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The Measurement of Self-Diffusion in Zinc*

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Measurements of self-diffusion along the *C* axis of zinc single crystals have been carried out. Long-lived radioactive Zn^{65} was used as an indicator. Measurements were made at six different temperatures, enabling a determination of the activation energy, which is 19,600 calories per mol. The diffusion coefficient at 410.4°C is 9.89×10^{-4} cm^2/day.

INTRODUCTION

DIFFUSION in metals is important both to the metallurgist and to the physicist.[1] It is important to the former because phenomena such as carburization of steel, production of corrosion- and heat-resisting substances, rates of hardening and transformation, and heat treatment of castings, all depend on diffusion rates. Self-diffusion is especially important because of the information it may reveal concerning creep in solids. It is important to the physicist because it will elucidate the mechanism of rate processes in solids, since it involves atomic movements.

Inquiries into the subject of self-diffusion (in which the atoms of a lattice are replaced by atoms of their own kind) led von Hevesy[2] and his collaborators to the use of radioactive isotopes as indicators. The property of radioactivity of an atom *A* permits its labeling or "tagging" and hence affords a means of studying its progress through the lattice of nonradioactive solvent *A*. By such means Hevesy, Seith, and Keil[2] studied self-diffusion in lead and Seith and Keil[3,4] studied self-diffusion in lead and bismuth, with thorium B (which is an isotope of lead) and thorium C (which is an isotope of bismuth).

Prior to the advent of artificial radioactivity the use of radioactive isotopes as indicators in studies of self-diffusion was limited to the heavier elements since these were the only ones which had active isotopes in nature. With artificially produced radioactive isotopes, however, means of studying the lighter elements, such as zinc and copper (elements of special interest to the metallurgist) are available. Self-diffusion in gold[5,6] and copper[7,8] has been studied by using artificial radioactive isotopes. The present paper deals with self-diffusion in zinc.

DESCRIPTION AND DISCUSSION OF PRESENT INVESTIGATION

Radioactive Zn^{65} is used as an indicator in this study. It is electrolytically deposited on a flat, polished, and etched surface of a single crystal of high purity zinc; the sample is then held for a fixed time at an elevated temperature to allow diffusion to proceed in the crystal, and finally cut into sections on a lathe at room temperature. The activity of each section is measured with a Geiger counter or an electroscope. From the weight of each section, the thickness can be computed, and from the thickness and activity the diffusion coefficient is obtained.

Zn^{65} (half-life eight months) can be obtained free from inactive Zn by proton bombardment of copper: $Cu^{65}(p, n)Zn^{65}$. The Zn^{65} produced by this proton-neutron reaction emits positrons and conversion electrons of a strong gamma-ray. Zn^{65} can also be produced from Zn^{64} by deuteron bombardment: $Zn^{64}(d, p)Zn^{65}$.

It is not possible to determine the diffusion coefficient by a method such as that of Hevesy,

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* This investigation has been carried out in cooperation with Dr. H. M. Day, Research Laboratory of the General Electric Company, Schenectady, New York. The preparation of accurately oriented, strain-free single crystals, and the precision heat treatments will be described in publications dealing with other phases of the diffusion problem.

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[1] R. F. Mehl, Trans. A. I. M. E. Inst. of Metals Div. **122**, 11 (1936).

[2] Hevesy, Seith and Keil, Zeits. f. Physik **74**, 197 (1932).

[3] W. Seith, Zeits. f. Elektrochemie **39**, 538 (1933).

[4] W. Seith and A. Keil, Zeits. f. Metallkunde **25**, 104 (1933).

[5] A. Sagrubskij, Physik. Zeits. Sowjetunion **12**, 118 (1937).

[6] H. A. C. McKay, Trans. Faraday Soc. **34**, 345 (1938).

[7] B. V. Rollin, Phys. Rev. **55**, 231 (1939).

[8] Steigman, Shockley and Nix, Phys. Rev. **56**, 13 (1939).

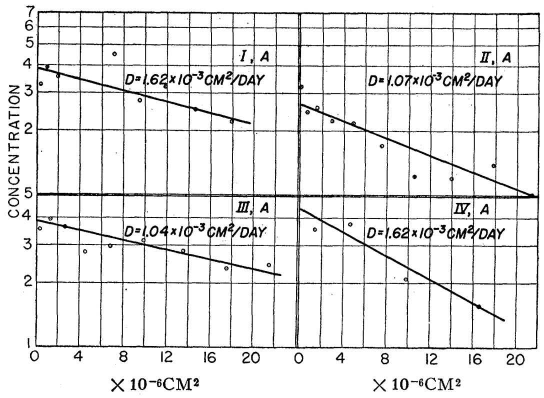

FIG. 1. Counter measurements on crystals of group *A*. Logarithm of concentration for each section plotted against square of mean depth in crystal. Temperature of heat treatment—412.5°C; time of heat treatment—12.5 hours for crystals I and II, 24 hours for crystal III, 6 hours for crystal IV; number of sections—ten, ten, ten, and six, respectively.

Seith and Keil,[2–4, 9] *viz.*, evaporation of Zn^{65} onto the surface of a crystal of ordinary zinc and measurement of the radioactive decay before and after diffusion, because there is no fixed range for electrons. It is possible, however, to solve the diffusion equation and take into account the approximately exponential character of the absorption of a continuous energy spectrum of electrons (the emitted radiation) in the substance employed, as Steigman, Shockley and Nix[8] did. This would lead to a very uncertain interpretation of the data in the case of Zn^{65}, for the ionizing radiation from this radioactive element is complicated by the emission of strong gamma-radiation. Methods may be devised, however, which do not depend on calculating the amount of diffusion which occurs from the decrease in intensity of the radiation measured at the surface. The procedure outlined at the beginning of this section is such a method.

Zn^{65} is separated from the copper from which it is produced by dissolving the surface of the copper containing the Zn^{65} in $1-1$ nitric acid. Chlorides are made of the Zn^{65} and copper, and the copper precipitated by hydrogen sulphide from a 0.3 normal HCl solution. Actually, there will be more copper ions present in the filtrate than Zn^{65} ions, because of the degree of efficiency of the precipitation process and because there is such a small quantity of Zn^{65} initially. Several precipitations are made until further bubbling of hydrogen sulphide through the solution brings down no more copper. The precipitate is tested in each case for its activity to ascertain whether any of the Zn^{65} is brought down with the copper. After this procedure practically all of the Zn^{65} remains in the solution, which is then concentrated down to dryness, and the residue dissolved in 5 cc of water. This solution serves as the electrolyte in the electrolysis process.

Single crystals were grown from high purity Zn and were used in the form of cylinders about 0.5 inch in diameter and 0.3 inch long. All the crystals had the same crystallographic orientation (diffusion interface perpendicular to the *C* axis), and their flat, etched, and polished surfaces were perfect reflectors. Each crystal served as the cathode during the electrolysis, a portion (0.5 cc in 3 cc of water) of the Zn^{65} solution mentioned above was the electrolyte, and a spiral platinum wire was the anode. The time of the electrolysis varied from forty-five minutes to six hours, the average voltage used was 4.5 volts, the average current 10 milliamperes. None of these factors seemed to be critical. During the electrolysis the crystals generally became tarnished.

A rotating cathode was used to provide stirring of the electrolyte to have a uniform distribution of the Zn^{65} ions throughout the solution, to prevent bubbles from gathering on the surface of the cathode, and to permit selective deposition of Zn^{65} in the presence of copper. A rotating cathode[10, 11] is indispensable for selective deposition of Zn^{65}, for it is well known that copper will plate out before zinc. A high speed rotating cathode obviates this. Also, the cathode was dipped in and out of the solution during the electrolysis to prevent the formation of bubbles, for they would destroy the intimacy of the contact between the surface of the zinc crystal and the Zn^{65}.

After electrolysis the impregnated crystals were held for a fixed time at elevated temperatures to allow diffusion to proceed. Variations in temperature during the course of the heat

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[9] G. v. Hevesy and W. Seith, Zeits. f. Physik **56**, 790 (1929).

[10] C. G. Fink and F. A. Rohrman, Trans. Am. Electrochem. Soc. **58**, 403 (1930).

[11] J. Steigman, Phys. Rev. **53**, 771 (1938).

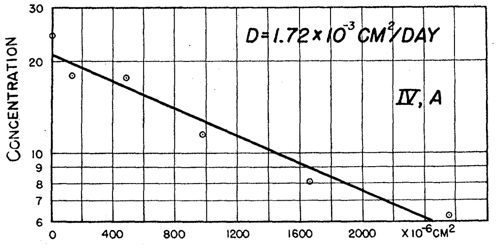

FIG. 2. Electroscope measurements on crystal IV, group A. Logarithm of concentration for each section plotted against square of mean depth in crystal. Temperature of heat treatment—412.5°C; time of heat treatment—6 hours; number of sections—six.

treatment were always less than 0.1°C. At room temperature the crystals were cut into sections approximately 0.002 inch thick on a lathe, the cut being parallel to the original face. The sections were in the form of ribbons, as cut by the lathe tool. It was not necessary to have the section of predetermined or accurately equal thickness; for each section was weighed, and the thickness computed from the weight, the known density of zinc (taken here to be 7.10 g/cc), and the area of the face from which the sections were turned. General freedom from edge effects was ensured by turning off the cylindrical surface of the crystal to a depth of approximately 0.005 inch before the sections were taken off.

The activity of each section was measured either with a Lauritsen[12] electroscope or with a Geiger-Müller counter. For the electroscope measurements each section was placed in the electroscope can. Most of the measurements were made with a thin glass-walled Geiger counter, directly under which each section was placed (in a small pill box) in approximately the same position. The background of this counter was approximately 17 counts per minute. After diffusion the activities of the first sections were at least 100 counts per minute above the background, the activities of the last sections at least 5 counts per minute above the background. About 2000 counts per section were taken, so that the precision ranged from one percent for the first sections to nine percent for the last.

It was not necessary to compare each measurement with a standard to allow for radioactive decay, as McKay[6] and Steigman, Shockley, and Nix[8] did. Because of the long half-life of Zn^{65} (eight months) the decay during any series of measurements is negligible. Also, it was not necessary to correct for the absorption of electrons in matter since each section was only approximately 0.002 inch thick (except for crystal IV, group A, where each section was 0.004 inch thick), and geometrically similar to every other section.

The electroscope and Geiger-counter measurements provided independent methods of determining the respective activities (and hence diffusion coefficients D) and the close agreement between these two methods (e.g., see results of crystal IV, group A) was construed to indicate reliability of the present technique in the study of the phenomenon in question.

The diffusion equation is

$$\partial c/\partial t = D\partial^2 c/\partial x^2 \tag{1}$$

if there is no evaporation to or from the surface. Here c is the concentration of Zn^{65}, t the time for

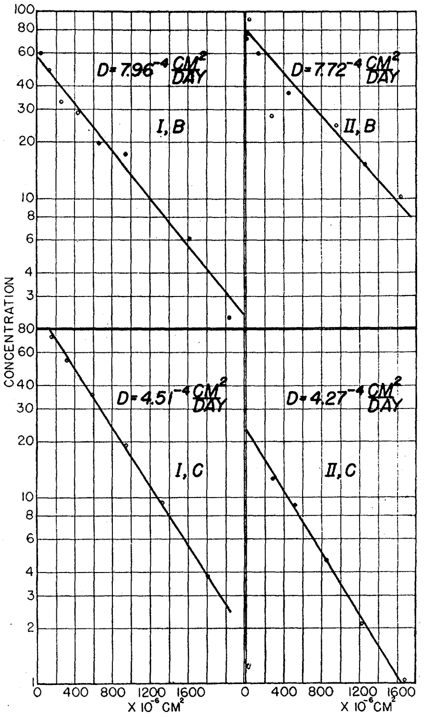

FIG. 3. Counter measurements on crystals of groups B and C. Logarithm of concentration for each section plotted against square of mean depth in crystal. Temperature of heat treatment—400°C and 374.4°C, respectively; time of heat treatment—6 hours and 7.5 hours, respectively; number of sections—ten.

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[12] C. C. Lauritsen and T. Lauritsen, Rev. Sci. Inst. 8, 438 (1937).

the diffusion, x the axial coordinate in the sample, and D the diffusion coefficient. D is assumed to be independent of c. The solution of this equation is given in this form:

$$c=(\pi Dt)^{-\frac{1}{2}}\exp\left[-x^2/4Dt\right], \tag{2}$$

in which the initial thickness of the active layer is assumed infinitesimal. If $\ln c$ is plotted against $\bar{x}^2$, which represents the square of the average depth of the section considered below the surface of the crystal, a straight line results of intercept $-\ln(\pi Dt)^{\frac{1}{2}}$, and of slope $-\frac{1}{4}Dt$. Thus, if c and x are known, D can be obtained directly from the graph, for a given t. The concentration in each section is obtained in relative units from the activity by dividing by the thickness of the section ($c_n=A_n/t_n$). This introduces an error of less than 1 percent (for the small distances dealt with in the experiment), which is well under the experimental error.

From Eq. (2)

$$Dt=\frac{\bar{x}_1{}^2-\bar{x}^2}{4\ln(c/c_1)}. \tag{3}$$

From the half-value of the concentration, i.e., the point where the concentration has fallen to one-half of its original value we have

$$Dt=0.361\bar{x}_{\frac{1}{2}}{}^2, \tag{4}$$

where $\bar{x}_{\frac{1}{2}}{}^2$ is the square of the abscissa where the half-value ordinate occurs.

$\bar{x}_{\frac{1}{2}}{}^2$ is determined from the graph (of $\ln c$ *vs.* $\bar{x}_n{}^2$) and t is known. Therefore D is obtained directly.

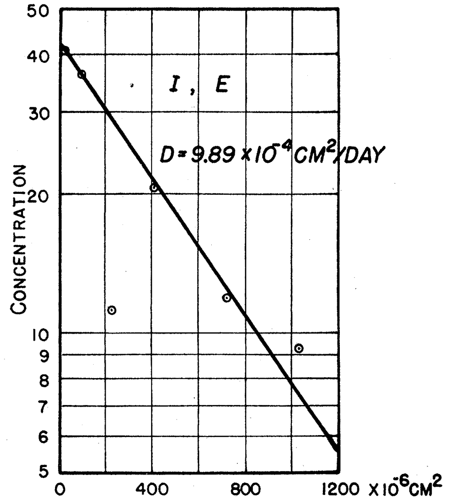

FIG. 5. Counter measurements on the only crystal of group E. Logarithm of concentration for each section plotted against square of mean depth in crystal. Temperature of heat treatment—410.4°C; time of heat treatment—3.5 hours; number of sections—ten.

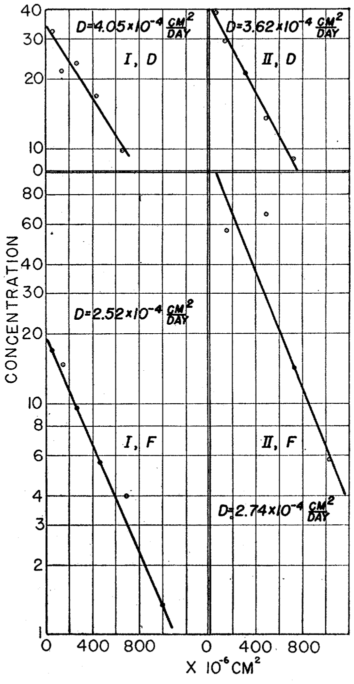

FIG. 4. Counter measurements on crystals of groups D and F. Logarithm of concentration for each section plotted against square of mean depth in crystal. Temperature of heat treatment—364.7°C and 355°C, respectively; time of heat treatment—8 hours and 9 hours, respectively; number of sections—ten.

RESULTS

The rate of diffusion was determined at six different temperatures for six groups of single crystals: Group A consisted of four crystals, group E, one, and all other groups of two crystals each.

Figure 1 displays the graphs of the counter measurements for the crystals I–IV of group A. Figure 2 is the graph for crystal IV, group A, for electroscope measurements. The agreement between the counter and electroscope measurements on the sections of this crystal is quite satisfactory. Figures 3, 4, and 5 are the graphs for crystals of groups B, C, D, E, and F.

The temperature dependence of D is given by

$$D=Ae^{-Q/RT}, \tag{5}$$

where A is the activation constant, Q the activation energy, R the gas constant, T the absolute temperature, and e is the logarithmic base.

$$\ln D=\ln A-(Q/RT). \tag{6}$$

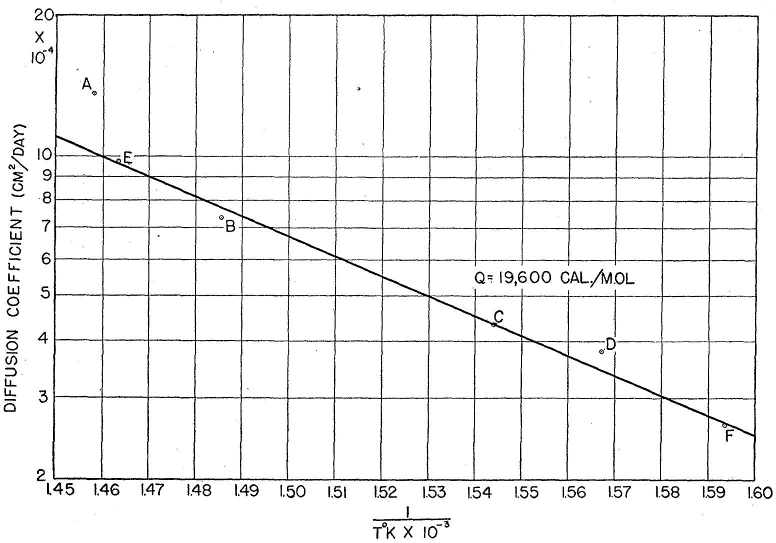

FIG. 6. Diffusion coefficient as a function of reciprocal temperature. The crystals of group A were heat treated before the precision furnance control had been developed.

If $\ln D$ is plotted against $1/T$ a straight line of intercept $\ln A$, slope $-Q/R$ results. Q, the activation energy is obtained directly from the graph. Figure 6 shows the temperature dependence of D (a plot of D against $1/T$). The value obtained for Q is 19,600 cal./mol.

Q can be calculated also from the Dushman-Langmuir[13] equation

$$D = Q/Nh\delta^2 e^{-Q/RT},$$

where δ is the interatomic distance, N is Avogadro's number, h is Planck's constant, D the diffusion coefficient, Q the activation energy, R the gas constant, T the absolute temperature, and e the logarithmic base. The average calculated value of Q is 22,200 cal./mol.

DISCUSSION OF RESULTS

Different boundary conditions prevailing at the interface between the diffusing solute and the ordinary zinc crystal will alter the results because of the possibility of the trapping of active zinc on the surface. Some of the plated zinc may be in good contact and start to diffuse immediately, some may be in poor contact and start to diffuse later, and some may not start at all. As a matter of fact, it is seen from the graphs that the first point of the curve for each crystal seems to be somewhat high. It is assumed that the greater part of the diffusion takes place normally. Justification for this assumption is in the agreement between the experimental and theoretical curves.

Possible sources of error in the determination of D are: (1) variations in the temperature of heat treatment (practically negligible since the furnace control was good to 0.1°C; (2) errors in weighing (less than 1 percent); (3) slightly different geometric orientations of the sections with respect to the counter in measuring activities; (4) assumption of independence of D and concentration c; (5) assumption that the thickness of the initial layer is not comparable with the depth of penetration (and hence the evaporation is not important); (6) statistical fluctuations in the counts made on each section; (7) location of the average line through the points; and (8) variation in time at the temperature of the heat treatment (a maximum of 3 percent).

CONCLUSION

The method described presents a very satisfactory way of determining the coefficient of self-diffusion D, and the activation energy Q, in zinc. It is especially useful in that it provides a simple and direct procedure for getting an average value for D.

The author expresses his gratitude to Professor Louis N. Ridenour, who initiated the experiment and under whose guidance the work de-

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[13] S. Dushman and I. Langmuir, Phys. Rev. 20, 113 (1922).

scribed here was carried out, to Dr. Harry M. Day, of the Research Laboratories of the General Electric Company, who prepared all of the crystals and performed the heat treatments, to Professors Frederick Seitz and Enos Witmer for their valuable discussions; and to the workers of WPA Project No. 21637 for assistance.

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FEBRUARY 15, 1941 PHYSICAL REVIEW VOLUME 59

The *L*-Emission Bands of Sodium, Magnesium and Aluminum

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The radiation emitted when conduction electrons fill vacancies in the L shell is spread over a band whose shape represents the energy distribution of the conduction electrons. This band has been studied spectrophotometrically for pure sodium, magnesium and aluminum. The observed shapes are in general agreement with theoretical predictions and confirm the results of previous experimental studies. In each case a "tail" has been observed at the low frequency end of the band, for which alternative explanations are offered. With the x-ray continuum as a standard of intensity, the total intensity of the L band increases nineteen-fold from sodium to aluminum.

THE electronic structure of a metal can be investigated by a study of the x-radiation emitted by the metal when one of its conduction electrons falls into a vacancy in an inner shell. Since the conduction electrons have energies throughout a range of several electron volts, this x-radiation is a band of corresponding width. The distribution in energy of the intensity in this band is related to the distribution in energy of the conduction electrons; thus the definite upper limit of the energy of the conduction electrons is evidenced by the fact that the x-ray emission band is sharply bounded at its high frequency end.

X-ray bands of this origin have been observed repeatedly. The recent work of Bearden and collaborators[1] provides examples in the region of 1.5A. In principle, it is preferable to observe the structure of the bands emitted in the ultra-soft x-ray region ($\lambda > 10A$), for here the frequency of the radiation is not large in comparison with the frequency spread of the emission band and high resolution technique is not necessary. Of several reports of bands emitted in this region, those of O'Bryan and Skinner[2] and of Skinner[3] are outstanding in that they present and discuss reliable photometric descriptions of the radiation from very clean surfaces of certain metals. In the emission of ultra-soft x-rays, the surface of the target must be extremely clean, since all photons except those from the surface are absorbed in the target. Foreign elements on the target not only introduce their own characteristic spectra, but also affect the characteristic radiation of the target element itself. The numerous reports of ultra-soft x-rays by Siegbahn and Magnusson[4] and others at Uppsala must be regarded as qualitative, since their targets were admittedly contaminated with carbon, nitrogen and oxygen.

The present work was undertaken as an attempt to confirm and extend previous work in the photometry of the band of radiation emitted as conduction electrons fall to L_{II} or L_{III} levels made vacant by electron bombardment.

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[4] M. Siegbahn and T. Magnusson, Zeits. f. Physik **62**, 435 (1930); **87**, 291 (1934); **88**, 559 (1934); **95**, 133 (1935).