Anisotropy of thermal expansion and electronic topological transitions in Zn and Cd under pressure

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Using first-principles local-density electronic structure calculations we investigate the evolution of the Fermi surface of hcp Zn and Cd under hydrostatic pressure. We find a sequence of electronic topological transitions (ETT) and a region of pressure where several of these ETT's almost coincide, which apparently leads to the experimentally observed anomalies in their lattice parameters. A change of sign of the anisotropic thermal expansion is predicted in this critical region for temperatures below the Debye temperature. [S0163-1829(99)04103-X]

Recent experimental observations[1–3] of anomalies in the pressure dependences of lattice properties in hcp Zn and Cd have renewed interest in the theoretical investigation of the electronic structure of these metals. Unfortunately, first-principles studies of the lattice properties of Zn and Cd under pressure[1,4–6] give rather contradictory results. First of all, it was shown[4] that while the local-density approximation (LDA) does not have sufficient accuracy to reproduce experimentally observed variations of the lattice constants, they can be described in excellent agreement with experiment making use of recent generalized gradient corrections (GGA).[7] While an anomaly in c/a was reproduced at around $c/a=1.75$ [compare to the experimental value of 1.733 $\approx\sqrt{(}3$ (Refs. 2 and 3)], possible reconstructions of the Fermi surface (FS) were not investigated in Ref. 4 and the specific points in the Brillouin zone (BZ), which are responsible for the anomalies were not identified. We shall here examine this in detail, and, in particular, study electronic topological transitions (ETT's) that occur when van Hove singularities (VHS) cross the Fermi level. Analyses, using LDA calculations, of the FS topology of Zn were done in Refs. 1 and 5. These authors, however, did not agree upon which ETT causes the observed lattice anomalies. For Cd,[6] no ETT corresponding to the lattice anomaly at $V/V_0=0.85$ was identified. Moreover, it follows from Refs. 1 and 5 that the lattice anomalies in hcp Zn are due to a single ETT [either at the L (Ref. 1) or K point[5] of BZ]. To our understanding, the situation cannot be so simple since it is known[8–11] that only rather weak singularities in the lattice constants at room temperature may be connected with a simple ETT in three-dimensional metals and the observed anomalies in Zn seem to be too strong to be connected with the usual single ETT. It is instructive to note that when one deals with stronger singularities such as in alkaline earth metals, the common action of several VHS's (e.g., their merging) is usually important.[12]

In this work, we present results of an accurate first-principles local-density electronic structure investigation of FS transformations in hcp Zn and Cd under hydrostatic pressure, identify the reason for the lattice anomalies, and predict an unusual behavior of the anisotropic thermal expansion of hcp Zn and Cd in the region of lattice anomalies at low temperatures.

Before describing the specific computational results, it is worthwhile to stress that the problem of the lattice properties anomalies in Zn and Cd under pressure is part of a general problem about the influence of peculiarities of the electronic structure of metals and alloys on their lattice properties. Initiated by the pioneering works by Hume-Rothery and Jones,[13] this problem can be formulated in modern terms as how the proximity of a VHS to the Fermi level (E_F) and the ETT associated with it[14] affects the lattice structure, elastic

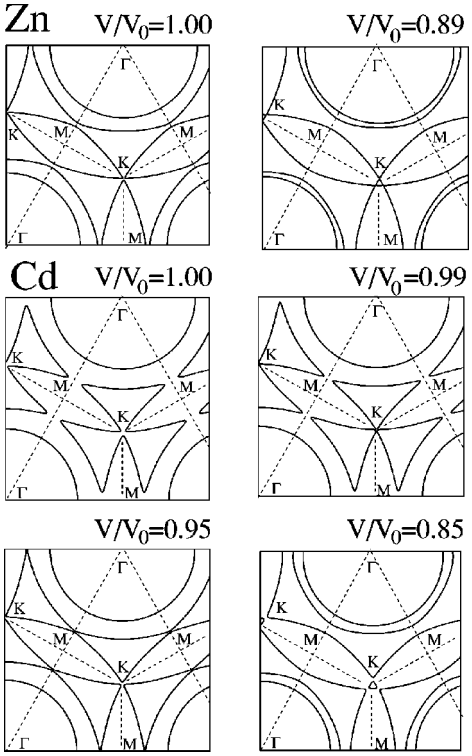

FIG. 1. Cross sections of the Fermi surface for hcp Zn and Cd for different volumes (with c/a optimized for each volume).

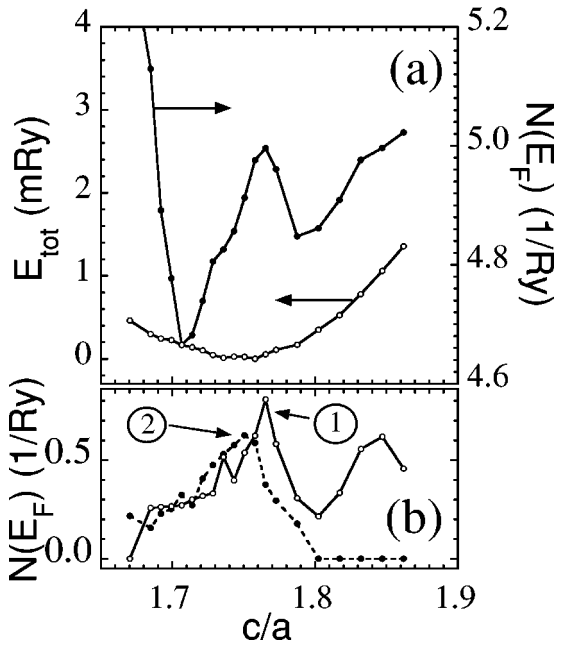

FIG. 2. Total energy (open circles) and total density of states at E_F (solid circles) for hcp Zn as a function of c/a at $V/V_0=0.88$ (a); contribution to $N(E_F)$ from a region of K (solid line) and L (dashed line) points (b).

moduli, phonon spectra, and other lattice properties. There are numerous theoretical works devoted to this problem using both model[8,9] and *ab initio*[10,11] approaches. It was shown that an ETT can lead to (i) a considerable softening of the shear moduli, even resulting in the total destabilization of a crystal structure,[10,11] (ii) less prominent but still noticeable anomalies in short-wavelength phonon modes,[8,9] and (iii) in thermodynamical properties of metals: heat capacity (see, e.g., Ref. 15 for $Cd_{1-x}Mg_x$ alloys) and thermal expansion. One result of the theory is the prediction of anisotropic thermal expansion for noncubic metals near an ETT at temperatures much lower than the Debye temperature. Expansion coefficients must in such cases be positive along one axis and negative along another[16,17]—as was experimentally confirmed for hcp Ti (Ref. 17) for $T<165$ K. This might be important from the point of view of possible applications since it means that any noncubic single-crystal metal in the immediate vicinity of an ETT should have a zero thermal expansion coefficient along some crystallographic direction at sufficiently low temperatures. Therefore new opportunities might appear in the search for new nonmagnetic Invar materials.

We investigated the change of the shape of the Fermi surface of Zn and Cd in a broad range of variations of the volume and c/a ratio using the full-potential linear muffin-tin-orbital method[18] with GGA corrections to the local-density functional.[7] Technical details of the calculations are described in Ref. 4. Critical points of Fermi surface transformations in hcp Zn and Cd under *ideal hydrostatic* pressure are seen from the cross sections of the FS presented in Fig. 1. At the equilibrium volume ($V/V_0=1.0$, with V_0 the experimental equilibrium volume), two qualitative differences are seen in the FS geometry (for FS topology terms, see Refs. 19 and 20): (i) the arms of the ''monsters'' are connected in the case of Zn, but are disconnected in Cd; (ii) the ''three-leg'' pieces of the FS around the K point are disconnected in Zn, but are connected in Cd. No needles are found for Zn at $V/V_0=1$. Although, this is not a well established fact,[21] the dHvA experiments[22] suggest that the needle cross-section area vanishes at $c/a\approx1.836$ (see Fig. 4 in Ref. 22), which is well below the c/a value of Zn at ambient pressure (and room temperature). With the increase of hydrostatic pressure, we detected for Zn the critical volume ($V/V_0=0.89$) where at least two ETT occur almost simultaneously (see Fig. 1), namely, the three-leg piece of the FS becomes connected and a new ellipsoidal piece (the ''needle'') appears, both around K. The situation is more complicated for Cd. First, at very slight compression ($V/V_0=0.99$), the three-leg piece of the FS becomes disconnected around the K point, then for $V/V_0=0.95$ one can see a reconnection of these pieces again and at the same time the arms of the ''monster'' become connected in the ΓM direction. This corresponds to the first anomaly in c/a found previously[4] and later confirmed.[6] With further increase of pressure, at $V/V_0\simeq0.85$ a needle appears around K. This volume corresponds to that predicted[4] and experimentally seen[3] as an anomaly in the c/a ratio. However, as we noticed above, the observed anomalies appear to be too strong to be connected with the single ETT. Note, for example that the K-point ETT in $Cd_{1-x}Mg_x$ alloys is almost invisible in the experimental dependence of the low-temperature heat capacity on x; the L-point ETT leads to an observable heat capacity anomaly, although it is not too sharp.[15] At the same time, we showed earlier[4] in the critical pressure region ($V/V_0=0.89$ for Zn and $V/V_0=0.85$ for Cd) that the total energy curve as a function of c/a becomes essentially flat [cf. Fig. 2(a)], which implies that domains with slightly different c/a may coexist in this pressure region. Hence, we paid special attention to this specific pres-

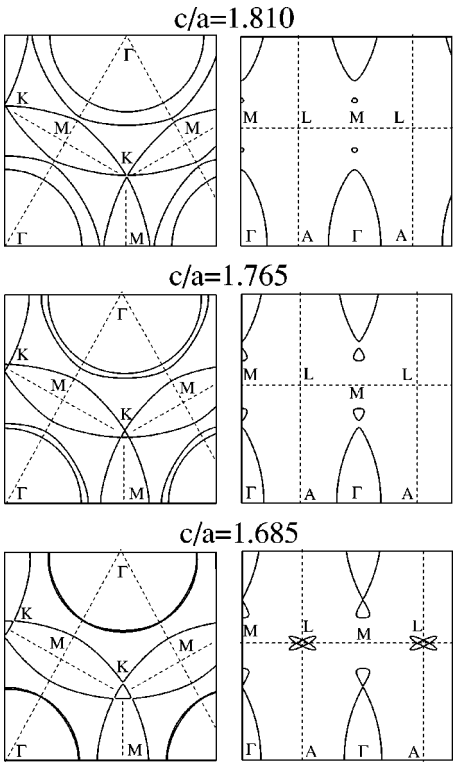

FIG. 3. Cross sections of the Fermi surface for hcp Zn for $V/V_0=0.88$ at different c/a.

sure region and the consequences of c/a variation on the FS geometry. Figure 3 exhibits the FS evolution for c/a values in the range where the total energy differs by less than ≈ 0.35 mRy [Fig. 2(a)] from its minimum value. The ETT's related to the structures 1 and 2 in Fig. 2(b), however, are encompassed by c/a in a range of ≈ 0.02, corresponding to an energy window of less than 0.01 mRy.

In contrast to previous calculations,[1,5] one can see that for Zn we now deal with *three* ETT's in the anomaly region. They are clearly seen in Fig. 2(b), which shows a contribution to the density of states at the Fermi energy, $N(E_F)$, calculated by integration over small (cylindrical) regions with the radii $0.07\times 2\pi/a$ a.u.$^{-1}$ around the K and L points using a Gaussian smearing parameter of 10 mRy. The first two described above [producing a single peak 1 in Fig. 2(b)] are connected with the saddle point (decay of the three-leg piece) and with the point of minimum energy (formation of the needle), respectively, with corresponding singular contributions to $N(E_F)$, as $\delta_1 N(E_F)\sim -\sqrt{E_{c1}-E_F}\,\theta(E_{c1}-E_F)$ and $\delta_2 N(E_F)\sim \sqrt{E_F-E_{c2}}\,\theta(E_F-E_{c2})$, where the step function $\theta(x)$ fulfills: $\theta(x>0)=1$, $\theta(x<0)=0$ and $E_{c,i}$ are the critical-point energies. At normal pressure, both singularities lie above E_F and move down under compression. The third ETT is connected with the L point [peak 2 in Fig. 2(b)], where two new pieces of the Fermi surface (butterflies) appear with the corresponding singular contribution to the density of states: $\delta_3 N(E_F)\sim \sqrt{E_F-E_{c3}}\,\theta(E_F-E_{c3})$. Taking into account the possibility of slightly nonhydrostatic conditions in the real experimental situation and the anomalous uniaxial softness of Zn and Cd, it is likely that all three ETT's take place in a critical pressure region. This might be the real reason for the relatively strong singularities in the lattice properties observed in Zn.

The peculiarities of this type of electronic structure lead to prominent anomalies in the low-temperature thermal expansion coefficient.[16,17] The general thermodynamic formulas for uniaxial crystals are

$$\alpha_\parallel=\left(\frac{\partial \ln c}{\partial T}\right)_p=\frac{1}{3BB_{22}}\left[(B_{22}-2B_{12})\frac{\partial S}{\partial u_1}+(2B_{11}-B_{12})\frac{\partial S}{\partial u_2}\right],$$

$$\alpha_\perp=\left(\frac{\partial \ln a}{\partial T}\right)_p=\frac{1}{3BB_{22}}\left[(B_{22}+B_{12})\frac{\partial S}{\partial u_1}-(B_{11}+B_{12})\frac{\partial S}{\partial u_2}\right],$$

$$\beta=\left(\frac{\partial \ln V}{\partial T}\right)_p=2\alpha_\perp+\alpha_\parallel=\frac{1}{BB_{22}}\left(B_{22}\frac{\partial S}{\partial u_1}-B_{12}\frac{\partial S}{\partial u_2}\right),$$

where P,V,T,S are the pressure, volume, temperature, and entropy, $du_1=d\ \ln V, du_2=d\ \ln(c/a), B_{ik}=(1/V)(\partial^2 E/\partial u_i \partial u_k)$ are elastic moduli, E is the total energy, $B=B_{11}-B_{12}^2/B_{22}$ is the bulk modulus. At low temperatures, the derivatives of the electronic entropy

$$\frac{\partial S}{\partial u_i}=\frac{\pi^2}{3}T\frac{\partial N(E_F)}{\partial u_i}$$

diverge as $(E_c-E_F)^{-1/2}$ at the ETT. Usually the density of states of noncubic metals is much more sensitive to the uniaxial stress than to the dilatation and $|\partial S/\partial u_2| \gg |\partial S/\partial u_1|$.[16] Our present calculations for Zn and Cd agree with this, the ratio being ≈ 6. Since for all crystals $2B_{11}-B_{12}>0$, and $B_{11}+B_{12}>0$, the signs of $\alpha_\parallel$ and $\alpha_\perp$ have to be opposite near an ETT.

At low temperatures, the lattice thermal expansion is determined by the derivatives of the Debye temperature, θ_D, with respect to deformations and has the same sign and power of the singular contributions since the singular contributions to θ_D and to $N(E_F)$ are proportional.[8–11] It appears that all three ETT described above for Zn give negative contributions to $[\partial N(E_F)]/[\partial(c/a)]$ since in all cases $[\partial \delta_i N(E_F)]/\partial E_{ci}<0$ and $\partial E_{ci}/[\partial(c/a)]>0$. The assumption about the higher sensitivity of the VHS positions to uniaxial stress than to the dilatation is also confirmed by our calculation. Hence, we predict that in the ''critical'' region at low temperatures $\alpha_\parallel\to-\infty$ and $\alpha_\perp\to+\infty$. Since at zero pressure we have $\alpha_\parallel>0$ and $\alpha_\perp<0$,[16] we predict a change of the sign of the anisotropy under pressure. A similar prediction of sign change in Cd_xMg_{1-x} versus x was made in Ref. 16. The region of negative $[\partial N(E_F)]/[\partial(c/a)]$ in Fig. 2 corresponds approximately to the region of three ETT's. One may expect from Fig. 2 that at further compression a second change of sign of the thermal expansion anisotropy may take place. In the case of Cd, we have to also consider the contribution of the VHS in the ΓM direction (the disconnection of monster arms) but the sign of its contribution to $[\partial N(E_F)]/\partial(c/a)$ is the same as for the other ETT's considered here.

To summarize, we presented results of first-principle investigations of the Fermi surface evolution in hcp Zn and Cd with pressure. We find FS topology changes with both uniaxial stress and dilatation producing three ETT's, which we argue may coexist due to the anomalous softness of the c axis. Thus, the picture appears to be more complicated than it was described in previous work. We predict also very in-

teresting features of the low-temperature thermal expansion coefficients, namely two inversions of sign of the anisotropy. They are connected with the important general features of noncubic metals near ETT and, if confirmed experimentally, might be used in a search for new nonmagnetic Invar materials.

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