Effect of Pressure on the Volume and Lattice Parameters of Magnesium*

G. L. Clendenen and H. G. Drickamer
Department of Chemistry and Chemical Engineering and Materials Research Laboratory, University of Illinois, Urbana, Illinois

(Received 20 April 1964)

The effect of pressure to 300 kbar has been measured on the volume and on the lattice parameters (c and a) of the hcp magnesium lattice. The a axis compresses in a regular manner, but the c axis compresses relatively rapidly to 70 kbar, then becomes continuously more incompressible in the range 70–120 kbars, which results in a distinct increase in c/a. The compressibility increases in the region 120–200 kbar and c/a is essentially constant. Beyond 200 kbar the c-axis compressibility decreases again and c/a increases rapidly. These results and earlier measurements of resistance as a function of pressure are interpreted qualitatively in terms of the theories of Jones and Goodenough and the Fermi surface as calculated by Falicov.

The effect of pressure has been measured on the volume and lattice parameters of magnesium to 300 kbar. Two sources of magnesium were used, powder from Fisher Chemical Company and turnings from a sample from Dow Chemical Company. No difference was noted. The high pressure x-ray methods have been previously described.[1] The pressure calibration is obtained by the addition of an appropriate marker of known compressibility. The markers used in this work were molybdenum and MgO. The density of molybdenum as a function of pressure is known from sock-wave velocity measurements.[2] The compressibility of MgO has been measured in this laboratory.[3] Some eighteen runs were made in all.

The calculations were largely based on the 101, 100, and 110 lines, with occasional checks made on other lines. The data were smoothed by plotting 2θ for the 101 reflection versus 2θ for each of the other reflections. Figures 1 and 2 are typical plots. Features to be especially noticed are the distinct discontinuity in slope near $2\theta_{101}=18.0°$, and the convexity of slope in the sections of the curve on either side of the discontinuity. Figure 3 shows a plot of $2\theta_{101}$ versus pressure.

In Fig. 4 the volume as a fraction of the atmospheric volume is plotted as a function of pressure. The curve shows a small but distinct irregularity in slope near 150 kbar but is otherwise quite smooth. Bridgman's[4] P-V data to 100 kbar and the data obtained from shock velocity measurements[2] are shown for comparison. Bridgman's data indicate a slightly lower compressibility; the shock wave data show a slightly higher value. A large temperature correction is necessary for the shock wave data, because of the high compressibility.

Figure 5 contains plots of c and a versus pressure. Figure 6 shows c/a. In both figures the resistance data of Stager[5] are shown. These are used in the discussion below. The results are summarized in Table I.

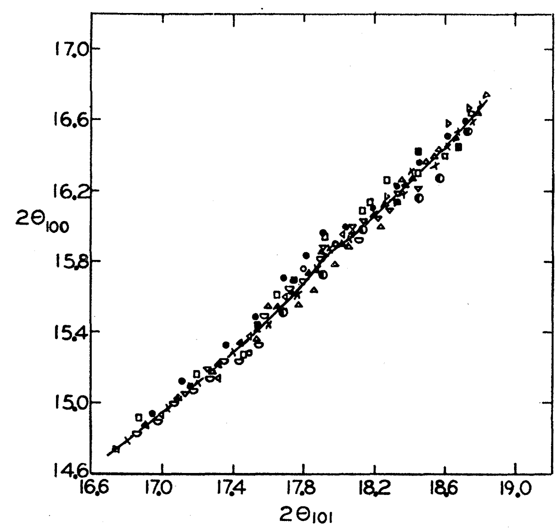

FIG. 1. Diffraction angle $2\theta_{100}$ versus $2\theta_{101}$—magnesium.

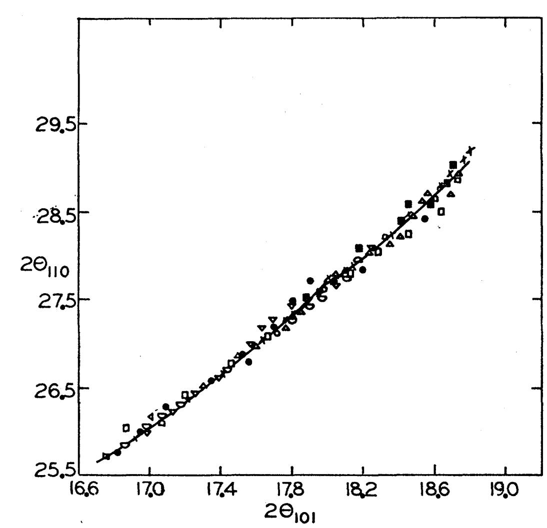

FIG. 2. Diffraction angle $2\theta_{110}$ versus $2\theta_{101}$—magnesium.

* This work was supported in part by the U. S. Atomic Energy Commission.

[1] E. A. Perez-Albuerne, K. F. Forsgren, and H. G. Drickamer, Rev. Sci. Instr. 33, 29 (1964).

[2] M. H. Rice, R. W. McQueen, and J. M. Walsh, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 1.

[3] E. A. Perez-Albuerne (private communication).

[4] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 76, 55 (1948).

[5] R. A. Stager and H. G. Drickamer, Phys. Rev. 131, 2524 (1963).

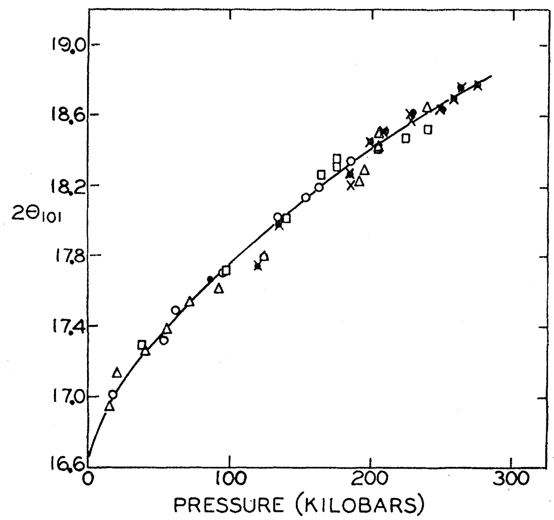

FIG. 3. Diffraction angle $2\theta_{101}$ versus pressure—magnesium.

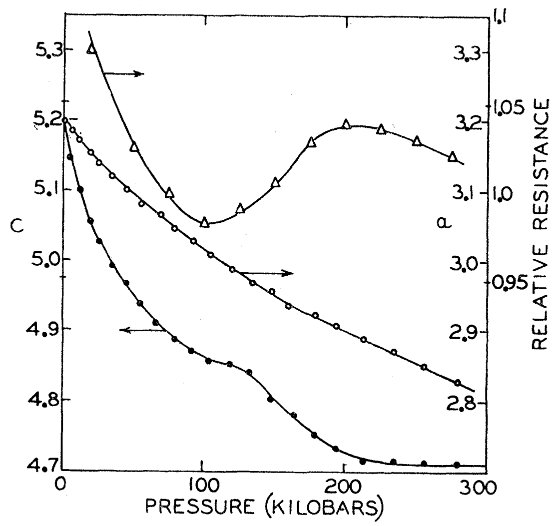

FIG. 5. Lattice parameters a and c and resistance versus pressure—magnesium.

From Fig. 5 it can be seen that the a axis varies smoothly with pressure, but that the c axis shows some unusual features which result in the peculiar shape of the c/a curve. There is a sharp drop in c/a in the first 20 kbar. At first we were inclined to attribute this initial drop in c/a to production of stacking faults or some similar phenomenon due to nonhydrostaticity. The change in c/a ratio is, however, entirely reversible and reproducible, and the peaks do not change in shape or relative intensity. From about 20–70 kbar the ratio is relatively independent of pressure. From 70–120 kbar the c axis becomes quite incompressible, resulting in a distinct rise in c/a. From about 120–200 kbar the c axis exhibits larger compressibility and c/a is essentially constant. Beyond 200 kbar the compressibility of the c axis decreases rapidly and c/a accordingly increases sharply.

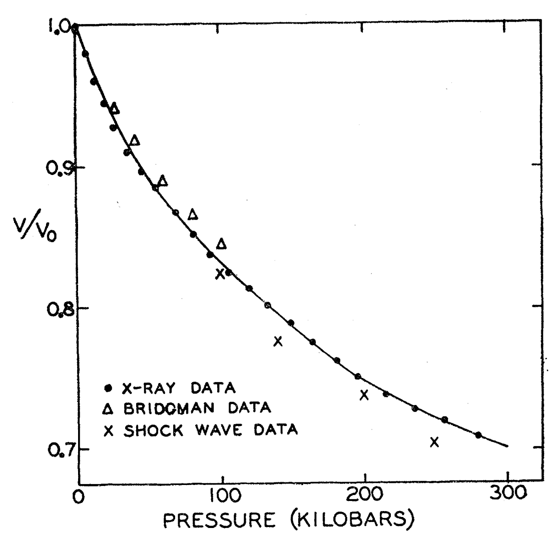

FIG. 4. Fractional change in volume versus pressure—magnesium.

In order to discuss these results it is necessary to review the available studies of the electronic structure of magnesium, in particular the relationship between the Fermi surface and the Brillouin zone boundaries.

Since the magneisum atom contains only filled shells, it would be an insulator if there were not holes in the second Brillouin zone and some overlap of electrons into the third or higher zones. Jones[6] discussed the arrangement on the basis of a spherical Fermi surface. His picture showed overlap at two points, but none in the [002] direction. He then accounted for the axial ratios of magnesium alloys on the basis of overlap in this direction because of the increased electron/atom ratio in the alloy. In particular, Jones showed that there

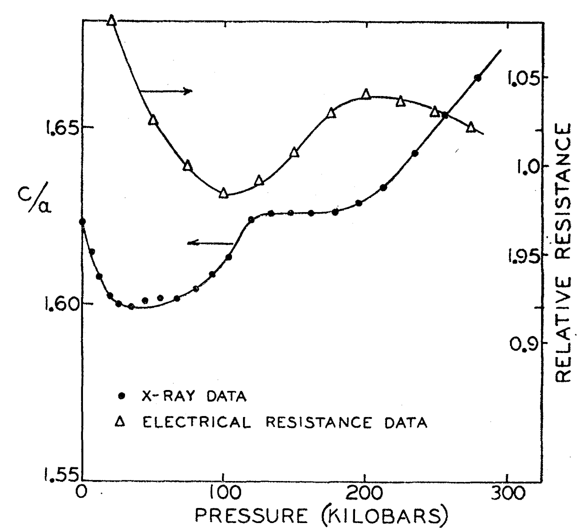

FIG. 6. Lattice parameter ratio c/a and resistance versus pressure—magnesium.

[6] H. Jones, Proc. Roy. Soc. (London) A147, 396 (1934).

TABLE I. Effect of pressure on volume and lattice parameters of magnesium.

P (kbar)	V/V_0	c	a	c/a
0	1.000	5.199	3.203	1.623
25	0.933	5.032	3.145	1.600
50	0.890	4.954	3.096	1.600
75	0.858	4.899	3.057	1.603
100	0.831	4.862	3.019	1.610
125	0.810	4.848	2.986	1.624
150	0.787	4.808	2.954	1.627
175	0.765	4.763	2.926	1.628
200	0.747	4.730	2.902	1.630
225	0.733	4.718	2.879	1.639
250	0.721	4.713	2.857	1.650
275	0.710	4.711	2.836	1.661
300	0.700	4.710	2.815	1.673

would be a lowering of the Fermi energy accompanying an overlap between the Fermi surface and the Brillouin zone wall. This theory was extended by Goodenough,[7] who pointed out that there could be attractive interaction between the Fermi surface and the zone boundary where they approached without overlapping, and that this interaction could affect the axial ratio and the axial compressibility.

Recent studies indicate that the picture based on a spherical Fermi surface is oversimplified. The calculations of Reitz and Smith[8] and the elastic constant measurements of Smith and his colleagues[9,10] showed that the Fermi surface must overlap the wall of the third Brillouin zone in pure magnesium at one atmosphere.

The detailed calculations of Falicov[11] indicate that the Fermi surface is very complex with a hole in the shape of a twelve-tentacled "monster" in the first and second zone, and electron pockets penetrating in the third and fourth zone in a number of spots including the plane perpendicular to the [002] axis.

In spite of the oversimplification involved in assuming a spherical Fermi surface, many of the qualitative arguments of Jones and Goodenough are almost certainly valid.

The discussions of Jones and of Goodenough give a particularly straightforward picture of the events between say 50 and 200 kbar. It should be kept in mind that compression of the c axis corresponds to expansion of the {002} face of the Brillouin zone. From 20–70 kbar c/a is substantially constant and the resistance decreases in a "normal" fashion. Beyond 70 kbar, a further compression of the c axis (expansion of the [002] axis) would result in extension of the second zone to envelop some of the Fermi surface originally in the third zone. As Jones has shown, this would involve an increase in energy, so the lattice distorts to prevent this overlap. Thus, c is relatively incompressible and c/a increases. Beyond 120 kbar it costs so much energetically to distort the lattice further that it is preferable to expand the {002} face and overlap part of the pocket of the Fermi surface back into the holes of the second zone. This, however, reduces the number of available conduction electrons. Accordingly, the resistance increases. In the region of highest pressure the c axis is again becoming incompressible, and c/a is increasing, quite possibly due to the approach of the {002} zone boundary to another piece of the Fermi surface.

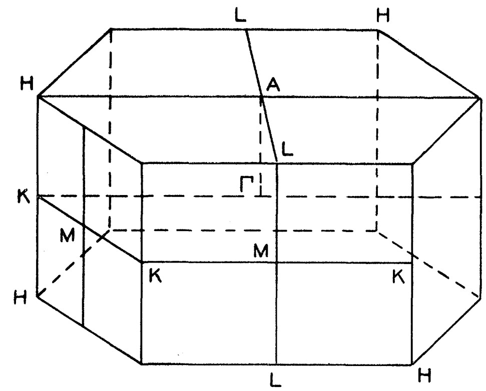

FIG. 7. Brillouin zone for hcp structure with certain symmetry points indicated.

Some qualitative observations can be made concerning the relationship of c/a ratio to Falicov's calculated Fermi surface. Figure 7 shows the hcp Brillouin zone with certain symmetry points marked using the usual nomenclature. Falicov's calculations show electron pockets in the third and fourth zones at Γ, at L, and at K. The holes in the first and second zone overlap the zone boundaries at H. In addition, the electron pocket at K approaches very closely the hole in this region. A discussion with Dr. Falicov[12] indicates the following qualitative features. (1) A decrease in c/a will be accompanied by decreases in the pockets at L and Γ, a shrinking of the hole at H, and an increase in size of the pocket at K. (2) An increase in c/a will be accompanied by an increase in the pocket at L and a decrease in the pocket at K. The increase in resistance in the region beyond 100 kbar can be accounted for by a decrease in total Fermi surface, quite possibly due to overlap between holes and electron pockets at the point K.

In essence, this last paragraph is a more specific rephrasing of the generalizations based on Jones' theory in terms of the Fermi surface of Falicov.

ACKNOWLEDGMENTS

The authors wish to thank J. Bardeen, C. S. Smith, F. Garcia-Molinar, and particularly L. Falicov for very helpful discussions.

[7] J. B. Goodenough, Phys. Rev. 89, 282 (1953).
[8] J. R. Reitz and C. S. Smith, Phys. Rev. 104, 1253 (1956).
[9] T. R. Long and C. S. Smith, Acta Met. 5, 200 (1957).
[10] R. E. Smunk and C. S. Smith, Phys. Chem. Solids 9, 100 (1959).
[11] L. Falicov, Phil. Trans. Roy. Soc. (London) A255, 55 (1962).
[12] L. Falicov (private communication).