Is There an Electronic Topological Transition in Zinc under High Pressure?

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An electronic topological transition (ETT) in Zn was recently deduced from an anomaly in the Lamb-Mössbauer factor f at 6.6 GPa [Potzel *et al.*, Phys. Rev. Lett. **74**, 1139 (1995)]. We show by inelastic neutron scattering up to 9.4 GPa that the pressure dependence of the low energy acoustic phonon modes Σ_4, Σ_3, and T_4 is completely regular without any singularity over the entire pressure range. No phonon softening was found beyond 6 GPa, in contrast to the Mössbauer studies. Lattice dynamical calculations demonstrate that, in general, the strong decrease of f cannot be due to the $q \sim 0$ phonon modes sensitive to the occurrence of an ETT. [S0031-9007(98)06729-5]

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The behavior of zinc and cadmium at reduced volume has attracted considerable interest over the last three decades [1–8]. These metals crystallize in the hcp structure with a nonideal c/a ratio which strongly decreases under pressure because of the pronounced anisotropy of their linear compressibilities. This may lead to drastic changes in their solid state properties. In particular, they are favorite candidates for observing the long searched "Lifshitz transition." As suggested in 1960 by Lifshitz [9], an electronic transition may occur in simple metals under high pressure due to a topology change of the Fermi surface as the Brillouin zone (BZ) is strongly deformed. Such an "electronic topological transition" (ETT) should cause anomalies in most thermodynamic properties, such as the bulk modulus, specific heat, and thermal expansion coefficient [9]. In the case of Zn and Cd, the low energy acoustic phonon frequencies should also be strongly affected if the ETT occurs at the L point of the BZ [10–12]. In these metals, a Kohn anomaly is known to exist at the zone center [11,12] since the Fermi level is close to the zone boundary along the (101) reciprocal vector $\mathbf{G}(101)$, i.e., $k_F \sim \frac{1}{2}|\mathbf{G}(101)|$. Hence, the condition for the appearance of a Kohn anomaly $\frac{1}{2}|\mathbf{q} + \mathbf{G}(hkl)| = k_F$ reduces to $\mathbf{q} \sim 0$, i.e., the anomaly occurs at the zone center. The frequency increase of the phonons is substantial, as seen, for example, in the anomalously high value of the elastic constant C_{44} of Zn and Cd [10–12]. As soon as the Fermi level goes beyond the band gap into the third BZ the frequencies are expected to regain their normal values. Measurements of de Haas–van Alphen oscillations show evidence for an ETT in Cd at ~1.7 GPa [4], but, despite numerous structural investigations under high pressure [1], no definite proof for its existence was found in these or any other metals.

Recently, however, a Mössbauer study reported the first observation of an ETT at 6.6 GPa and 4 K in zinc [5,6]. In these measurements, the Lamb-Mössbauer factor f is seen to increase by a factor ~4 from 0 to 6.6 GPa, followed by a sharp drop to about half of its maximal value. It indicates a strong *decrease* of the low energy (acoustic) phonon frequencies at 6.6 GPa and was interpreted as the occurrence of an ETT at the L point. This contrasts with the findings of a high pressure neutron study to 8.8 GPa [8], which reported an anomalous *increase* of a low energy phonon mode beyond 6.8 GPa. The high pressure behavior of the acoustic phonon frequencies hence remains controversial. In this context a structural study of Zn to 126 GPa [2,3] should be mentioned. A small anomaly of the a-lattice parameter was detected at 9.1 GPa, where c/a becomes equal to $3^{1/2}$. Very recent *ab initio* calculations can reproduce an anomaly when c/a is close to this value, but its relation to an ETT remains unclear [13].

A detailed study of the lattice dynamics of Zn is now experimentally possible due to new developments in high pressure techniques for inelastic neutron scattering [14]. Disklike single crystal samples 3.6 mm in diameter and 1.8 mm thick (~17 mm^3 in volume) were used. They were embedded in a lead pellet and compressed similar to previous experiments [14]. All data were collected at the Laboratoire Léon Brillouin in Saclay (France).

In the first experiments, the single crystal was oriented with the $(\bar{1}20)$ reflection vertical, which allows measurements of the Σ_3 mode with polarization along the c axis and wave vector parallel to [100]. The pressure was determined using the measured variation of the c axis [using the (004) reflection] and Takemura's [2,3] 300 K data. Data were collected for reduced wave vectors $\xi = 0.075$ (Fig. 1), 0.10 (both to 9.4 GPa), $\xi = 0.15$ (to 9.1 GPa), and $\xi = 0.20$ (to 3.9 GPa). We define the edge of the first Brillouin zone as $\xi = 0.5$. Typical scan times were between 30 min and 3 h at low pressures and between 2 and 5 h for the highest pressures. The quality of the single crystals hardly deteriorated with pressure, as indicated by the width of the (004) reflection. It increased from 0.8° at ambient to 1.0° at the highest pressures. In a second measurement, a single crystal was oriented with the c-axis vertical, which gives access to the Σ_4 and T_4 modes with polarization in the hexagonal plane and wave vector

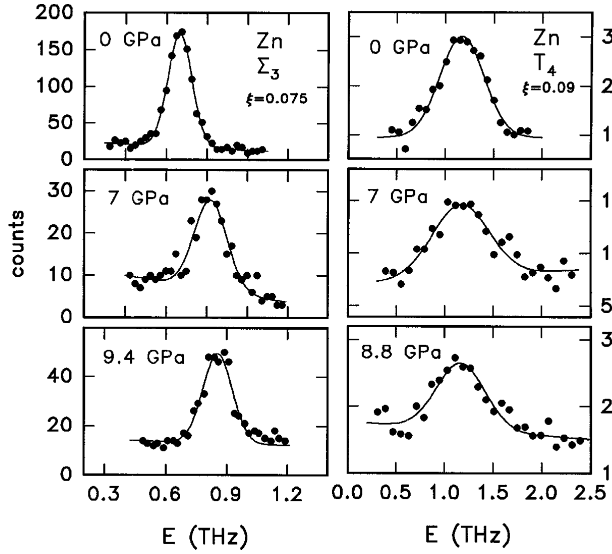

FIG. 1. Constant-Q scans across the Σ_3 and T_4 phonon branch for three different pressures. The line represents a least squares fit to a Gaussian including a linear background.

in the high symmetry directions [100] and [110], respectively. Data were collected at $\xi = 0.09$ (T_4, Fig. 1) and $\xi = 0.10$ (Σ_4) up to 8.8 GPa. Pressure values were determined by measuring the variation of the a-lattice parameter and again using Takemura's calibration [2,3].

The pressure dependence of the modes is strongly anisotropic (Fig. 2). The frequencies ω of modes with polarization along the c axis increase by 25% up to 9 GPa, whereas the modes with polarization in the hexagonal planes show almost no variation over the same pressure range. This fact can be conveniently expressed by mode Grüneisen parameters $\gamma(j, \mathbf{q}) = -\partial \ln \omega(j, \mathbf{q})/\partial \ln V$, where j designates the mode, $\mathbf{q}$ the wave vector, and V the volume. From linear regression fits of the data in Fig. 2 we find $\gamma(\Sigma_3) = +2.8 \pm 0.10$ (which seems to be independent of $\mathbf{q}$), $\gamma(T_4) = +0.5 \pm 0.15$, and $\gamma(\Sigma_4) = 0.0 \pm 0.3$. Extrapolation of the data points of $\gamma(\Sigma_3)$ and $\gamma(T_4)$ to $\mathbf{q} = 0$ shows excellent agreement with the ultrasonic measurements (Fig. 3), whereas $\gamma(\Sigma_4)$ seems to be somewhat lower than expected. Symmetry requires that $\gamma(\Sigma_4) = \gamma(T_4)$ for $\mathbf{q} \to 0$, i.e., the elastic properties must be isotropic in the hexagonal plane.

The drastic decrease of the Lamb-Mössbauer factor f was seen in Refs. [5,6] at 4 K and 6.6 GPa. In this experiment, the pressure was measured *in situ* using the superconducting transition temperature of lead [6]. The occurrence of the ETT is related to the values of the lattice parameters a and c at these conditions and is therefore shifted to higher pressures at room temperature due to the thermal expansion of the lattice. The difference in a and c between 4 and 300 K corresponds to 1.3 GPa [2,3]; i.e., at 300 K, the ETT is expected to occur at approximately 7.9 GPa. A more accurate estimate is obtained by taking into account the temperature dependence of the bulk modulus B and its pressure derivative B'. Ledbetter quotes $\partial \ln B/\partial \ln T = -3 \times 10^{-4}\ \mathrm{K}^{-1}$ [20], i.e., a 8.7% increase of B between 295 and 4 K. This agrees well (8.2%) with the more reliable procedure proposed by Vinet *et al.* [21]. In any case, we find a pressure shift of ~1.5 GPa and conclude that *if the ETT was observed at 4 K at 6.6 GPa, it should occur at 300 K at* ~8.0 *GPa with an uncertainty much less than 1 GPa.*

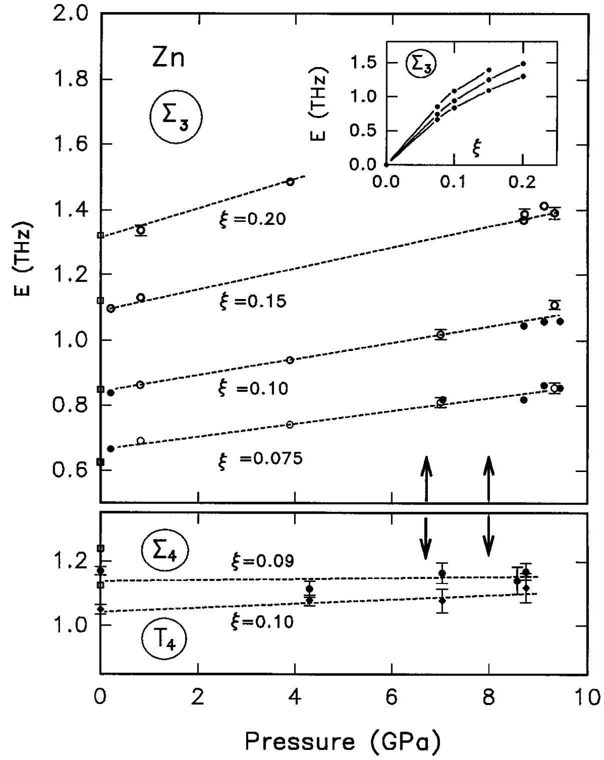

FIG. 2. Variation of mode frequencies under pressure of modes Σ_3, Σ_4, and T_4. The inset shows the corresponding part of the dispersion curve of Σ_3 at 0, 4, and 9 GPa. Dots and circles represent runs using different single crystals. Open squares indicate published ambient pressure values obtained at 80 K [15]. If not plotted, error bars are smaller than symbol size. The vertical arrows indicate the pressure where phonon anomalies were reported to occur at 4 K (6.6 GPa) [5,6] and where they should appear at 300 K (8 GPa; see text).

Figure 2 shows no evidence for any anomaly in this pressure range, in any mode. The most crucial results are those for Σ_3 to 9.4 GPa, since this mode involves the C_{44} elastic constant, which is expected to be sensitive to the occurrence of an ETT [5,6,10] at the L point. The phonon frequencies increase continuously beyond 8 GPa, with *no* phonon softening occurring for any wave vector. Our data prove, in particular, that there is no "rapid divergence" of the $\xi = 0.075$ frequency beyond 6.8 GPa either, as reported by Morgan *et al.* [8]. This mode behaves completely regularly and no singularity occurs up to at least 9.4 GPa.

There is of course a possibility that the lattice dynamics of Zn at 4 K differs from that at 300 K. However,

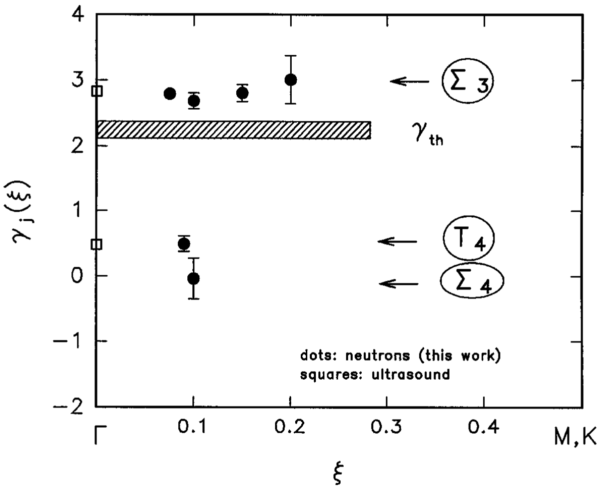

FIG. 3. Mode Grüneisen parameters from neutron data (points, [16]) compared to ultrasonic results (squares, [17]). The shaded area indicates the range of the thermodynamic value γ_{th} obtained from calorimetric [18] and shock wave measurements [19].

there is no experimental evidence for this. No structural phase transition occurs in this temperature range and the dispersion curves obtained at 300 K [11] are identical to those at 80 K [11,15]. In particular, the Kohn anomaly in sound, whose disappearance is suggested [5,6] to be responsible for the decrease in f, is still observable at 300 K [11].

In the following we relate our neutron results to the quantity determined in Refs. [5,6], the Lamb-Mössbauer factor f. We recall that f is the fraction of recoilless emitted photons, and is, similarly to the Debye-Waller factor, given by [22,23]

$$f = \exp\{-k_\gamma^2 \langle \mathbf{x}^2 \rangle\}, \tag{1}$$

where $\mathbf{k}_\gamma$ is the wave vector of the emitted γ radiation ($E_\gamma = 93.3$ keV) and $\langle \mathbf{x}^2 \rangle$ is the mean square atomic displacement in the direction of $\mathbf{k}_\gamma$. For a monatomic crystal $\langle \mathbf{x}^2 \rangle$ is [22]

$$\langle \mathbf{x}^2 \rangle = (V\hbar/16\pi^3 m) \sum_j \int d^3\mathbf{q} [\mathbf{e}_\gamma \cdot \mathbf{e}_j(\mathbf{q})]^2 \times [1 + 2n_j(\mathbf{q})]/\omega_j(\mathbf{q}), \tag{2}$$

where $\mathbf{e}_j(\mathbf{q})$ is the eigenvector and $n_j(\mathbf{q})$ the Bose factor of mode j and wave vector $\mathbf{q}$, and $\mathbf{e}_\gamma = \mathbf{k}_\gamma / k_\gamma$. In a hexagonal crystal, $\langle \mathbf{x}^2 \rangle$ has extremal values $\langle \mathbf{x}^2 \rangle_\parallel$ and $\langle \mathbf{x}^2 \rangle_\perp$ parallel and perpendicular to the c axis. We now evaluate $\langle \mathbf{x}^2 \rangle$ by two different means, first by a Debye model, and then by an exact calculation using a lattice dynamical model.

In Debye's model $\langle \mathbf{x}^2 \rangle$ is assumed to be isotropic and is given by [22]

$$\langle \mathbf{x}^2 \rangle = (3\hbar^2/4mk_B)(1/\theta), \tag{3}$$

where θ is the Debye temperature and the other constants have their usual meaning. As pointed out by Pynn [24], the 0 K Debye temperature of a hcp structure can be evaluated by

$$\theta = (\hbar/k_B)(9N/A)^{1/3}, \tag{4}$$

where N is the atomic density and A is a function of the five elastic constants C_{ij}. This model, although approximate, retains the anisotropic elastic properties of Zn. Taking C_{ij} values from Ledbetter [25] we find $\theta = 319$ K, compared to values of θ between 309 and 326 K from calorimetric measurements at low temperatures [26]. We may also evaluate the thermodynamic Grüneisen parameter $\gamma_{th} = -\partial \ln\theta / \partial \ln V$, since the volume dependence of all elastic constants contained in A is known [25]. We find $\gamma_{th} = 2.28$, again in excellent agreement with $\gamma_{th} = 2.3$ from measurements of the thermal expansion at 4 K [18] and values between 2.11 and 2.38 from shock wave data [19]. On the other hand, from Eqs. (1) and (3) we deduce $\gamma_{th} = -\partial \ln\theta/\partial \ln V = -\partial \ln(\ln f)/\partial \ln V \sim 3$ from Refs. [5,6]. In other words, *the initial rate of increase of f with pressure can be reasonably well explained by the pressure dependence of the elastic constants* and is entirely consistent with our data.

This model allows us to estimate how much the elastic constants have to soften to produce the 50% decrease of f observed in the Mössbauer experiments at 6.6 GPa. In our experiments, we measured only C_{44} and $C_{66} = \frac{1}{2}(C_{11} - C_{12})$, related to the shear modes Σ_3 and Σ_4. We calculated therefore f using (1), (3), and (4) for four scenarios: (i) only C_{44} decreases, (ii) only C_{66} decreases, (iii) both C_{44} and C_{66} decrease by the same relative amount, and we finally also calculated (iv) the effect of a decrease of *all* elastic constants by the same relative amount, despite the experimental evidence [2,3] that the bulk modulus $B = 2(C_{11} + C_{12} + 2C_{13}) + C_{33}$ is completely regular. *In all cases, a 50% drop in f requires a drop in one or several elastic constants of at least 30% and hence a 15% decrease in the phonon frequencies.* For typical phonon frequencies of ~1 THz, it is at least 10 times larger than the standard errors of our neutron measurements.

The anomalous behavior of the Lamb-Mössbauer factor f is believed to originate from the giant Kohn anomaly at the zone center. The setup of our experiments prevented the investigation of acoustic phonon modes very close to Γ. Therefore, if the Kohn anomaly at $\mathbf{q} = 0$ is sufficiently narrow, it may have escaped detection in our measurements. In order to examine this possibility we performed lattice dynamical calculations on the basis of a Born–von Kármán model [27] extending to the eighth shell (16 parameters) which fits the observed [15,28] phonon dispersion to ~0.07 THz.

This model gives the anisotropic atomic displacement factor $\langle \mathbf{x}^2 \rangle$ (by sampling the contributions of the eigenmodes over the Brillouin zone [see (2)]) and allows us to estimate the contribution of the $q \sim 0$ phonon modes to them. For low temperature (4 K) one obtains $\langle \mathbf{x}^2 \rangle_\perp = 0.002\,08$ Å^2 and $\langle \mathbf{x}^2 \rangle_\parallel = 0.0035$ Å^2, in good agreement with the experimental values of 0.002 26(5) and 0.0037(5) [29]. Also the experimentally less precisely determined room temperature values [23] are well described. To estimate the influence of long wavelength phonon modes to $\langle \mathbf{x}^2 \rangle$, we separated the summation into two parts with frequencies smaller and larger than 1 THz, respectively. There is no doubt that any mode related to the giant Kohn anomaly belongs to the low frequency range [11] and our neutron scattering measurements extend below this limit. At 4 K, the modes <1 THz contribute only 2% and 4% to $\langle \mathbf{x}^2 \rangle_\perp$ and $\langle \mathbf{x}^2 \rangle_\parallel$, respectively. This comes essentially from the fact that, although the modes are weighted by $1/\omega$, the relevant phase volume represents only 1 per mil of the entire Brillouin zone. At higher temperatures the low-energy phonons get additional weight through the Bose factor thereby increasing the importance of the low-frequency region.

These calculations therefore suggest that the minor contribution of modes which could be associated with the giant Kohn anomaly rules out the interpretation given for the anomalous behavior of the Lamb-Mössbauer factor. The initial increase of f, which indicates a decrease of $\langle \mathbf{x}^2 \rangle$ by 25% between 0 and 6.6 GPa, clearly exceeds the effect of all modes related to the giant Kohn anomaly. Instead, it has to be attributed to the normal hardening of the lattice. The observed decrease of f at 6.6 GPa requires a 20% increase in the atomic displacement parameter (mainly $\langle \mathbf{x}^2 \rangle_\perp$), which is 5 to 10 times larger than the entire contribution of modes sensitive to the Kohn anomaly. Or, alternatively, if the observed decrease of f comes from phonons below 1 THz, their frequencies have to soften on average to (10–20)% of their original values.

We finally want to point out that the pressure transmitting medium in Refs. [5,6] was Ag_2SO_4. Under pressure, this compound undergoes a sluggish phase transition, as indicated by the anomalous behavior of the shear strength [30] and confirmed by recent neutron diffraction studies [31] which leads to a highly disordered (amorphous?) structure beyond $\sim$6.5 GPa. The transition seems to be first order with a volume collapse of (2–5)%. Since the change of f is, after severe background corrections [6], deduced from a change in transmission from typically 99.92% to 99.96% [5,6], it is tempting to attribute its reported decrease to an artifact coming entirely from the pressure transmitting medium used in these experiments. We encourage further high pressure Mössbauer studies to answer this question.

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