SOLID STATE PHYSICS PROGRAM

PRESSURE DERIVATIVES OF THE ELASTIC CONSTANTS OF CADMIUM

by J.A. CORLL

OFFICE OF NAVAL RESEARCH
TECHNICAL REPORT NO. 6
CONTRACT Nonr-1141 (05)
PROJECT NR 017-309

JUNE 1962

CASE INSTITUTE OF TECHNOLOGY
UNIVERSITY CIRCLE
CLEVELAND 6, OHIO

ABSTRACT

The pressure derivatives of the elastic stiffness constants of cadmium have been measured by the ultrasonic pulse echo technique. In terms of dC/dP the results are: C_{11}, 9.29; C_{33}, 7.26; C_{66}, 2.59; C_{44}, 2.38; C_{12}, 4.10; C_{13}, 5.66; and $C_{11} + C_{12} + 2C_{33} - 4C_{13}$, 5.27. These values are comparable with those previously found for polyvalent aluminum and magnesium. An attempt was made to fit to cadmium the theory of Reitz and Smith for the elastic constants of magnesium. A fit could not be made, presumably because of the high overlap electron populations which arise from the anomalously high (c/a) ratio of cadmium. Consequently the pressure data could not be interpreted in terms of this model as was the same data for magnesium.

INTRODUCTION

The elastic constants of metals with valence two and three present an interesting and unreconciled theoretical problem. It seems clear that the proximity of the Fermi surface to the Brillouin zone boundary will produce effects in the elastic property which are very large compared with the same effects in monovalent metals. Many details of the complex Fermi surface of these metals have recently become available from several modern techniques. Before these results were available, an older and far simpler view of the electronic structure had been used, initially by Leigh[1], in the interpretation of the experimental elastic properties of aluminum[1], magnesium[2,3,4] indium[5] and beryllium[6]. This simple model is reasonably successful in accounting for the elastic properties of these metals but it does not seem possible to reconcile it with the now known complex structure of the Fermi surface, except possibly in the case of magnesium.

The effect of pressure on the elastic constants of aluminum and magnesium[7] has been studied and plausibly interpreted in terms of the simple model with some advance in understanding. Cadmium is a metal with the HCP structure like magnesium and beryllium but with an anomalously high (c/a) ratio. The

elastic properties has recently been studied as a function of temperature by Garland Silverman[8]. It was felt that a study of the effect of pressure, besides being intrinsically useful, would provide a particularly severe test of the simple model in view of the anomalous (c/a) ratio. This feeling has been confirmed; we have not been able to fit the simple model even to the elastic constants themselves, much less to go on to the interpretation of the effect of pressure.

A further, but minor, reason for the pressure study lay in the possibility of a phase transformation in the accessible pressure range. Long ago Bridgman[9] reported anomalies in the linear compressibility and electrical resistance of cadmium single crystals. Jamieson[10] failed, however, to find X-ray evidence for a transformation at pressures up to 16,000 bars. A phase transformation would be expected to produce catastrophic effects in the elastic property of single crystals, but none have been observed in experiments carried to 9000 bars, thus confirming the X-ray evidence.

EXPERIMENTAL PROCEDURE

The crystals used in this research were grown from cadmium donated by the McGean Chemical Company of Cleveland, Ohio. Spectrographic analysis by the Herron Testing Laboratories, (Cleveland, Ohio) showed the sample to contain the following impurities; Fe $<$ 0.01%, Cu $<$ 0.01%. The crystals were grown by passage of a high thermal gradient through a preformed cadmium slug in a small furnace which was especially constructed for this purpose. The motion of the thermal gradient was effected by slowly decreasing the power into the heating coils of the furnace. No motion of the furnace or slug was involved. During the growth an argon atmosphere was maintained in the furnace. The growth of cadmium crystals was found to be relatively easy and once a growth procedure was established, single crystal slugs were obtained on almost every trial. Grain boundaries, if any, were visible when the cadmium slug was removed from the graphite crucible; an etch of one or two per cent nitric acid in alcohol enhanced these and served to verify that no other boundaries were present.

The single crystal slugs were approximately 1 in. in diameter and 4 in. long; from these slugs, specimens with a desired orientation were removed using a string saw and a saturated solution of ammonium nitrate in water. The specimen shape was a

right circular cylinder approximately 5/8 in. in diameter and 1 in. long. The specimens were then mounted in a steel lapping ring with the desired propagation direction perpendicular to the face of the lapping ring. The proper orientation of the specimen was checked by means of a back reflection Laue X-ray photograph while the specimen was mounted in the lapping ring. At this point the surfaces of the specimen were carefully cut off with an end mill until only a few thousands of an inch protruded from the lapping ring. The protruding surfaces were then removed by alternate grinding on fine metallographic polishing paper and etching, until the specimen surfaces were flush with the lapping ring. Removal from the lapping ring completed the sample preparation. This method of preparing the acoustic reflecting surfaces is justified by the fact that a fuzzy, but still discernable single crystal X-ray pattern may be obtained from the surface at the end of preparation.

Since cadmium is hexagonal it was necessary to make measurements in more than one crystalographic direction to obtain all five elastic constants and their pressure derivatives. The final dimensions and orientations of the specimens are given in Table 1. The normals to the reflecting surfaces of the A

Table 1. Specimen Length and Orientation. Twice the crystal length is the distance traveled by the ultrasonic pulse between time measurements, and θ is the angle between the normal to the reflecting surface and the "c" axis.

Crystal	Length	θ
A	2.3888 cm	$89^\circ\ 36'$
C	2.2555 cm	$0^\circ\ 5'$
H	2.3787 cm	$44^\circ\ 57'$

crystal are approximately parallel to an "a" axis and the normals to the reflecting surfaces of the C crystal are approximately parallel to the "c" axis. The normals to the reflecting surfaces of the H crystal are approximately 45° from the "c" axis and lie in a zone whose axis is an "a" axis.

The wave velocities and their pressure derivatives were measured by the ultrasonic pulse echo technique which is fully described in previous papers from this laboratory[11,12] The velocity measurements are related[4] to the elastic constants in a hexagonal crystal by the following equations.

$$C'_{11} = (\rho v^2)_{11} - \left(\frac{(C'_{15})^2}{C'_{11} - C'_{55}} \right)$$

$$C'_{66} = (\rho v^2)_{66} \qquad (1)$$

$$C'_{55} = (\rho v^2)_{55} + \left(\frac{(C'_{15})^2}{C'_{11} - C'_{55}} \right)$$

The primed C's refer to a coordinate system which rotated with respect to the conventional coordinate system such that X' makes an angle θ with the "c" axis and is the direction of propagation and Y' lies in the basal plane. The term $(\rho v^2)_{11}$ refers to the longitudinal wave and the terms $(\rho v^2)_{66}$ and

$(\rho v^2)_{55}$ refer to the two transverse wave. The term $(\rho v^2)_{66}$ refers to particle motion perpendicular to the "c" axis and the term $(\rho v^2)_{55}$ refers to particle motion in a plane containing X' and the "c" axis. The pertinent relations between the primed and conventional elastic constants are

$$C'_{11} = \sin^4\theta\, C_{11} + \cos^4\theta\, C_{33} + 2\cos^2\theta \sin^2\theta\, (C_{13} + 2C_{44})$$

$$C'_{66} = \sin^2\theta \left(\frac{C_{11} - C_{12}}{2}\right) + \cos^2\theta\, C_{44} \qquad (2)$$

$$C'_{55} = \sin^2\theta \cos^2\theta\, (C_{11} - 2C_{13} + C_{33}) + (\sin^2\theta - \cos^2\theta)^2\, C_{44}$$

$$C'_{15} = \sin^3\theta \cos(-C_{11} + C_{13} + 2C_{44}) + \cos^3\theta \sin\theta(-C_{13} + C_{33} - 2C_{44})$$

$$C'_{16} = 0$$

$$C'_{56} = 0$$

The choice of specimen orientations listed in Table 1 simplify the above equations and solution of equations(1) and (2) yields the conventional elastic constants obtained in this work.

Table 2 displays the values of the elastic constants at 27°C which were obtained in this work. The density, ρ, of 8.648 g cm^{-3} that was used in reducing the data was computed

Table 2. The adiabatic elastic constants of cadmium in units of 10^{12} dyne/cm^2 at 27°C compared with the values of Garland and Silverman[8]. Also shown are measured values of the pressure derivatives dC/dP and of the related quantity -dlnC/dlnr defined in the text.

	Garland and Silverman	This work		
	C	C	dC/dP	-dlnC/dlnr
C_{11}	1.138	1.145	9.29	11.2
C_{33}	0.506	0.511	7.26	19.6
C_{66}	0.373	0.374	2.59	9.6
C_{44}	0.200	0.200	2.38	16.4
C_{12}	0.392	0.396	4.10	14.3
C_{13}	0.400	0.401	5.66	19.5
C_H	0.941	0.958	5.27	7.6

from the lattice constants of Jette and Foote[13] converted to Angstrom units to give "a" = 2.9789 Å, "c" = 5.6167 Å, together with Avogadro's number 6.02305×10^{23}, and the chemical atomic weight 112.41 g $mole^{-1}$. These results are compared with the recent pulse echo measurements of Garland and Silverman[8]; after correspondence with Professor Garland we have multiplied the values quoted in their paper by $(1.00202)^{-6}$ to correct an error made in their conversion of the Jette and Foote lattice constants to Angstrom units.

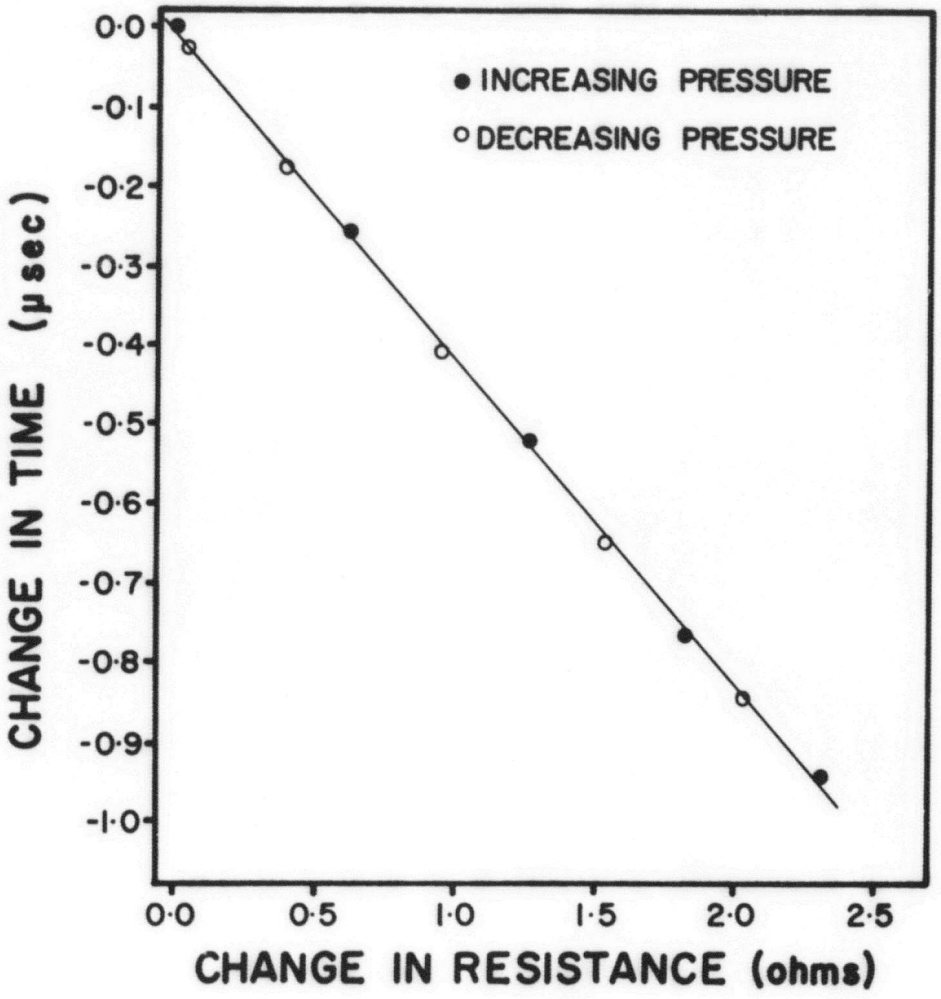
Measured values of (ρv^2) are reproducible to 0.2 per cent as determined by repeated measurement on the same crystals. A far better test of accuracy is a comparison of constants determined independently from two different crystals. The constant C_{44} is nearly directly determined from both crystal A and crystal C; these numbers differed by 0.5 per cent, the average being quoted in Table 2. Upon taking into account other sources of uncertainty not assessed by such a test an accuracy figure of 1.0 per cent may be set on the values quoted in Table 2. In this light the comparison of the data from the two laboratories is good.

Also listed in Table 2 is the combination $C_H = (C_{11} + C_{12} + 2C_{33} - 4C_{13})$ which is important in this work and which corresponds to a strain which changes the (c/a) ratio, leaving the volume and symmetry of the crystal unchanged. The isothermal linear compressibilities and the bulk modulus are needed in the reduction of pressure data. These values, computed from the elastic stiffness constants of Table 2 and Handbook[13] values of the linear expansivities and heat capacity are:

$k_{\parallel}^T = 1.653 \times 10^{-12}$ cm^2/dyne, $k_{\perp}^T = 0.261 \times 10^{12}$ cm^2/dyne, and $B_T = 0.460 \times 10^{12}$ dyne/cm^2.

The pressure derivative measurements were made in high pressure apparatus developed by Daniels[15], and the pressure bomb and the general theory for pressure measurements are described in previous papers from this laboratory[12,16]. The range of pressures used in this work extended to 5000 atmospheres; the pressure was measured by the (linear) change of resistance with pressure of a manganin resistance gage. The pertinent data recorded was the change of arrival time of a late ultrasonic echo versus the change in resistance of the manganin resistance gage. A typical plot of this data is shown in Fig. 1.

Fig. 1. Pressure data for longitudinal wave (C_{33}) propagation in crystal C, showing the change in arrival time of the ultrasonic echo versus the change in resistance of the pressure gage.



The pressure derivatives were obtained by combination of the derivatives of equations (1) and (2) with

$$\frac{d}{dp}(\rho v^2) = \frac{-2(\rho v^2)}{K}\left(\frac{1}{T}\frac{dT}{dR}\right) + (\rho v^2)\left[\frac{1}{B_T} - 2k_\theta^T\right] \qquad (3)$$

where R is the resistance of the pressure gage, T is the transit time of the ultrasonic echo, K is the pressure gage constant, and k_θ^T is the linear isothermal compressibility in the direction of propagation.

The reduction of the pressure data was greatly simplified by the orientations of the crystals (see Table 1). In the cases of the A and C crystals the derivatives of equations (2) immediately reduce to the desired dC/dP's with only very small perturbations. The only measurements determined with the H crystal are C_{13} and dC_{13}/dP and the reduction of pressure data for this crystal is a bit more involved due to the change of orientation (θ) of the crystal surfaces with pressure. The choice of $\theta = 45^\circ$ greatly simplified the dC_{13}/dP computation and the perturbation due to the change in θ with pressure amounted to approximately 1 per cent of the measured $d(\rho v^2)_{55}/dP$.

The raw pressure data were generally without hysteresis or significant curvature as is shown in Fig. 1. Several of the pressure runs were repeated and gave a reproducibility of slope of 2 per cent. On the other hand the independent and directly determined values of dC_{44}/dP are available from crystals A and C; these differed by only 1 per cent. The value for dC_{44}/dP quoted in Table 2 is the average of these two determinations. Taking into account other sources of error a maximum uncertainty of 5 per cent may be placed on the values of dC/dP reported in Table 2.

Comparisons of the dC/dP values for cadmium with the previously reported dC/dP values for aluminum and magnesium[7] show cadmium values to be on the same order of magnitude and to have approximately the same ratio between compressional and shear stiffnesses as the values for aluminum and magnesium.

As already mentioned, the application of pressure to hexagonal cadmium causes a change in (c/a) ratio in addition to a volume change. This complication in the deformation is much more important in cadmium than in magnesium because the linear compressibility of cadmium is quite anisotropic. In order to compare the pressure measurements for cadmium with

those for other metals on the basis of strain rather than pressure change we have set $dP = -B_T d\ln V = -3B_T d\ln r$, thus defining $d\ln r$. The quantities $-d\ln C/d\ln r$ in Table 2 then measure the fractional change in stiffness divided by an average linear strain. For all constants this quantity is large in cadmium.

INTERPRETATION AND CONCLUSIONS

In several previous papers[2,5,17] from this laboratory it has been possible to account theoretically for the elastic constants of several metals by assuming three contributions to the elastic shear strain energy of the crystal: (1) a purely electrostatic (or Coulomb) term representing the difference of electrostatic energy of the ion cores in the strained and unstrained geometry, (2) a term arising from a short range repulsive interaction of the ion cores, and (3) an additional term due to changes in Fermi energy, caused by movements of the Brillouin zone planes as the metal is sheared.

In cadmium the ion radius is small compared to the atomic radius (0.97:1.49) and in this work it was assumed that interactions between the ion cores did not contribute to the elastic stiffnesses, an assumption also made for other polyvalent metals, magnesium, aluminum and indium. The calculation of the Fermi energy contribution to the elastic stiffness in cadmium follows the model of Leigh[1]; the modification for the hexagonal close packed structure is fully explained in a previous paper from this laboratory on magnesium by Reitz and Smith[2]. This calculation is made in two steps which are treated independently; (I) a full zone contribution and (II) an overlap-hole

contribution. The full zone calculation treats the Brillouin zone as fully occupied and energy changes occur through movement of Brillouin zone planes. The overlap-hole contribution provides for displacement of the Fermi surface during shearing and the simultaneous transfer of electrons from certain positions to others.

These contributions to the elastic constants were calculated for two types of strain: (1) a C_{66} strain which changes the angle between any pair of orthogonal axes in the basal plane leaving the volume and "c" axis of the crystal unchanged, and (2) a C_H strain which changes the (c/a) ratio leaving the volume of the crystal unchanged. In terms of the convenient strain parameters the basis vectors for the hexagonal lattice in real space become:

$$\underline{a}_1 = a\,\eta^{\frac{1}{2}}\,(1,0,0)$$

$$\underline{a}_2 = a\,\eta^{\frac{1}{2}}\,(-1/2, \sqrt{3}/2\,\eta\,, 0)$$

$$\underline{c} = c\,(0,0,1)$$

and $C_{66} = \left(\frac{d^2W}{d\eta^2}\right)_{\eta=1}$

for C_H strain

$$\underline{a}_1 = a\, \xi^{1/3}\, (1,0,0)$$

$$\underline{a}_2 = a\, \xi^{1/3}\, (-1/2,\ \sqrt{3}/2,\ 0)$$

$$\underline{c} = c\, \xi^{1/3}\, (0,0,\xi^{-1})$$

and $$C_H = \left(\frac{d^2W}{d\xi^2}\right)_{\xi=1} (9/2)$$

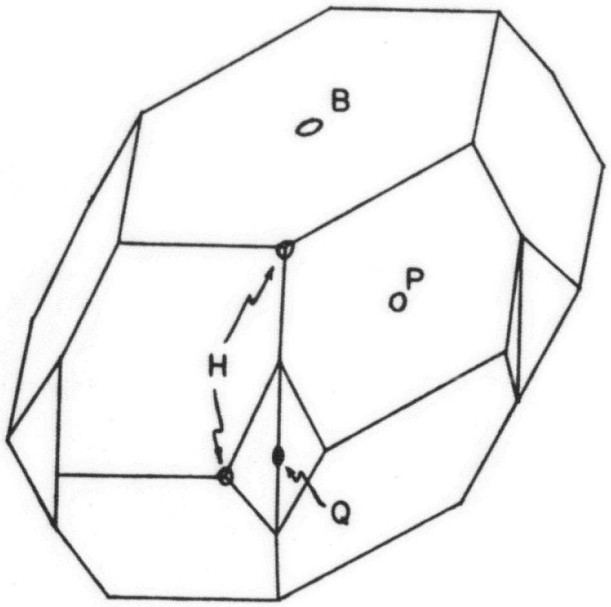
A further condition is obtained by considering the first derivatives of the energy with respect to the strains. The conditions for equilibrium with no applied stress are

$$\left(\frac{dW}{d\eta}\right)_{\eta=1} = 0 \quad \text{and} \quad \left(\frac{dW}{d\xi}\right)_{\xi=1} = 0$$

In the case of the C_{66} strain all three contributions have first derivatives which are independently zero; in the case of the C_H strain the Coulomb and the full zone Fermi first derivatives yield negative contributions and must be matched by a positive contribution from the overlap-hole term to comply with the equilibrium condition, which thus becomes an independent and useful condition.

A C_{44} type strain lowers the symmetry of the crystal such that the calculations become quite involved. No attempt was made to account for the C_{44} shear constant.

Fig. 2. The second Brillouin zone of cadmium. The small spheroids indicate the assumed positions of electron overlap and holes. Only one position of each type is shown. The two H positions are of the same type.



Coulomb Term: The contributions of the Coulomb energy (W_c) to the stiffnesses C_H and C_{66} were calculated at the observed (c/a) ratio of 1.8855 by an extension of Ewald's method[18] on the assumption that the doubly-charged ion-cores may be approximated by point charges in an electron sea of uniform density. The effective charge of the ion-cores was taken to be 2Ze and the results of the calculations are recorded in Table 3 as a function of Z^2. The fact that c/a is different from the ideal value of $(8/3)^{1/2}$ substantially modifies the calculated coulomb stiffness C_H.

Full Zone Term: In calculating the contributions of the full zone Fermi energy (W_F^I) the energies of the electron states are taken to be proportional to the free electron energies; the constant of proportionality being the inverse effective-mass ratio (m/m*). The parameter α_o is introduced as the inverse effective-mass ratio (m/m*) for the full zone. The details of the calculations are given in the Appendix and the results are recorded in Table 3 as a function of α_o.

Overlap-Hole Term: In the calculation of the contribution from the overlap-hole energy (W_F^{II}), the B and P types of overlaps and the H type of hole were assumed (see Fig. 2.). The Q type overlap has not been observed in cadmium by low field De Haas

Table 3. The Coulomb and full zone contributions to the elastic constants of cadmium in units of 10^{12} dyne/cm^2. The values are calculated for the observed (c/a) ratio 1.8855. Experimental observed elastic constants are listed for comparison.

	C_H	C_{66}	$\frac{dW}{d\zeta}$
Coulomb contribution	$4.821Z^2$	$0.355Z^2$	$-0.113Z^2$
full zone contribution	$2.066\alpha_o$	$0.255\alpha_o$	$-0.063\alpha_o$
experimental values	0.958	0.374	0.000

Table 4. First and second derivatives of the various overlap and hole energies in cadmium with respect to the C_H shear parameter ξ and the C_{66} shear parameter η, evaluated at zero strain and (c/a) = 1.8855.

Type	number of spheroids	$x = \xi$	$x = \eta$
		$\left(\frac{dE_i}{dx}\right)$	
B	1	$(4/3)E_B$	0.0
P	4	$-0.3182E_P$	$-0.4129E_P$
P	2	$-0.3182E_P$	$0.8258E_P$
H	4	$-0.1888E_H$	$0.0663E_H$
H	2	$-0.1888E_H$	$-0.1326E_H$
		$\left(\frac{d^2E_i}{dx^2}\right)$	
B	1	$(4/9)E_B$	0.0
P	4	$0.9950E_P$	$1.2387E_P$
P	2	$0.9950E_P$	0.0
H	4	$1.2354E_H$	$1.3320E_H$
H	2	$1.2354E_H$	$1.0267E_H$

van Alphen work and is therefore not taken into consideration in this model.[19] The B type overlap was considered to be large in comparison to the P type overlap and the number of hole states was, of course, taken as equal to the sum of the overlap electrons. The numerical value of the overlap-hole contribution is a function of several parameters. These are n_i the number of states per pair of overlaps or holes, N_i the density of states at the Fermi surface per pair of overlaps or holes, and E_i the energy at the points where the overlaps or holes first occur. The derivatives, $dW_F^{II}/d\xi$, $d^2W_F^{II}/d\xi^2$, $d^2W_F^{II}/d\eta^2$ are lengthy functions of the n_i, N_i and of derivatives of the E_i with respect to strain parameter. These expressions are given in the paper by Reitz and Smith[2]. The derivatives of the E_i with respect to strain parameter were computed as part of the program for the full zone term that is described in the Appendix. These derivative results, evaluated for c/a = 1.8855, are listed in Table 4.

The useful equations of the model are listed below:

$$n_B + 6\, n_P + 6\, n_H = 0 \qquad (4)$$

$$N_B + 6\, N_P + 6\, N_H = N_f \qquad (5)$$

$$dW_c/d\xi + dW_F^I/d\xi + dW_F^{II}/d\xi = 0 \qquad (6)$$

$$d^2W_c/d\xi^2 + d^2W_F^I/d\xi^2 + d^2W_F^{II}/d\xi^2 = C_H \qquad (7)$$

$$d^2W_c/d\eta^2 + d^2W_F^I/d\eta^2 + d^2W_F^{II}/d\eta^2 = C_{66} \qquad (8)$$

The density of states at the Fermi level may be calculated from measurements of the electronic specific heat. The data reported by Clement[20], gives the total density of states per unit energy range at the Fermi level as $N_f = 8.73 \times 10^{33}$ erg^{-1} cm^{-3}.

In order to explore for solutions, Equations 6, 7 and 8 can be graphed with the free parameters Z^2 and α_o as coordinates. In this form the slopes of the lines are the ratio of the numerical coefficient of α_o to the coefficient of Z^2 (Table 3), and the Z^2 intercepts are related to the appropriate derivative of W_F^{II} (a function of n_i, N_i, E_i). Values of the n_i and E_i were first estimated from free electron theory (the n_i then automatically complying with Equation 4) and reasonable values of the N_i that satisfy Equation 5 were chosen. This graph is shown in Fig. 3 and the lack of intersections demonstrates the unavailability of simultaneous solutions for the three equations with a physically possible value of Z^2.

Fig. 3. Plots of Z^2 versus α_o for Equations 6, 7, and 8 of the text. Free electron values of the overlap-hole parameters E_i and n_i have been used, together with reasonable values of the N_i which satisfy Equation 5.

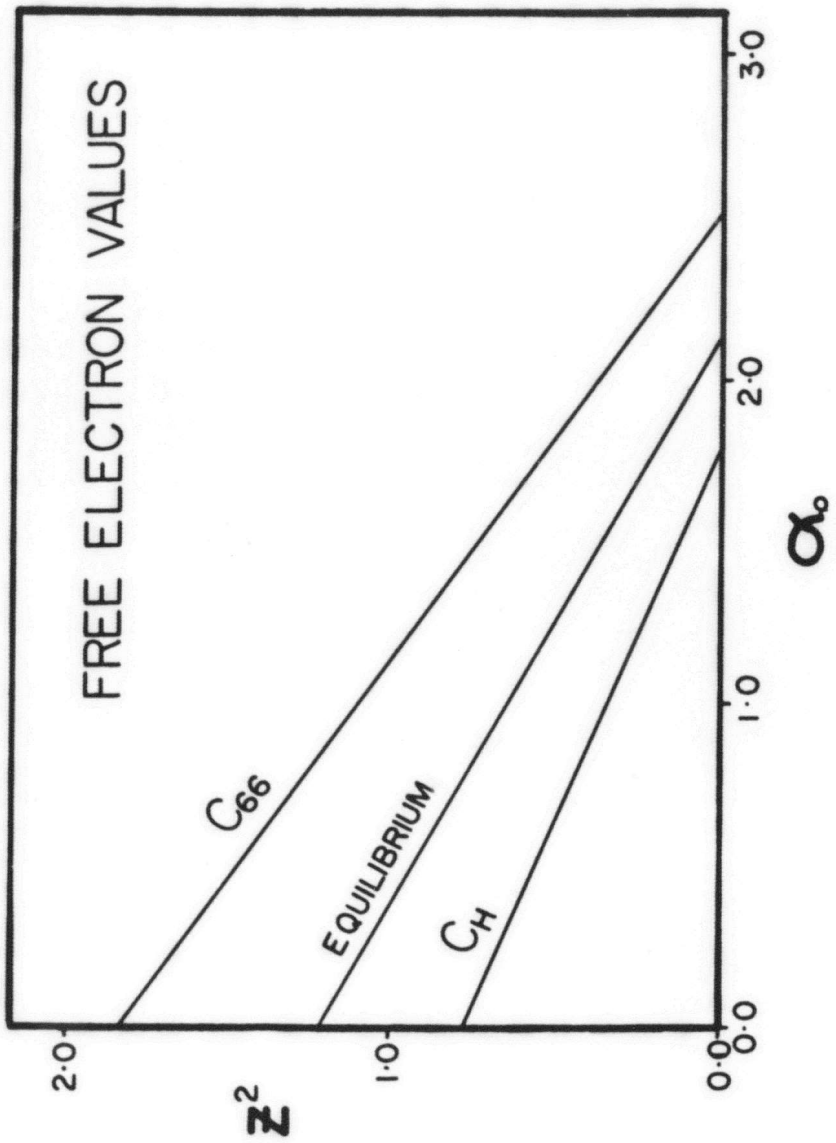
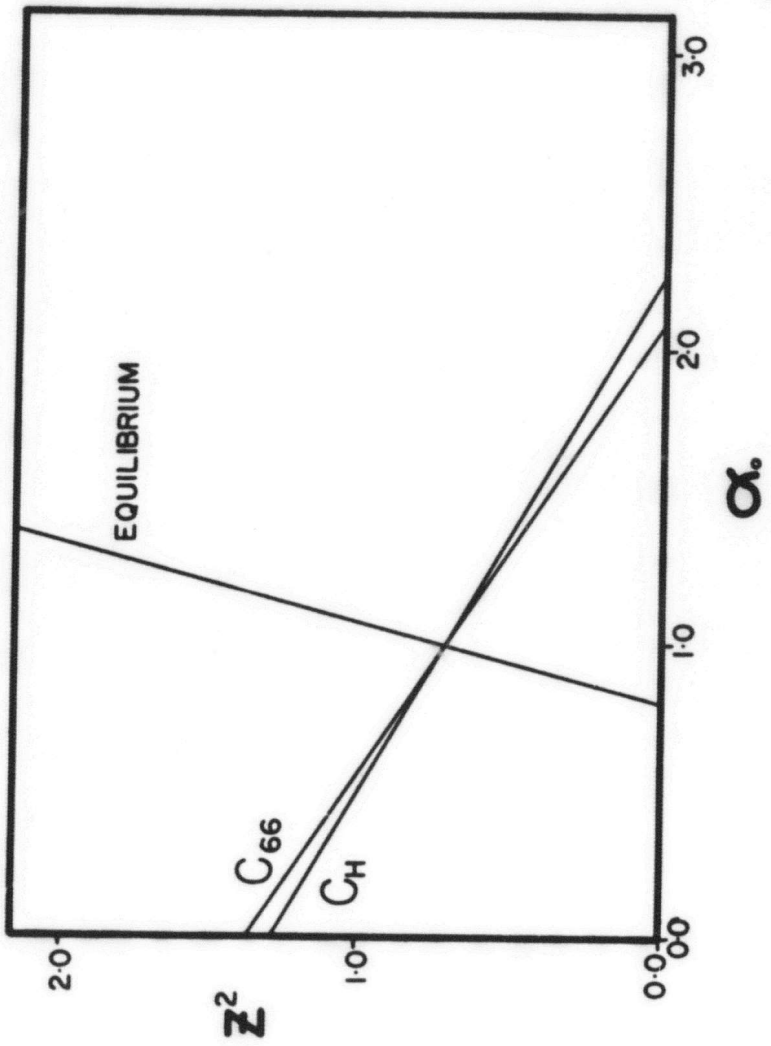


Fig. 4. Plots of equations 6, 7 and 8 for magnesium. The values of the n_i, N_i, and E_i used are those quoted by Eros[3]. The striking difference between the equilibrium equations for cadmium and magnesium is due to the major change in the first derivatives of the Coulomb contributions to C_H.



Next many physically reasonable variations in the parameters n_i, N_i and E_i were tried thus altering the intercepts on the plot. It was found that either the (c/a) equilibrium equation (6) and the C_H equation (7) could be satisfied, or the (c/a) equilibrium equation (6) and the C_{66} equation (8) could be satisfied, but the C_H equation (7) and the C_{66} equation (8) could not be simultaneously satisfied with the required positive value of Z^2.

From the above discussion one must conclude that a model more advanced that this one is necessary to interpret the elastic constants of cadmium. It is not unreasonable that the model used should break down for a high (c/a) ratio material like cadmium for one of the basic assumptions of the model is the rigid motion of <u>small</u> overlaps and holes with the Brillouin zone planes. A reciprocal space calculation comparing the free electron sphere to the Brillouin zone of cadmium estimates the number of overlap states (or the number of hole states) at approximately 1$\frac{1}{4}$%.

Even though the B overlap is quite large, the approach used in this work might conceivably give a good estimate of the effect of this overlap. We believe in fact that the major difficulty is encountered in handling the motion of the holes.

If the holes are as large as indicated by the free electron calculation, they are probably spread out along the intersection of the slant faces (see Fig. 2) and are no longer confined to the corners. Considering the complex topology of such a hole surface, the terms in Table 4 referring to the hole energies have little validity. (Low field de Haas van Alphen work in cadmium indeed reveals annomalies in the hole observations.[19])

For the reason described above the model of Leigh could not reasonably be expected to apply in detail to cadmium. Some features of the model can be expected, however, to estimate two major physical contributions to the shear stiffnesses and equilibrium condition. These contributions are the Coulomb and full zone terms. We have accordingly proceeded in the following way: a) arbitrary, but reasonable values of $\alpha_o = 1.00$, $Z^2 = 0.60$ have been assigned to the parameters which appear in these contributions. These simple and plausible values correspond with those which were found necessary to fit the model to experiment in the cases of aluminum[7], magnesium[7] and indium[5]. b) the Coulomb and full zone contributions to equations (6), (7) and (8) were then computed, and subtracted from the experimental values. c) the remainder is assigned to the overlap-hole terms in equations (6), (7) and (8). The results of this process are shown in Table 5. Presumably the

Table 5. Contributions to the elastic shear constants of cadmium in units of 10^{12} dyne/cm^2.

	C_H	C_{66}	$\left(\frac{dW}{d\zeta}\right)_{\zeta=1}$
Coulomb term, $Z^2 = 0,60$	2.893	0.213	-0.067
Full zone term, $\alpha_o = 1.00$	2.066	0.254	-0.063
Overlap-hole term	-4.001	-0.093	0.130
Total (Experimental)	0.958	0.374	0.000

general order of magnitude of these terms may some day be accounted for by a detailed treatment of the topologically complex Fermi surface of cadmium.

It may be pointed out that the overlap-hole contribution to C_H is relatively larger than in magnesium and this contribution to C_{66} is relatively smaller than in magnesium. These observations comply with the model in the sense the B overlap (which is strongly effected in a C_H strain) is proportionally much larger in cadmium and the P overlap (which is strongly effected in a C_{66} strain) is proportionally much smaller in cadmium.

In view of the failure of the rigid band model to account for the elastic stiffnesses themselves, it is not possible to go on to interpret the observed change of stiffness with pressure in terms of the model, as has been done successfully for aluminum and magnesium[7] . Such interpretation would have been difficult in any case because the application of hydrostatic pressure to hexagonal cadmium produces a shear strain described by ζ , in addition to volume strain, because the linear compressibility is quite anisotropic. There is one major feature of the pressure effects, to which attention should be called, as it may have theoretical significance. The values of $n = -\,d\ln C/d\ln r$ for the shear constants listed in Table 6 are

Table 6. Values of $\pi = -\,d\ln C/d\ln r$ for the shear elastic constants of the polyvalent metals aluminum[7], magnesium[7] and cadmium.

Constant	$\pi = -\,d\ln C/d\ln r$		
	Al	Mg	Cd
C_{66}	15.2	8.4	9.6
C_{44}	17.8	9.9	16.4
C_H	---	11.6	7.6

seen to be in the same numerical range for the three polyvalent metals, aluminum, magnesium and cadmium, for which pressure measurements have been made. Furthermore these numbers are anomalously high, on elementary considerations, as was first pointed out by Schmunk and Smith[7]. Since the Coulomb energy per unit volume varies as r^{-4} and the Fermi energy per unit volume as r^{-5}, one expects at first sight $\pi_C = 4$, $\pi_F = 5$ with an experimental π somewhere between these values. Values of π_C inferred from similar pressure experiments on sodium, aluminum, and magnesium have been in the neighborhood of 8, it is true, but such a number alone is not sufficient to account for the large experimental values in cadmium. For aluminum and magnesium it was shown that plausible electron population shifts with pressure could account on the Leigh model for the large pressure effect observed. It seems possible that such shifts, quite apart from the Leigh model, would contribute to the large effects observed in cadmium.

Calculations of the elastic stiffnesses following the model of Leigh have been found to be unsuitable in the case of cadmium. The major source of inapplicability is believed to be associated with the handling of the contributions to the elastic stiffnesses from the large hole pockets in the Brillouin zone. Since the contributions from the Coulomb energy and the full zone energy are fairly reliable, the model has been turned around to estimate the contributions from the overlap-hole energies by subtracting the Coulomb and full zone contributions from the experimental values.

Because of the failure of the model for the constants themselves, no attempt was made to calculate the effect of hydrostatic pressure on them. The experimental pressure dependance of the elastic constants of cadmium are recorded in Table 2 and it is noted that for cadmium as well as other polyvalent metals, aluminum and magnesium, the values of $\pi = - d\ln C/d\ln r$ are anomalously large.

APPENDIX

CALCULATION OF FULL ZONE TERM

Following Reitz and Smith[2] the energy of the full zone may be calculated by considering the zone to be made up of right tetrahedrons. The contribution to the Fermi energy of each tetrahedron is

$$(W_F^I) = (\alpha_o/4\pi^3)(\hbar^2/2m)(pqr/10)\left[p^2+q^2/2+r^2/6\right] \qquad (1)$$

where α_o is the inverse effective mass of the full zone and p, q, and r are the lengths of the mutually othogonal edges of the tetrahedron. The lengths p, q, and r may be expressed in terms of the lattice parameter "a", the (c/a) ratio and the pertinent strain parameter, x, such that

$$p = \frac{2\pi}{a} P\left(\frac{c}{a},x\right)$$

$$q = \frac{2\pi}{a} Q\left(\frac{c}{a},x\right)$$

$$r = \frac{2\pi}{a} R\left(\frac{c}{a},x\right)$$

And equation (1) reduces to

$$(W_F^I) = (\alpha_o h^2/10ma^5)\left[P^2QR + PQ^2R/2 + PQR^2/6\right] \qquad (2)$$

Equation (2) may now be differentiated twice with respect to the strain parameter to obtain the Fermi contribution of each tetrahedron to the elastic constant.

Because of the algebraic form of equation (2) in terms of the strain parameter the expressions for derivatives of equation (2) become rather involved and actual numerical calculation becomes very laborious indeed. Therefore the numerical calculation was programmed in Algol and carried out on a Burroughs 220 computor. The programing was set up such that the (c/a) ratio of the material was a varible of the program and hence the calculations could be repeated for any hexagonal close-packed material merely by changing one card and rerunning the program.

For the C_H type shear seven types of tetrahedrons were used and for the C_{66} type shear eighteen types of tetrahedrons were used. The first derivative of equation (2) for each type of tetrahedron was taken by hand and evaluated by the computor. A check on this was obtained by having the computor also take

the first derivatives of equation (2) by a delta process. The second derivatives of equation (2) were obtained by having the computor use a delta process on the first derivative equations which were taken by hand. The Algol language carries eight digits through all operations and with proper choice of increment, we were able to obtain three to four significant figures in the delta process operations.

The program was run not only for cadmium but also for magnesium and beryllium. The calculation for magnesium was made with the ideal (c/a) ratio to enable comparison with the results of the hand calculation quoted by Reitz and Smith[2]. The comparison was favorable, checking both first (C_H shear) and second derivative values quoted within 1 per cent. The calculation for beryllium was made with a (c/a) ratio of 1.568 to enable comparison with the values quoted by Bernstein[6]. In this case there is a major disagreement. The results of these comparisons are displayed in Table A1.

Table A1. Full zone contributions to the elastic shear constants of hexagonal metals. Units of 10^{12} dynes/cm^2. $\alpha_o = 1.0$. Values of (c/a) used are: Mg, (8/3) ; Be, 1,568; Cd, 1.8855.

	Metal	C_H	C_{66}
This work	Mg	1.400	0.190
Reitz and Smith	Mg	1.405	0.192
This work	Be	7.546	*
Bernstein	Be	5.208	0.843
This work	Cd	2.066	0.254

* not calculated

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