

## Elastic Constants of Cadmium from 4.2°K to 300°K\*

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The adiabatic elastic constants of cadmium single crystals have been measured by an ultrasonic pulse technique. The values extrapolated to 0°K are:  $c_{11}=13.08$ ,  $c_{33}=5.737$ ,  $c_{44}=2.449$ ,  $c_{12}=4.048$ ,  $c_{13}=4.145$  in units of  $10^{11}$  dynes/cm<sup>2</sup>. A Debye characteristic temperature,  $\theta_0$ , of  $213^\circ \pm 1^\circ$ K has been calculated from these 0°K elastic constants. The temperature dependence of the linear compressibilities,  $K_{11}$  and  $K_L$ , has also been calculated.

## I. INTRODUCTION

THE low-temperature elastic constants of a single crystal can be used directly to calculate a Debye characteristic temperature,  $\theta_0$  (elastic), which is valuable in interpreting or confirming the data obtained from low-temperature heat-capacity measurements.<sup>1</sup> In addition, since the elastic constants can be related to the atomic force parameters used in theoretical calculations (such as the Born-von Karman theory of lattice dynamics<sup>2,3</sup>), the elastic constants provide a convenient and sensitive experimental test of force models for a solid.

The elastic constants of magnesium and of zinc have been measured recently in this laboratory<sup>4,5</sup> and elsewhere.<sup>6,7</sup> Magnesium has a hexagonal close-packed structure with a ( $c/a$ ) ratio of 1.623, which is close to the ideal axial ratio of 1.633; and it is almost elastically isotropic. Zinc, on the other hand, has an axial ratio of 1.855 and is highly anisotropic in its elastic properties. Since cadmium ( $c/a=1.886$ ) is very similar to zinc in structure and in thermal properties, the elastic constants of cadmium are of value in increasing our understanding of both of these unusual hexagonal metals. In particular, it was desired to compare the elastic and calorimetric Debye temperatures and to provide data for investigating the appropriateness of certain force models.<sup>8</sup>

The five elastic constants— $c_{11}$ ,  $c_{33}$ ,  $c_{44}$ ,  $c_{66}$ ,  $c_{13}$ —of a cadmium single crystal have been measured down to liquid helium temperature by an ultrasonic pulse tech-

nique.<sup>4,9</sup> In all, seven waves (long wavelength acoustical modes) were measured on two separate cadmium crystals; these give the five independent constants and two internal checks. Four of the waves were pure longitudinal or pure transverse modes in the directions parallel and perpendicular to the  $c$  axis. For each of these four waves the velocity ( $U$ ) is directly related to one of the elastic constants  $c_{11}$ ,  $c_{33}$ ,  $c_{44}$ , or  $c_{66}$  by a simple expression of the form  $c_{ij}=\rho U^2$ , where  $\rho$  is the density.<sup>3</sup> To obtain  $c_{13}$  and two checks on the consistency of our data, three other waves were propagated in a direction at an angle of  $22^\circ$  to the  $c$  axis. The acoustical wave velocities for propagation at an angle  $\theta$  to the  $c$  axis<sup>10</sup> are given by

$$\rho U_t^2 = c_{66} \sin^2 \theta + c_{44} \cos^2 \theta, \quad (1)$$

$$2\rho U^2 = c_{11} \sin^2 \theta + c_{33} \cos^2 \theta + c_{44} \pm \{ (c_{11} - c_{44})^2 \sin^4 \theta + (c_{33} - c_{44})^2 \cos^4 \theta + 2 \sin^2 \theta \cos^2 \theta [(c_{11} - c_{44})(c_{44} - c_{33}) + 2(c_{13} + c_{44})^2] \}^{\frac{1}{2}}. \quad (2)$$

The velocity of a pure transverse wave polarized perpendicular to the  $c$  axis is denoted by  $U_t$ . The other two waves are of mixed character: the plus sign in Eq. (2) gives a quasi-longitudinal wave velocity,  $U_{ql}$ , and the minus sign gives a quasi-transverse velocity,  $U_{qt}$ . All seven wave velocities were measured as a function of temperature from 4.2°K to 300°K.

## II. EXPERIMENT

Two cadmium single crystals, denoted by I and II, were obtained from Monocrystals Company<sup>11</sup> in the form of right circular cylinders 1 inch in diameter and 1.75 inches long. Part of the surface was etched on each crystal, and the orientation was determined from back-reflection Laue x-ray photographs. The  $c$  axis was found to be almost perpendicular to the cylinder axis for both I and II. An unsuccessful attempt was made to cleave crystal II at liquid nitrogen temperatures. Failure to obtain cleavage along the basal plane is ascribed to the softness of cadmium (relative to zinc which cleaves easily) and to the unfavorable orientation of these

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<sup>1</sup> G. A. Alers and J. R. Neighbours, *Revs. Modern Phys.* **31**, 675 (1959).

<sup>2</sup> J. de Launay, *Advances in Solid-State Physics*, edited by F. Seitz and D. Turnbull, (Academic Press, New York, 1956), Vol. 2.

<sup>3</sup> L. J. Slutsky and C. W. Garland, *J. Chem. Phys.* **26**, 787 (1957); **28**, 331 (1958).

<sup>4</sup> L. J. Slutsky and C. W. Garland, *Phys. Rev.* **107**, 972 (1957).

<sup>5</sup> C. W. Garland and R. Dalven, *Phys. Rev.* **111**, 1232 (1958).

<sup>6</sup> S. Eros, Atomic Energy Commission Technical Report No. 7, Contract at (11-1)-623, Case Institute of Technology, December, 1959 (unpublished).

<sup>7</sup> G. A. Alers and J. R. Neighbours, *J. Phys. Chem. Solids* **7**, 58 (1958).

<sup>8</sup> W. E. Wallace, *J. Chem. Phys.* **23**, 2281 (1955).

<sup>9</sup> H. B. Huntington, *Phys. Rev.* **72**, 321 (1947).

<sup>10</sup> L. Gold, *J. Appl. Phys.* **21**, 541 (1950).

<sup>11</sup> Monocrystals Company, 1721 Sherwood Blvd., Cleveland, Ohio.

samples. At this point a cylinder of plastic (Stycast 40) was polymerized around each of the crystals. This was not only convenient for fly-cutting the samples while they were held fixed in a two-circle goniometer but was necessary to avoid deformation on clamping them for later fly-cuts. After the cleavage attempt on Cd II, there were several small nicks at one end of the crystal, and the Laue spots were slightly doubled and less sharp. Cadmium II was oriented within 12' of arc as closely as possible with these spots, and a basal plane was fly-cut as a reference plane. Cadmium I was then oriented within 12' of arc, and two pairs of planes, one pair parallel and the other perpendicular to the  $c$  axis, were fly-cut. Machine cuts of 3 mils were reduced to 0.5 mil toward the end of a cut; the surfaces were then finished with 20 cuts of about 0.2 mil. For Cd I at 25°C, the path length along the  $c$  axis was  $2.1954 \pm 0.0008$  cm; the pathlength perpendicular to the  $c$  axis was  $4.2126 \pm 0.0015$  cm for the  $c_{11}$  measurement and was reduced to  $3.0508 \pm 0.0020$  cm for the  $c_{66}$  measurement.

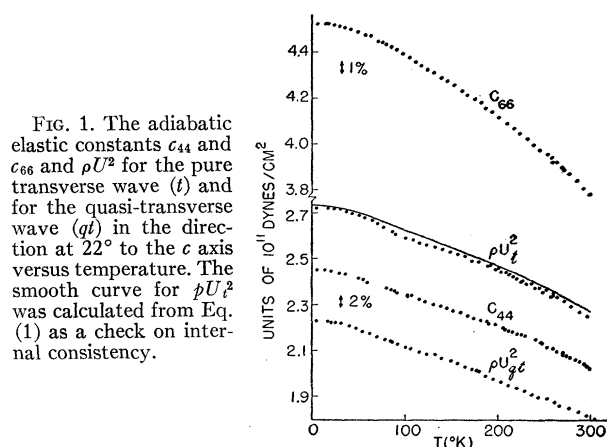


FIG. 1. The adiabatic elastic constants  $c_{44}$  and  $c_{66}$  and  $\rho U^2$  for the pure transverse wave ( $t$ ) and for the quasi-transverse wave ( $gl$ ) in the direction at 22° to the  $c$  axis versus temperature. The smooth curve for  $\rho U^2_l$  was calculated from Eq. (1) as a check on internal consistency.

Two parallel planes whose normal was at an angle of 22° from the  $c$  axis were fly-cut on Cd II, and a path length of  $1.3653 \pm 0.0034$  cm was obtained. This angle was chosen because  $c_{13}$  determined from velocities in a 22° direction is least affected by any uncertainty in the angle. Since the time delays were short and the echoes poorer than the very fine echoes obtained with Cd I, the three wave velocities in the 22° direction have a greater uncertainty assigned to them.

Although the experimental method and equipment for measuring ultrasonic velocities and temperatures have been given previously,<sup>4</sup> some new details of technique might be mentioned here. Our procedure was to make measurements while the sample, which was suspended in an inner Dewar, was being cooled by liquid nitrogen in an outer Dewar. By slowly raising the nitrogen level, one could achieve a very slow rate of cooling (less than 0.2°K per minute). After the crystal had cooled to about 85°K, it was submerged in liquid helium to obtain a measurement at 4.2°K. The helium was

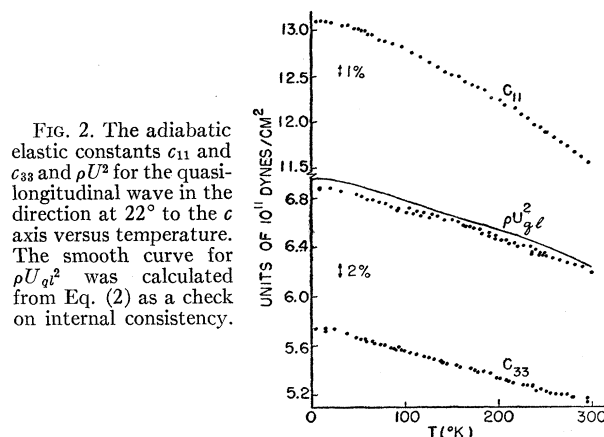


FIG. 2. The adiabatic elastic constants  $c_{11}$  and  $c_{33}$  and  $\rho U^2$  for the quasi-longitudinal wave in the direction at 22° to the  $c$  axis versus temperature. The smooth curve for  $\rho U^2_{gl}$  was calculated from Eq. (2) as a check on internal consistency.

allowed to evaporate and data were then taken on a warm-up to liquid nitrogen temperature. A final measurement was made with the crystal submerged in liquid nitrogen. No data were taken between 4.2°K and 20°K because of low thermocouple sensitivity and rapid warm-up in this range. Temperatures were measured to better than 0.2°K outside this range.

Fisher "NONAQ" stopcock grease provided a very satisfactory transducer seal for all measurements except some of the transverse wave measurements from 260°K to room temperature, for which phenyl salicylate (salol) was used. Excellent seals can be achieved by rewarming the seal after the crystal has been installed in the sample holder. The seal was then allowed to cool and harden slowly. This technique often made a great improvement in the number and quality of the echoes.

Since rectified echo pulses were ranged it is necessary to make transit-time corrections to account for changes which occur in the leading edge of the pulse after several trips through the sample. These corrections were obtained from room-temperature data on a third single crystal, Cd III, which was also obtained from Monocrystals Company. This crystal was not oriented; planes were fly-cut perpendicular to the cylinder axis, and measurements of the round-trip transit time were made for six path lengths from 7 to 1.25 cm. The apparent velocities of longitudinal and transverse waves were obtained with both salol and "NONAQ" seals; no systematic difference between the results for the two seals was observed. A plot of  $(1/U_{app})$  versus  $(1/L)$  gave a line with a slight upward slope corresponding to a correction of  $+0.04 \pm 0.03$   $\mu$ sec for longitudinal waves. Similarly, the correction was found to be  $+0.045 \pm 0.05$

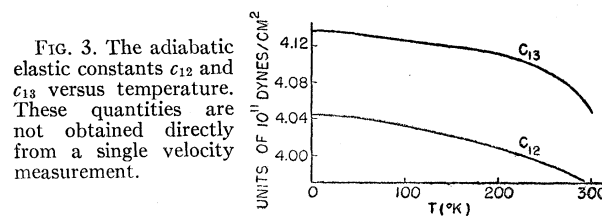


FIG. 3. The adiabatic elastic constants  $c_{12}$  and  $c_{13}$  versus temperature. These quantities are not obtained directly from a single velocity measurement.

TABLE I. The adiabatic elastic constants,  $c_{ij}$ , and values of  $\rho U_{qt}^2$  in the  $22^\circ$  direction for cadmium, in units of  $10^{11}$  dynes/cm<sup>2</sup>. Adiabatic linear compressibilities  $K_{11}$  and  $K_L$ , are given in units of  $10^{-13}$  cm<sup>2</sup>/dyne. Entries in the first five columns are taken from smooth curves through the experimental data points; entries in the last four columns are those calculated at each temperature and have not been smoothed. The number of significant figures does not indicate the absolute accuracy of the value.

$T(^{\circ}\text{K})$	$c_{11}$	$c_{33}$	$c_{66}$	$c_{44}$	$\rho U_{qt}^2$	$c_{12}$	$c_{13}$	$K_{11}$	$K_L$
0	13.08	5.737	4.516	2.449	2.225	4.048	4.145	13.83	2.491
20	13.07	5.725	4.513	2.443	2.220	4.044	4.143	13.86	2.486
40	13.02	5.690	4.494	2.424	2.204	4.032	4.126	13.97	2.483
60	12.97	5.644	4.463	2.398	2.178	4.044	4.127	14.13	2.449
80	12.89	5.600	4.425	2.370	2.149	4.040	4.129	14.28	2.422
100	12.80	5.553	4.379	2.342	2.120	4.042	4.127	14.44	2.399
120	12.69	5.509	4.330	2.315	2.091	4.030	4.120	14.57	2.389
140	12.58	5.465	4.280	2.288	2.060	4.020	4.121	14.73	2.363
160	12.47	5.420	4.227	2.262	2.030	4.016	4.120	14.88	2.344
180	12.36	5.376	4.171	2.232	2.000	4.018	4.115	15.04	2.325
200	12.24	5.336	4.113	2.203	1.969	4.014	4.113	15.18	2.308
220	12.11	5.293	4.052	2.172	1.938	4.006	4.108	15.31	2.300
240	11.97	5.253	3.988	2.140	1.907	3.994	4.100	15.44	2.925
260	11.82	5.212	3.920	2.104	1.876	3.980	4.083	15.57	2.305
280	11.67	5.169	3.848	2.065	1.842	3.972	4.071	15.71	2.301
300	11.52	5.122	3.774	2.025	1.809	3.972	4.053	15.88	2.299

$\mu\text{sec}$  for transverse waves. These corrections were assumed independent of temperature and subtracted from all the observed delay times.

A density of  $8.7491 \pm 0.0016$  g cm<sup>-3</sup> at  $25^\circ\text{C}$  was calculated from the 1935 x-ray lattice parameters of Jette and Foote.<sup>12</sup> Corrections of the order of 1% in the density and in the path lengths as a result of thermal expansion were calculated from the data of Gruneisen and Goens.<sup>13</sup>

### III. RESULTS

Experimental data points are shown in Figs. 1 and 2 for the four elastic constants obtained directly from a single velocity measurement ( $c_{11}$ ,  $c_{33}$ ,  $c_{44}$ ,  $c_{66}$ ) and for the values of  $\rho U^2$  of the three waves propagated in a direction at  $22^\circ$  to the  $c$  axis. The smooth curves drawn for  $\rho U_t^2$  and  $\rho U_{qt}^2$  are calculated from the smooth-curve values of the other waves, and they agree with the experimental points within the limits of error assigned; these two waves constitute the two possible checks on the internal consistency of our data. The temperature variation of  $c_{12}$  and  $c_{13}$ , constants which are not obtained from a single velocity measurement, are shown in Fig. 3.

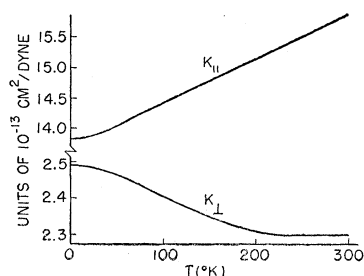


FIG. 4. The adiabatic linear compressibilities parallel and perpendicular to the  $c$  axis,  $K_{11}$  and  $K_L$ , versus temperature. These values were calculated from Eqs. (3) and (4) using the elastic constants in Table I.

The constants  $c_{66}$  and  $c_{12}$  are not independent, since  $c_{12}$  is calculated from the relation  $c_{66} = (c_{11} - c_{12})/2$ . Because of the relatively large uncertainty in our  $\rho U_{qt}^2$  data,  $c_{13}$  can be calculated with the best accuracy from the quasi-transverse wave data alone [Eq. (2) with the minus sign]. Correction was made for the slight change in the  $22^\circ$  direction with temperature which is due to the anisotropy of the thermal expansion; at  $0^\circ\text{K}$ , this angle becomes  $21^\circ 46'$ . This change of  $14'$  in the direction of propagation leads to a correction of only 0.1% in  $c_{13}$ . It should be noted that a negative value of  $c_{13}$  which would satisfy Eq. (2) can be ruled out by the elastic stability criteria.

The adiabatic linear compressibility,  $(-1/L_0) \times (\partial L / \partial P)$ , parallel and perpendicular to the  $c$  axis ( $K_{11}$  and  $K_L$ ) was calculated from the smooth-curve elastic constants. The appropriate formulas are:

$$K_{11} = (c_{11} + c_{12} - 2c_{13})/C, \quad (3)$$

$$K_L = (c_{33} - c_{13})/C, \quad (4)$$

where  $C \equiv c_{33}(c_{11} + c_{12}) - 2c_{13}^2$ . The temperature variation of these compressibilities is shown in Fig. 4.

Values of the adiabatic elastic constants,  $\rho U_{qt}^2$ , and the compressibilities are tabulated at  $20^\circ$  intervals from  $0^\circ\text{K}$  to  $300^\circ\text{K}$  in Table I. An error analysis was carried out in which uncertainties in the path lengths, in the experimental time delays, and in the transit-time corrections were considered. The resulting limits of error for directly measured quantities are given in Table II. It should be pointed out that the uncertainty in the transit-time correction does not lead to a random error in the various quantities. It is reasonable to assume that the longitudinal and transverse transit-time corrections should be very similar; thus all waves velocities would be changed systematically in the same direction by any

<sup>12</sup> E. R. Jette and F. Foote, J. Chem. Phys. 3, 605 (1935).

<sup>13</sup> E. Gruneisen and E. Goens, Z. Physik 29, 141 (1924).

change in the transit-time corrections. A propagation-of-errors treatment gives a limit of error of 1.1% in  $c_{12}$ , 2.1% in  $c_{13}$ , 1.5% in  $K_{11}$ , and 4.3% in  $K_1$ .

In Table III, the results obtained in this investigation are compared with other determinations<sup>14,15</sup> of the room-temperature elastic constants. A comparison can also be made with compressibility data obtained on polycrystalline cadmium. The isothermal volume compressibility,  $K = (-1/V_0)(\partial V/\partial P)_T$ , calculated from our data at 293°K is  $21.70 \pm 0.16$  in units of  $10^{-13}$  cm<sup>2</sup>/dyne; other investigators have reported room-temperature values of  $K = 21.0$  (Bridgman<sup>16</sup>),  $21.0$  (Richards<sup>17</sup>), and  $22.5$  (Adams et al.<sup>18</sup>).

#### IV. DISCUSSION

The low-temperature elastic data for cadmium resembles that for most metals in that there is a larger percentage variation in the shear constants than in the compressional constants. Cadmium is, however, very highly anisotropic in its elastic properties; this is shown in Table IV, where the ratios  $c_{66}/c_{44}$ ,  $c_{33}/c_{11}$ , and  $K_{11}/K_1$  for cadmium are compared with those for three other hexagonal-close-packed metals—beryllium,<sup>19</sup> mag-

TABLE II. Limits of error in quantities calculated directly from a single velocity. The contribution from the uncertainty in the transit-time correction (*A*) and the contribution from all other sources (*B*) are shown separately.

	$c_{11}$	$c_{33}$	$c_{66}$	$c_{44}$	$\rho U_{qt}^2$	$\rho U_t^2$	$\rho U_{qt}^2$
<i>A</i> (%)	0.25	0.35	0.35	0.35	0.55	0.60	0.60
<i>B</i> (%)	0.20	0.30	0.25	0.30	0.80	0.80	1.30
Total (%)	$\pm 0.45$	$\pm 0.65$	$\pm 0.60$	$\pm 0.65$	$\pm 1.35$	$\pm 1.40$	$\pm 1.90$

nesium,<sup>4,6</sup> and zinc.<sup>5,7</sup> The elastic anisotropy of cadmium is very similar to that of zinc as one might expect from a comparison of their axial ratios.

The temperature dependence of the linear compressibilities is also interesting, and again the behavior for cadmium is very similar to that reported for zinc.<sup>7</sup> Since the atoms are more closely packed in the basal plane than along the  $c$  axis it seems reasonable that the ( $K_{11}/K_1$ ) ratio should be greater than one, but Fig. 4 shows that as the lattice expands with increasing temperature cadmium becomes more compressible along the axial direction and at the same time less compressible in the basal plane. For both cadmium and zinc,  $K_{11}$  increases almost linearly with increasing temperature;  $K_1$  for zinc is almost constant in the range 0°K to 300°K, with a slight dip at 200°K, while  $K_1$  for cadmium shows a steady decrease. This difference between cadmium and zinc may not be real since there is a greater

TABLE III. The adiabatic elastic constants of cadmium single crystals at room temperature obtained from the present measurements (P) compared with values obtained by Bridgman<sup>a</sup> (B) and by Gruneisen and Goens<sup>b</sup> (GG). All results are given in units of  $10^{11}$  dynes/cm<sup>2</sup>.

Obs.	Temp.	$c_{11}$	$c_{33}$	$c_{44}$	$c_{66}$	$c_{12}$	$c_{13}$
P	293°K	11.58	5.140	2.039	3.801	3.975	4.060
GG	293°K	12.1	5.13	1.85	3.65	4.8	4.42
B	room	10.9	4.59	1.56	3.45	4.0	3.75

<sup>a</sup>See reference 15.

<sup>b</sup>See reference 14.

uncertainty in  $K_1$  values than in  $K_{11}$  values. It should be noted that the isothermal linear compressibility perpendicular to the  $c$  axis would be almost independent of temperature, while the isothermal compressibility parallel to the  $c$  axis would increase more rapidly with temperature than does the adiabatic value,  $K_{11}$ . Certainly such compressibility results make it clear that the forces acting between atoms in a basal plane are different from those acting between atoms which lie in different planes. This would be consistent with the model proposed by Wallace,<sup>8</sup> which assumes a system of resonating covalent bonds between atoms in the basal plane. Interpretation of the elastic constants of both cadmium and zinc based on such a model is under investigation.

The Debye characteristic temperature at 0°K,  $\theta_0$ , can be calculated from the elastic constants at 0°K by averaging the inverse cube of the elastic wave velocities over all directions of propagation. For the one pure transverse wave this average may be evaluated analytically<sup>4,20</sup>; for the quasi-longitudinal and quasi-transverse waves the averaging must be done numerically. An elastic  $\theta_0$  value of 212.5°K was obtained by interpolation in the tables presented by Wolcott,<sup>20</sup> and a direct numerical calculation gave a  $\theta_0$  value of 213.3°K. Taking into account the uncertainties in elastic constants, we find an elastic value of  $\theta_0 = 213^\circ \pm 1^\circ$ K. The heat capacity of cadmium has been measured in the range 1°K to 20°K by Smith and Wolcott<sup>21</sup> and they report a calorimetric value of  $\theta_0 = 188^\circ$ K. Another recent low-temperature specific heat measurement<sup>22</sup> yields a  $\theta_0$  value of  $189^\circ \pm 4^\circ$ K. This disagreement between elastic and calorimetric  $\theta_0$  values

TABLE IV. The axial ratio ( $c/a$ ), the elastic constant ratios ( $c_{66}/c_{44}$ ) and ( $c_{33}/c_{11}$ ), and the ratio of adiabatic linear compressibilities ( $K_{11}/K_1$ ) for cadmium compared with those for other hexagonal-close-packed metals. Values of ( $c/a$ ) are room-temperature values; all other ratios are given at 0°K.

	$c/a$	$c_{66}/c_{44}$	$c_{33}/c_{11}$	$K_{11}/K_1$
Be	1.585	0.818	1.143	0.92
Mg	1.623	1.018	1.047	1.04
Zn	1.855	1.494	0.386	7.9
Cd	1.886	1.844	0.439	5.6

<sup>20</sup> N. Wolcott, J. Chem. Phys. **31**, 536 (1959).

<sup>21</sup> P. L. Smith and N. M. Wolcott, Phil. Mag. **1**, 854 (1956).

<sup>22</sup> T. M. Scrivinasan, Proc. Indian Acad. Sci. **49**, 61 (1959).

<sup>14</sup> E. Gruneisen and E. Goens, Z. Physik **26**, 235 (1924).

<sup>15</sup> P. W. Bridgman, Proc. Natl. Acad. Sci. (U. S.) **10**, 411 (1924).

<sup>16</sup> P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 9 (1944).

<sup>17</sup> T. W. Richards, J. Am. Chem. Soc. **37**, 1643 (1915).

<sup>18</sup> L. H. Adams, E. D. Williamson, and J. Johnston, J. Am. Chem. Soc. **41**, 12 (1919).

<sup>19</sup> J. F. Smith and C. L. Arbogast, J. Appl. Phys. **31**, 99 (1960).

for cadmium is very similar to that found for zinc<sup>1</sup> where  $\theta_0$  (elastic) is 328°K, and  $\theta_0$  (calorimetric) is 309°K. Although the reason for the discrepancies is not certain it still seems possible that they may arise from the difficulty of interpreting the low-temperature heat ca-

capacity of highly anisotropic metals. For both zinc and cadmium there is a sizeable  $T^5$  lattice contribution as well as the large electronic heat capacity; both of these factors must be taken into account carefully in obtaining the  $T^3$  contribution that determines  $\theta_0$ .

## Diffusion Rate of Li in Si at Low Temperatures\*

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The method of ion drift in the electric field of an  $n$ - $p$  junction has been used to measure the diffusion constant of Li in Si between 25°C and 125°C, taking particular care to avoid chemical and electrical interactions which might affect the results. When these data are combined with previous high-temperature data, there is obtained  $D = (2.5 \pm 0.2) \times 10^{-3} \exp[-(0.655 \pm 0.01)e/kT]$  cm<sup>2</sup>/sec, the data extending over eight decades in  $D$ . The results are compared with those from ion-pair relaxation experiments, and it is shown that the latter are consistent with the ion-drift results.

### INTRODUCTION

THE method of ion drift in the electric field of a reverse-biased  $n$ - $p$  junction<sup>1</sup> offers a sensitive technique, based on a simple model, for diffusion measurements at low temperatures. This method can be adapted to the measurement of the diffusion rate of free Li<sup>+</sup> in Si through the use of techniques which minimize or eliminate possible interactions between the Li<sup>+</sup> and other constituents present in the Si.

Because of the simplicity of the technique and of the model upon which it is based, the results should be highly reliable. They can be compared with values deduced from previous measurements<sup>2</sup> in this temperature range which are based on a particular model<sup>3</sup> of ion-pairing kinetics. Such a comparison is of particular interest inasmuch as two different approaches have been suggested<sup>3,4</sup> to the analysis of such diffusion-limited "precipitation" (or, in this case, ion-pair recombination), these approaches leading to different values for the diffusion constant when applied to Maita's data. In essence, the former<sup>3</sup> approach visualizes the recombination as correlated, with each Li<sup>+</sup> to be associated uniquely with a particular acceptor, while the latter<sup>4</sup> approach considers the Li<sup>+</sup> ions to be initially randomly located, with nothing to inhibit their motion from the neighborhood of one acceptor to another.

### I. Ion-Drift Measurements

#### *Experimental Method*

In the present experiments, the diffusion constant is deduced from the rate at which the Li<sup>+</sup> ions drift in the electric field of a reverse-biased  $p$ - $n$  junction. The  $p$ - $n$  junction is prepared in a preliminary step by diffusing Li into the surface of a piece of  $p$ -type Si. The drift rate of the Li<sup>+</sup> ions, at a given temperature, is determined by measuring the rate of change of the capacitance of the junction. Complete details, with a full discussion of the experimental techniques, is given in reference 1, together with a description of the surface treatment normally used in making measurements on high-resistivity Si such as that used here.

#### *Effects of Li-Impurity Reactions*

At the low Li concentrations and low diffusion temperatures used in this experiment, it is possible for Li acceptor, Li oxygen, Li dislocation, or perhaps even other unknown interactions to affect the diffusion rate. Before one can be sure that the results are descriptive of free Li, these possibilities must be eliminated.

The presence of any such interaction will generally lead to an activation energy for diffusion which is different from that of free Li; however, such an interaction should be absent at high temperatures because of the relatively small binding energies involved. The facts that the present low-temperature data fall along a straight line (as shown later in Fig. 2) and that this line extrapolates through the previously determined high-temperature diffusion data<sup>5</sup> serve, therefore, as general

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<sup>1</sup> E. M. Pell, J. Appl. Phys. **31**, 291 (1960).

<sup>2</sup> J. P. Maita, J. Phys. Chem. Solids **4**, 68 (1958).

<sup>3</sup> H. Reiss, C. S. Fuller, and F. J. Morin, Bell System Tech. J. **35**, 535 (1956).

<sup>4</sup> F. S. Ham, J. Phys. Chem. Solids **6**, 335 (1958).

<sup>5</sup> C. S. Fuller and J. C. Severiens, Phys. Rev. **96**, 21 (1954); also, E. M. Pell, Phys. Rev. **119**, 1014 (1960).