LYNC-RW 65-0960

J. Phys. Chem. Solids Pergamon Press 1965. Vol. 26, pp. 63–68. Printed in Great Britain.

THE EFFECT OF PRESSURE ON THE RESISTANCE AND LATTICE PARAMETERS OF CADMIUM AND ZINC*

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(*Received* 9 *July* 1964; *in revised form* 5 *August* 1964)

Abstract—The electrical resistance of cadmium and zinc have been measured to 500 kbars. Lattice parameters have been obtained for cadmium to 300 kbars and for zinc to about 160 kbars. Cadmium has a minimum in resistance near 150–155 kbars and a maximum above 200 kbars. For zinc, the minimum and maximum are at somewhat lower pressures. For both substances, the *a* axis is quite incompressible at low pressure. The compressibility increases and then decreases again at still higher density. The *c* axis compressibility exhibits a distinct irregularity at intermediate density. *c/a* decreases rapidly at low density, levels or increases slightly and then falls again. It does not seem possible to explain the results satisfactorily in terms of the simpler pictures involving electron stresses which are used to explain alloying effects.

A HEXAGONAL close packed arrangement of rigid spheres has an ideal *c/a* ratio of 1·633. Cadmium and zinc crystallize in the *hcp* structure, but with a considerably extended *c* axis, so that the *c/a* values (at 25°C and one atm) are 1·886 and 1·856 respectively. The effect of pressure to over 500 kbars has been measured on the resistance of these elements. In addition, the lattice parameters of cadmium have been measured to 300 kbars. X-ray diffraction measurements have also been made on zinc, but both the accuracy and the pressure range are limited (to about 160 kbars) because the molybdenum radiation which it is necessary to use in our apparatus gives very poor diffraction lines with zinc. The experimental techniques used both for resistance$^{(1,2)}$ and for X-ray diffraction$^{(3)}$ have been previously described. The cadmium was 99·99% pure material from A. D. Mackay. The zinc was high purity material from the National Bureau of Standards.

Figures 1 and 2 show resistance plotted against pressure. For cadmium, the resistance drops with increasing pressure in a 'normal' manner, exhibits a minimum near 150–155 kbars, and a maximum above 200 kbars. At high pressure, the resistance drops monotonically. Zinc behaves in a very similar manner except that the minimum is displaced to lower pressures (110–120 kbars). It is of interest to point out that magnesium, which also has the *hcp* structure but with nearly ideal *c/a* (1·623) at 1 atm, exhibits closely analogous resistance behavior.$^{(4)}$

The lattice parameters of cadmium were calculated from the 101 and 102 lines. The 100 and 002 lines were used as checks as well as the 112 and 201 lines at low pressures before they overlapped, and the 110 and 103 lines at high pressures after they separated. Figure 3 shows V/V_0 vs. pressure. MgO was used as a marker. There is a distinct irregularity in the region 90–130 kbars. Shock wave data$^{(5)}$ are shown for comparison. Above the irregularity, our data show less compression than the shock wave measurements. This is in contrast to the X-ray results for iron,$^{(6)}$ magnesium$^{(7)}$ and a number of other substances where MgO was also used frequently as a marker. Fourteen runs were made in all, and the scatter in the data are an order of magnitude less than the difference at the highest pressure. The results are all discussed in terms of V/V_0 which is calculated directly from the measured data. Table 1 lists values of *c*, *a*, *c/a* and

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* This work was supported in part by the United States Atomic Energy Commission.

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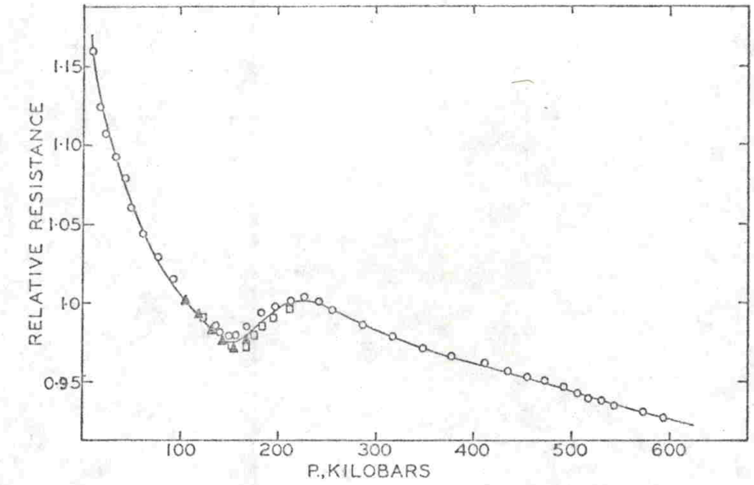

FIG. 1. Resistance vs. pressure–cadmium.

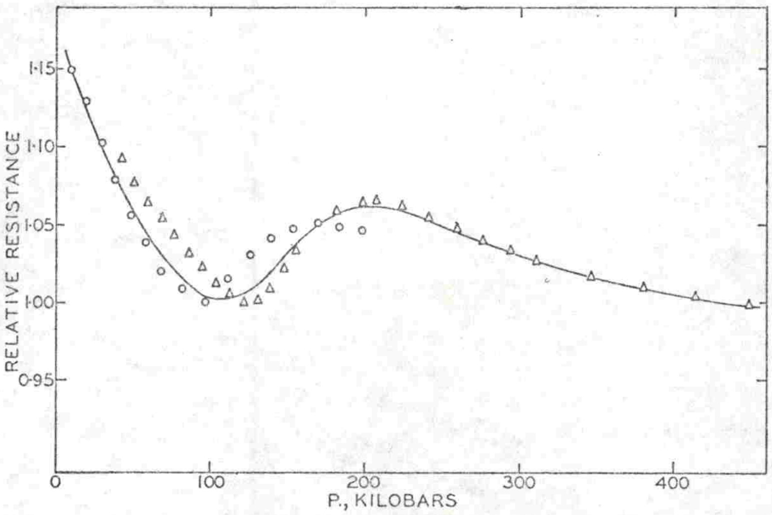

FIG. 2. Resistance vs. pressure–zinc.

pressure as a function of V/V_0. In Fig. 4 are shown c, a and relative resistance as a function of V/V_0. Figure 5 exhibits c/a and relative resistance plotted vs. V/V_0.

The a axis is at first very incompressible. At about $V/V_0 = 0{\cdot}96$–$0{\cdot}95$ its compressibility increases markedly; near $V/V_0 = 0{\cdot}89$–$0{\cdot}88$ it becomes more incompressible, while at higher density the compressibility again increases. The behavior of the c axis tends to mirror that of the a axis with high compressibility at first, which decreases markedly and then shows a sharp increase near $V/V_0 = 0{\cdot}89$–$0{\cdot}88$. This compensation is only partial as there is a distinct kink in the p vs. V/V_0 curve near $V/V_0 = 0{\cdot}85$–$0{\cdot}88$. The axial ratio c/a shows a large drop in the region $V/V_0 = 1{\cdot}0$–$0{\cdot}90$, then it levels near $V/V_0 = 0{\cdot}90$ and drops rather abruptly beyond $V/V_0 = 0{\cdot}88$.

The X-ray measurements for zinc are shown in Table 2 and Figs. 6 and 7. Qualitatively, the results are very similar to those for cadmium. In the low pressure region, the a axis is relatively

Table 1. *Smoothed data for cadmium*

V/V_0	C (Å)	a (Å)	c/a	P (kbars)
1·00	5·617	2·979	1·886	0
0·97	5·472	2·972	1·841	8
0·95	5·380	2·967	1·813	17
0·93	5·292	2·960	1·788	30
0·91	5·217	2·948	1·770	46
0·89	5·156	2·931	1·759	68
0·87	5·112	2·913	1·755	95
0·86	5·087	2·904	1·752	112
0·85	5·045	2·898	1·741	129
0·83	4·970	2·884	1·723	166
0·81	4·895	2·871	1·705	210
0·79	4·817	2·858	1·685	266
0·78	4·798	2·852	1·682	300

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incompressible (although not as incompressible as the cadmium *a* axis). Its compressibility increases markedly near $V/V_0 = 0·96$ and decreases again in the region beyond $V/V_0 = 0·90$. The *c* axis has at first a relatively high compressibility. In the region $V/V_0 = 0·94–0·91$ it shows a very small compressibility, and then its compressibility increases rapidly at higher densities. c/a decreases from 1·856 at atmospheric pressure to about 1·80 near $V/V_0 = 0·95$. It exhibits a small maximum

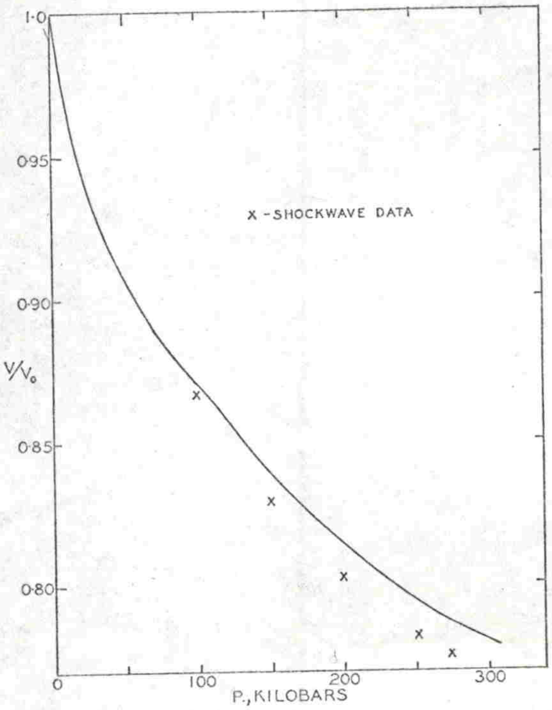

FIG. 3. V/V_0 vs. pressure–cadmium.

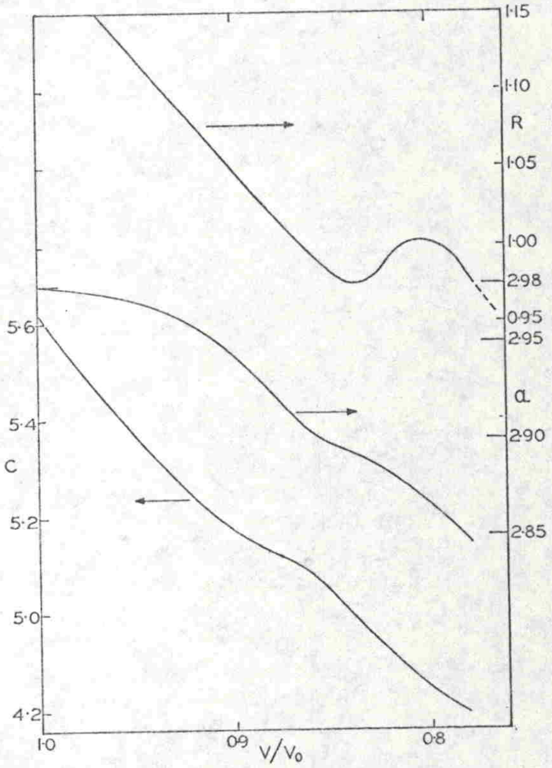

FIG. 4. *c*, *a* and resistance vs. V/V_0 cadmium.

Table 2. Smoothed data for zinc

V/V_0	c (Å)	a (Å)	c/a	P (kbars)
1·00	4·947	2·665	1·856	0
0·99	4·906	2·662	1·843	7
0·98	4·869	2·659	1·831	15
0·97	4·835	2·655	1·821	23
0·96	4·804	2·651	1·812	32
0·95	4·777	2·644	1·807	40
0·94	4·758	2·635	1·806	48
0·93	4·755	2·621	1·814	58
0·92	4·746	2·610	1·818	68
0·91	4·730	2·600	1·819	79
0·90	4·705	2·593	1·814	90
0·89	4·670	2·587	1·805	104
0·88	4·617	2·582	1·788	118
0·87	4·576	2·579	1·774	132
0·86	4·538	2·577	1·761	147
0·85	4·500	2·576	1·747	162
0·84 (?)	4·464 (?)	2·575 (?)	1·733 (?)	180

near $V/V_0 = 0{\cdot}91$–$0{\cdot}92$, then it decreases to the highest pressures obtainable.

JONES(8,9) has developed a theory of the stress introduced when a part of the Fermi surface overlaps a Brillouin zone boundary. This stress inhibits expansion of the boundary and therefore

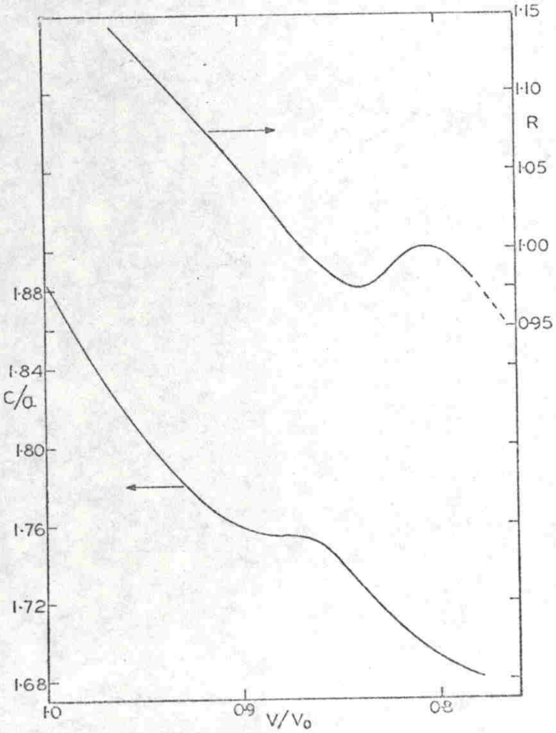

FIG. 5. c/a and resistance vs. V/V_0–cadmium.

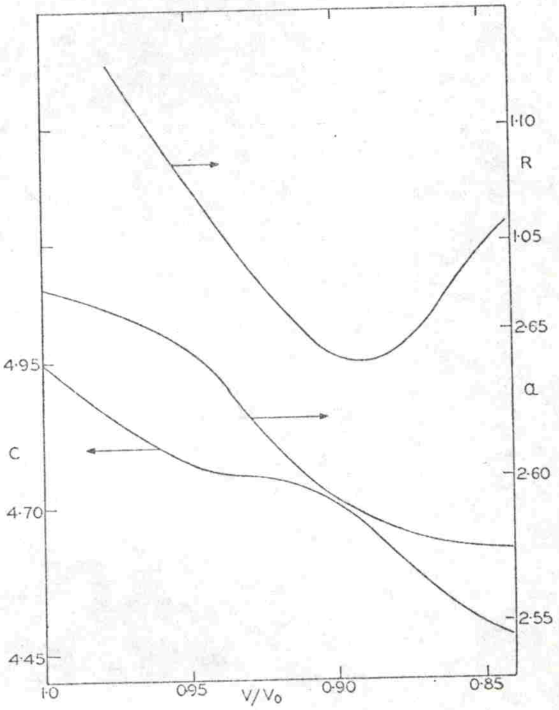

FIG. 6. c, a and resistance vs. V/V_0–zinc.

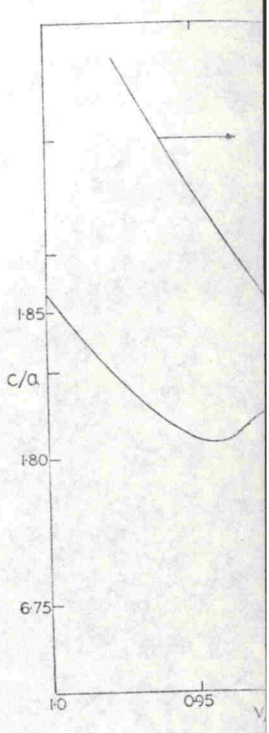

FIG. 7. c/a and re

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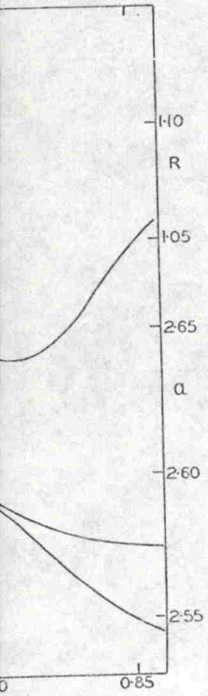

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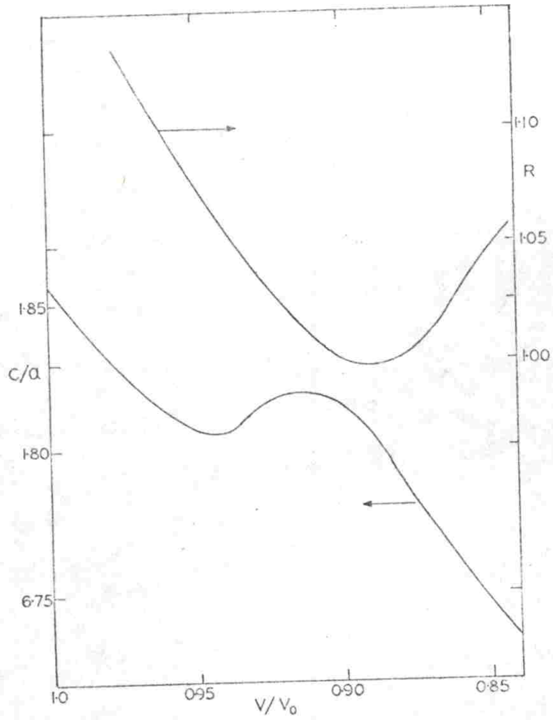

FIG. 7. c/a and resistance vs. V/V_0–zinc.

reduces the compressibility of the corresponding axis in real space. GOODENOUGH(10) has extended the study to show that there is an attractive force between a Brillouin zone boundary and a Fermi surface approaching it, but not in contact, which reduces compressibility of the corresponding axis. Contact without overlap introduces a repulsive force due to distortion of the Fermi surface which permits greater expansion of the Brillouin zone boundary. A small amount of overlap introduces a 'partial pressure' of electrons which again inhibits the expansion. At large overlap the net interaction is negligible.

It is a relatively straightforward procedure, as HARRISON(11) has shown, to construct the Fermi surface for the *hcp* structure for a free electron model. Figure 8 shows the Brillouin zone for the *hcp* structure with important symmetry points marked. For the ideal c/a ratio and two electrons per atom, there is a complex structure of holes in the second zone known as the 'monster'. It consists essentially of a ring of holes passing through points like Σ with tentacles stretching out to the points marked H. In the third and fourth zones, there are several electron pockets including a large pillow shaped pocket at Γ, cigar shaped pockets at K and complex pockets known as 'stars' at L.

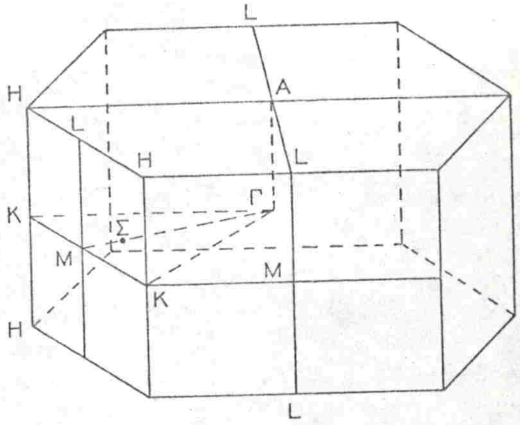

FIG. 8. Brillouin zone for *hcp* structure showing symmetry points.

HARRISON(11,12) has made OPW calculations for zinc. GIBBONS and FALICOV(13) have used extensive magneto-acoustic measurements and de Haas–van Alphen data to construct the Fermi surface and discuss electronic properties of zinc and cadmium. while there are a number of quantitative differences, the free electron picture is qualitatively correct for zinc. For cadmium, as predicted by the free electron picture, the pockets at K are gone, but the most striking feature is that the 'monster' is pinched off at the points Σ so it is not continuous throughout the zone. This phenomenon is not predicted by free electron theory.

Calculations based on the free electron model using experimentally determined values of c and a show that, with increasing density, there is an increase in the size of the pockets at K and L and a small increase in the 'pillow' at Γ.

It is not at present possible to relate our experimental results to the theories of Jones and of Goodenough or to the Fermi surface calculations in any definitive manner. Jones and Goodenough discuss approach and overlap of the Fermi surface with a zone plane, but, in the free electron model, our calculations show that the overlap of the 002 plane by the pillow at Γ does not change significantly with changing volume and c/a. Changing overlap at Brillouin zone edges and corners give higher order effects whose importance is hard to estimate.

The calculations of Harrison, and of Gibbons and Falicov show significant differences in the Fermi surfaces of cadmium and zinc. Yet the high pressure behavior of these two metals is qualitatively quite similar both as regards resistance and axial compressibility except that the a axis in cadmium is markedly less compressible than the a axis of zinc at low pressure. Effects other than the kinetic energy of the Fermi electrons may be important.

For both metals the rise in resistance occurs just beyond the knee in the c/a vs. density curve. It would seem most probable that the rise is associated with the transfer of an electron pocket from the third zone to the hole in the second zone reducing the number of free electrons. However, changes in the Fermi velocity and related effects cannot be eliminated.

As noted earlier, magnesium also exhibits a minimum and maximum in resistance at high pressure. The resistance minimum for magnesium also occurs at densities just higher than those for which the c/a ratio shows a distinct hump. It would seem that there should be a common explanation for the behavior of all three metals.

Acknowledgements—R. B. Aust obtained much of the resistance data for zinc. The authors would like to acknowledge helpful discussions with E. A. Perez-Albuerne and R. L. Clendenen of this laboratory.

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