Anisotropic Diffusion of Silver and Indium Tracers in Zinc Single Crystals*

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The sectioning technique was used to measure the anisotropic diffusion of tracers in zinc single crystals. The diffusion of silver-110 was measured over the temperature range from 271° to 413°C. Referring the diffusion constants to the direction of the hexagonal symmetry axis of the zinc crystal structure, the results are:

$$D_{||} = (0.32 \pm 0.02) \exp[-(26.0 \pm 0.1) \times 10^3 / RT] \text{ cm}^2/\text{sec},$$
$$D_{\perp} = (0.45 \pm 0.07) \exp[-(27.6 \pm 0.2) \times 10^3 / RT] \text{ cm}^2/\text{sec}.$$

The diffusion of indium-114 was measured over the range from 171°C to 416°C. The results are:

$$D_{||} = (0.062 \pm 0.008) \exp[-(19.1 \pm 0.1) \times 10^3 / RT] \text{ cm}^2/\text{sec},$$
$$D_{\perp} = (0.14 \pm 0.02) \exp[-(19.6 \pm 0.1) \times 10^3 / RT] \text{ cm}^2/\text{sec}.$$

These show that silver diffuses at a rate about one-tenth that of zinc self-diffusion while the indium diffuses at a rate about ten times as great. Also, $D_{||} > D_{\perp}$ for the silver diffusion as it is for zinc self-diffusion, while for the indium diffusion, $D_{\perp} > D_{||}$. These results are interpreted to indicate a vacancy mechanism of tracer migration with the possibility of a strong tracer-vacancy association occurring in the case of the indium.

INTRODUCTION

A NUMBER of measurements of self-diffusion rate have been reported in noncubic metals where diffusion is anisotropic. Specifically, measurements have been made in zinc,[1] magnesium,[2] cadmium,[3] thallium,[4] and indium.[5] The primary motivation for these experiments has been to demonstrate the mechanism of diffusion by comparing the ratio of independent diffusion constants, i.e., the anisotropy, as determined experimentally, with that calculated theoretically for any one given mechanism. This theoretical anisotropy depends only on lattice geometry and the jump direction. Except in the case of zinc, the experiments have generally been inconclusive. The theoretical and experimental anisotropies do not agree. Even by assuming that different pairs of several kinds of atomic jumps are occurring and trying to fit the data generally leads to more than one possible combination. In the case of the self-diffusion in zinc, however, the data indicate quite clearly that a vacancy mechanism is operating with vacancy jumps occurring to nearest neighbors in the basal plane and from plane to plane.

Numerous workers have been investigating the effect of the valence of an impurity atom on its diffusion rate in single crystals of the monovalent, cubic metals copper and silver.[6-10] Lazarus has proposed a theory based on a vacancy mechanism which fits the data reasonably well.[11] It appeared that zinc would be a good noncubic metal in which to do analogous experiments. Lazarus' calculations for the cubic, monovalent metals are not applicable to divalent, hexagonal zinc, but the qualitative aspects of the theory's predictions should be fulfilled. These are, generally, that impurities of greater valence than that of the host matrix should diffuse at a faster rate and those of smaller valence at a slower rate than that of self-diffusion if a vacancy mechanism is operating. This effect is caused by an attraction that a screened impurity atom of greater valence has for a vacancy while impurities of smaller valence tend to repel vacancies.

A further incentive for making impurity diffusion measurements in an anisotropic metal is that a series of these, using tracers of the same valence but different atomic size, may shed more light on the effect of tracer size on the diffusion constant. Measurements of this kind made on cubic metals[9,12] have shown very little change in diffusion constant and practically no change in diffusion activation energy for the various tracers of the same valence. This is rather surprising when one considers the localized strain that must develop in the structure around a wrong-sized impurity atom.

THEORY

In the absence of electric or magnetic fields, the driving force for the diffusion of a component of a solid is the gradient of its chemical potential. For an ideal solution or for very low concentrations, the chemical potential gradient is proportional to the concentration gradient. Thus for isothermal diffusion under these con-

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[10] C. A. Mackliet, Phys. Rev. 109, 1964 (1958).
[11] D. Lazarus, Phys. Rev. 93, 973 (1954).
[12] T. Hirone, N. Kunitoni, M. Sakamoto, and H. Yamaki, J. Phys. Soc. Japan 13, 838 (1958).

ditions we may write Fick's first law:

$$\mathbf{J} = -\mathbf{D} \cdot \text{grad} C, \tag{1}$$

where: $\mathbf{J}$ = flux of diffusing particles per unit area, $\mathbf{D}$ = diffusion tensor, and C = concentration per unit volume of the diffusing species. If one refers $\mathbf{D}$ to its principal axes, assumes it is independent of the concentration and then invokes the continuity condition on the particle flux, one arrives at the diffusion equation:

$$\frac{\partial C}{\partial t} = D_{xx}\frac{\partial^2 C}{\partial x^2} + D_{yy}\frac{\partial^2 C}{\partial y^2} + D_{zz}\frac{\partial^2 C}{\partial z^2}, \tag{2}$$

where the D's are the principal values of the diffusion tensor. In the experimental situation of this experiment, a flat surface is prepared normal to the axis of a cylindrical crystal. This surface is plated with the radio-tracer which is then allowed to diffuse into the sample. Under these circumstances, the appropriate solution to Eq. (2) is[13]

$$C(x,t) = \frac{C_0}{(\pi D t)^{\frac{1}{2}}} \exp\left(-\frac{x^2}{4Dt}\right), \tag{3}$$

where C_0 = initial surface concentration of activity, t = time of diffusion, x = distance from the originally plated surface, and D = diffusion constant appropriate to the direction of diffusion. Experimentally, the diffusion constant in any direction is almost invariably observed to behave with temperature as

$$D = D_0 \exp-(Q/RT), \tag{4}$$

where D_0 = a constant, Q = activation energy, R = gas constant, and T = absolute temperature.

In terms of the independent elements of the diffusion tensor,[14]

$$D = D_{xx}\gamma_x^2 + D_{yy}\gamma_y^2 + D_{zz}\gamma_z^2, \tag{5}$$

where the γ's are the direction cosines between the direction of diffusion and the principal axes of the diffusion tensor. If the crystal has a symmetry axis threefold or higher, the diffusion perpendicular to this axis is isotropic and, relative to this axis, Eq. (5) may be written:

$$D = D_{\shortparallel}\cos^2\theta + D_{\perp}\sin^2\theta, \tag{6}$$

where θ is the angle between the diffusion direction and the symmetry axis.

The contribution that any atomic jump in a lattice makes to $D_{\shortparallel}$ and $D_{\perp}$ may be calculated from random walk theory. Ignoring the correlation terms, the results

are[1,15]

$$D_{\shortparallel} = \frac{1}{2}\sum_{\beta=1}^{\alpha}\Gamma_\beta\xi_\beta^2\langle\cos^2\theta_\beta\rangle_{\text{av}}, \tag{7}$$

$$D_{\perp} = \frac{1}{4}\sum_{\beta=1}^{\alpha}\Gamma_\beta\xi_\beta^2\langle\sin^2\theta_\beta\rangle_{\text{av}}, \tag{8}$$

where α = number of different jump lengths possible, ξ_β = jump length, Γ_β = probability per unit time that a jump of length ξ_β occurs, and θ_β = angle between the symmetry axis and the direction of a jump of length ξ_β. According to Wert and Zener,[16] Γ_β is given by

$$\Gamma_\beta = \nu_\beta \exp(-\Delta G_\beta/kT), \tag{9}$$

where ν_β = vibration frequency of an atom in a direction leading across a saddle point of energy to a new equilibrium site and ΔG_β = isothermal work done on slowly moving a plane from the equilibrium to the saddle position assuming that the diffusing atom vibrates only in this plane. For any one kind of atomic jump, the ratio of Eqs. (7) and (8) is independent of Γ_β and hence may be calculated from geometrical factors alone. If the data are not fitted in this way, one may assume that two types of atomic jumps are occurring and put the experimental results into the equations to evaluate ν_β and ΔG_β for the two types.

The types of possible jump mechanisms usually considered are:

1. The vacancy mechanism wherein an atom and an adjacent vacancy exchange places.

2. The interstitial mechanism wherein an atom moves about among the normally unoccupied sites of the structure.

3. The ring mechanism which is a coordinated motion of two or more atoms such that each exchanges places with an adjacent atom. This motion effects a net displacement of any one atom but no mass transfer.

Reference 1 may be consulted for the details of applying these ideas to calculations of diffusion in zinc.

EXPERIMENTAL PROCEDURE

Single crystals of 99.999+% pure zinc, about 5 in. long and 0.5 in. in diameter were grown in evacuated Pyrex tubes by the Bridgman technique. The zinc was purchased from the New Jersey Zinc Company. Those crystals having hexagonal axis within about 20° of being parallel or perpendicular to the specimen axis were retained for further processing. These were cut into samples about 1 cm long with a string-saw, using concentrated nitric acid as a cutting agent.

One end of the sample was faced off in a lathe and all cold-worked material removed by polishing and etching. When an x-ray reflection photograph showed the surface to be strain free, the sample was annealed

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[14] J. F. Nye, *The Physical Properties of Crystals* (Clarendon Press, Oxford, 1957).

[15] A. D. LeClair and A. B. Lidiard, Phil. Mag. **1**, 518 (1956).

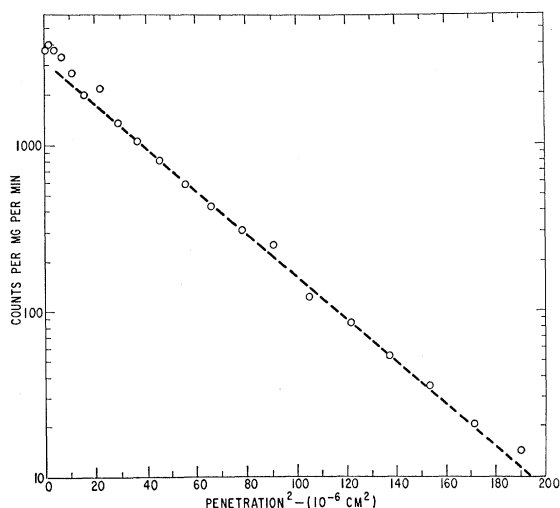[16] C. A. Wert and C. Zener, Phys. Rev. **76**, 1189 (1949).

FIG. 1. Sample penetration plot for Ag[110] diffusing at 82° to hexagonal axis of zinc crystal. Temperature was 320.8°C. Time of diffusion was 2.706×10^5 sec.

in vacuum for 24 hr at about 85% of the melting temperature. The samples were examined for grain growth, and if satisfactory, were repolished. Surfaces so prepared were accurately flat to better than 0.0001 in. The crystallographic direction perpendicular to the prepared surface was determined by x-ray reflection.

After protecting the sides of the sample with an acetone soluble paint, the prepared surface was chemically plated with one of the radioactive tracers, silver-110 or indium-114. The plating was done simply by dipping the sample into a solution containing the radioactive ions. In the case of silver-110, this was a standard commercial silver-cyanide electroplating solution. For the indium-114 a solution of indium trichloride in distilled water was found to be satisfactory. The indium and silver films used were typically of the order of 0.5μ thick.

In the indium case it was found that plating had to be done quickly from a solution rich in indium ions, or the resulting plate would not diffuse into the bulk. We assume that this is due to the thin indium film undergoing a reaction to form a stable compound which effectively ties it down to the surface. The nature of this reaction is not known, nor do we know whether it occurs in the plating bath or in the glass capsule at the start of the diffusion anneal.

After being cleaned of paint, pairs of samples, placed so that their plated surfaces faced each other across a Pyrex disk spacer, were sealed off under vacuum in Pyrex capsules. One of these samples was of an orientation such that diffusion occurred nearly parallel to the hexagonal axis, and in the other, the diffusion occurred nearly perpendicular to the hexagonal axis. The diffusion anneal was performed in furnaces whose temperature was controlled to ± 0.2°C over long periods of time.

After removal from the furnace, the samples were

mounted in a lathe, and the sides were ground away with abrasive paper to eliminate the effect of side diffusion. The sample was sectioned by turning off thin layers of material parallel to the originally plated surface. These turnings were put into small plastic-coated stainless steel cups, weighed, and then dissolved in 50% HCl. The resulting solution was spread over the bottom of the cup and dried. The beta activity of the resulting layer of crystals was measured with a thin end-window Geiger tube and a standard scaling circuit and counter.

The specific activity of each section was assumed to be that at the center. The thickness of the sections was calculated, using the area of the sample face, the density of zinc, and the mass of the section. After correcting the activities for counter dead time, the logarithm of each was plotted against the square of the penetration distance at which it occurred. Figures 1 and 2 show sample penetration plots. Equation (3) shows how the slope of the line through this data is related to the diffusion constant and the time of diffusion.

The diffusion constants measured for differently oriented samples diffused at the same temperature was used with Eq. (6) to calculate D_{II} and $D_{\perp}$ at that temperature. The logarithms of these diffusion constants are plotted as a function of the reciprocal temperature in Fig. 3. A plot of the self-diffusion results of Shirn, Wajda, and Huntington[1] are included in the same figure for comparison.

The diffusion constants plotted in Fig. 3 have been corrected for the fact that the time the samples spent in the furnace is not the same as the time at the diffusion temperature due to heat-up time. Corrections were also made for the fact that the sections taken were generally not exactly parallel to the originally plated surface and also for the fact that the calculated specific activity is not that which occurs at the center of a section because of the finite thickness of the section.

The uncertainty in an individual diffusion-constant measurement is due to many causes. In this experiment, the most important sources of error are, in order of increasing importance, (1) the uncertainty in the thickness
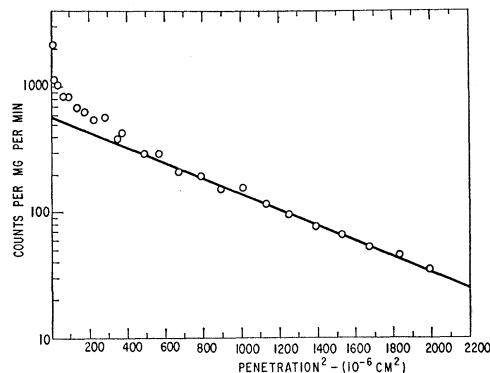

FIG. 2. Sample penetration plot for In[114] diffusing at 72.5° to hexagonal axis of zinc crystal. Temperature was 352.0°C. Time of diffusion was 9.420×10^3 sec.
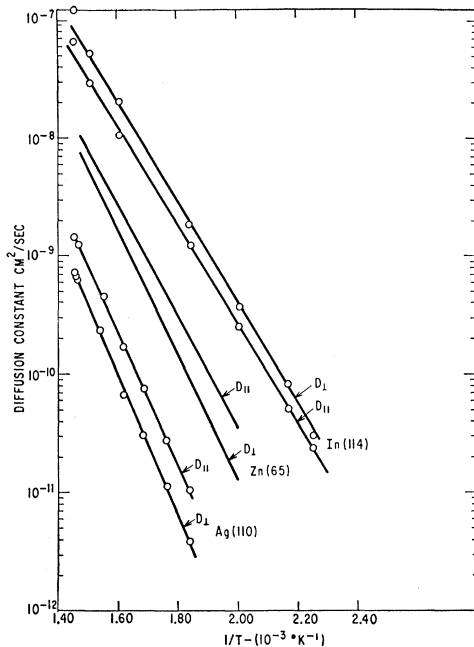
FIG. 3. Diffusion constant versus reciprocal temperature for Ag[110] and In[114] tracers diffusing parallel and perpendicular to the hexagonal axis in zinc single crystals. Self-diffusion results of Shirn et al. shown for comparison.

of the first section, (2) uncertainty in the area of the sample face, and (3) the small amount of arbitrariness in the choice of a straight line to represent the penetration data. All errors being considered, the uncertainty in a diffusion constant measured for silver-110 is about $\pm 8\%$ and for indium-114 about $\pm 13\%$. The larger error in the indium case is due to somewhat more scatter in the penetration data plus the incidence of anomalously high activities in the first few sections which made the choice of a straight line to fit the data more uncertain than for the silver data.

RESULTS

Using a least-squares technique to fit the data shown in Fig. 3 to Eq. (4) yields the results shown in Table I. The self-diffusion results of Shirn et al. are included for comparison. The probable errors indicated are calculated from the scatter of the data about the least-square lines. The D_0 values given include a small correction for lattice expansion at the diffusion temperature.

The high-temperature (416.4°C) points for the indium diffusion were not included in the least-squares analysis because their anomalously high value would have a disproportionately large effect on the results. The data for these points are very good and lead us to conclude that the effect is real, although more evidence for this high-temperature diffusion enhancement is necessary.

The change in the ratio of D_{11} to $D_{\perp}$ on going from the higher to the lower temperature investigated is: (1) from 2.3 to 3.1 for silver, (2) from 1.2 to 2.5 for zinc

self-diffusion, (3) from 0.63 to 0.77 for indium. The fact that the ratio is temperature dependent implies that more than one kind of atomic jump must be occurring. If this were not so, the activation energies for diffusion in both directions would be equal.

DISCUSSION OF RESULTS

Figure 3 clearly shows that the diffusion rate of the smaller valence impurity, silver, is less than the self-diffusion rate, while that of the impurity of greater valence, indium, is greater. These facts are in agreement with the predictions of Lazarus' model; hence they strongly imply that these impurities are diffusing by a vacancy mechanism.

Calculations were made to fit the data to vacancy and ring mechanisms. This was done by assuming that the measured diffusion constant in a given direction is due to contributions from two kinds of atom jumps each with its own characteristic D_0 and Q. Hence:

$$D_{11}(T) = {}_{11}D_{01} \exp(-Q_1/RT)$$
$$+ {}_{11}D_{02} \exp(-Q_2/RT), \quad (10)$$

$$D_{\perp}(T) = {}_{\perp}D_{01} \exp(-Q_1/RT)$$
$$+ {}_{\perp}D_{02} \exp(-Q_2/RT), \quad (11)$$

where the subscripts 1 and 2 refer to the type of jump. Now since for a given kind of jump one can calculate the quantity,

$$({}_{11}D_0/{}_{\perp}D_0)_{1 \text{ or } 2}, \quad (12)$$

by using Eqs. (7) and (8), then one can simplify Eqs. (10) and (11) to the forms:

$$D_{11}(T) = {}_{11}D_{01} \exp(-Q_1/RT)$$
$$+ {}_{\perp}D_{02}({}_{11}D_0/{}_{\perp}D_0)_2 \exp(-Q_2/RT), \quad (13)$$

$$D_{\perp}(T) = {}_{11}D_{01}({}_{\perp}D_0/{}_{11}D_0)_1 \exp(-Q_1/RT)$$
$$+ {}_{\perp}D_{02} \exp(-Q_2/RT). \quad (14)$$

The criteria for a good fit are that not only must the calculated values of the D_0's and Q's reproduce the measured curve within the experimental error, but also, following the ideas of Zener[17] and general observations about good diffusion data, the calculated values of D_0 must be roughly of the order of unity.

The silver data could be fitted by assuming that a

TABLE I. Frequency factors and activation energies for tracer diffusion in zinc single crystals.

Isotope	Diffusion direction	D_0 (cm²/sec)	Q (cal/mole)
Ag[110]	$\parallel$	0.32 ± 0.02	$(26.0 \pm 0.1) \times 10^3$
Ag[110]	$\perp$	0.45 ± 0.07	$(27.6 \pm 0.2) \times 10^3$
In[114]	$\parallel$	0.062 ± 0.008	$(19.1 \pm 0.1) \times 10^3$
In[114]	$\perp$	0.14 ± 0.2	$(19.6 \pm 0.1) \times 10^3$
Zn[65]	$\parallel$	0.1	$(21.8 \pm 0.2) \times 10^3$
Zn[65]	$\perp$	0.5	$(24.3 \pm 0.5) \times 10^3$

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

vacancy jumped either to a nearest neighbor in the basal plane or to a nearest neighbor in an adjacent basal plane. It was attempted to fit the data to ring mechanisms involving three atoms in two combinations, all three in one basal plane and two on one plane and the third on an adjacent plane. The results indicate a negative D_0 for one of these, which is, of course, impossible.

The indium data could be fitted by either the vacancy or ring mechanisms of the type described as being used in the silver calculations. This inability to discriminate between mechanisms is due to the small difference in activation energy for indium diffusion in the two directions. In this case, however, one may infer that a vacancy mechanism is operating from the fact that $D_\perp > D_{||}$ for indium, while $D_{||} > D_\perp$ for silver and zinc diffusion. The argument is as follows.

A vacancy in the zinc structure looks like a screened negative charge and so should be repelled from impurity atoms whose valence is less than that of zinc, since these also look like screened negative charges. A vacancy should be attracted to impurity atoms of valence greater than that of zinc, since these look like screened positive charges. For the silver diffusion, the repulsion between a vacancy and a silver atom would make the next-nearest-neighbor position to the preferred one for the vacancy with respect to the silver atom. This position puts the vacancy on the basal plane adjacent to the one occupied by the silver atom; hence silver jumps with a large component parallel to the hexagonal axis would become more probable than those perpendicular to it. One would then expect that aside from the change in the magnitude of the diffusion constant of silver due to valence effects, the ratio of $D_{||}$ to $D_\perp$ at a given temperature should be greater than is the case for zinc self-diffusion. This is what we observe.

For the case of an atom like indium, however, the attraction between it and a vacancy would make the preferred position of the vacancy the nearest neighbor position on the same basal plane as the indium atom. This should result in a reduction of the ratio of $D_{||}$ to $D_\perp$ from that found for zinc self-diffusion. This is indeed what has been measured. The reduction has in fact been so great that $D_\perp$ has become larger than $D_{||}$. This fact, together with the very large increase of the diffusion constant of indium over the self-diffusion constant, implies that the indium atom-vacancy attraction is a strong one. The two may be associated for long periods of time and so diffuse through the zinc structure as a unit.

CONCLUSIONS

We conclude that the diffusion of indium and silver in single crystals of zinc occurs by a vacancy mechanism involving atom jumps to nearest-neighbor positions in the basal plane and to next-nearest-neighbor positions on adjacent basal planes. In the case of indium, there is a good possibility that the indium atom and vacancy are strongly associated and tend to diffuse through the structure as a unit. The most frequent orientation of this unit is the one where both members lie on the same basal plane. The qualitative predictions of Lazarus' theory for the effect that the valence of an impurity has on its diffusion rate are fulfilled for diffusion in the anisotropic, divalent zinc matrix.