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On the high pressure axial ratio anomaly in zinc and the roles of temperature and different electronic topological transitions

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Abstract

We report electronic structure calculations on zinc at various compressions. Our calculations show that an electronic topological transition (ETT) associated with the anomaly in the axial ratio (c/a) at high pressures is sensitive to $\boldsymbol{k}$ sampling used in the calculations, exchange–correlation potential and temperature. We show that K-point ETT does not contribute to the anomaly, and thus disagree with the model of contributions from many ETTs. Hence only the L-point ETT is significant. We suggest that, even though temperature smearing of the Fermi function reduces the signatures of ETT, it does not wipe out the anomaly at room temperature.

Zn crystallizes in the hexagonal close packed (hcp) structure with large axial ratio ($c/a = 1.856$) at ambient conditions, which leads to anisotropy in the Fermi surface topology, transport and other physical properties. The application of pressure reduces the anisotropy with the axial ratio approaching the ideal value, and any departure from its smooth decrease is termed the (c/a) anomaly. A highly debated controversy in Zn, persisting for over a decade, is whether any such anomaly exists near 10 GPa pressure [1–15]. Moreover, Zn exhibits a giant Kohn anomaly (GKA) [16] at ambient pressure, and there is disagreement among the various groups [6, 8–10, 12, 14] about its destruction under pressure due to an electronic topological transition (ETT). A further controversy is whether ETT is the cause of the (c/a) anomaly [8, 10, 12–14] or not.

The first theoretical prediction of the (c/a) anomaly under pressure, using first principles electronic structure calculations, was made by Meenakshi *et al* [2] who attributed it to the shift of the p-component van Hove peak in the density of states through the Fermi level (E_F). These studies helped to resolve the disagreement between the experimental data of two groups [3, 4], with subsequent experimental and theoretical investigations supporting their conclusions. Prominent among these follow-up investigations were, angle-dispersive x-ray diffraction (ADXRD) data [5] and observation of an anomaly in the Lamb–Mössbauer factor in high pressure Mössbauer spectroscopy, supported by the linear augmented plane wave (LAPW) calculations showing ETT at the L point of the Brillouin zone (BZ) at about the

same pressure [6]. The ADXRD data showed the anomaly at $(c/a) = \sqrt{3}$, which led to the suggestion that the high degeneracy of the reciprocal lattice vectors at this particular axial ratio might have been responsible for the anomaly [5].

For the similar metal Cd, Godwal *et al* [8] predicted two (c/a) anomalies under compression, the first at $V/V_0 = 0.95$ occurring due to the K-point ETT at a (c/a) value different from $\sqrt{3}$, and the second corresponding to $V/V_0 = 0.85$. Their work thus ruled out the reciprocal lattice vector degeneracy at $(c/a) = \sqrt{3}$ as the cause of the anomaly.

Until recently, all the 0 K theoretical investigations supported the existence of a (c/a) anomaly under compression in Zn [2, 7, 10, 12]. But its correlation to ETT was debated and uncertainties still exist in this regard. Fast *et al* [7] obtained much more prominent anomalies than observed experimentally in the variation of lattice constants with pressure, and related them to ETT at the K point of the BZ. They also ruled out the reciprocal lattice vector degeneracy as the cause of the anomaly. Later, the room-temperature high pressure x-ray diffraction experiments [11] under better hydrostatic pressure conditions (with helium as the pressure-transmitting medium) did not show any (c/a) anomaly. Moreover, the phonon dispersion measurements [9] from neutron inelastic scattering experiments failed to detect the destruction of GKA and hence the ETT that causes it.

At this stage, the general interpretation was that ETT and the (c/a) anomaly exist at low temperatures, as indicated by the Lamb–Mössbauer factor [6] and supported by 0 K theoretical calculations, but temperature would wipe out its signature at room temperature, and the controversy seemed to have been resolved. But the observation by Olijnyk *et al* [13] of an anomaly at room temperature in the phonon linewidth of optical phonons in the Raman spectra with helium as the pressure-transmitting medium re-opened the controversy. The phonon linewidth showed a decrease with increasing pressure in their experiments up to 10 GPa, and then suddenly started increasing, thus indicating the initiation of additional modes of relaxation for the optical phonons. Occurrence of ETT would give rise to additional channels of relaxation by electronic excitations in that region. But they did not observe any anomaly in the optical phonon frequency variation up to 58 GPa. This was, however, explained by the phonon frequency and mode Grüneisen parameters (γ) calculations of Li and Tse [12], which showed significant softening near 10 GPa in a transverse acoustic phonon mode only. Li and Tse supported the interpretation [2] that the (c/a) anomaly arises due to the combined effects of 2 or 3 ETTs (at K and L points of the BZ). They further correlated the ETTs to the (c/a) anomaly by pointing out that the softening of the acoustic mode would affect the compressibility of a and c, thus leading to the observed anomaly[1]. There are also suggestions that domains of different (c/a) ratios co-exist near about 10 GPa [10], due to multiple minima in the variation of total energy as a function of (c/a) at fixed volume.

As all the relevant band structure calculations are at 0 K, a detailed understanding of the role of temperature in the occurrence of ETT and the (c/a) anomaly is essential to resolve the controversies. We have adopted the full potential linear augmented plane wave method (FP-LAPW) [17] in our calculations, and employed the generalized gradient approximation (GGA) for exchange–correlation terms [18]. A large number of $\boldsymbol{k}$ points (20 000 in the full BZ) were found necessary and employed for BZ sampling. The calculations were carried out for 0 K. The (c/a) ratio at each volume compression was varied to estimate the optimum axial ratio. The cold (0 K) P_c–V curve was obtained by neighbourhood fitting of the calculated

[1] But the very recent FPLAPW calculations of Neumen *et al* [15], with gigantic $\boldsymbol{k}$ sampling, do not support an axial ratio anomaly in Zn, in contrast to [12] in which comparatively dense $\boldsymbol{k}$ sampling was also employed. However, the spin–orbit interaction was neglected in [15], which, according to Kechin [14], would lead to two different types of Fermi surface sheets due to ETT. This phenomenon could be significant in affecting the anisotropy of compressibility and could give rise to a (c/a) anomaly.

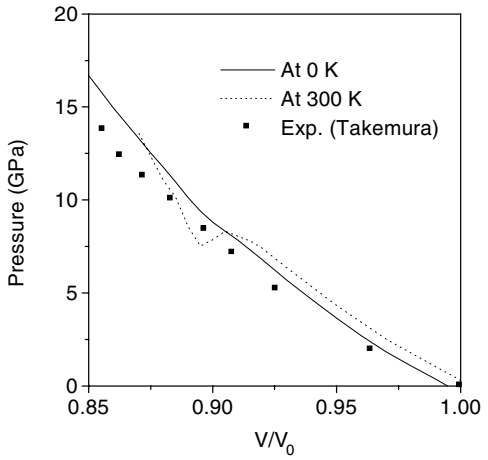

Figure 1. Equation of states for Zn.

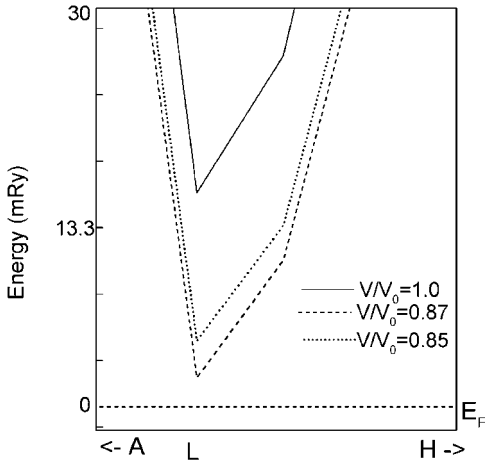

Figure 2. Position of the band minimum at the L point with respect to E_F for different compressions.

total energies at various volume compressions to low degree polynomials, and thus obtaining the required derivatives. E_{lt} was obtained using the Debye–Grüneisen model, following the procedure adopted by Godwal and Jeanloz [19], by using pressure variation of the Debye temperature from its ambient value of 208 K, and the lattice contribution to pressure was estimated from the pressure variation of an average Grüneisen γs [12] and using the relation

$$P_{lt} = \gamma E_{lt}/V.$$

This term was added to the cold pressure to obtain the total P–V curve. The calculated room temperature P–V curve in the controversial region around 10 GPa is shown in figure 1 along with the cold P_c–V curve obtained by electronic structure calculations. The anomalous structure in the curve correlates well with the (c/a) anomaly [2]. It may be noted that the prominent anomaly in the room temperature EOS is due to the strong anomaly in the pressure variation of γ obtained by Li and Tse [12]. It is possible that approximations used in those calculations, such as the harmonic approximation in the phonon frequency computations, might have overestimated the anomaly in their calculations, especially as the experiments have not observed the enhanced anomaly depicted in figure 1. Alternatively, the anisotropic stresses in the samples might have hindered the observation of the anomaly in room temperature P–V variation. Thus our calculations show that temperature does not hinder the occurrence of the anomaly.

Our calculations also clarify some controversies on the ETTs responsible for the (c/a) anomaly. The band structure details of our calculations show that the ETTs at the K point of the BZ occur at much lower pressures, than that at the L point. This result is in agreement with Kechin's [14] analysis of various ETTs, which provided domains for different ETTs separated by constant (c/a) boundaries in the P–T phase diagram, based on self-consistent calculations by the tight binding linear muffin-tin orbital method. Thus we disagree with the model of 2 or 3 ETTs contributing together to the (c/a) anomaly in Zn, and are of the opinion that only L-point ETT contributes. This conclusion is in agreement with the fact that only zone centre softening of the acoustic phonon mode was obtained in the calculations of Li and Tse [12]. If the K-point ETT were also to contribute to the anomaly, additional softening of the phonon mode at the K point should have occurred.

Regarding the L-point ETT, the pertinent eigenvalue, which is about 16 mRyd above the Fermi level (E_F) at ambient pressure at 0 K, gets closer to it within 2 mRyd (at $V/V_0 = 0.87$),

and then moves up to higher energies again (see figure 2). Our local density approximation (LDA) for exchange correlation showed that its closest approach to E_F is shifted to higher compression. Thus the ETT at the L point is very sensitive to the exchange correlation. Hence, efforts beyond GGA based DFT may help to resolve the issue.

We now comment upon the model, which advocates that the (c/a) anomaly could be due to the simultaneous existence of domains of different axial ratios. Our calculations show that the L-point ETT, which is responsible for the observed anomaly in the variation of axial ratio, could occur at lower pressure if the (c/a) ratio is reduced from the optimum value obtained by total energy calculations at fixed volume. Though multiple minima or a broad minimum would exist in the total energy variation as a function of (c/a) near 10 GPa pressure, the alternative (c/a) values should all correspond to higher values than the energy minimized optimum value. For these higher values of (c/a), the ETT does not occur and hence does not lead to acoustic phonon softening [12], or to the observed broadening of the Raman linewidths of the optical phonons [13]. Thus the occurrence of domains with different (c/a) values is not consistent with the association of ETT with the anomaly. Thus with ETT as the driving mechanism for the (c/a) anomaly, the domains of different (c/a) cannot co-exist.

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