Self-Diffusion in Sodium Single Crystals

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The objective of this investigation was the study of self-diffusion in single-crystal sodium using tracer techniques and the determination of the diffusion constant and activation energy. Precise values of these quantities can be obtained by using Fick's second law of diffusion and the relation

$$D = D_0 \exp \left(-\frac{Q}{RT}\right)$$

provided the concentration of the diffusing isotope is kept very small. However, in the above relation, the quantities $D_0$ (diffusion constant) and $Q$ (activation energy) may vary with the composition of the crystal and with impurity content but are independent of temperature.

MATERIALS AND METHODS

Sodium single crystals of 99.99% purity were grown by the Czochralski method at the Virginia Institute for Scientific Research, Richmond. The crystals were cylindrical in shape and ranged from 3/4 inch to 1 inch in diameter. In all of these experiments we found that the technical preparation of crystals such as embedding, cutting, and polishing was very important.

The single sodium crystal was cleansed in methanol and isopropyl alcohol and then placed in an etching bath of xylene with about one part in fifty of isopropyl alcohol. After several minutes the crystal structure became clearly visible when the specimen was illuminated with directional white light. If the specimen were a single crystal, a slow rotation with respect to a fixed light source would reveal a continuous variation of reflecting blaze planes and less reflecting areas. The particular planes subject to preferential etching were not determined. Crystal orientation was not investigated due to limitations in experimental facilities. After the crystal was embedded in paraffin to prevent subsequent deformation, it was mounted in a microtome and a reference surface was cut with a string saw (private communication with R. Bowers, D. Pinnow, and S. Tallman, Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York). An electrolytic method of polishing the crystal surface was well suited for the final preparation of the sodium single crystal. The electrolyte used was cp anhydrous ethylenediamine (Putnam and Kobe, 1938), a highly basic ionising solvent which dissolved some of the alkali salts. Electro-polishing of the crystal surface and the deposition of the tracer isotope Na22 were carried out in an inert atmosphere.

After polishing, a thin film of Na22 was deposited on the surface of the specimen. Then specimens were subjected to diffusion anneal at a constant temperature for known lengths of time. The temperature of the annealing bath was controlled by a thermostatic bath capable of maintaining temperatures to within ± 0.05 C. The annealing time on the average was 10⁶ sec. After the diffusion anneal, the specimens were remounted in the microtome and sectioned into uniform slices of 50 µ thickness for radioactive assay. Three crystal samples were prepared for diffusion measurements by the previously described techniques.

RESULTS AND DISCUSSION

A summary of the diffusion data is shown in table 1. The diffusion coefficients $D$ are obtained by plotting $\ln C$ vs $(\bar{X})^2$. The $\ln C$ has been plotted as a function of the square of the average depth of each section and is shown in figures 1 and 2 for annealing temperatures at 293 K and 304 K respectively.

![Fig. 1-Variation of concentration with square of average depth for annealing temperature at 293 K.](image1)

![Fig. 2-Variation of concentration with square of average depth for annealing temperature at 304 K.](image2)

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The diffusion coefficients were obtained by analyzing the data on RPC 4000 computer. The logarithm of the diffusion coefficients obtained are plotted against the reciprocal of the absolute temperature as shown in figure 3. The slope of this curve gives the activation energy, and the intercept at 1/T = 0 gives the diffusion constant. This plot yields the values $D_s = 0.313 \text{ cm}^2/\text{sec}$ and $Q = 11,000 \text{ Cal/mole}$.

The results of this investigation for sodium single crystals can be compared with the results obtained for polycrystalline sodium by Nachtrieb, Weil, and Catalano (1952). Their results have been reproduced in figure 3 and give 10,450 Cal/mole for the activation energy and 0.242 cm$^2$/sec for the diffusion constant. From figure 3 it is observed that the values of $D$ for single crystals lie consistently below the values obtained for polycrystals. Similarly, the values for the activation energy and diffusion constant in single crystals of sodium are greater than those for polycrystals; this may be due to traces of impurities in the crystals. However, the measured values of activation energy for single-crystal sodium are in good agreement with the values reported from the measurements of nuclear resonance line width in sodium by Gutowsky and McGarvey (1952; Gutowsky, 1951) are a little larger than those reported by Nachtrieb et al. (1952), and by Barr et al. (1951). No further comparison of the activation energies can be made since the kind, number, and effect of defects in the single-crystal sodium are not known. The ratio of the associated enthalpy to the melting point of solids, according to Zener (1952; Wert and Zener, 1949), and van Liempt (1935), applied to cubic metals should be around 32 Cal/mole, which is in good agreement with the value of 30 Cal/mole shown in table 1.

**SUMMARY**

In summary, no unique conclusion could be drawn concerning the mechanism of diffusion in sodium from diffusion rates and activation energies alone. Such a decision must be based upon the direct measurement of mean jump frequency.

**Acknowledgements**

We wish to express our sincere thanks to the Virginia Institute for Scientific Research and the Scientific Computation Laboratory, Medical College of Virginia, for their invaluable cooperation and help.

**REFERENCES**


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**TABLE 1**

<table>
<thead>
<tr>
<th>Temperature on Absolute Scale $^\circ K$</th>
<th>Diffusion Coefficient (D) cm$^2$/sec</th>
<th>Activation Energy (Q) Cal/mole</th>
<th>Standard Error of Q</th>
<th>Diffusion Constant ($D_0$) cm$^2$/sec</th>
<th>Standard Error of $D_0$ cm$^2$/sec</th>
<th>$\Delta H / Tm$</th>
</tr>
</thead>
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<tr>
<td>293.0</td>
<td>$2.01 \times 10^{-9}$</td>
<td>11,000.0</td>
<td>$\pm 170.0$</td>
<td>0.313</td>
<td>$\pm 0.018$</td>
<td>30.0</td>
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<tr>
<td>304.0</td>
<td>$4.07 \times 10^{-9}$</td>
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</tr>
<tr>
<td>314.0</td>
<td>$7.17 \times 10^{-9}$</td>
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</tbody>
</table>

*Since $Q$, the activation energy, is the sum of two enthalpy terms, $Q = (\Delta H + \Delta H_m) = \Delta H$, it was replaced by $\Delta H$. Associated enthalpy $\Delta H$ is expressed in Cal/mole. $Tm$ is the melting point of sodium on Kelvin scale.*

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Fig. 3—Variation of $D_{Na}$ with the reciprocal of absolute temperature. The polycrystal curve is reproduced from data of Nachtrieb, Catalano, and Weil (1952).