

Anisotropic Diffusion of Mercury in Zinc*

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The diffusion of mercury has been studied in high-purity zinc as a function of temperature, using the sectioning technique. The diffusion coefficients as measured in single crystals are given by $D_{11} = (0.056 \pm 0.002) \times \exp[-(19700 \pm 48)/RT]$ cm²/sec, and $D_{\perp} = (0.073 \pm 0.006) \exp[-(20180 \pm 94)/RT]$ cm²/sec, where D_{11} and D_{\perp} are the diffusion coefficients parallel and perpendicular to the hexagonal axis, respectively. Compared to the diffusion of cadmium in zinc, where $D_{\perp} > D_{11}$, mercury diffuses with a slightly smaller activation energy, and with $D_{11} > D_{\perp}$. The results are discussed on the basis of the basal and nonbasal vacancy mechanisms, and the influence of the ion size of the diffusing atom is examined to explain the diffusion anisotropy.

INTRODUCTION

DIFFUSION of a variety of impurities in single crystals of high purity zinc has already been studied using the sectioning technique, and the experimental data are available in the literature. The diffusion of trivalent tracers, indium¹ and gallium,² and of monovalent tracers, silver,¹ gold,³ and copper,² is found to be qualitatively consistent with Lazarus's theory,⁴ later refined by LeClaire⁵ and then extended by Ghate⁶ to explain quantitatively the impurity diffusion in zinc. The theory is based on the electrostatic interaction between a screened impurity and its neighboring vacancy.

The diffusion of cadmium which has the same valence as that of the host matrix, zinc, has been investigated by Ghate.³ It was found that cadmium diffuses faster than zinc with D_{\perp} greater than D_{11} . Here D_{11} and D_{\perp} are the diffusion coefficients parallel and perpendicular to the c axis of the hexagonal structure of zinc. These results are also consistent with the vacancy mechanisms (basal and nonbasal) and the fact that the diffusivity of cadmium is greater than that of zinc agrees quite satisfactorily with LeClaire's theory⁷ of homovalent diffusion. The larger diffusivity of cadmium is attributed to a higher potential at the impurity because of its different core potential from that of zinc. The potential increase is equal to the difference between the electron ground-state energies of zinc and cadmium atoms.

The present investigation was undertaken in order to obtain more information on homovalent diffusion in zinc; the diffusivity of mercury is reported in this paper.

EXPERIMENTAL

Single-crystal specimens, about $\frac{1}{2}$ in. in length and $\frac{1}{2}$ in. in diam, were prepared from 99.999% pure zinc

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¹ J. H. Rosolowski, *Phys. Rev.* **124**, 1828 (1961).

² A. P. Batra and H. B. Huntington, *Phys. Rev.* **145**, 542 (1966).

³ P. B. Ghate, *Phys. Rev.* **131**, 174 (1963).

⁴ D. Lazarus, *Phys. Rev.* **93**, 973 (1954).

⁵ A. D. LeClaire, *Phil. Mag.* **7**, 141 (1962).

⁶ P. B. Ghate, *Phys. Rev.* **133**, 1167 (1964).

⁷ A. D. LeClaire, *Phil. Mag.* **10**, 641 (1964).

supplied by the American Smelting and Refining Company. Hg²⁰³ radioisotope, obtained from the Oak Ridge National Laboratory, was used as the tracer. A thin layer of mercury, about 0.1 μ in thickness, was deposited on the well annealed samples from a plating solution⁸ containing the tracer. The standard sectioning technique was used to measure the diffusivity. The temperature of the diffusion anneal was controlled to within $\pm 0.3^\circ\text{C}$. Some of the samples were analyzed by a well-type NaI(Tl) scintillation counter; the others were counted with a thin-end-window Geiger counter. The experimental procedures have been described in detail in a previous publication.²

RESULTS

The diffusion runs were performed in the temperature range from 260 to 413°C. Typical penetration profiles are shown in Fig. 1, where the logarithm of the specific activity is plotted as a function of the square of the penetration distance. These plots indicate evaporation of the tracer from the sample surface since the first few data points lie below the line drawn through the points far removed from the surface of the sample. The diffusion coefficients D_{11} and D_{\perp} [$D = (4 \times \text{slope} \times \text{time of diffusion anneal})^{-1}$] are calculated from such plots and these are listed in Table I. In Fig. 2, the logarithm of the diffusion coefficient is plotted vs the reciprocal temperature; the Arrhenius plots for cadmium diffusion and self-diffusion are included for comparison.

TABLE I. Diffusion of Hg²⁰³ in zinc.

Temperature (°C)	1000/T (°K ⁻¹)	D_{11} (cm ² /sec)	D_{\perp} (cm ² /sec)
412.7	1.458	2.92×10^{-8}	2.79×10^{-8}
409.4	1.465	2.83×10^{-8}	2.63×10^{-8}
400.2	1.485	2.31×10^{-8}	2.09×10^{-8}
379.1	1.533	1.36×10^{-8}	1.22×10^{-8}
357.3	1.586	7.81×10^{-9}	6.55×10^{-9}
297.9	1.751	1.57×10^{-9}	1.29×10^{-9}
260.2	1.875	4.83×10^{-10}	4.18×10^{-10}

⁸ *Modern Electroplating*, edited by F. A. Lowenheim (John Wiley & Sons, Inc., New York, 1963).

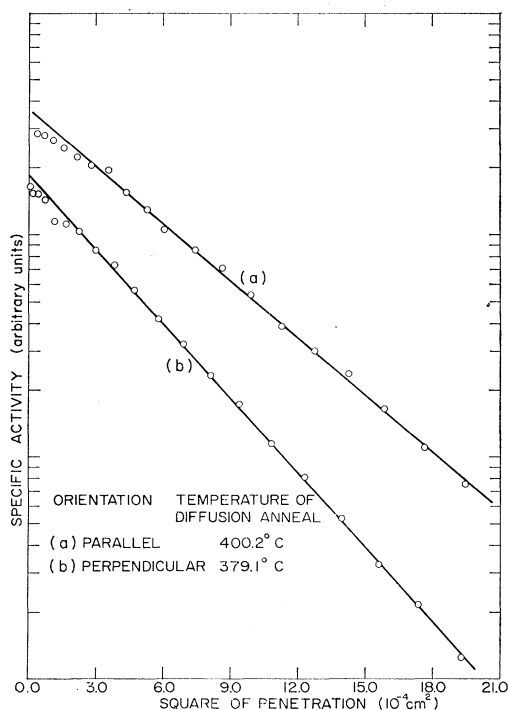


Fig. 1. Sample penetration profiles for Hg^{203} diffusing in zinc.

The temperature dependence of the diffusion coefficients can be expressed as

$$D_{11} = (0.056 \pm 0.002) \exp[-(19700 \pm 48)/RT] \text{ cm}^2/\text{sec},$$

$$D_{\perp} = (0.073 + 0.006) \exp[-(20180 \pm 94)/RT] \text{ cm}^2/\text{sec}.$$

DISCUSSION

Zinc, cadmium, and mercury are all divalent. As Fig. 2 shows, the diffusivity of mercury in zinc is greater than that of zinc itself and has the same sign of anisotropy, that is, D_{11} is greater than D_{\perp} . Compared to the diffusion of cadmium where D_{\perp} is greater than D_{11} , mercury diffuses with both a smaller activation energy (4.1% for parallel diffusion and 1.2% for perpendicular diffusion) and a smaller pre-exponential factor.

It was found that mercury also diffuses in silver⁹ and in copper¹⁰⁻¹² with an activation energy smaller than that of cadmium and zinc, although the effect in copper is less pronounced (3.7% versus 9.0%). It was suggested for the mercury in the silver case⁹ that the low activation energy might result from dislocation diffusion at low temperatures or it might be a valence effect. Though one cannot definitely rule out or accept the view that the

⁹ A. Sawatzky and F. E. Jaumot, Jr., Trans. AIME **209**, 1207 (1957).

¹⁰ C. T. Tomizuka, quoted by D. Lazarus, Solid State Phys. **10**, 117 (1960).

¹¹ T. Hirone, N. Kunitomi, M. Sakamoto, and H. Yamaki, J. Phys. Soc. Japan **13**(8), 838 (1958).

¹² J. Hino, C. T. Tomizuka, and C. Wert, Acta Met. **5**(1), 41 (1957).

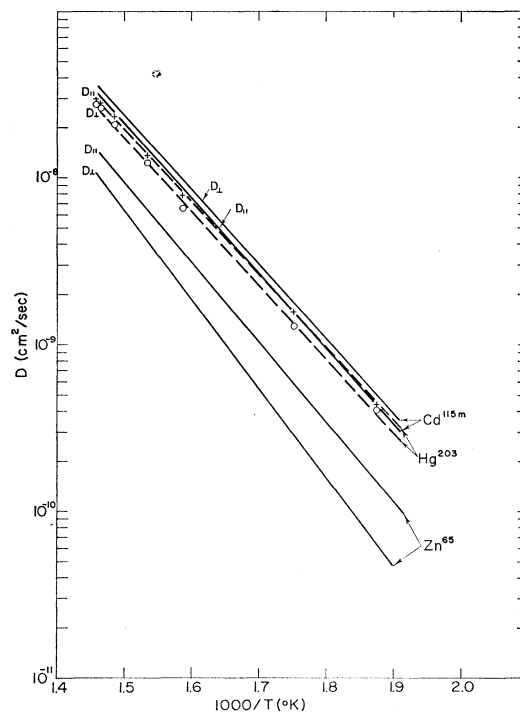


Fig. 2. Temperature dependence of Hg^{203} diffusing in zinc single crystals. Results of self-diffusion and diffusion of Cd^{115m} are shown for comparison.

observed effect arises from the short-circuiting segments in the single crystals,¹³ we are inclined to believe that it results from the valence effect.

The different diffusion rates for solute atoms of the same valence as that of the solvent result from different cores and ion sizes. The contribution of these cores and size effects to the diffusion of elements of valence different from that of the solvent cannot, therefore, be ignored. When an impurity is present substitutionally in a matrix, it has an effective valence which is different from its chemical valence and which is determined by the impurity and the solvent. It is, therefore, quite reasonable to expect different activation energies for diffusion of impurities of the same chemical valence.

An explanation of the relative activation energies of diffusion of mercury and cadmium in zinc can be made if one assumes that the effective positive charge of the mercury ion is slightly greater than that of the cadmium ion, when both are present substitutionally in zinc. LeClaire's theory⁷ of homovalent diffusion predicts the effective charge on mercury and cadmium ions in zinc matrix to be +0.29 and +0.72, respectively. These numbers cannot be taken seriously because of the inherent approximations in the theory and the uncertainties in the Fermi energy for these elements used to calculate the height of the potential barrier at the impurity.

¹³ C. T. Tomizuka, Acta Met. **6**, 660 (1958).

For the more electropositive elements, one expects for the vacancy mechanisms that D_{\perp} will be greater than D_{\parallel} , as for example in cadmium diffusion where D_{\perp} is observed to be greater than D_{\parallel} . However, the opposite is experimentally observed for the diffusion of mercury. Clearly, cadmium and mercury lie close to the condition for isotropic diffusion. From charge considerations alone, it is hard to reconcile the observed anisotropy of the mercury diffusion with its lower activation energy. However, size of the diffusing ion may make an appreciable contribution to the anisotropy. In the diffusion of noble metals (copper, silver, and gold) in zinc, different magnitudes of anisotropy were attributed to a size effect.² Since the c/a ratio for zinc (about 1.86) is greater than that for close packing (about 1.63), the movement of large atoms is probably impeded in the

close-packed basal planes more than in plane-to-plane motion. The influence of this size effect might cause anisotropy with D_{\parallel} greater than D_{\perp} . The ionic radii¹⁴ of cadmium and mercury ions are 0.97 and 1.10 Å, respectively. Since both cadmium and mercury diffusions show very little anisotropy, it is possible that the larger atoms of mercury are responsible for the non-reversal of anisotropy of mercury from that of zinc.

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We wish to express our appreciation and thanks to C. J. Santoro for his help during the measurements.

¹⁴L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals* (Cornell University Press, Ithaca, New York, 1960).

Specific Heat of Sodium from 300 to 475°K

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The specific heat of 99.99% pure sodium has been measured from 300 to 475°K using an adiabatic calorimeter. The melting point of pure sodium is estimated as $371.01 \pm 0.005^{\circ}\text{K}$ and the latent heat as 620.95 ± 0.30 cal/g-at. The specific-heat and melting results are in good agreement with earlier drop-calorimetry results of Ginnings, Douglas, and Ball. If the rapid increase of specific heat in the solid is ascribed to the thermal generation of lattice vacancies, a formation energy of 8.2 ± 1.2 kcal/mole is obtained. A new and simple derivation is given of the basic equation used in Mastrangelo and Dornte's method for analyzing the melting of substances with solid soluble impurities.

INTRODUCTION

THE enthalpy of sodium in the range 0 to 900°C was measured by Ginnings, Douglas, and Ball¹ using a drop calorimeter. These authors derived specific-heat values by differentiating their results and also summarized previous specific-heat and melting measurements on sodium. The present author used the results of Ginnings *et al.* together with other results at lower temperatures² in order to estimate the heat of formation of thermally generated lattice vacancies in sodium.³ The microscopic and macroscopic thermal-expansion coefficients of sodium were measured by Sullivan and Weymouth,⁴ who obtained a heat of formation of lattice vacancies significantly smaller than the specific heat result. Since the results of Ginnings *et al.* for solid sodium were based on very few enthalpy determinations

and since the specific-heat results (obtained by differentiation) might not be very accurate at the extreme end of the range, it seemed desirable to make direct specific-heat measurements on the solid; such measurements are reported in this paper. The results agree well with those of Ginnings *et al.* While this work was in progress, the thermal-expansion experiment was repeated by Feder and Charbnau,⁵ who obtained a heat of formation in agreement with the earlier, and present, specific-heat results.

EXPERIMENTAL

The measurements were made in a continuous-heating adiabatic calorimeter, described elsewhere.⁶ The sample was purchased from Koch-Light (Colnbrook, Bucks, England) and the stated impurities were Ca < 5 ppm, Fe 5 ppm, Mg < 20 ppm, K < 100 ppm. The calorimeter was filled in the manner described.⁶ The weight of the sodium sample was 28.909 g. The estimated accuracy of results⁶ varies from 0.1% at room temperature to 0.2% at 475°K.

¹ D. C. Ginnings, T. B. Douglas, and A. F. Ball, *J. Res. Natl. Bur. Std. (U.S.)* **45**, 23 (1950).

² D. L. Martin, *Proc. Roy. Soc. (London)* **A254**, 433 (1960).

³ D. L. Martin, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1964), p. 255.

⁴ G. A. Sullivan and J. W. Weymouth, *Phys. Rev.* **136**, A1141 (1964).

⁵ R. Feder and H. P. Charbnau, *Bull. Am. Phys. Soc.* **11**, 46 (1966); *Phys. Rev.* **149**, 464 (1966).

⁶ D. L. Martin and R. L. Snowdon, *Can. J. Phys.* **44**, 1449 (1966).