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BRIEF REPORTS

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c/a anomalies and electronic topological transitions in Cd

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The total-energy calculations are carried out to obtain the axial ratio (c/a) variation with compression for cadmium. We find two anomalies as compared to a single anomaly at $V/V_0=0.85$ observed in the experimental data. The first anomaly at $V/V_0=0.95$ is due to electronic topological transition (ETT) and correlates well with the anomaly observed in the existing resistivity data. We find the $4d$-orbital overlap, coupled with transfer of electrons from d to s states as the cause of second anomaly. This observation is in contrast to the existing understanding in zinc, where the c/a anomaly is attributed to the destruction of a giant Kohn anomaly by ETT. Nondestruction of giant Kohn anomaly in cadmium at high pressures is in disagreement with the current view in the literature that its Fermi surface is identical to that of zinc. [S0163-1829(97)02044-4]

Zn and Cd metals have been the subject of intense theoretical and experimental investigations, mainly because they crystallize in hexagonal closed packed (hcp) structure with unusually large c/a ratios ($c/a=1.856$ for Zn and 1.886 for Cd) and hence many of their solid state properties are highly anisotropic.[1–4] The application of pressure affects the bonding anisotropy, and hence alters a variety of physical phenomena.[5–7] One of the main changes occurs in the topology of Fermi surface, which causes changes in transport and other physical properties. Under ambient conditions, Cd has almost identical Fermi surface topology as that of Zn except that the horizontal arms of the second band hole surface is pinched off to separate the sections near the lateral zone edges, and the third band electron sheet needles at the K points in the Brillouin zone (BZ) are absent.[1] As these features of the Fermi surface sheets of Zn appear in Cd under pressure at about 1.7 and 3.5 GPa, respectively,[6] it is presently thought that Cd should undergo similar changes as Zn under compression but at higher pressures.

A significant feature of Cd and Zn is the presence of giant Kohn anomaly at ambient pressure. A giant Kohn anomaly can occur if for a certain reciprocal lattice vector $\mathbf{G}_0$, the Fermi surface lies in a local band gap[5,8] with $2\mathbf{k}_F=\mathbf{G}_0$ for some Fermi surface radius $\mathbf{k}_F$. As a consequence, the anomaly occurs at long-wavelength acoustic and optic phonons (i.e., $\mathbf{q}=0$), and can be very pronounced. The main focus of the recent studies has been to relate the observed experimental anomalies to the destruction of giant Kohn anomaly[8] due to electronic topological transition[9] (ETT) under pressure. In a recent low-temperature ($T=4.2$ K), high-pressure Mössbauer experiment on Zn, Potzel *et al.*[5] observed that the Lamb-Mossbauer factor (LMF) drops off sharply at a pressure of 6.6 GPa. As the LMF is more sensitive to low-frequency phonons, it was argued that softening of the low-frequency acoustic and optical phonons is the reason for abrupt decrease in LMF. Potzel *et al.*[5] also find from their scalar relativistic linear augmented plane wave (LAPW) calculations that at a pressure of 6.6 GPa, an ETT occurs that destroys the giant Kohn anomaly and causes changes in the phonon spectrum. Thus Mössbauer experiments suggest that the lattice dynamics of Zn are strongly influenced by ETT at high pressure. This is further supported by the recent inelastic neutron scattering studies of Morgan *et al.*[10] from single crystals of Zn under pressure at room temperature, which clearly show that a phonon softening occurs at a pressure of 9 GPa due to the collapse of the giant Kohn anomaly via ETT. Very recently the measurements of c/a values of Zn have been made by Takemura[7] from high-precision powder diffraction experiments involving state of the art techniques consisting of diamond anvil cell, synchro-

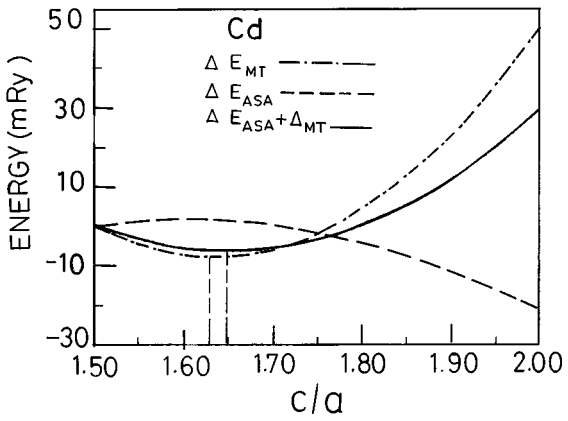

FIG. 1. Variation of the atomic sphere approximation contribution and muffin-tin correction to the total energy as a function of c/a at $V/V_0=1.0$ for cadmium.

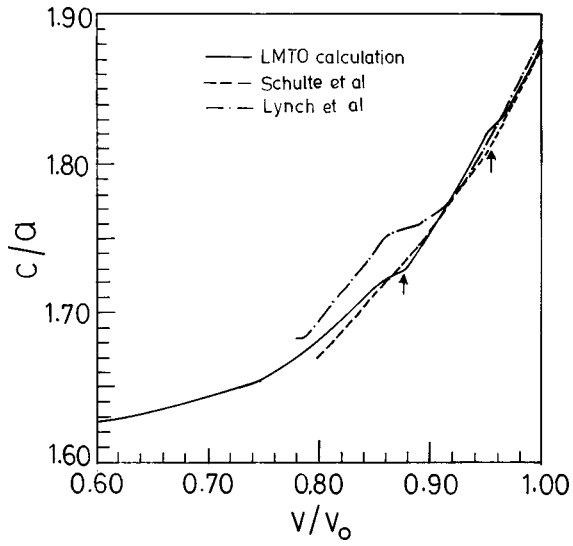

FIG. 2. The c/a variation with V/V_0 for cadmium. The solid line is calculated from total-energy calculations and is compared with two experimental data sets [- · - : Lynch *et al.* (Ref. 12) ; — : Schulte *et al.* (Ref. 14)].

tron radiation, and imaging plate. He finds excellent correlation between the measured and our previous theoretical estimates[11] of c/a values. The presence of the c/a anomaly under pressure as predicted by us has been confirmed experimentally and our findings of relating it to the electronic transition have been supported by Potzel *et al.*[5] In fact the relative volume (V/V_0, V_0 being the volume at normal pressure) range where the c/a anomaly occurs is in agreement with the destruction of the giant Kohn anomaly.

Due to the intense activities in relating the destruction of the giant Kohn anomaly to the observed anomalies in Zn, the present work on a similar metal Cd is aimed at studying whether the c/a anomaly observed in Lynch *et al.*'s[12] and Takemura's[13] data is related to the vanishing of the giant Kohn anomaly under pressure. As the energy dispersive x-ray diffraction work of Schulte, Nikolaenko, and Holzapfel[14] and neutron inelastic scattering work by Morgan *et al.*[10] have created doubt about the presence of the c/a anomaly in Zn, the present work is also partly aimed at theoretical calculations of c/a under compression for Cd, which has an electronic structure similar to Zn at ambient conditions.[1] We find that the giant Kohn anomaly in Cd persists at high pressures, in contrast to Zn, and the cause of the anomaly in the c/a ratio observed in the experimental data at $V/V_0=0.85$ and around 10 GPa is not its destruction following ETT. In addition, we find a weak anomaly in the axial ratio around $V/V_0=0.95$ due to the ETT in agreement with resistance anomaly at 3.5 GPa.[6] Our present studies reveal that Fermi surface changes in Cd under pressure are not identical to those of Zn.

We employed the scalar-relativistic linear muffin-tin orbital (LMTO) method[15] within the local density approximation (LDA) for self-consistent electronic structure studies. A frozen core with $4d^{10}5s^2$ valence configuration is taken with Barth-Hedin exchange correlation[16] and with s, p, d, and f components retained in the angular momentum expansion of the muffin-tin orbitals. The calculations included the combined corrections to the atomic sphere approximation (ASA).[17] The c/a ratio is obtained by finding the minimum of total energy at each volume. The calculations for Cd using 462 **k** points in the BZ at each compression were carried out in hcp structure by varying the c/a ratio from 1.9 to its ideal value 1.63. The results of such calculations at $V/V_0=1.0$ are displayed in Fig. 1. It is seen that the ASA values of total energy do not show a minimum. This is because the ASA total energy functional includes only the $l=0$ contribution to the total intercellular Coulomb interaction and that vanishes for monoatomic solids. In order to improve upon this approximation, the intercellular interaction in muffin-tin approximation[18] was computed in a manner discussed in our earlier studies[11] on Zn. This correction term as shown in Fig. 1 when added to ASA values of total energy gave a minimum at $c/a=1.65$. However, it has been well established[18,11] that this correction term may not always be adequate. We therefore adjusted it to reproduce the experimental c/a value of 1.886 at normal pressure. This parameter of the muffin-tin correction term was then kept fixed for all other compressions. At normal pressure, our calculated electronic structure agrees well with the available experimental and theoretical data[1,6,19,20] on Cd, and also displays some of the well-known

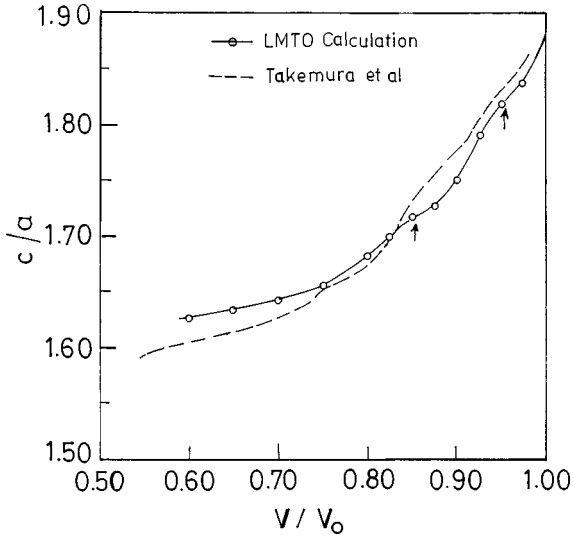

FIG. 3. The calculated c/a variation as compared with the recent imaging plate experimental data of Takemura (Ref. 13).

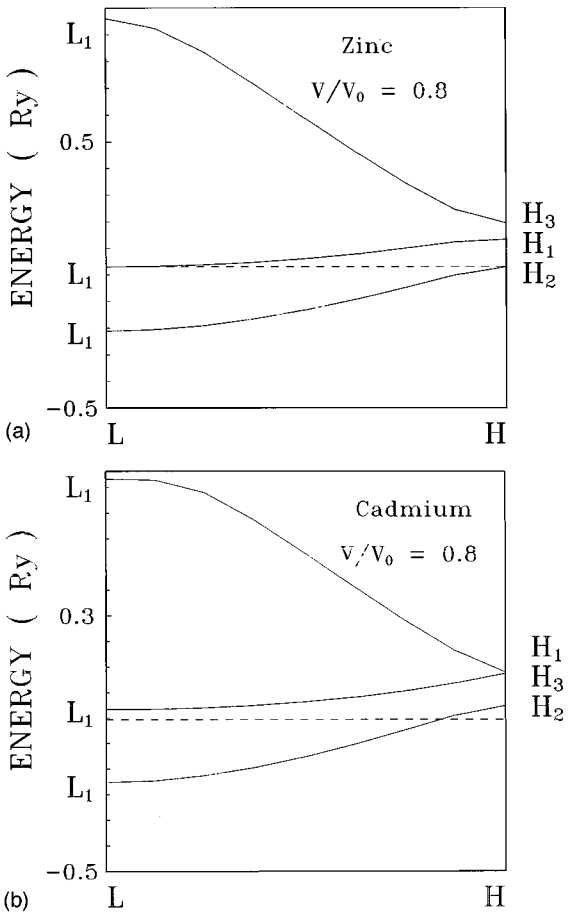

FIG. 4. Electron energy bands along the symmetry line L-H on the BZ boundary surface for (a) zinc, and (b) cadmium. Both the calculations were carried out at relative volume ratio $V/V_0=0.8$. The dashed line indicates the Fermi level E_F.

features of the pressure variation of the Fermi surface topology. For example, the linking of the horizontal arms of the second band hole Fermi surface as observed in de Haas–van Alphen (dHvA) experiments,[6] which is also associated with the peak in the thermoelectric power data[21] around 1.7 GPa pressure. Secondly, the appearance of the K-point needle in the third zone electron sheet of the Fermi surface, which gives an anomaly in the pressure dependence of resistivity at pressure of 3.5 GPa at room temperature.[6]

In Fig. 2 we have compared the c/a values as a function of compression with experimental data of Lynch *et al.*[12] and Schulte *et al.*[14] Our calculations show two anomalies in the variation of c/a as a function of compression. The first anomaly is around $V/V_0=0.95$ and seems to be absent in both the experimental data sets depicted in the figure. However, as pointed out earlier, an anomaly in the resistivity data had been reported at 3.5 GPa pressure,[6] and also our own resistivity and thermoelectric power measurements confirm the existence of this anomaly. The details of these experimental results will be published elsewhere.[22] In fact our electronic structure calculations as a function of compression reveal that around this pressure the K_1 level moves from an unoccupied to an occupied state, and this ETT had also been correctly given as the explanation in Ref. 6 for the appearence of needles in their dHvA experiments. The second c/a anomaly occurs at $V/V_0=0.85$ where Lynch and Drickamer's data[12] show a strong anomaly. Our c/a values are seen to compare better with Lynch and Drickamer's data[12] than that of Schulte, Nicolaenko, and Holzapfel,[14] which does not show the anomaly. We have further compared, in Fig. 3, the c/a values with high precision imaging-plate-based powder diffraction data of Takemura.[13] Our c/a values correlate very well with his data though there is no clear indication of the first anomaly in his data.[23] The second anomaly occurs at $V/V_0=0.85$ and is in excellent agreement with the experimental results. The c/a value at this anomaly is 1.7 and is in fair agreement with Takemura's value[13] of $\sqrt{3}$. It may be noted that our calculations give slightly higher c/a values at higher compressions and tend to approach the ideal c/a value of 1.63 for the hcp structure.

In order to find the possible connection of the c/a anomaly with the destruction of giant Kohn anomaly (due to ETT at the L point), we have studied variations of FS topology around the L point in various directions. Figure 4 depicts the electron energy bands near the FS along the L-H direction for (a) Zn and (b) Cd at the compression of $V/V_0=0.8$, as all the anomalies of experimental data occur below this compression, and reveals the contrasting features in Zn and Cd about the destruction of the giant Kohn anomaly. In Cd, the Fermi level (E_F), which is in the so-called local band gap[5] at the L point of BZ surface at normal pressure (not shown in the figures, see Ref. 1 for details), continues to remain so at high compressions;[24] whereas it is clearly seen in Zn that the L level in the vicinity of E_F that is unoccupied at normal compression (see Ref. 1) moves down across the Fermi level [Fig. 4(a)] thus destroying the giant Kohn anomaly. This qualitatively contrasting nature of the variation in the relevant L point energy level with respect to E_F is not expected to change in a more accurate full potential calculation, or by applying corrections to LDA through the generalized gradient approximation. Note that our calculations apply identical approximations for Zn and Cd; the nature of the variation in Zn, mentioned above, agrees with the experimental findings and the full potential calculations[5]; the c/a values are comparable for Zn and Cd, and more importantly, the c/a values decrease towards the ideal value under compression, and hence the ASA results become more reliable at higher pressures. Hence, at least in Cd, the c/a anomaly at $V/V_0=0.85$ is not due to the destruction of the giant Kohn anomaly at the L point of the BZ. The details of our electronic structure calculations show a continuous, though slow transfer of electrons from d to s,p states due to the relative shifts and broadenings of these bands. In the region of the anomaly the $4d$ bandwidth increases rapidly and a change of 1 eV from its value at normal pressure is seen. Also, about 0.1 electron/atom is transferred from d to the more delocalized s-p states. This causes the turnover in the $4d$-partial pressure from negative (filled band) to positive contribution around this anomaly. This observation is similar to our findings in indium,[25] but is not significant in Zn in the region of c/a anomaly.

In summary, we simulated the axial ratio variation with pressure for Cd and found that its variation shows anomalies. We have shown that the main anomaly observed around $V/V_0=0.85$ is not due to the destruction of the giant Kohn anomaly at the L point of the BZ, which is in contrast to the

current understanding in Zn. Our calculations show that the value of c/a at this anomaly in Cd is 1.7. Also, we obtain a weaker anomaly around $V/V_0=0.95$ ($c/a=1.82$), which has not been observed experimentally, and hence, more elaborate experimental investigations and careful analysis around this compression would be useful.

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[24] We have verified by carrying out the calculations at $V/V_0=0.6$, that the unoccupied L level just above E_F continues to remain above the Fermi level at higher compressions, and in fact, moves a little away from E_F.

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