follows that the theory developed by Aronov[4] is correct only as far as the relations (43) and (44) are fulfilled.

In conclusion we would like to mention that in the measurements of the optical absorption in Ge in crossed fields by Vrehen and Lax[5,6] the light-hole–electron transitions can be described by the effective-mass approximation. Indeed, for $E\sim 5\times 10^4$ V/cm, $\mathcal{H}\sim 10^5$ G, $a\sim 5\times 10^{-8}$ cm, $m^*\sim 0.04m_0$, we have $eEa/\hbar\omega_c^*\sim 0.1$. Heavy holes having the effective mass approximately 10 times larger than that of the light holes, cannot be described by EMA under the above experimental conditions.

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Diffusion of Copper and Gallium in Single Crystals of Zinc*

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The sectioning technique was used to study the diffusion of radioactive tracers in high-purity zinc single crystals. Diffusion both parallel and perpendicular to the hexagonal axis was measured. The diffusion of Cu^{64} was measured over the temperature range from about 338°C to 415°C with the results

$$D_{\parallel}=(2.22\pm 0.57)\exp[-(29.53\pm 0.29)\times 10^3/RT]\ \mathrm{cm}^2/\mathrm{sec},$$
$$D_{\perp}=(2.00\pm 0.54)\exp[-(29.92\pm 0.30)\times 10^3/RT]\ \mathrm{cm}^2/\mathrm{sec}.$$

The diffusion of Ga^{72} was measured over the range from about 240°C to 403°C with the results

$$D_{\parallel}=(0.016\pm 0.001)\exp[-(18.40\pm 0.06)\times 10^3/RT]\ \mathrm{cm}^2/\mathrm{sec},$$
$$D_{\perp}=(0.018\pm 0.001)\exp[-(18.15\pm 0.08)\times 10^3/RT]\ \mathrm{cm}^2/\mathrm{sec}.$$

Copper diffused at a rate faster than gold but slower than silver. As in silver and gold, $D_{\parallel}>D_{\perp}$; but the anisotropy was much smaller in Cu than in Ag or Au. The measured values of gallium fall somewhat below those for indium and show $D_{\perp}>D_{\parallel}$. The relative diffusion rates are qualitatively in accord with the predictions of LeClaire's theory of homovalent diffusion. The sign of anisotropy is explained in terms of the electrostatic interaction between the diffusing ion and the vacancy, and the reduced anisotropy of copper diffusion is interpreted as evidence of a size effect.

INTRODUCTION

In the last few decades much effort has been expended in the study of impurity diffusion in order to develop a better understanding of the diffusion mechanisms. Considerable work has been reported in literature on impurity diffusion in cubic metals, particularly the noble metals, and the over-all pattern seems to be well understood on the basis of the screened interaction model proposed by Lazarus[1] and later modified by LeClaire.[2] There has been less information available on diffusion in anisotropic crystals which possess more than one rate of diffusion in the same lattice structure.

Experimental data on self-diffusion[3] and on the diffusion of indium, silver,[4] cadmium, and gold[5] impurities in noncubic divalent zinc single crystals are available. The general trend of the activation energies with the valence of the diffusing atom was found to be in qualitative accord with Lazarus' theory.

Following the approach of Lazarus, Ghate[6] developed the screened interaction model for impurity diffusion in zinc and calculated the difference ΔQ in the activation energies for impurity diffusion and self-diffusion. He considered the diffusion of both trivalent and monovalent impurities, parallel and perpendicular to the hexagonal axis. The results of this calculation check fairly well in the case of indium and gold but a considerable discrepancy exists for silver. The lack of quantitative agreement is probably due to the fact that the theory does not take into account the differences in the electronic constitution of the inner core of the diffusing and the host ions and their relative sizes. These factors do contribute to the diffusion parameters as is evident from the results of diffusion of homovalent

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* This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-1044.

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[2] A. D. LeClaire, Phil. Mag. **7**, 141 (1962).

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impurities. It was found, for example, that cadmium tracer diffuses faster than zinc tracer in zinc.[5]

In order to explain the diffusion of homovalent impurities, LeClaire[7] extended his model. He attributed ΔQ directly to the differences in core potential of solvent and solute. In this simple treatment, the impurity is represented by a square well of depth U equal to the difference between the electron ground state energies of solvent and solute atoms. It is shown that this energy, for monovalent metals, can be written as

$$E^0 = -(H+\bar{F}+\mathrm{I}_1), \tag{1}$$

and for divalent metals, it is replaced by

$$E^0 = -\tfrac{1}{2}(H+2\bar{F}+\mathrm{I}_1+\mathrm{I}_2). \tag{2}$$

where H is the heat of sublimation, $\bar{F}$ is the mean Fermi energy per electron, and I_1 and I_2 are the first- and second-ionization potentials, respectively. Thus

$$U = E_A{}^0 - E_B{}^0, \tag{3}$$

where subscripts A and B refer to the solvent and the solute atoms, respectively.

A negative U implies a potential hump at the impurity which repels the electrons and thereby acquires a positive charge. Since the vacancy carries an effective negative charge, there will be an electrostatic attraction between the impurity and the vacancy resulting in a faster rate of diffusion. A positive U leads to slower diffusion.

LeClaire has calculated ΔQ for impurity diffusion of noble metals into one another and the results are in remarkable agreement with the experimental measurements.

The diffusivities in zinc of the tracers, copper and gallium, are reported here. The addition of the copper data to previously published results on silver and gold completes the diffusion data for elements of the I*B* subgroup and the work on gallium helps confirm the general behavior expected of III*B* elements diffusing in zinc.

EXPERIMENTAL

Cylindrical single crystals, about $\frac{1}{2}$-in. in diameter, were grown by the Bridgman furnace technique from 99.999% pure zinc supplied by the American Smelting and Refining Company. Only those crystals which had their cylindrical axes closely parallel or perpendicular to the hexagonal axis were retained for the experimental work. Specimens were then prepared in a manner similar to that outlined by Rosolowski.[4]

The Cu^{64} and Ga^{72} radioisotopes were obtained from the Oak Ridge National Laboratory. The appropriate tracer was electroplated on the well-annealed samples; a cyanide bath was used for copper plating whereas for gallium plating, an alkaline solution was used.[8] The thickness of the plated layer was estimated to be less than 1000 Å.

For each diffusion anneal, two samples (one of parallel and the other of perpendicular orientation) were vacuum-sealed in a Pyrex capsule. The samples were so placed that their active faces were separated by a thin Pyrex disk. The temperature during the course of the diffusion anneal was controlled automatically to within ±0.2°C and was measured by a chromel alumel thermocouple which was calibrated against a U. S. National Bureau of Standards standardized platinum platinum-rhodium thermocouple. For high temperature runs with gallium, it was found necessary to make warm-up time corrections to determine the effective diffusion time.[9]

After a diffusion run the specimens were mounted on a precision lathe and reduced in diameter by about 40 mils to eliminate the effects of the tracer atoms which had diffused along its lateral surface. About 15 to 20 sections were then turned off from every sample. The chips from each section were collected on a stainless steel planchet and weighed on a Mettler balance with a precision of 0.02 mg.

The beta activity of each section was counted with a thin end-window Geiger counter and a RIDL scaler. The counting data were corrected for the counter dead time, background, and also for the decay of the activity during the course of counting. This last correction was necessary since both the isotopes have short half-lives (Cu^{64}: 12.8 h, and Ga^{72}: 14.2 h).

RESULTS

Zinc has a hexagonal structure. The diffusion coefficient $D(\theta)$ in a direction making an angle θ with the hexagonal axis can be written as

$$D(\theta) = D_{\parallel}\cos^2\theta + D_{\perp}\sin^2\theta, \tag{4}$$

where $D_{\parallel}$ and $D_{\perp}$ refer to the diffusion coefficients parallel and perpendicular to the hexagonal axis of the lattice, respectively. Thus knowledge of $D(\theta)$ in two different directions enables us to calculate both $D_{\parallel}$ and $D_{\perp}$.

Under the experimental conditions, the concentration c of tracer atoms at a perpendicular distance x from the active layer is given by[10]

$$c = [c_0/(\pi Dt)^{1/2}]\exp(-x^2/4Dt), \tag{5}$$

where t is the time during which the diffusion took place, D the diffusion coefficient, and c_0 the concentration of the tracer originally present in the radioactive layer.

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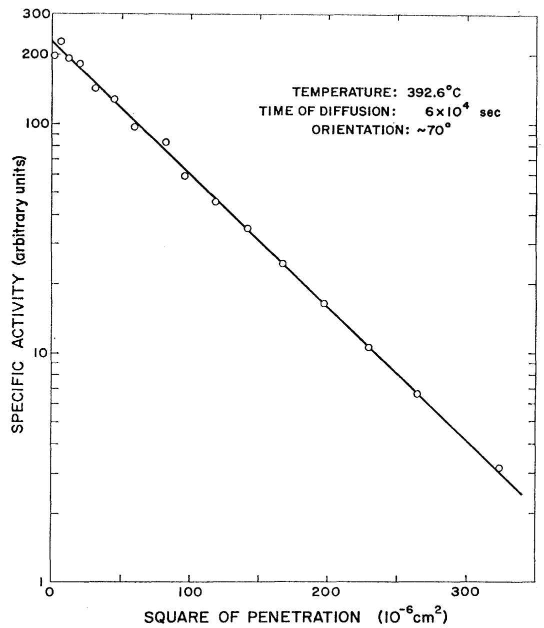

FIG. 1. Sample penetration curve for diffusion of Cu^{64} in zinc.

$D(\theta,T)$ can thus be calculated from the slope of the linear plot of $\ln c$ versus x^2. Typical penetration plots are shown in Figs. 1 and 2. Diffusion coefficients were calculated from such plots and are given in Tables I and II for copper and gallium, respectively, together with the annealing temperatures. Figure 3, which also includes the results of the earlier investigations on self-diffusion and diffusion of indium, silver, and gold tracers, shows the logarithm of the diffusion coefficient plotted as a function of the reciprocal temperature.

TABLE I. Diffusion of Cu^{64} in zinc.

Temperature (°C)	$1000/T$ (°K)$^{-1}$	$D_{\parallel}$ (cm^2/sec)	$D_{\perp}$ (cm^2/sec)
415.1	1.453	9.05×10^{-10}	6.73×10^{-10}
408.0	1.468	7.75×10^{-10}	...
405.7	1.473	...	4.33×10^{-10}
392.6	1.502	4.19×10^{-10}	2.96×10^{-10}
383.4	1.523	3.58×10^{-10}	2.23×10^{-10}
371.2	1.552	2.26×10^{-10}	1.26×10^{-10}
361.7	1.575	1.36×10^{-10}	9.29×10^{-11}
347.6	1.611	9.68×10^{-11}	5.53×10^{-11}
337.7	1.637	5.61×10^{-11}	4.49×10^{-11}

TABLE II. Diffusion of Ga^{72} in zinc.

Temperature (°C)	$1000/T$ (°K)$^{-1}$	$D_{\parallel}$ (cm^2/sec)	$D_{\perp}$ (cm^2/sec)
403.0	1.479	1.89×10^{-8}	2.69×10^{-8}
381.3	1.528	1.26×10^{-8}	...
377.9	1.536	9.30×10^{-9}	...
353.4	1.596	6.20×10^{-9}	7.85×10^{-9}
316.1	1.697	2.33×10^{-9}	3.11×10^{-9}
297.3	1.753	1.40×10^{-9}	1.92×10^{-9}
287.0	1.785	1.04×10^{-9}	1.45×10^{-9}
268.5	1.846	5.94×10^{-10}	9.15×10^{-10}
257.6	1.884	4.49×10^{-10}	6.37×10^{-10}
239.6	1.950	2.30×10^{-10}	3.29×10^{-10}

TABLE III. Arrhenius parameters for diffusion of Cu^{64} and Ga^{72} in zinc single crystals.

Isotope	Diffusion direction	D_0 (cm^2/sec)	Q (kcal/mole)
Cu^{64}	$\parallel$	2.22 ± 0.57	29.53 ± 0.29
Cu^{64}	$\perp$	2.00 ± 0.54	29.92 ± 0.30
Ga^{72}	$\parallel$	0.016 ± 0.001	18.40 ± 0.06
Ga^{72}	$\perp$	0.018 ± 0.001	18.15 ± 0.08

The error in D due to sectioning, counting, and drawing the best straight line through the experimental points in the penetration profiles is estimated to be ±5%. The temperature of the anneal could be specified to within ±0.4°C which leads to the total uncertainty of ±6.5% in the measurement of $D(T)$.

The temperature dependence of the diffusion coefficient D generally follows an Arrhenius-type relation

$$D=D_0\exp(-Q/RT)\,, \qquad (6)$$

where D_0 is the frequency factor, Q the activation energy, R the gas constant, and T the absolute temperature. The diffusion parameters D_0 and Q for copper and gallium were calculated by the best least-squares fit to the data. These are listed in Table III.

DISCUSSION

Figure 3 shows that the diffusivity of copper in zinc lies between that of gold and silver but with much smaller anisotropy than either. The copper tracer diffuses faster than the gold tracer and slower than the silver tracer.

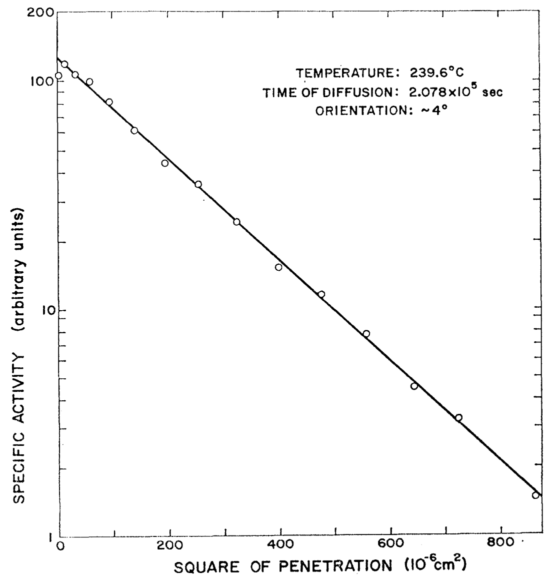

FIG. 2. Sample penetration curve for diffusion of Ga^{72} in zinc.

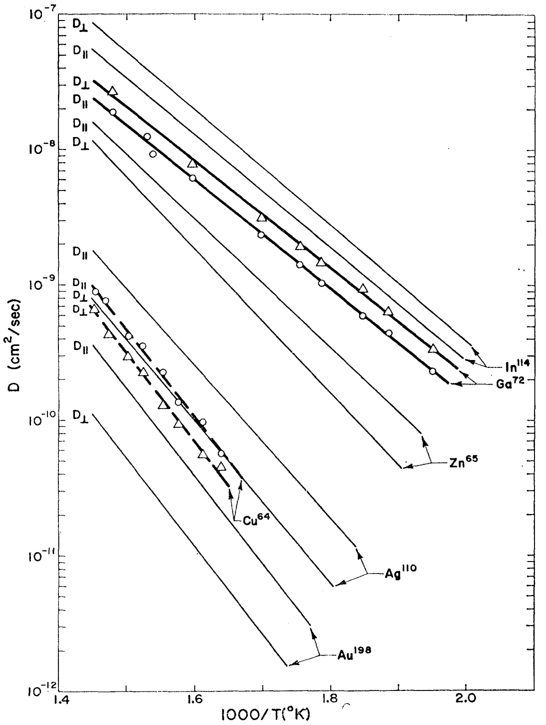

FIG. 3. Temperature dependence of Cu^{64} and Ga^{72} diffusion in zinc single crystals. Results of self-diffusion and diffusion of Ag^{110}, In^{114}, and Au^{198} are shown for comparison.

We note that the results for these elements, which are in the same column of the periodic table, behave qualitatively as predicted by LeClaire's theory. Using Eq. (1), he calculated the electron ground state energies for silver, copper and gold atoms[7] and found them to be -13.74, -15.46, and -16.23 eV, respectively. With these estimates, he was able to explain successfully the experimentally observed diffusion of these elements into one another. Therefore, when these impurities are dissolved substitutionally in the zinc matrix, it is reasonable to believe that the excess charge of the impurity ion within its cell increases from gold to copper to silver ($-1 \leqslant Z_{\mathrm{Au}} < Z_{\mathrm{Cu}} < Z_{\mathrm{Ag}} < 0$). This increase can be attributed to the different core potentials and can be qualitatively understood as follows.

Valence considerations alone lead to the conclusion that a noble-metal ion in zinc behaves like a screened negative charge, but the effect of the core should also be taken into account. The impurity can therefore be represented by a potential well whose depth is determined not only by the valence but also by the core potential. A decrease in the electron ground-state energy implies an increase in the depth of the potential well. Thus more electrons are attracted to the ion and its effective charge is more negative. This will result in lower diffusivity, if one assumes that the diffusion is taking place via the vacancy mechanism. Looking at the values of the ground-state energies for these elements, one therefore concludes that our results agree qualitatively with the theoretical predictions.

Both gallium and indium differ in valence by $+1$ from the zinc matrix. The measured values for gallium diffusion fall somewhat below those for indium. Therefore, one would expect the excess charge on the gallium ion to be less than that of the indium ion when both are present substitutionally in zinc ($0 < Z_{\mathrm{Ga}} < Z_{\mathrm{In}} \leqslant 1$).

The electron ground-state energies for gallium and indium are about -30.3 and -26.9 eV, respectively. In calculating these energies, we have ignored the contributions of the exchange, correlation and Coulomb energies, but as pointed out by LeClaire,[7] these corrections should be nearly the same for metals of the same valence. According to these estimates, the diffusion of gallium in indium should be less than self-diffusion. It is, therefore, not unreasonable to expect the diffusivity of gallium to be less than that of indium in zinc.

The Arrhenius plots, for both copper and gallium, of $D_{\parallel}$ and $D_{\perp}$ versus $1/T$ are almost parallel to each other in their respective temperature range. The anisotropy, namely $D_{\parallel}/D_{\perp}$, for copper diffusion is about 1.5 and should be compared with the reported values of approximately 2.7 ± 0.4 for silver and 3.3 ± 0.3 for gold. The anisotropy of gallium is about 0.72 ± 0.02 as compared to the corresponding value of 0.70 ± 0.07 for indium diffusion.

The sign of the anisotropy is consistent throughout with the vacancy mechanism. In case of the monovalent impurities (copper, silver and gold) in zinc, there is an electrostatic repulsion between the impurity ion and the vacancy. They, therefore, prefer to stay as neighbors in the adjacent basal planes rather than the same basal plane and there is a greater impurity-vacancy exchange rate along the hexagonal axis. This explains in general, even more strongly than for the self-diffusion of zinc, why $D_{\parallel}$ is greater than $D_{\perp}$. In case of the trivalent impurities (gallium and indium) in zinc, we observe higher diffusivity in a direction perpendicular to the hexagonal axis. This can similarly be explained in terms of the electrostatic attraction between the impurity ion, which behaves as a screened positive charge, and the vacancy.

The observed anisotropy of copper diffusion is appreciably smaller than that of silver and gold diffusion. We are inclined to interpret this fact as an evidence of the size effect. Copper, silver, and gold are all face-centered cubic metals with almost similar chemical properties, but they differ in their atomic or ionic sizes; the ionic radii[11] are, respectively, 0.96, 1.26, and 1.37 Å. Motion in the close-packed basal planes of the largest atoms of the noble metals, namely, gold atoms, is impeded more than the motion parallel to the hexagonal axis. Thus the anisotropy is greater than for

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

smaller atoms, namely, silver and copper atoms, which are able to move with relative ease in the basal planes.

If only nonbasal jumps were to contribute to the perpendicular diffusion of noble elements, one would expect the anisotropy to be $\cong 5.2$ for zinc.[6] From the observed values of anisotropy, one concludes that both types of atomic jumps, basal and nonbasal, are responsible for perpendicular diffusion.

We compare below the experimental values of the differences in the activation energies (ΔQ) for self-diffusion and for diffusion of copper and gallium in zinc with the theoretical predictions[6] based on the simple screened interaction model.

For copper:

$$
\begin{aligned}
(\Delta Q_{\parallel})_{\text{expt}} &= 7.73 \text{ kcal/mole},\\
(\Delta Q_{\parallel})_{\text{theory}} &= 8.48 \text{ kcal/mole},\\
(Q_{\parallel})_{\text{expt}} &= 29.53 \text{ kcal/mole},\\
(Q_{\perp})_{\text{expt}} &= 29.92 \text{ kcal/mole},\\
(Q_{\parallel})_{\text{theory}} &\cong (Q_{\perp})_{\text{theory}} = 30.29 \text{ kcal/mole}.
\end{aligned}
$$

The theoretical and experimental values for $(\Delta Q_{\parallel})$, $(Q_{\parallel})$, and $(Q_{\perp})$ differ by about 10%, 2.5%, and 1.3%, respectively.

For gallium:

$$
\begin{aligned}
(\Delta Q_{\parallel})_{\text{expt}} &= -3.4 \text{ kcal/mole},\\
(\Delta Q_{\parallel})_{\text{theory}} &= -2.61 \text{ kcal/mole},\\
(\Delta Q_{\text{basal}})_{\text{expt}} &= -11.64 \text{ kcal/mole},\\
(\Delta Q_{\text{basal}})_{\text{theory}} &= -8.55 \text{ kcal/mole}.
\end{aligned}
$$

The theoretical and experimental values for $(\Delta Q_{\parallel})$ and $(\Delta Q_{\text{basal}})$ differ by about 24% and 34%, respectively.

The disagreement between theoretical and experimental values reflects the fact that the theory does not include core and ion size effects.

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Interatomic Forces in Various Solids

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Inferences are made concerning the nature and range of interatomic forces in several solids, by the use of the observed dispersion relations of the lattice vibrations together with the simple analytical properties of the sum of the squares of all the lattice vibrations corresponding to the same point in reciprocal space. Eleven metals, one alloy, and four semiconductors are treated. The method enables one to separate long-range electromagnetic (i.e., multipole) forces from "overlap" ones. The results suggest in several cases that the former are required to describe the interactions in a realistic way.

1. INTRODUCTION

THE thermal motion of atoms in a crystal is determined by the forces existing between them, and the observation of the spectrum of these vibrations should therefore be a tool for inferring the nature of these forces. The process of obtaining this inference is necessarily an inductive rather than a deductive one. Thus, a given force scheme (i.e., an assumed set of "force constants" or "coupling parameters" which tell how the displacement in some direction of any atom in the lattice will affect the motion of any other atom in the lattice) produces one unique set $\omega_i(\mathbf{q})$ of $3n$ lattice vibrations for each wave vector $\mathbf{q}$ ($i=1, \cdots, 3n$, $n=$ the number of atoms per unit cell) which one can straightforwardly compute, provided that one agrees on basic theoretical assumptions such as the Born–von Karman theory and the harmonic approximation. The reverse process, which has to be followed in practice, is not a unique one, however; at least as long as the number of experimental observations of $\omega(\mathbf{q})$ is finite and is subject to experimental error, it is always possible to fit the experimental data with any number of possible force schemes. To pick the "correct" force scheme from these, other criteria are necessary—such as goodness of fit, assumption of nature of forces believed for other reasons to exist in certain crystals, shortness of range, simplicity, or general "reasonableness." Mathematically, the "dispersion relation" $\omega_i(\mathbf{q})$ is the $3n$ solutions of an equation of order $3n$ in ω^2, with the force constants

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