature in Fig. 2. The individual errors in D quoted in Table I are a sum of the error in the slope of the penetration profile and the error in the anneal time. They do not include any estimate of the error in the cross-section area of the sample. As noted in Ref. 2, this error is difficult to estimate for a particular sample but could be of the order of 1%.

A least-squares fit of the dat in Table I gave the following Arrhenius relation:

$$D = 0.16 \pm 0.01\, e^{-(9360 \pm 50)/RT} \,. \qquad (3)$$

The values of the diffusion coefficients obtained in Ref. 3 are in good agreement with the present data. The higher activation energy of 9750 kcal/mole (Ref. 3) is reduced to the value given in Eq. (3), within experimental error, when the two values at 40 and 54 °C are omitted. These two values lie above the Arrhenius line of Eq. (3) by considerably more than their individual experimental error.

DISCUSSION

The only other measurements with which a comparison can be made are those of Kohler and Ruoff.[4] The spread in their values from 8.3 to 11 kcal mole^{-1}, over the small temperature range examined, prevents the possibility of observing curvature in the Arrhenius relation. Similarly, their measurements of activation volume were over too small a range of pressure (0–1 kbar) to observe any departure from linearity in a log D vs pressure plot. The evidence of the recent activation-volume measurements on sodium[2] would suggest that the Kohler and Ruoff value for the activation volume for potassium (0.55× the atomic volume) is a sum of activation volumes for two diffusion processes.

The straight line given by Eq. (3) is shown in Fig. 2. Percentage deviations of each diffusion coefficient from this straight line together with their individual errors are shown in the lower part of Fig. 2. These deviations strongly suggest that the Arrhenius plot is curved, and a fit was made to a two-exponential equation using a variable metric-fitting routine.[5] In this way, we obtain

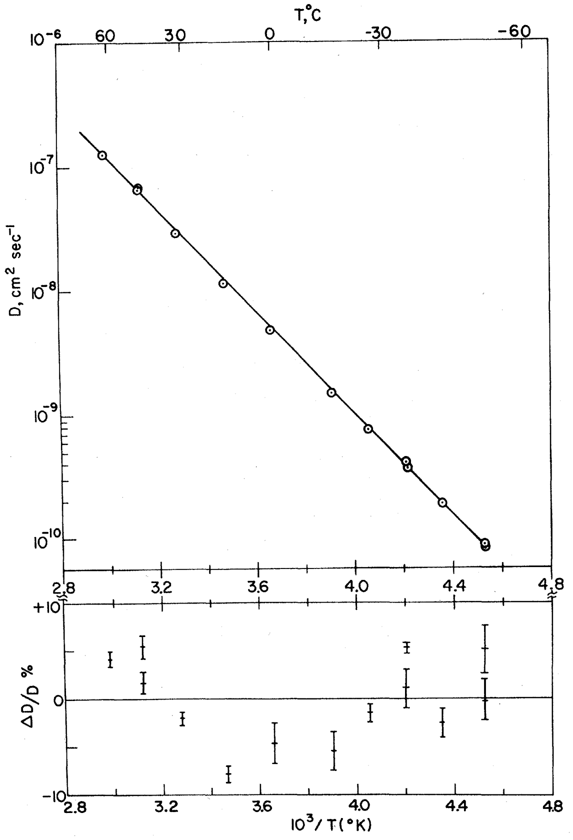

FIG. 2. Diffusion of ^{42}K into potassium as a function of temperature.

$$D = 1.0\, e^{-11220/RT} + 0.05\, e^{-8890/RT} . \tag{4}$$

Statistically this is not a better fit than a single-exponential fit, and confirmation of the curvature of the Arrhenius plot could probably be obtained only by extending the present measurements to lower temperatures. Unfortunately, the short half-life ^{42}K (12.4 h) and the minimum section thickness ($\sim 10\ \mu$) set the present limit for the lowest temperature.

The curvature for potassium was compared with that for sodium,[2] using a normalized temperature scale (T/T_m, °K). A linear Arrhenius fit of the data above $0.75T_m$ was made for both the sodium and potassium data. At $0.65T_m$ (the lowest data point for potassium) the deviation of the diffusion coefficients of both potassium and sodium from their respective Arrhenius lines were approximately 20%. This again would suggest that the diffusion behaviors of potassium and sodium are similar, although the evidence for curvature is not as conclusive for potassium.

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Calculated Low-Energy Electron-Diffraction Intensities for (111) and (110) Surface of Al[†]

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Reflected low-energy electron-diffraction spectra are calculated for the (111) and (110) surfaces of Al using the band-structure-matching approach without taking into account inelastic effects. The main effort was put into the calculation of a realistic pseudopotential (no adjustable parameters). The results are compared with experiment and found to be in over-all agreement with respect to the widths and positions of the peaks, provided we identify a single experimental peak with a group of calculated ones.

I. METHOD OF CALCULATION

In a recent Letter[1] we reported the results of an elastic calculation of low-energy electron-diffraction (LEED) intensities for the (001) surface of Al using the band-structure-matching formalism.[2] We have now applied the same method to calculate the reflected LEED spectra as a function of energy for the (111) and (110) surfaces of Al.

The band structure of Al in the energy range between 0 and 10 Ry has already been extensively discussed elsewhere.[3] Let us only mention here that it was calculated using a pseudopotential based on the orthogonalized-plane-wave (OPW) approximation without any adjustable parameters.[4] Full nonlocality and $\vec{k}$ dependence of the pseudopotential was retained throughout all calculations. The crystal potential contained all of the usual contributions,[4] with the exception that instead of Slater's approximation in calculating the core-electron–conduction-electron exchange we employed an OPW approximation, where the conduction electron was described by a single OPW, and the core electron by a Hartree-Fock wave function taken from Frose-Fisher.[5]

The band structure along the Λ direction was