Anomaly in c/a Ratio of Zn under Pressure

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Recently an anomaly in the c/a ratio for hcp Zn was observed as a function of hydrostatic compression [Takemura Kenichi, Phys. Rev. Lett. **75**, 1807 (1995)]. The anomaly is even more pronounced for the lattice parameter a in the hexagonal plane. By means of accurate first principles calculations we demonstrate that at a specific volume the distances between the atoms within the hexagonal planes of Zn actually *increase* when the volume is decreased. By an explicit separation of the various contributions from different volume segments of the Brillouin zone we conclude that the electronic states around the K point are those responsible for the observed anomaly. [S0031-9007(97)04132-X]

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During five decades Zn has been studied because of its interesting properties but only recently a delicate crystallographic anomaly was discovered [1,2]. The electronic structure of Zn has been investigated by means of various models, *ab initio* calculations, as well as by a number of experimental techniques. The Fermi surface of Zn is well known, but only a few accurate *ab initio* calculations of the Fermi surface have been performed. As will be shown below the Fermi surface behavior of Zn is intimately coupled to the observed anomaly in the pressure dependence of the axial c/a ratio. In the present work we reproduce theoretically the room temperature measurements [1,2] of Zn.

We base our analysis on highly accurate state-of-the-art total energy calculations, which in the past have proven to be very reliable in reproducing structural properties [3]. The theoretical calculations are based on a full-potential linear muffin-tin-orbital (FP-LMTO) method. The main approximation used in this approach is the local density approximation (LDA) for which we have applied the implementation by Hedin and Lundqvist for approximating the exchange and correlation functional [4]. Thus our calculations are based on density functional theory [5,6]. A Gaussian broadening technique is used to increase the convergence speed in k space. We have chosen Gaussians with a width between 5 and 20 mRy without observing any changes in our results. The effective one-electron wave functions are treated fully relativistically for the core electrons and scalar relativistically for the valence electrons. The $4s$, $4p$, and $3d$ orbitals form the valence band states and the rest of the electrons are treated as part of the ion core. From tests at a few volumes we have found that an inclusion of the spin-orbit coupling for the valence states does not change the behavior of the optimized c/a ratios. At this point we also mention that recently other theoretical papers [7] have been published for Zn addressing other topics than what is discussed here.

Using our theoretical method we have calculated the total energy for the crystal under variation of both the volume and c/a ratio of the hcp structure. For each volume an energy minimum was determined with respect to the c/a ratio. From these calculations we then obtain the compression dependence of the a and c axes of Zn and this is illustrated in Fig. 1. Note from the figure that at a volume reduction of about 0.88 the distance between atoms within the hexagonal plane *increases* with pressure. In Fig. 1 we also show the experimental room temperature data from the work of Ref. [1]. Note that the experiments do show

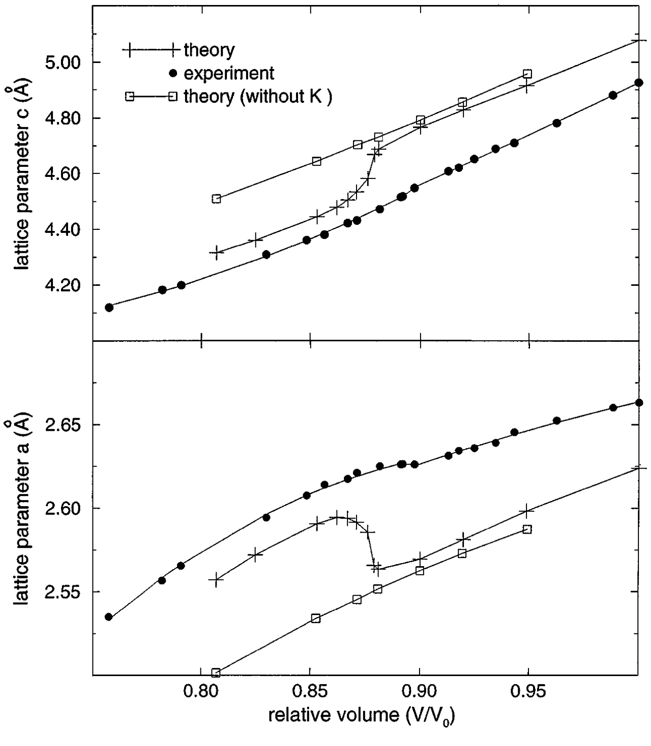

FIG. 1. Lattice parameters, a and c, as a function of volume compression. The experimental data are denoted by filled circles and the theoretical data are represented by plus signs. The theoretical data where k points close to the symmetry point K are excluded are given by open squares.

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an anomaly at a compression which is close to our theoretical data, but that this anomaly is not as pronounced as in theory and manifests itself by a nondecreasing flat region in the compression dependence of the a axis. It is clear from Fig. 1 that both in theory as well as in experiment the anomaly is larger for the interatomic distance within the hexagonal plane compared with the behavior in the c direction. Below we will present an explanation for this highly unexpected behavior presented in Fig. 1 as well as give an argument for why experiments at room temperature merely display a flat region in the compression dependence of the axial length, whereas theory shows an increase in the a axis at 88% of the experimental equilibrium volume. The reason for this discrepancy is due to temperature effects not accounted for in the theoretical treatment. As we will demonstrate below, the calculated anomaly originates from a redistribution among the occupied electron states, and therefore temperature will tend to smear out the abruptness of this rearrangement. At this stage we stress that the calculated and observed anomaly in the crystallographic axes at a relative volume of 88% (90% in the experiments) do not represent a crystallographic phase transition; Zn remains in the hcp structure in the entire volume interval.

In order to analyze the reason behind the c/a anomaly, we have performed model calculations where parts of the Brillouin zone are omitted in the self-consistent calculation. It is found that when k points in a small volume of the Brillouin zone (BZ) around the symmetry point K are excluded, this effect disappears as can be seen in Fig. 1. Neglecting other parts of the BZ does not influence the c/a anomaly in any significant way. Thus we find, for instance, that the electronic states around the L point play no role for the c/a anomaly, in contrast to what was suggested in Ref. [7].

Since we now know that it is the electronic states around the K point which drive the anomaly, it is tempting to relate it to the Lifshitz $2\frac{1}{2}$ transition, [8] i.e., due to an electronic topological transition (ETT). That the calculated anomaly in Zn is closely related to an electronic topological phase transition, as may be deduced from the Fermi surface (FS), is shown in Fig. 2 for Zn at two different volumes, one above and one below the transition. The FS in Fig. 2(a) is for a volume slightly larger than the transition volume whereas the data in Fig. 2(b) are for a volume slightly smaller than the transition volume. The most conspicuous change in the Fermi surface is around the K point where the needle shaped branch becomes much fatter and cigar shaped. Detailed studies of the band structures confirm this picture. Some states which are unoccupied for larger volumes pass through the Fermi energy just before the volumes where the anomaly occurs. This lead to a Fermi surface with an altered topology; i.e., it is an ETT.

In addition to the experiments of Ref. [1], the unique structural behavior of Zn under pressure should be detectable by means of ultrasound measurements of the elastic constants as a function of compression. The anomaly should show up particularly in the combination of elastic constants, $(C_{33} - C_{13})/(C_{11} + C_{12} - 2C_{13})$, which should be unusually low at the critical volume. This combination of elastic constants reflects the ratio of the compressibility of the a and c axes of the hcp structure. Also, at critical compressions, response to shear is usually anisotropic (and soft); thus the anomaly in Zn should be evident in the higher order elastic constants near the critical compression. Moreover, phonon measurements (which have been performed on Zn at ambient conditions [11]) should signal the long wavelength Kohn anomaly [10] at the critical compression. We also note that, as shown by Lifshitz [8], the transport properties may change drastically as the Fermi surface topology changes. In Ref. [12] the electrical conductivity tensor of Zn and Cd in a magnetic field was measured to show how the Fermi surface changed with pressure. Similar experiments performed at higher pressures could detect the pressure induced ETT in Zn.

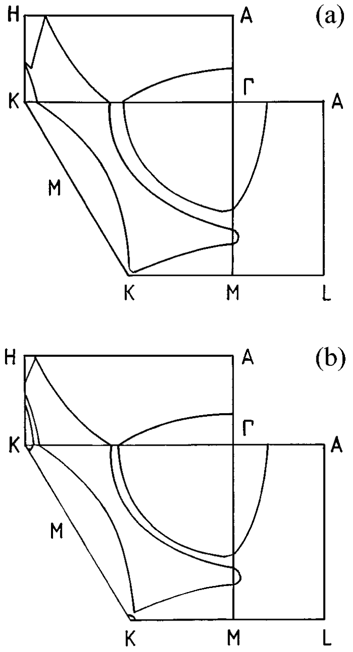

FIG. 2. Calculated Fermi surface of Zn at two different volumes branching the $2\frac{1}{2}$ transition, at $\frac{V}{V_0} = 0.88$ (a) and $\frac{V}{V_0} = 0.87$ (b), respectively, where $V_0 = 15.2$ Å^3 per atom. The symbols represent different high symmetry points of the Brillouin zone [13].

The electronic topological transition described in the present Letter shows that, in contrast to what is commonly assumed, the interatomic distances (c/a and b/a ratios, internal atomic positions, and so forth) do not necessarily change in a continuous way when applying an external pressure, even though the crystal structure remains the same. This holds both for experimental work, as is evident from Ref. [1], and for theoretical work, as demonstrated here. To be more specific we found it absolutely crucial to exercise extreme caution when sampling the Brillouin zone, where many k points were needed to reproduce the experiments. It is likely that other materials exhibit similar phenomena provided sufficient care is taken in the theoretical and experimental investigations of them, and we speculate that Zn is not an isolated example of an unusual behavior in the compressibility.

The theory outlined here gives a picture which is different from the analysis of Ref. [1], where it was speculated that the unique crystallographic properties of compressed Zn are correlated to a specific c/a ratio of $\sqrt{3}$. We show here that this has nothing to do with the observed structural properties. Our calculated anomaly occurs at a c/a ratio which deviates slightly but undoubtedly from $\sqrt{3}$. Instead we show that an electronic topological transition is what drives the peculiar structural properties of compressed Zn.

The discrepancy between the theoretical and experimental values of the volume is somewhat larger for Zn than what we find for other elements, and this error is well known to arise from the LDA. The error in the theoretical equilibrium volume may be connected to the fact that we observe the anomaly at a slightly different volume, compared to experiment. However, although the volume is underestimated with 9%, the calculated c/a value is only deviating 1.5% from the experimental value at 0 K. This is important to observe because the occupation of the K point, which is intimately connected to the structural anomaly, is sensitive to the c/a ratio but almost independent of the volume. It follows that our theoretical work should describe the structural anomaly rather accurately.

We finally note that since thermal broadening of the electron states will smear out the sharp features of the Fermi surface, elevated temperatures are expected to reduce the effect of the Fermi surface nesting and also smooth the effect of a sudden change of the Fermi surface close to the K point. The change in screening properties of Zn will thus be less pronounced at elevated temperatures. This explains why in the room temperature experiments the anomaly in structural properties accompanying the electronic topological transition is less pronounced than in our theoretical work. The room temperature also introduces other effects not taken into account in our study, e.g., the anomaly can broaden if different domains with slightly different c/a ratios coexist.

A careful experimental study at very low temperatures would therefore be highly desirable in order to complement our results. We point out that the effect discussed here is also likely to be found in Cd and it may be important also in other materials.

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