Electronic phase transitions in cadmium at high pressures

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Abstract. Elemental solid Cd crystallizes in the hcp structure with a large c/a value of 1.89. This leads to anisotropy in the Fermi-surface topology, electron-transport and other physical properties. Application of pressure reduces this anisotropy, with the c/a ratio decreasing to the ideal value corresponding to a spherical Fermi surface. There is long standing interest in the detection of departures of c/a from a smooth variation with pressure, and in associating such anomalies with electronic topological transitions. Angular x-ray diffraction measurements were carried out on Cd up to 25 GPa at room temperature. Variations of c/a with pressure reveal anomalies near 2, 7, 15 and 22 GPa; we find anomalies in the pressure–volume compression curve close to these pressures, which are also associated with electronic topological transitions determined from first-principles calculations. Independent in-situ x-ray powder-diffraction determinations of melting for Cd show departures from Lindemann predictions above 1 GPa, consistent with the occurrence of electronic topological transitions.

1. Introduction
Electronic phase transition also known as electronic topological transition (ETT) in materials results whenever the topology of Fermi surface is affected due to temperature, pressure or alloying. The resulting shift in the Fermi level (E_F) relative to electronic band extrema leads to subtle electronic phase transitions and causes anomalies in physical properties [1]. Zinc and cadmium crystallize at ambient conditions in the hcp structure with an unusually large c/a ratio of lattice parameters with highly anisotropic Fermi surface. Pressure is supposed to alter this anisotropy and hence these materials have been studied intensely under pressure for the observation of electronic phase transitions both experimentally [2-13] and theoretically [14-22]. Inspite of such frantic efforts spanned over two decades the existence of ETT still remains highly controversial. For Zinc which has been studied more
Intensely than cadmium there is broad consensus among the theoretical groups about the existence of ETT, however the experimental groups appear to be divided due to the fact that the resulting compressibility anomaly (or anomaly in $c/a$) is small if it exists at all.

The available limited high pressure studies for Cd suggest that the structural effects of electronic phase transitions are more visible than in Zn and extended over a larger pressure range [22]. Takemura’s [6] data on Cd with methanol-ethanol and water mixture as pressure medium although covers the pressure range up to 174 GPa, a close look at the pressure volume curve reveal that there are no data points in the range 5-12 GPa where the strong ETT is predicted [16-17,22]. Pratesi et al’s [23] energy dispersive high pressure x-ray diffraction data for Cd up to 17 GPa with mineral oil as pressure transmitting medium indicate anomalies in lattice parameters and $c/a$ ratio. Further, the past high pressure x-ray diffraction studies by Speziale et al [24] on Cd$_{0.80}$Hg$_{0.20}$ alloy, a system with the same structure as Cd but with $c/a$ ratio of 1.9 (1.1 % larger than Cd) at ambient conditions showed the presence of anomalies in the pressure dependence of lattice parameters in the extended pressure range which were associated with electronic phase transition according to the electronic structure calculations [24]. However alloying of Cd with Hg could have changed the band filling and hence the number of connectivity of the Fermi Surface sheets leading to the smearing of the electron states and the observable effects [25]. This possibility can not be ruled out because of the lack of our experimental knowledge about electronic structure at high pressures. Hence it is important to study pure Cd for which there is motivation from thermo electric power measurements [9], x-ray diffraction [23] and first principles total energy calculations [22] which indicate possibility of detecting the onset of ETT in Cd by studying the pressure dependence of its elastic properties. We study pure cadmium at room temperature using angle dispersive x-ray diffraction with argon as pressure medium. The primary aim is to improve the accuracy of our measurements compared to Pratesi et al [23] using different pressure medium and to compare it with the available data of Takemura [6] up to the pressure of 25 GPa and correlate the compressibility anomalies with ETTs predicted by theory.

2. Experimental details
Rhenium gasket indented to a 50 μm thickness and 100 μm hole served as the sample chamber. The sample material about the size of the sample chamber was cut out from a Cadmium wire. The sample along with few specks of ruby was loaded in a rhenium gasket. For hydrostatic measurements, argon was loaded cryogenically to serve as a pressure-transmitting medium. High-pressure experiments were performed using a symmetric diamond-anvil cell (DAC) beamline 12.2.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory [26]. Powder x-ray diffraction patterns were collected in angle-dispersive geometry using monochromatic radiation ($\lambda = 0.48594 \pm 0.00004$ Å) and a MAR345 image-plate detector at a distance of 295.54 (± 0.01) mm from the sample. The x-ray beam size was approximately 10 μm in the horizontal and vertical directions. Pressure was determined by the ruby-fluorescence method, using the calibration of Mao et al [27]. The software package FIT2D [28] was used both for beam-position and sample-to-detector distance calibrations, and for collapsing the two-dimensional diffraction images to one-dimensional patterns. As various pressure media used to collect the high pressure data on Cd freeze in the pressure range we have explored [34] we have compared and analyzed all the data sets together.

3. Results and discussion
Each of the x-ray diffraction patterns collected exhibits ~9 diffraction lines from the sample. We used all these observed sample lines to determine the unit-cell parameters and the density of Cd at each experimental pressure. The diffraction patterns show that the sample remains in the hcp phase up to 25 GPa (figure 1). Structural parameters as a function of pressure are given in table 1.
Table 1. Structural data of Cd for high pressure. The lattice parameters and the axial ratio at ambient pressure at room temperature are \( a = 2.9788(4) \) Å, \( c = 5.6164(6) \) Å and \( c/a = 1.8853(3) \).

| P(GPa) | \( a (\text{Å}) \) | \( c(\text{Å}) \) | \( c/a \) | \( V/V_0 \) |
|--------|-----------------|----------------|---------|--------------|
| 2.0(2) | 2.9673(2)       | 5.4867(8)     | 1.8491(4) | 0.9694(6)    |
| 5.0(3) | 2.9404(4)       | 5.3023(13)    | 1.8033(6) | 0.9199(8)    |
| 6.5(4) | 2.9358(2)       | 5.2389(6)     | 1.7845(3) | 0.9061(6)    |
| 10.5(5)| 2.9089(7)       | 5.1345(8)     | 1.7651(7) | 0.8718(9)    |
| 13.6(6)| 2.9074(1)       | 4.963(7)      | 1.7070(3) | 0.8418(5)    |
| 14.0(6)| 2.9089(7)       | 4.9799(8)     | 1.7120(7) | 0.8455(9)    |
| 17.7(7)| 2.8886(2)       | 4.8627(5)     | 1.6834(3) | 0.8142(5)    |
| 20.3(8)| 2.8731(2)       | 4.8091(7)     | 1.6738(4) | 0.7966(5)    |
| 23.3(8)| 2.8606(3)       | 4.7930(9)     | 1.6755(5) | 0.7870(6)    |

Figure 1. Evolution of diffraction patterns with pressure for cadmium.

Figure 2. Isothermal compression of Cd. The line is the Birch-Murnaghan 300 K isotherm fitted to the data collected in present studies. Error bars are equivalent to the size of the symbols.
A third-order Birch–Murnaghan fit [29] to the pressure dependence of the unit-cell volume fixing the initial volume to the measured value $V_0 = 43.159 (\pm 0.02) \text{ Å}^3$ (figure 2) yields bulk modulus $K_{T_0} = 46 (\pm 6) \text{ GPa}$ and pressure derivative $K_{T_0}' = 6.4 (\pm 1.2)$, where subscripts 0 and $T$ indicate zero pressure and isothermal conditions, respectively. These values are in excellent agreement with values measured by others for Cd, $K_{T_0} = 46 (\pm 5) \text{ GPa}$, $K_{T_0}' = 6 (\pm 1)$ [6-8].

It is observed from figure 2 that there are no experimental points in Takemura’s [6] measurements in ~5-12 GPa pressure region where the strong anomaly is predicted. Pratesi et al’s [23] energy dispersive data with mineral oil as pressure medium lies above Takemura’s data. Our data is in between these two data sets with better agreement with Pratesi et al’s data upto 10 GPa and close to Takemura’s data above 12 GPa. Pratesi et al’s data start systematically deviating above 10 GPa from Takemura’s and our data. We do not find any observable anomaly in the P-V data. These data sets observed together for the variation of lattice parameters ‘a’ and ‘c’ show anomalous behavior near 8-9 GPa and 14-15 GPa (figure 3). The $c/a$ ratio (figure 4) decreases monotonously from 1.885 to 1.67 through our experimental pressure range of 0-25 GPa. However, the pressure dependence of $c/a$ shows two clear discontinuities, at 8-10 GPa ($c/a = 1.757 - 1.753$) and 14-15 GPa ($c/a = 1.71 - 1.69$). The anomaly is clearly seen in Pratesi et al’s data of $c/a$ variation with pressure, which is at close pressure intervals near 8 and 15 GPa. Looking at the variation of $c/a$ ratio from 18 to 25 GPa we notice an anomaly near 22-23 GPa. If we observe all the data sets together in figures 3 and 4 then we also find anomaly close to 2 GPa.

![Figure 3. Pressure variation of lattice parameters (‘a’ and ‘c’) with pressure. Comparison is made with Pratesi et al’s [23] and Takemura’s data [6]. Pratesi et al’s data clearly reveal anomalies. Error bars are equivalent to the size of the symbols.](image-url)
Figure 4. Pressure variation of c/a ratio with pressure. We compare our data with Pratesi et al.’s [23] and Takemura’s data [6]. Pratesi et al.’s data which is in close pressure intervals clearly reveal anomalies in pressure variation of c/a ratio. Error bars are equivalent to the size of the symbols.

In order to better highlight the anomalies in the compression of Cd, we have plotted the data in terms of Eulerian strain ($f = 0.5[(V_0V^{-1})^{2/3} - 1]$) and normalized pressure ($F = P[3f(1+2f)^{5/2}]^{-1}$) calculated by fixing the value of $V_0$ to 43.159 ($\pm$ 0.03) Å$^3$ (figure 5). This representation effectively shows the slope of the $P$–$V$ data, such that the intercept gives the bulk modulus at zero pressure, $K_{T0}$ [29]. The $F$–$f$ plot of our data with uncertainties again suggests that there are at least two discontinuities in the compression curve, at 6-8 GPa ($f = 0.03-0.040$) and at 14-16 GPa ($f = 0.06-0.065$). It is also observed that these anomalies are also observed in Pratesi et al’s [23] and Takemura’s data [6] at comparable pressures. Further Takemura’s data shown in figure 5 also show anomalies close to 2-3 GPa ($f = 0.018-0.020$) and 22-23 GPa ($f = 0.089-0.091$).

The two anomalies we find in our data separate regions of the compression curve characterized by similar pressure dependence of the bulk modulus (proportional to the slope of the $F$–$f$ plot). Fits of the two regions of the $F$–$f$ curve of our data for the pressure region (6-8 GPa); $K_{T0} = 42.5$ ($\pm$ 3) GPa and $K_{T0}' = 4.7$ ($\pm$ 1); and $K_{T0} = 48$ ($\pm$ 4) GPa and $K_{T0}' = 1.7$ ($\pm$ 0.8) for the high-pressure region (14-16 GPa). The $F$–$f$ fit for the anomaly in Takemura’s data for the low pressure (2-3 GPa) yield $K_{T0} = 40$ ($\pm$ 2) GPa and $K_{T0}' = 9$ ($\pm$ 2.5). We note that bulk modulus and its pressure derivative across the two anomalies in our data (figure 5) are different from each other.
Figure 5. Plot of normalized pressure, $F$, versus Eulerian strain, $f$, for Cd ($F = P[3(1+2f)^{5/2}]^{-1}$, $f = 0.5[(V_0/V)^{2/3} - 1]$). The figure also includes extra points corresponding to two measurements at the same pressure (2 and 13.6 GPa) which resulted in slightly different uncertainties in volumes. The lines show linear fits of the two regions of the compression curve (see text).

These anomalies are in excellent agreement with self consistent pseudopotential electronic structure calculations carried out using Quantum Espresso Code [30] which predicts change in the topology of Fermi surface and anomalies in axial ratio, elastic constants and linear compressibility around 2, 7, 15 and 22 GPa [22,30]. However, Takemura [6] and Pratesi et al [23] interpret their data in terms of a single anomaly at $c/a \approx 1.74$ near 8 GPa.

Independent in-situ x-ray powder-diffraction determinations of melting of Cd up to 10 GPa using resistively heated diamond anvil cell by Raju et al [31-32] and previous melting studies by ex-situ methods [33, 34] show departures from Lindemann predictions [35] above 1 GPa, and are consistent with the occurrence of electronic topological transitions near 2 and 8 GPa in Cd, it is possible that they are responsible for the departure of melting curve from Lindemann law.

Our present studies combined with Takemura’s [6] and Pratesi et al’s [23] data support four electronic phase transitions up to 25 GPa and differ from the observation of Takemura and Pratesi et al who report only one ETT. The anomalies we have observed are in agreement with the predictions from first principles theories.

4. Conclusions

Variation of lattice parameters, axial ratio and equation of state is in agreement with available data to the pressure range of 25 GPa. Our results combined with available data on Cd suggest the occurrence of anomalies in the compressibility at 2, 8, 15 and 22 GPa pressures. Highly accurate first principles electronic structure calculations associate these anomalies with changes in the Fermi surface topology. Thus, our experimental results of high pressure x-ray diffraction by annealing the sample at each pressure step along with our independent melting curve results [32] combined with theoretical calculations support the view that the anomalies of structural parameters and elastic moduli of pure Cd are caused by electronic topological transitions (ETTs).
References:

[1] Lifshitz I M 1960 Sov. Phys. JETP 11, 1130
[2] Linch R W, and Drickamer H G 1965 J. Phys Chem. Sol. 26, 63
[3] Potzel W, Steiner M, Karzel H, Schiessl W, Kofferlein M, Kalvius G M, Blaha P 1995 Phys. Rev. Lett. 74 1139
[4] Takemura K 1995 Phys. Rev. Lett. 75 1807
[5] Morgan J G, Von Dreele R B, Wochner P, Shapiro S M 1996 Phys. Rev. B 54 812
[6] Takemura K 1997 Phys. Rev. B 56, 5170
[7] O. Schulte, A. Nikolaenko, and W.B. Holzapfel 1991 High Pres. Res. 6, 169
[8] Schulte O and Holzapfel W B 1996 Phys. Rev. B 53, 569
[9] Godwal B K, Meenakshi S, Rao R S and Vijayakumar V 1998 J. Phys. Chem. Sol. 59, 747
[10] Takemura K 1999 Phys. Rev. B 60, 6171
[11] Klötz S, Braden M, Besson J M 1998 Phys. Rev. Lett. 81 1239
[12] Olijnyk H, Jephcoat A P, Novikov D L, Christensen N E 2000 Phys. Rev. B. 62, 5508
[13] Takemura K, Yamawaki H, Fujihisa H and Kikegawa T 2002 Phys. Rev. B 65, 132107
[14] Meenakshi S, Vijayakumar V, Godwal B K, and Sikka S K 1992 Phys. Rev. B 46, 14359
[15] Fast L, Ahuja R, Nordström L, Wills J M, Johansson B, Eriksson O 1997 Phys. Rev. Lett. 79 2301
[16] Godwal B K, Meenakshi S, Rao R S 1997 Phys. Rev. B 56 14871
[17] Novikov D L, Katsnelson M I, Trefilov A V, Freeman A J, Christensen N E, Svane A, Rodriguez C O 1999 Phys. Rev. B 59 4557
[18] Li Z, Tse J S 2000 Phys. Rev. Lett. 85 5130
[19] Neumann G S, Stixrude L, Cohen R E 2001 Phys. Rev. B 63 54103
[20] Godwal B K, Modak P and Rao R S 2003 Solid State Comm. 125, 401
[21] Qiu S L and Marcus P M 2003 J. Phys.: Condens. Matter 16, 6405
[22] Pratesi G, DiCicco A, Minicucci M and Itie 2005 J. Phys. Condens. Matter 17, 2625
[23] Speziale S, Jeanloz R, Clark SM, Meenakshi S, Vijayakumar V, Verma A K, Rao R S, Godwal B K 2008 J. Phys. Chem. Solids 69 2325
[24] Koudela D, Richter M, Mobius A, Koepernik K and Eschrig H 2006 Phys. Rev. B 74 214103
[25] Kunz M, MacDowell A A, Caldwell W A, Cambie D, Celestre R S, Domning E E, Duarte R M, Gleason A E, Glossinger J M, Kelez N, Plate D W, Yu T, Zaug, JM, Padmore H A, Jeanloz R, Alivisatos A P and Clark S M 2005 J. Synch. Rad. 12(5) 650-658
[26] Mao H K, Xu J and Bell P M 1986 J. Geophys. Res., B91, 4673
[27] Hammersley A P et al. 1996 High Press. Res. 14 235
[28] Angel R J, Buzak M, Zhao J, Gatta G D and Jacobsen S D 2007 J. Appl. Cryst. 40 26
[29] F. Birch Phys. Rev. B 1947 71 809
[30] Srinivasan V, Godwal B K , Grossman J C, and Jeanloz R 2012 (Submitted Phys. Rev. B)
[31] Raju S V, Zaug J M, Chen B, Yan J, Knight J W, Jeanloz R, and Clark S M 2011 J. Appl. Phys. 110 023521
[32] Raju S V, Godwal B K, Geballe Z, Williams Q and Jeanloz R, (2012, Submitted to Phy. Rev. B)
[33] Errandonea D 2010 J. Appl. Phys. 108 033517
[34] F. A. Linde mann, Z. Phys. 11, 609 (1910)

Acknowledgements

We thank the U.S. Department of Energy, Director, Office of Science, and Office of Basic Energy Sciences, under Contract No. DEAC02-05CH11231 and COMPRES for supporting this research at the Advanced Light Source.