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Diffusion of Zinc in Single Crystals of Silver*

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The diffusion of Zn in Ag has been measured in the temperature range from 640°C to 925°C, using high-specific-activity Zn^{65} as a tracer. The data indicate that the diffusion coefficient is given to within 2% by the equation, $D=0.54\exp(-41\,700/RT)$ cm^2/sec.

INTRODUCTION

IN order to understand the basic mechanism involved in diffusion in metals, or alternately, in order to decide among the various theoretical explanations for the differences in diffusion rates in alloys containing the same base metal, it has become necessary to obtain data of considerably higher accuracy than much of that presently in the literature. It has been demonstrated recently[1] that data of high accuracy can be obtained by using single crystals of a monovalent cubic metal for the solvent, and high-specific-activity tracer as solute to keep the solute concentration small.

In conjunction with the need for data of higher accuracy, there is a need for systematic data on the effect on diffusion rates of the valence, atomic size, and crystal structure (interatomic forces) of the solute. The recent work cited[1] investigated the effect of valence, without considering the other two factors. Thus, the logical choice as a first step in increasing the accurate systematic data in the literature was a solute of the same valence and crystal structure but of different atomic size than that used previously. The present report gives the data for diffusion of zinc in silver, and supports the contention that it is possible to obtain data of high accuracy.

EXPERIMENT

Single crystals of silver (99.99% pure, obtained from Handy and Harman) were grown by using a modified Bridgeman technique. Particular attention was paid to obtaining crystals free from excessive substructure. Experience has indicated that it requires considerable care to obtain single crystals essentially free from dislocation boundaries; and it has been observed[2] that these boundaries materially affect diffusion rates, particularly at lower temperatures. Acceptable single crystals were cut into short cylinders, etched, formed accurately in the lathe on which they were to be sectioned later, lightly polished, etched, and annealed at 850°C for one hour to remove residual strains. After a final etch to check monocrystallinity, the ends of the specimens were plated on one end with high-specific-activity Zn^{65}, obtained from the Oak Ridge National Laboratory. The estimated thickness of the plated layer ranged from 20 to 200 A.

The specimens were then placed in pairs, with active faces together, in evacuated Vycor tubes. The specimens were held accurately in place in the tubes by Vycor rods welded to the tube walls, and thermocouples affixed to the tubes in positions corresponding to the diffusion interfaces. During the diffusion anneals, the temperatures of the furnaces were controlled by Celectrays with the variation at any sample not exceeding ±1°C.

After diffusion, 30 to 60 mils were removed from the sides of the cylindrical samples in order to eliminate edge effects. Uniform sections, 0.001 cm thick, were then removed using a precision jeweler's lathe, and the activity of each section determined with a thin mica end-window Geiger tube in a standard scaling circuit. The cuts were then weighed to check their thickness and finally, the total weight of all sections was compared with the known total amount removed from the sample. In the rare cases where these values did not agree, the weights were used as proportional thickness measurements and the activity determined as (counts/minute) per milligram, so that the specific activity is not affected by small losses of material during transfer. The entire counting geometry was, of course, accurately reproduced for each count and each section was "counted" at least twice.

RESULTS

Diffusion runs were made at six temperatures in the range from 640°C to 925°C, for times ranging from eight hours to slightly more than ten days. A linear curve was obtained, for all samples, when the logarithm of

TABLE I. Summary of data.

Sample	Temp. (°C)	Time (sec)	D (cm^2/sec)
1	924	2.88×10^4	1.32×10^{-8}
2	924	2.88×10^4	1.28×10^{-8}
3	847	6.57×10^4	3.86×10^{-9}
4	847	6.57×10^4	3.84×10^{-9}
5	801	6.12×10^4	1.77×10^{-9}
6	801	6.12×10^4	1.73×10^{-9}
7	748	10.44×10^4	6.33×10^{-10}
8	748	10.44×10^4	6.44×10^{-10}
9	702	29.52×10^4	2.36×10^{-10}
10	702	29.52×10^4	2.43×10^{-10}
11	643	86.76×10^4	6.09×10^{-11}
12	643	86.76×10^4	5.88×10^{-11}

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[1] See, for example, C. T. Tomizuka and L. Slifkin, Phys. Rev. **96**, 610 (1954).

[2] F. E. Jaumot, Jr., and R. L. Smith, J. Metals (to be published).

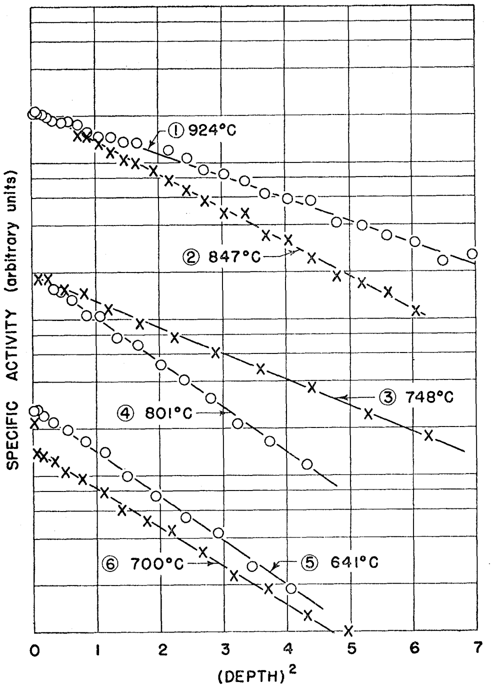

FIG. 1. Penetration-depth curves for diffusion of Zn in Ag. Scale factors: Curves 1 and 2—5×10^{-4} cm^2; Curve 4—2.5×10^{-4} cm^2; Curve 6—2×10^{-4} cm^2; Curves 3 and 5—10^{-4} cm^2. In all cases, only every other section has been plotted, and in curves 2 and 4 the initial points have been omitted to avoid confusion.

the concentration was plotted against the square of the penetration distance, indicating little effect of any imperfections in the crystals. Typical concentration-depth curves are shown in Fig. 1. A "least-squares fit" of these data allowed the diffusion coefficient to be calculated directly. Table I summarizes the results for individual samples and Fig. 2 gives a plot of the logarithm of the diffusion coefficients as a function of the reciprocal of the absolute temperature.

DISCUSSION OF RESULTS

Inasmuch as the effects of any imprefections in the sample are magnified at low temperatures, the data at the higher temperatures should yield more accurate values of the activation energy, Q, and the frequency factor, D_0. On this basis, Q and D_0 were obtained from a least-squares fit of the data for the four highest temperatures (samples one through eight) and values of 41 690 cal/mole and 0.538 cm^2/sec, respectively, were obtained. A least-squares fit of all the data gives $Q=41\,660$ cal/mole and $D_0=0.528$ cm^2/sec. With an estimated probable error of $\pm2\%$ in D, $+0.5\%$ in Q, and $\pm10\%$ in D_0, the data can be represented, well within these errors, by

$$D=0.54\exp(-41\,700/RT)\ \mathrm{cm^2/sec}.$$

The mean deviation of the individual points from the value given by this equation is 1.3%, with a maximum deviation of 2% (sample No. 11). The deviations are markedly reduced by using the more detailed values given above, but these are not warranted in view of the estimated accuracy of the measurements.

Since one of the primary motivations of the present diffusion program is to determine the effect of the atomic size of the solute on diffusion parameters, it is interesting to compare the results for Zn with those previously reported for Cd,[1] even though it is obviously impossible to draw conclusions from one comparison. Zinc is smaller in both atomic radius (based on distance of closest approach of atoms in the pure solid) and ionic radii than Cd, but has the same valence and the same crystal structure. Tomizuka and Slifkin[1] give for diffusion of Cd in Ag

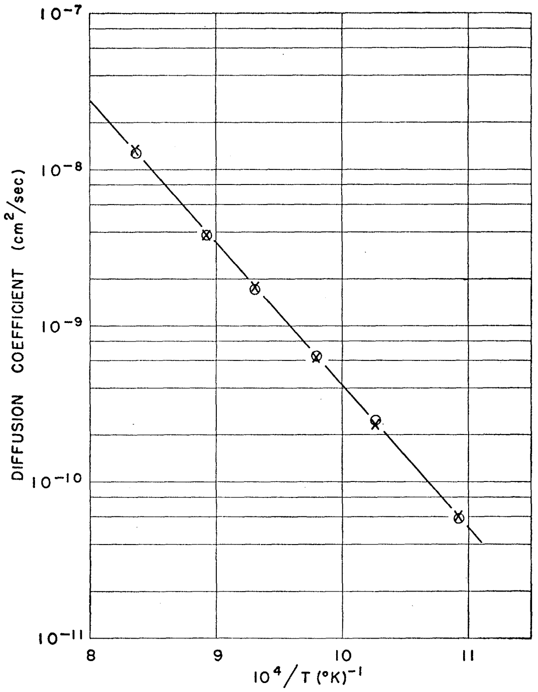

FIG. 2. The diffusion data plotted as log D *versus* $1/T$.

$$D=0.454\exp(-41\,700/RT)\ \mathrm{cm^2/sec},$$

with the same estimated error as given for the present work. The indication, although far from conclusive, is that the atomic size has little effect on the activation energy, and certainly its effect is less than the effect of valence. On the other hand, it would seem that the frequency factor is affected, since it would require that the maximum error in both determinations be called into play in order to bring the two values of D_0 into coincidence. More work is needed to substantiate these very tentative conclusions.

The present work agrees with that of Tomizuka and Slifkin in that the values of D_0 and Q for solute diffusion are much nearer those for self-diffusion than has generally been reported in the literature. Since these authors discussed this point in detail, there is no need to do so here.

Finally, calculating D_0 from Zener's theory[3] and using the value of the vibration frequency, ν, obtained from the Debye temperature for zinc, one obtains 0.537 cm^2/sec. Similarly, using Nowick's method[4] for calculating Q from the highest-temperature data, one obtains 41 690 cal/mole. These values are in obviously fortuitous agreement with the experimental data.

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[3] C. Zener, J. Appl. Phys. **22**, 372 (1951).

[4] A. Nowick, J. Appl. Phys. **22**, 1182 (1951).

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Amphoteric Impurity Action in Germanium*

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A new type of impurity action in germanium is described. This is "amphoteric" impurity action, to be contrasted with "donor" and "acceptor" action of the usual impurities in germanium. An amphoteric impurity, of which gold is shown to be an example, is an element that may either donate or accept electrons in the semiconductor, depending upon the nature and amount of other impurities present, that is, upon the position of the Fermi level as determined by these impurities. Previously the acceptor action of gold in germanium had been described, and it was shown there were two acceptor levels, 0.15 and 0.55 ev above the valence band. Morton, Hahn, and Schultz have found evidence of a third state which they interpret as the first acceptor level. In the present investigation, the existence of a third state is confirmed, and it is shown, with rather high degree of certainty, to be a donor level 0.05 ev above the valence band. This appears to be the first nonhydrogenic donor state yet observed in germanium. When gold is added to germanium containing third column elements in amounts less than the gold content, the carrier density remains constant, but the carriers acquire an ionization energy of 0.05 ev. Good agreement was obtained with several sources of gold. This behavior, it appears, can be explained most simply by assuming that neutral gold atoms may give up electrons to low-lying empty states to form Au^+. The upper gold states when filled are still interpreted as Au^- and Au^{--}.

INTRODUCTION

The acceptor action of gold in germanium has been described in several papers.[1] In this work it was shown that gold was capable of taking up electrons at two energy levels, situated about 0.15 and 0.55 ev above the valence band. It was suggested that these levels were probably due to the formation of, first Au^- and then Au^{--}. These states were shown to be highly different in ionization energy from the states due to ordinary donor and acceptor impurities in germanium. Because of the great depth of these levels, a wide variety of new applications were opened up, including studies of trapping and secondary photoconductivity, and studies utilizing the high resistivity available at 77°K.

Morton, Hahn, and Schultz[2] have recently investigated the action of gold in germanium, and, in addition to confirming the existence of the above acceptor levels, have found evidence for a third state. They interpret their results as indicating an acceptor level 0.05 ev above the valence band, which takes up electrons to form Au^-. The upper two levels when filled with electrons would then be Au^{--} and Au^{---}.

There are several difficulties in accepting this interpretation of these results. In the first place, the original investigations[1] had indicated, with an accuracy somewhat better than 25%, that there were only two acceptors per gold atom, these levels being present in approximately equal numbers. Secondly, there is an intrinsic difficulty in assuming an Au^{---} center only 0.5 ev above the valence band. The electrostatic repulsion of the two electrons toward a third electron should be rather large.

Because of these difficulties, an investigation was made of the third gold level. This work confirmed the existence of such a level, but indicated that it was a donor level 0.05 ev above the valence band. With this change of interpretation, all the results were found to be consistent with previous studies on gold-doped germanium. Besides fitting in well with the finding of two acceptor states per gold atom, the new hypothesis agreed with previous results that when gold was added to pure germanium, the product was always *p*-type. This follows from the great depth of the donor level, and its inability to contribute directly to the number of conducting electrons. The state shows up only in *p*-type material, where it furnishes a supply of electrons for trapping holes, and for furnishing acceptor levels associated with re-excitation of holes back to the valence band.

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* Work performed at General Electric Research Laboratory, Schenectady, New York.

[1] W. C. Dunlap, Jr., Phys. Rev. **91**, 1282 (1953); **97**, 614 (1955).

[2] Morton, Hahn, and Schultz, Atlantic City Photoconductivity Conference, November, 1954 (John Wiley and Sons, Inc., New York, 1956).