Phonon Anomaly in High-Pressure Zn

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The equation of states and phonon dispersions of hexagonal zinc have been calculated by the plane-wave pseudopotential method within the generalized-gradient approximation. Weak discontinuities are found in the pressure-volume relation as well as the c/a-volume curve. Phonon dispersions of Zn under pressure have been obtained with a direct method and the results are consistent with the neutron scattering data. At $V/V_0 \approx 0.88$, the calculated frequencies of the acoustic phonons near the zone center softened substantially as a result of an electronic topological transition. The theoretical result is consistent with the observed anomaly in the Lam-Mössbauer factor at low temperature.

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The hexagonal close-packed (hcp) structures of nontransition metallic Zn and Cd have been extensively studied for many years [1–4], since the axial c/a ratios, 1.856 for Zn, and 1.89 for Cd, are much larger than the ideal ratio, $c/a = \sqrt{8/3} = 1.633$. The unusually large c/a ratio makes many physical properties of Zn and Cd highly anisotropic. It is clear that the electronic structure of Zn plays an important role in the manifestation of these properties. The asymmetry of the electronic charge distribution caused by the p-band mixing has been shown to be the origin of the large c/a ratio for Zn [2,5]. The axial ratio of Zn decreases under pressure and has been investigated with both experiment [6–13] and theory [14–16]. An earlier study by Lynch and Drickamer [6] reported unusual changes in the c/a axial ratios under pressure. In Zn, an anomaly in the c/a ratio and electrical resistance at about 7 GPa was reported. This observation was attributed to pressure induced changes in the topology of the Fermi surface. Such an electronic topological transition (ETT) is anticipated to affect low-frequency acoustic and optical phonons near the zone center. This suggestion, however, was in apparent contradiction with a study by Schulte *et al.* using energy dispersive diffraction [7] where no discontinuinity in c/a was observed. Later, Takemura [8] repeated the measurement with high-pressure powder x-ray diffraction experiments at room temperature. Their results seem to reaffirm the earlier report where the volume dependence of the c/a ratio in Zn changes its slope at $V/V_0 = 0.893$ (9.0 GPa). More recently, under a better hydrostatic condition achieved by using a helium pressure-transmitting medium, the c/a anomaly was no longer observed [9]. Apart from structural measurements, neutron inelastic-scattering experiments have been performed on Zn under pressure at room temperature. While Morgan *et al.* [12] found a discontinuity in the phonons under pressure, supporting the ETT model, Klotz *et al.* [13] failed to observe the anomaly or softening in the phonon frequency of Zn under pressure. The only experimental study which supports the ETT model is a low temperature (4 K) Mössbauer study [10]. In this experiment, the Lam-Mössbauer factor f was found to increase by a factor of 4 from 0 to 6.6 GPa at 6.6 GPa ($V/V_0 \approx 0.92$), followed by a sharp drop to about half of its maximal value and eventually recovered to the normal behavior at $V/V_0 \approx 0.84$. This observation indicated a strong decrease of the low-frequency acoustic phonon frequencies near 6.6 GPa, possibly, due to the ETT.

The conflicting experimental results have stimulated several subsequent theoretical investigations on the structure and electronic properties of Zn and Cd at high pressure [14–16]. Although these first-principle calculations employed different approximations for exchange correlations and potentials, all the theoretical results indicated a c/a ratio anomaly at about $V/V_0 = 0.90$. The analysis of the band structure suggested an electronic topological transition occurred at either the K or L points in the Brillouin zone.

It is important to note that all the studies performed at 0 K (theoretical calculations) and 4 K (Mössbauer spectroscopy) support the ETT model, while recent experiments performed at room temperature found no anomaly in the c/a ratio and phonons. Therefore it is possible that the temperature factor may play a crucial role. The ETT and c/a ratio anomaly might be smeared out or become difficult to detect at room temperature [9]. A direct measurement of the c/a or acoustic phonons at high pressure and low temperature may help to resolve the discrepancy.

In this Letter, electronic structure calculations were performed to investigate the c/a ratio and phonon dispersions of Zn under pressure by a plane-wave pseudopotential method with generalized-gradient approximation (GGA) [17]. All calculations of total energy and Hellmann-Feynman forces were carried out by using the VASP code [24]. The VASP code applies the standard method in which the Kohn-Sham equations are solved self-consistently using a pseudopotential and plane-wave basis, based on the density-functional theory. We used ultrasoft pseudopotentials [25] for Zn, which were generated with the atomic configuration of $3d^{10}4s^2 4p^0 4f^0$, with a cutoff radius of 1.40 Å. The cutoff energy of 350 eV was employed in

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the calculations of total energies of the Zn primitive unit cell with different volumes and the optimization of c and a at a constant volume. A $25 \times 25 \times 25$ k-point mesh was used for the summation over the Brillouin zone. Preliminary calculations shown that the c/a ratio is very sensitive to the k-point mesh.

The full phonon dispersions and mode Grüneisen parameters under pressure were obtained from direct calculations [18] of Hellman-Feymann forces. A $4 \times 4 \times 2$ supercell with 64 atoms was employed. The cutoff energy was set to 250 eV and a $(4 \times 4 \times 4)$ k-point mesh [26] which gave 24 to 48 k-points in the irreducible Brillouin zone. Increasing the cutoff energy to 350 eV and the k-point mesh to $(6 \times 6 \times 6)$ does not change the phonon dispersions more than 1.0%. Further calculation using even larger $(7 \times 7 \times 7)$ mesh does not alter the results presented here in any significant manner. The Hellmann-Feynman forces are calculated for all atoms in the supercell with one atom displaced from the equilibrium position by about 0.5% of the lattice constant. One Zn atom was displaced along x, y, and z, respectively, generating $3 \times 3 \times 64$ Hellmann-Feynman force field data from which the interatomic force constants (IFCs) were generated by establishing the hexagonal symmetry. The interaction range was limited to the distance from the central atom of the supercell to the surface atom; it contained up to the twelfth nearest neighbors in the $4 \times 4 \times 2$ supercell. Sixty-seven independent IFCs were obtained. The dynamical matrix was constructed to calculate the phonon dispersions. Details of obtaining force constants and phonon dispersions have been described in Ref. [18]. This method has been applied successfully to calculate the phonons not only for insulators [19] and semiconductors [20] but also for metals [21] and alloys [22,23] as well.

Figure 1a shows the pressure-volume relation for Zn within the GGA. The results are in good agreement with previous full potential linearized muffin-tin orbital (FP-LMTO) calculations [16]. In the earlier calculations, it was demonstrated that GGA gave the best description of the equation of states and the c/a ratio for Zn. It is clear from Fig. 1a that an anomaly, albeit weak, can be observed in the P-V curve. Figure 1b compares the calculated c/a ratio as a function of volume with the recent experimental results. The agreement in the overall trend is reasonable with the theoretical values systematically higher than the experimental data. Consistent with previous theoretical investigations, the onset of a small anomaly at $V/V_0 = 0.88$ was predicted. It should be pointed out the discontinuity in c/a predicted by the present calculation is much weaker than that given in Ref. [15]. The k-point mesh used in previous calculations was not indicated in the papers. However, as noted above, an insufficient number of k-points may affect the convergence of the c/a ratios. A much denser $45 \times 45 \times 45$ mesh has also been used in the calculation, and we found that the c/a anomaly is still persistent. An important observation from our calculations is

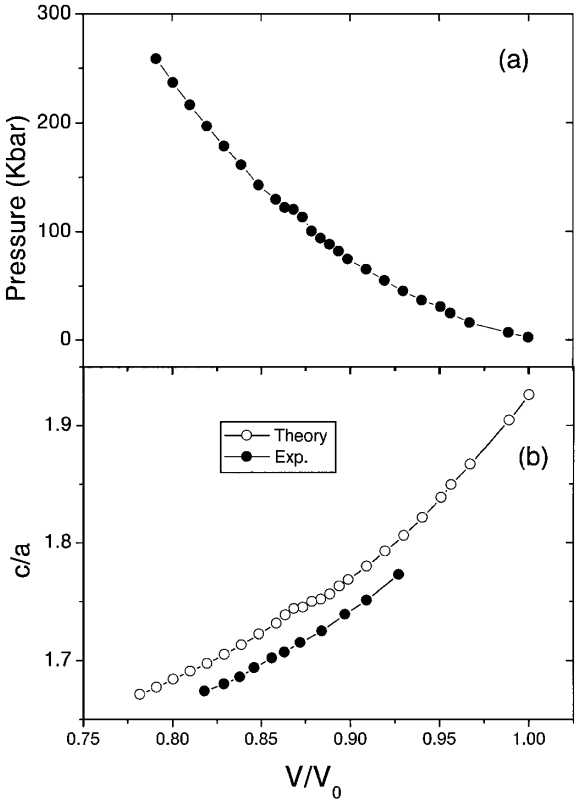

FIG. 1. (a) Zero temperature pressure-volume relation for Zn. (b) Calculated and experimental c/a ratio for Zn as a function of relative volume. The experimental data are taken from Ref. [9].

that the calculated discontinuinity ("kink") in c/a is less than 0.005. This small difference may be very difficult to detect by experiment.

The results presented here are in substantial agreement with the FP-LMTO calculations of Novikov *et al.* [16]. In this study, the electronic structure, Fermi surface, and density of states at the Fermi level $[N(E_F)]$ of Zn under pressure indicate the ETT's at both the K and L points. At the K point, the three-leg piece of the Fermi surface becomes connected and a new needle appears at the L point [16]. Furthermore, the bottom of the conduction band touches the Fermi level at the critical volume. An examination of the calculated band structure and $N(E_F)$ clearly shows that there are similar ETT's at $V/V_0 = 0.88$. The question is how the c/a anomaly related to the ETT's?

To answer this question, it is essential to understand the phonon spectra under pressure. An ETT may induce giant Kohn anomalies resulting in a drastic softening of low-frequency phonon modes as observed in the Mössbauer experiments [10,11]. Figure 2 shows the phonon dispersions calculated at the lattice constants of Zn at 80 K in order to compare with the experimental phonon dispersions [27] at the same temperature. The calculations reproduced very well the experimental phonon dispersions for all branches in every symmetrical direction. The largest discrepancies ($<$0.4 THz) occur near the K point, where the calculated

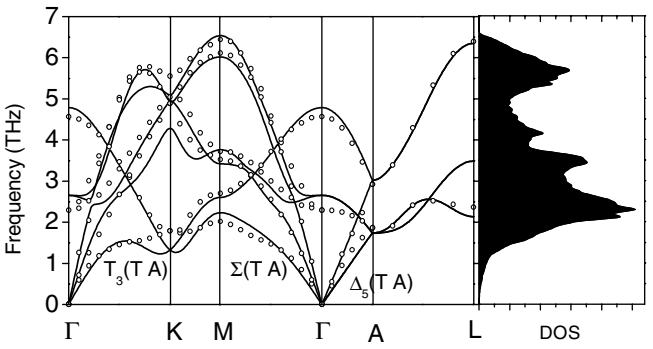

FIG. 2. Phonon dispersions for Zn at ambient pressure (full curve—theory; open circle—experiment). The lattice constants at 80 K are taken from Ref. [27].

transverse acoustic modes are slightly softer than that observed. The good agreement between theory and experiment is possibly because Zn is a nontransition metal where the $3d$ band is fully occupied and, therefore, the interaction range is shorter than that of a transition metal. From the calculated force constants, we noted that the longest interaction included in our calculation is about 2 orders smaller than the shortest interaction. The calculated phonon density of states is shown in Fig. 2. Several interesting features for the phonons of Zn are that the frequencies of acoustic modes are quite low (less than 2.0 THz), while the optic modes are strongly dispersive and no sharp peak is observed at the high frequency as often observed in many metals.

The pressure dependence of phonons can be represented by the mode Grüneisen parameters $\gamma_n(\mathbf{q})$,

$$\gamma_n(\mathbf{q}) = -\frac{d[\ln\omega_n(\mathbf{q}, V)]}{d[\ln V]}, \qquad (1)$$

where $\omega_n(\mathbf{q}, V)$ is the frequency of the nth vibration mode at wave vector q and V is the volume of the unit cell. The results are shown in Fig. 3 at $V/V_0 = 0.88$ where the c/a anomaly occurs. It is noted that the Grüneisen parameters of all optical modes are between 0.0 and 2.0 and almost q independent, while the lowest acoustic mode has substantial softening around the Γ point and along several symmetrical directions. This observation confirms the predictions of the ETT model [11]. The room temperature Grüneisen parameters of the acoustic Σ_3 mode along Γ to the M point have been measured by Klotz *et al.* [13] from inelastic neutron scattering experiments. No discontinuity was observed up to 9.4 GPa. The absence of the anomaly in the experiment may be due to a temperature effect. Unfortunately, it was not possible to evaluate the temperature dependence of the phonons within the quasiharmonic approximation. We have also computed the average value of Grüneisen parameters of the lowest acoustic mode along the Γ-K, Γ-M, and Γ-A directions as functions of the unit cell volume. The results are given in Fig. 3b. It shows clearly that the mode average Grüneisen

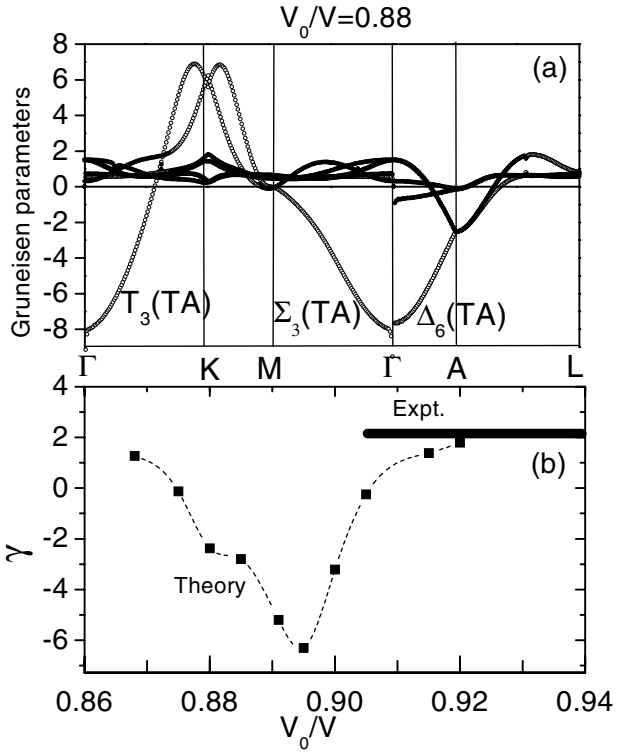

FIG. 3. (a) Mode Grüneisen parameters for Zn at $V/V_0 = 0.88$. (b) Mode average Grüneisen parameters of the lowest acoustic modes of Zn as a function of relative volume. The experimental values are from Ref. [13].

parameter varies sharply and changes sign (becomes negative) around $V/V_0 = 0.895$. This anomaly is close to the discontinuity in the P-V curve at $V/V_0 = 0.88$ (10 GPa). This phonon softening, in principle, should be observable near 10 GPa at low temperature. Unfortunately, the experimental measurements were performed only up to 9.4 GPa at 300 K. Moreover, the experimental data between 7 and 9 GPa were rather sparse and it is plausible that the abrupt softening of the acoustic phonon modes predicted here may have been inadvertently missed. We have checked the phonon softening with a larger ($7 \times 7 \times 7$) k-point mesh at $V/V_0 = 0.89$, the average Grüneisen parameter $\gamma = -0.38$. Therefore, increasing the k-point for integration does not change the phonon anomaly.

The softening of acoustic modes will affect the compressibility of a and c leading to the discontinunity observed in the c/a ratio. It is because the vibration of the acoustic modes represents the movement of the mass center of the primitive unit cell. In a recent high-pressure x-ray diffraction experiment [9] on Zn at room temperature, Takemura did not observe the c/a ratio discontinuity. However, this does not necessarily preclude the possibility of a c/a ratio discontinunity at low temperature. The variation c/a under pressure depends on the compressibility of both c and a, which are related to the lattice vibrations along the c axis and in the basal plane, respectively. Since the softening of the acoustic mode is more pronounced

near the zone center with vibrational frequencies less than 1.0 THz (see Fig. 3), thus perhaps at low temperature, where only low-frequency modes are dominant, the effects of acoustic mode softening could be observed. At higher temperature, when high-frequency modes with "more normal" Grüneisen parameters are activated, this may smear out the effects of acoustic mode softening.

In summary, the c/a anomaly and an ETT in Zn under pressure were confirmed with plane-wave ultrasoft pseudopotential calculations. Phonon dispersions and Grüneisen parameters were obtained for the first time. A sudden softening of acoustic modes near the Γ point was found at the pressure where the c/a ratio shows a discontinuity. This novel phenomenon is shown to be related to an electronic topological transition.

Very recently, we noted an experimental and theoretical study [28] on the zone center (Γ point in Fig. 2 and Fig. 3a) optical modes under pressure. In agreement with our results, there is no phonon anomaly up to 58 GPa. The Grüneisen parameter of the zone center transverse-optical mode from experiment (about 2.2 at critic pressure) is very close to our value of 1.8. Future experiments on acoustic modes at low temperature and under pressure are clearly desirable.

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[1] S. Daniuk, T. Jarlborg, G. Kontrym-Sznajd, J. Majsnerowki, and H. Stachowiak, J. Phys. Condens. Matter **1**, 8397 (1989).
[2] D. Singh and D. A. Papaconstantopoulos, Phys. Rev. B **42**, 8885 (1990).
[3] P. Blaha, K. Schwarz, and P. H. Dederichs, Phys. Rev. B **37**, 2792 (1988).
[4] W. Potzel, W. Adlassnig, J. Moser, C. Schäfer, M. Steiner, and G. M. Kalvius, Phys. Rev. B **39**, 8236 (1989).
[5] J. A. Moriarty, Phys. Rev. B **10**, 3075 (1974).
[6] R. W. Lynch and H. G. Drickamer, J. Phys. Chem. Solids **26**, 63 (1965).
[7] O. Schulte, A. Nikolaenko, and W. B. Holzapfel, High Press. Res. **6**, 169 (1991).
[8] K. Takemura, Phys. Rev. Lett. **75**, 1807 (1995); Phys. Rev. B **56**, 5170 (1997).
[9] K. Takemura, Phys. Rev. B **60**, 6171 (1999).
[10] W. Potzel, M. Steiner, H. Karzel, W. Schiessel, M. Köfferlein, G. M. Kalvius, and P. Blaha, Phys. Rev. Lett. **74**, 1139 (1995).
[11] M. Steiner, W. Potzel, H. Karzel, W. Schiessel, M. Köfferlein, G. M. Kalvius, and P. Blaha, J. Phys. Condens. Matter **8**, 3581 (1996).
[12] J. G. Morgan, R. B. Von Dreele, P. Wochner, and S. M. Shapiro, Phys. Rev. B **54**, 812 (1996).
[13] S. Klotz, M. Braden, and J. M. Besson, Phys. Rev. Lett. **81**, 1239 (1998).
[14] S. Meenakshi, V. Vijayakumar, B. K. Godwal, and S. K. Sikka, Phys. Rev. B **46**, 14 359 (1992).
[15] L. Fast, R. Ahuja, L. Nordström, J. M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. Lett. **79**, 2301 (1997).
[16] D. L. Novikov, A. J. Freeman, N. E. Christensen, A. Svane, and C. O. Rodriguez, Phys. Rev. B **56**, 7206 (1997); D. L. Novikov, M. I. Katsnelson, A. V. Trefilov, A. J. Freeman, N. E. Christensen, A. Svane, and C. O. Rodriguez, Phys. Rev. B **59**, 4557 (1999).
[17] Y. Wang and J. P. Perdew, Phys. Rev. B **44**, 13 298 (1991).
[18] K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. **78**, 4063 (1997).
[19] K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. B **61**, 272 (2000).
[20] K. Parlinski and Y. Kawazoe, Phys. Rev. B **60**, 15 511 (1999).
[21] A. Eichler, K. P. Bohnen, W. Reichardt, and J. Hafner, Phys. Rev. B **57**, 324 (1998).
[22] Z. Q. Li and J. S. Tse, Phys. Rev. B **61**, 14 531 (2000).
[23] A. van de Walle, G. Ceder, and U. V. Waghmare, Phys. Rev. Lett. **80**, 4911 (1998).
[24] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11 169 (1996).
[25] G. Kresse and J. Hafner, J. Phys. Condens. Matter **6**, 8245 (1994).
[26] H. Monkhorst and J. Pack, Phys. Rev. B **13**, 5188 (1976).
[27] L. Almqvist and R. Stedman, J. Phys. F **1**, 785 (1971).
[28] H. Olijnyk, A. P. Jephcoat, D. L. Novikov, and N. E. Christensen, Phys. Rev. B **62**, 5508 (2000).