

basis of a two-charge model. The physical meaning of the two-charge parameters is briefly discussed in Sec. III. By a suitable choice of the two parameters satisfactory agreement is obtained for the intensities of the four A_2 vibrations as shown in Table XIII. The Raman intensities of the four A_1 vibrations have been calculated on the basis of a simple model in Sec. IV. With no adjustable parameters satisfactory agreement with experiment is obtained for the relative intensities as shown in Table XIV. The theoretical and experimental strengths and frequencies for both the Raman and infrared are summarized and compared graphically in Fig. 2.

It has been customary to demonstrate the validity of the valence-force model entirely from the calculated frequencies. Such a comparison is shown in Table X. However, in the present work it has been shown that the Raman intensities are more sensitive to the normal modes than are the frequencies. Evidently the infrared

intensities are also very sensitive to the normal modes. Therefore the successful calculation of the intensities constitutes a much stronger confirmation of the normal modes and the valence-force model than just a comparison of frequencies. The picture of quartz as a valence crystal is further substantiated by the success of the two-charge model in representing the effects of the twelve charges allowed by symmetry.

There remains the task of applying these techniques to the modes of species E . Much could be learned from such a study, since these modes are active in both infrared and Raman effects, and the experimental intensities are now known.⁹ It would be interesting to test the β -quartz theory for the infrared intensities of the E modes suggested in the Introduction. Looking beyond the interest in quartz itself, we hope that these ideas will prove helpful in the general understanding of the vibrational spectra of molecules and valence crystals.

Effect of Dislocations on Self-Diffusion in Germanium

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The effect of dislocations on the rate of diffusion of radioactive Ge^{71} in intrinsic germanium single crystals has been studied at temperatures near 740°C . The dislocations were introduced by either of two methods: (A) distorting the surface by lapping under pressure, thus producing a network of dislocations; (B) bending the specimens so as to introduce up to 2×10^6 parallel edge dislocations per cm^2 . Both deformation treatments produce an enhancement of self-diffusion relative to that in undeformed crystals. In both cases the diffusion can be described in terms of an enhanced volume diffusion with apparent diffusion coefficients up to 38% larger than the value for undeformed intrinsic specimens.

INTRODUCTION

THE role of dislocations in enhancing atom diffusion has not been demonstrated clearly. One method by which information has been sought is in the study of diffusion along small-angle tilt boundaries, using the Burgers model to describe the boundary in terms of individual dislocations. It was Hoffman and Turnbull^{1,2} whose observations implied that the rate of self-diffusion in silver along grain boundaries may, indeed, be explained by defining an intrinsic diffusivity for dislocation pipes. Somewhat contradictory to this are the findings of others, particularly Smoluchowski and co-workers.³ Their measurements indicate that the effect of individual dislocations is inconsequential in all

systems which they studied. The role of an array of parallel edge dislocations which do not form a boundary was first studied by Hendrickson and Machlin.⁴ An appreciable enhancement of diffusion due to the dislocations was reported. Their results were later contradicted, however, by Murray⁵ of the same laboratory who had tried to duplicate and extend them. Finally, for the case of a random network of dislocations, Hart⁶ and Mortlock⁷ suggested that single crystals at low temperatures may exhibit enhanced diffusion, but without a change in the mathematical form of the concentration profile. The resulting diffusion constant at low temperatures should then be larger than that found by the extrapolation of high-temperature data. Tomizuka⁸ claims that the curvature in the Arrhenius

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¹ D. Turnbull, *Report of Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955), p. 203.

² R. E. Hoffman, *Acta Met.* **4**, 97 (1956).

³ R. Smoluchowski, *Report of Bristol Conference on Defects in Crystalline Solids, July, 1954* (The Physical Society, London, 1955), p. 147.

⁴ A. A. Hendrickson and E. S. Machlin, *J. Metals* **6**, 1035 (1954).

⁵ G. T. Murray, thesis, 1958, Columbia University, New York, (unpublished).

⁶ E. W. Hart, *Acta Met.* **5**, 598 (1957).

⁷ A. J. Mortlock, *Acta Met.* **8**, 132 (1960).

⁸ C. T. Tomizuka, *Acta Met.* **6**, 660 (1958).

TABLE I. Experimental results.

Run No.	Deformation	Disloc. density (cm ⁻²)	Annealing prior to diffusion	Temp. of diffusion <i>T</i> (°C)	Penetration depth $2(Dt)^{1/2}$ (microns)	Lattice diffusivity <i>D^a</i> (units of 10 ⁻¹⁴ cm ² /sec)	Apparent diffusivity <i>D'</i>	(<i>D'</i> - <i>D</i>)/ <i>D</i> (%)
1	(A)	?	None	754	2.38	1.76	2.4	38
2	(A)	?	65 hr at 850°C	754	2.38	1.76	1.8	0
3	(B)	2×10 ⁶	none	747.4	3.65	1.45	1.5	0
4	(B)	2×10 ⁶	none	751.6	3.46	1.64	1.9	16
5	(B)	2×10 ⁶	none	751.6	3.46	1.64	1.9	16
6	(B)	2×10 ⁶	20 days at 750°C	751.6	3.46	1.64	2.0	22
7 ^b	(B)	2×10 ⁶	20 days at 750°C	720.4	2.68	0.58	0.65	12

^a Values of *D* from reference 9.^b Run No. 7 taken for different penetration depth and temperature than the comparable runs Nos. 4, 5, and 6. This may explain the comparatively low value of (*D'* - *D*)/*D*.

plot observed for diffusion of antimony in silver and self-diffusion of silver are due to this cause. However, other interpretations, such as a temperature-dependent activation energy for diffusion, are also possible.

Because of the availability in this laboratory of a sensitive technique which had previously been used to measure self-diffusion in nearly dislocation-free, intrinsic germanium crystals, it seemed worthwhile to try to look for dislocation effects in this material.

EXPERIMENTAL METHODS

The technique is a residual activity technique described in more detail elsewhere.⁹ A thin layer of radioactive Ge⁷¹, which emits primarily monochromatic x rays, is first evaporated onto a flat surface of a crystal in high vacuum, after which the crystal is subjected to a diffusion anneal. Thin sections of the sample are then removed successively and the intensity of radiation *I*(*x*) coming from the remainder of the crystal is measured as a function of the thickness, *x*, of the removed portion. The relative residual activity *R*(*x*), defined by $R = I(x)/I(0)$ is, for the case of volume diffusion, given by

$$R(x) = \frac{I(x)}{I(0)} = \exp(\mu x) \frac{1 - \operatorname{erf}[x/2(Dt)^{1/2} + \mu(Dt)^{1/2}]}{1 - \operatorname{erf}[\mu(Dt)^{1/2}]}, \quad (1)$$

where *t* is the duration of diffusion, *D* is the diffusion coefficient, and μ is the linear absorption coefficient of the x radiation from Ge⁷¹ ($= 240 \pm 5 \text{ cm}^{-1}$). As used, the method is capable of measuring diffusion with penetration depth, $2(Dt)^{1/2}$, as low as 10⁻⁴ cm with an error of only about 5%.

The single crystals used contained less than 10¹⁶ cm⁻³ of electrically active impurities and less than 10⁸ dislocations/cm² (as indicated by CP4 etching). Dislocations were introduced by either of two methods: (A) distorting the surface by lapping under a pressure of about 2 kg/cm² (measurements of the rate of etching indicate that a distorted layer of about 12 μ is obtained);

(B) bending single-crystal bars about the $[\bar{1}12]$ axis in vacuum of about 1 μ Hg. If the conditions specified by Vogel¹⁰ are met, slip occurs on (111) planes in the [110] direction only, and parallel edge dislocations along the $[\bar{1}12]$ direction are introduced, at least in those portions of the bar which are not too far off the neutral zone of bending. Etch pit counts in the (111) plane, which is nearly perpendicular to these dislocations, show that they are produced in densities of up to 2×10⁶ cm⁻². On other {111} planes the etch pit densities were found to be at least two orders of magnitude smaller, indicating that the dislocations obtained were almost entirely in a parallel array.

Diffusion anneals were carried out in vacuum ($\leq 10^{-5}$ mm Hg) and the temperature was controlled to $\pm 0.3^\circ\text{C}$ and known to $\pm 0.5^\circ\text{C}$. All counting was carried out in a well-defined and reproducible counting geometry and with reference to decay standards.

RESULTS AND DISCUSSION

Measurements were made at temperatures near 740°C. The pertinent data are summarized in Table I. Both types of deformation produce an enhanced diffusion. Further, all penetration curves can be fitted by expression (1) for volume diffusion with a coefficient $D'(T) \geq D(T)$, where *D*(*T*) is the coefficient for "pure lattice diffusion," i.e., that observed on dislocation-free specimens at the same temperature.

Runs 1 and 2 (Table I) were carried out on specimens deformed by method A. For the first sample the value of *D'* obtained was 38% larger than *D*. The second sample was annealed at 850°C for about three days prior to diffusion. *D'* was found to be, within experimental error, the same as *D*. This shows that the enhancement of diffusion in lapped specimens can be annealed out by a pretreatment at 850°C.

Runs 3 to 7 were carried out on specimens deformed by bending, method B. In all cases the direction of diffusion is parallel to the direction of the dislocations introduced by bending, i.e., $[\bar{1}12]$. *D'* is up to 22%

⁹ H. Widmer and G. R. Gunther-Mohr, *Helv. Phys. Acta* (to be published).

¹⁰ F. L. Vogel, *Trans. Am. Inst. Mining Met. Engrs.* **206**, 946 (1956).

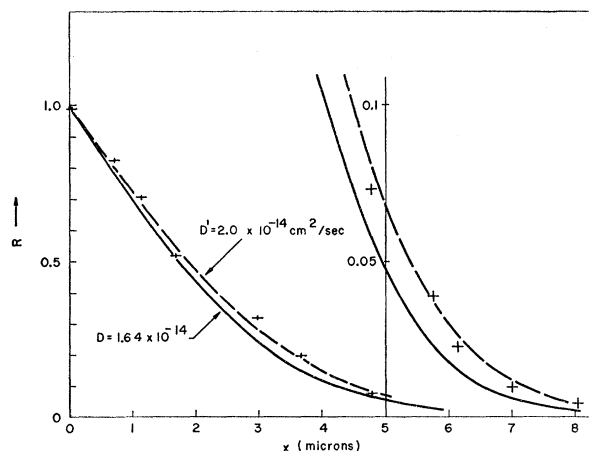


FIG. 1. Relative residual activity $R(x)$ measured on a bent specimen containing 2×10^6 parallel-edge dislocations/cm². The portion of the curves for x larger than about 4μ is drawn with the ordinate magnified by a factor of 10.

larger than the value, D , for pure lattice diffusion. That the enhancement is not eliminated by annealing the specimens at 750°C prior to diffusion, is shown by runs 6 and 7 in Table I. Annealing at higher temperatures was not tried since it would lead to polygonization.¹⁰ Etch pit counts, which were carried out after diffusion, show that the concentration of dislocations parallel to the bend axis remained of the same order of magnitude during diffusion as that originally introduced by bending. Polygonization was observed only in regions far from the neutral zone of bending, but not in those parts of the specimens on which diffusion was measured. Typical data for a bent specimen are shown in Fig. 1. The solid line is R vs x [equation (1)] for pure lattice diffusion. The dashed line represents the best fit to Eq. (1) to the data for $x < 5 \mu$. It is noteworthy that the later experimental points for $x > 5 \mu$ all lie on this curve within experimental error, even for values of R as low as 0.01. It must be concluded that a concentration

profile of the same mathematical form as that for pure lattice diffusion, i.e., $\propto \exp(-x^2/4Dt)$, is valid within experimental error under the present condition of dislocation enhanced diffusion.

The observed enhancement cannot be attributed to experimental errors since, in some cases, deformed specimens were annealed together with, and analyzed in reference to, undeformed samples. In the case of the lapped samples, the result is consistent with Hart's suggestion, assuming that the network spacing is small compared to the mean penetration depth ($\approx 2 \mu$). In the case of bent crystals the close fit to Eq. (1), which is characteristic of pure lattice diffusion, is a surprising result since Hart's analysis does not apply. Specifically, there is no network formed, and the spacing of the parallel edge dislocations is large compared to the mean penetration depth. On the other hand, Fisher's¹¹ analysis which predicts a concentration profile $\propto e^{-ax}$ should not be valid either, since it was derived for very different boundary conditions. Nevertheless, we endeavored to see if the data were consistent with a concentration profile proportional to e^{-ax} , and found that this was not so.

In summary, the present work has shown an unmistakable enhancement of self-diffusion by a comparatively low ($2 \times 10^6/\text{cm}^2$) concentration of parallel-edge dislocations. The fact that the diffusion equation (1), which is valid for pure volume diffusion, is obeyed accurately cannot immediately be understood. Attempts are being made to examine the problem under realistic boundary conditions to see if the results can be interpreted by means of a simple dislocation model.

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¹¹ J. C. Fisher, J. Appl. Phys. 22, 74 (1951).