

function of  $Z$ , but strictly linear in  $Z$  within each period of the periodic system. The linear equations, relating back-scattering to  $Z$  within each period, when solved simultaneously, indicate discontinuities at  $Z=10, 18, 36$ , and  $54$ , corresponding to the rare gases which terminate the periods.

The back-scattering from compounds is accurately predicted from the scattering of their constituent atoms. In this connection an equivalent atomic number  $\bar{Z}$  is computed for the compound. For the compound  $B_nC_m$ ,

$$\bar{Z} = \frac{n(A_B Z_B) + m(A_C Z_C)}{\text{molec. wt. of } B_nC_m}, \quad (1)$$

where  $A_B$  and  $A_C$  are the atomic weights of B and C. So defined,  $\bar{Z}$  is simply the sum of each atomic number multiplied by the weight percent of that atom which is present in the compound. The value of  $\bar{Z}$  for calcite ( $\text{CaCO}_3$ ) is 12.565. This indicates that back-scattering from calcite should be intermediate between Mg ( $Z=12$ ) and Al ( $Z=13$ ). Linear interpolation between the back-scattering for calcite and these two metals yields a value of  $\bar{Z}$  within 0.08 percent of the calculated value. Equally accurate results have been obtained for quartz ( $\text{SiO}_2$ ), halite ( $\text{NaCl}$ ), fluorite ( $\text{CaF}_2$ ), kernite ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ ), and celestite ( $\text{SrSO}_4$ ). Other minerals yield the predicted value with lesser precision, unless careful corrections are made for impurities.

There are small but definite differences in the back-scattering from various planes of a crystal. This has been verified in quartz and aragonite ( $\text{CaCO}_3$ ). In general, the scattering is greater the smaller the interplanar distance, though not simply in the ratio of the respective interplanar distances. The nature of this possible dependence upon lattice constants is being examined in greater detail. As might be expected, Eq. (1) predicts an average value.

Back-scattering from organic compounds is equally well predicted, but with results which are low in increasing proportion to their hydrogen content. Fortunately, the decrease in back-scattering is directly proportional to the hydrogen content and precise corrections can be made.

The scattering of beta particles by matter is an extremely complex phenomenon. Theoretical considerations have indicated that one can hope to understand the process *only* when the experimental procedure approximates the condition of single scattering.

These results, however, indicate that, even for multiple scattering, there are generalizations and regularities enabling one to predict the relative scattering for any element or compound.

Details of these and related investigations will be submitted to this journal shortly.

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<sup>1</sup> George Hevesy and F. A. Paneth, *A Manual of Radioactivity* (Oxford University Press, London, 1938), p. 46.

<sup>2</sup> H. H. Seliger, *Phys. Rev.* **78**, 491 (1950).

### Self-Diffusion in Germanium\*

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ALTHOUGH the mechanism of substitutional diffusion in close-packed metal lattices is generally believed to be one of vacancy motion, no such acceptance prevails in the case of germanium. To provide information concerning this question we have undertaken a study of self-diffusion in germanium, preliminary results of which are reported in this letter.

Diffusion specimens in the form of thin slabs of about 1-cm<sup>2</sup> area were cut from a zone-melted single crystal. Both faces of each specimen were polished to 4/0 paper on a precision grinding machine<sup>1</sup> which is capable of polishing the faces parallel to within a tolerance of about 0.5 $\mu$ . About 1 $\mu$ C of Ge<sup>71</sup> was plated onto each face from a hot alkaline oxalate solution of GeO<sub>2</sub>.<sup>2</sup> The

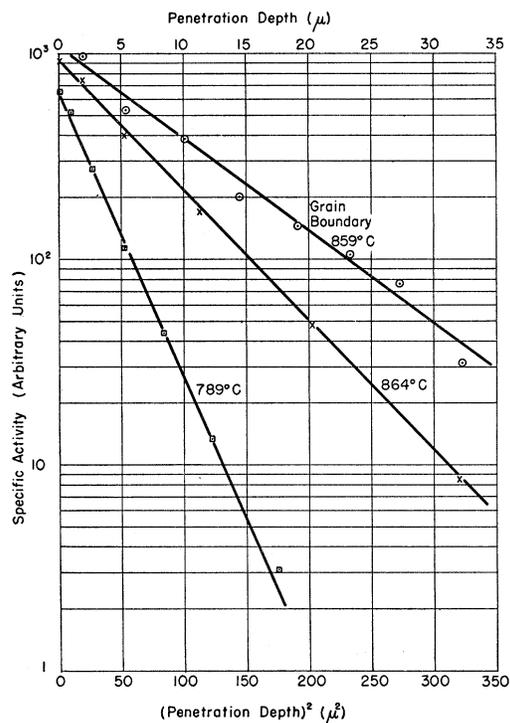


FIG. 1. Typical penetration data. The upper scale of the abscissa refers to the upper curve which represents grain boundary diffusion. The lower curves illustrate volume diffusion.

specimen, supported by a quartz flat, was sealed off in a small, evacuated Vycor tube and placed in a constant temperature furnace ( $\pm 1^\circ\text{C}$ ). After diffusion, the specimen was sectioned on the grinder. The mass and thickness of each cut were determined from the weight loss of the specimen. The concentration of Ge<sup>71</sup> in each cut was determined by assaying the polishing paper with a Tracerlab TGC-3 tube. Typical penetration data are shown in Fig. 1.

Because of the small values of the diffusion constant  $D$ , the penetration depths, measured by  $(Dt)^{1/2}$ , were often only a few microns. If the alignment error in sample mounting were as much as a few tenths of a micron, it would produce an apparently high  $D$ ; therefore, at each temperature, several measurements were made and only the lower values of  $D$  accepted. These data are shown in Fig. 2 and are described by the equation  $D = 87 \exp(-73500/RT)$  cm<sup>2</sup>/sec. Significantly, the penetration data for the lowest  $D$  at a given temperature generally showed the least scatter. The validity of the experimental method was checked by measuring  $D$  for indium in Ag at 613°C. Here, with  $(Dt)^{1/2} = 32\mu$ , the value of  $D$  obtained agreed to 1 percent with the data of Tomizuka<sup>3</sup> taken by conventional techniques.

The value (87) of  $D_0$ , good to order of magnitude, is higher than usually found for self-diffusion in metals and much greater than the 0.3 cm<sup>2</sup>/sec predicted by the theory of Zener.<sup>4</sup> It is comparable to the value of 10 reported by Dunlap and Brown<sup>5</sup> for Sb in Ge.

If one assumes a vacancy mechanism and takes 50 kcal/mole as the energy of formation of a vacancy,<sup>6</sup> then our activation energy indicates the activation energy of mobility to be about 23.5 kcal/mole. From the expression for the vacancy fraction as a function of temperature given by Mayburg and Rotondi,<sup>6</sup> one estimates a diffusion coefficient for vacancies:

$$D_v = D_{\text{self}} \times 1/(\text{vacancy fraction}) = 3.9 \exp(-23,500/RT) \text{ cm}^2/\text{sec}.$$

For two runs, the specific activity varied exponentially with the first power of the depth, as is found in grain boundary diffusion.<sup>7</sup>

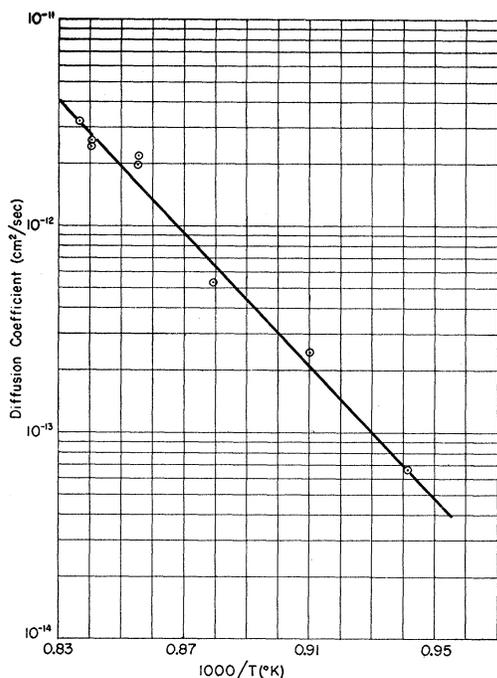


FIG. 2. Diffusion coefficient as a function of  $1/T$ .

Clarke and Hopkins<sup>8</sup> have shown that polishing Ge can produce a distorted surface layer of the order of  $10^{-4}$  cm deep. Presumably, such a layer could be induced to recrystallize. If some grain growth followed, grain boundary diffusion would result. The grain boundary  $D$ 's calculated by means of Fisher's theory<sup>7</sup> were of order  $10^{-8}$  cm<sup>2</sup>/sec, about  $10^4$  larger than the respective volume  $D$ 's.

These experiments are being extended, using longer diffusion times, etched surfaces to preclude recrystallization, and finer alignment techniques.

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<sup>1</sup> Letaw, Slikin, and Portnoy (to be published).

<sup>2</sup> Schwarz, Heinrich, and Holstein, *Z. anorg. u. allgem. Chem.* **229**, 146 (1936).

<sup>3</sup> C. T. Tomizuka (to be published).

<sup>4</sup> C. Zener, *J. Appl. Phys.* **22**, 372 (1951).

<sup>5</sup> W. C. Dunlap, Jr., and D. E. Brown, *Phys. Rev.* **86**, 417 (1952).

<sup>6</sup> S. Mayburg and L. Rotondi, *Phys. Rev.* **91**, 1015 (1953); R. Logan, *Phys. Rev.* **91**, 759 (1953).

<sup>7</sup> J. C. Fisher, *J. Appl. Phys.* **22**, 74 (1951).

<sup>8</sup> E. Clarke and R. Hopkins, *Phys. Rev.* **91**, 1566 (1953).

### Neutron Diffraction Study of the Anisotropy Transition in $\alpha\text{-Fe}_2\text{O}_3$ †

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MORIN,<sup>1</sup> Néel,<sup>2</sup> and others have noted an anomaly in the magnetic behavior of  $\alpha\text{-Fe}_2\text{O}_3$  at approximately  $-25^\circ\text{C}$ . Shull<sup>3</sup> has examined this material by means of neutron diffraction at room temperature and  $-190^\circ\text{C}$  and finds evidence for an antiferromagnetic structure in which the threefold axis of the crystal, which is of rhombohedral symmetry, is the stable direction of the spin system at the lower temperature. At the higher

temperature, the spins lie in the (111) plane and may be oriented toward one of the nearest neighbors in or close to that plane. The anomaly below room temperature is thus interpreted as a transition point at which the antiferromagnetic crystalline anisotropy changes. However, the temperature of the transition appears to vary markedly in the various investigations. Urquhart and Goldman<sup>4</sup> have reported unusual field-dependent strain effects in the neighborhood of the transition. It appeared desirable, therefore, to investigate this transition and its possible dependence on field, choice of crystal, etc., by means of neutron diffraction. One natural single crystal, the same one used in the investigation of Urquhart and Goldman, and a synthetic crystal on which Anderson *et al.*<sup>5</sup> have made resonance measurements were studied.

The intensity of the (111) diffraction peak depends completely on the magnetic state of the system.<sup>3</sup> When the magnetic vectors are in the (111) plane and the usual antiferromagnetic symmetry is observed, there is an appreciable intensity to this peak. However, if the spins are oriented perpendicular to this plane, the magnetic scattering for this reflection vanishes and the line virtually disappears. The experiment was done using the spectrometer previously described.<sup>6</sup> The crystal was mounted on a goniometer and oriented in the neutron beam so as to obtain the maximum intensity. A vacuum-jacketed quartz vessel was then lowered over the crystal, and air that had been passed through a mixture of solid  $\text{CO}_2$  and alcohol was passed over the crystal. The temperature was controlled by regulating the flow of air and was measured by means of two copper-constantan thermocouples in contact with different parts of the crystal. The temperature could be controlled to within  $0.2^\circ\text{C}$  during the scanning of a peak.

The data thus obtained are shown in Figs. 1 and 2. In Fig. 1

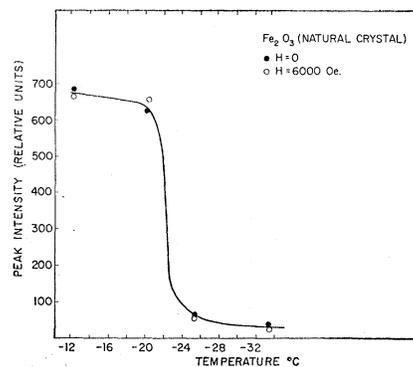


FIG. 1. Temperature dependence of the integrated intensity of the (111) reflection from a natural single crystal of  $\text{Fe}_2\text{O}_3$ .

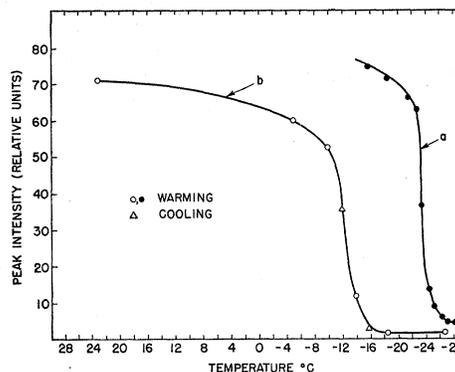


FIG. 2. Variation with temperature of the (111) peak height for single crystals of  $\text{Fe}_2\text{O}_3$ . Curve *a* represents a natural crystal (same as in Fig. 1) and curve *b* a synthetic crystal.