Electronically Driven Soft Modes in Zinc Metal

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^{67}Zn Mössbauer studies under hydrostatic pressures up to 16 GPa coupled to scalar-relativistic linear augmented plane wave calculations show that in Zn metal an electronic topological transition occurs at ~6.6 GPa. At the transition of the electronic subsystem the hyperfine interactions remain virtually unchanged, but the lattice dynamics is drastically affected, in particular, the Lamb-Mössbauer factor abruptly drops by a factor of 2. The latter result is described by a sudden destruction of a giant Kohn-anomaly which accompanies the electronic topological transition.

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The electronic structure of hexagonal closed packed (hcp) metals is of fundamental interest, in particular in systems like Zn and Cd with an unusually large c/a ratio, where many of their solid-state properties are highly anisotropic [1–4]. A further consequence of the c/a ratio being far away from the ideal value ($c/a = \sqrt{8/3} \approx 1.633$) is the presence of a pronounced electric field gradient (EFG) at the nuclei of the lattice atoms. Modern theoretical band-structure calculations are able to describe EFG's for all hcp elementary metals, including Zn, in good agreement with experiment [3]. These calculations show that the EFG is mainly determined by the nonspherical distribution of the valence electrons, in particular of p electrons.

Not only hyperfine interactions but also the lattice dynamics of metals depends strongly on the properties of the electronic subsystem. A strong structural anisotropy of hexagonal metals is expected to lead [5,6] to a close compensation of two main contributions to the interionic interaction which determine the lattice dynamics, the direct Coulomb ion-ion interaction, and the indirect interionic interaction via conduction electrons. This strongly affects low-energy phonons. The highly anisotropic metals Zn and Cd have practically identical phonon dispersion relations if normalized to the corresponding plasma frequencies. They are characterized by a giant Kohn anomaly in the long-wavelength regime [5–7]. Kohn anomalies reflect the interplay between phonons (wave vector $\mathbf{q}$) and conduction electrons (wave vector $\mathbf{k}_F$ at the Fermi surface [8]. For a free-electron gas, for example, they occur at $|\mathbf{q} + \mathbf{G}| = 2|\mathbf{k}_F|$, where $\mathbf{G}$ is a reciprocal lattice vector. For $|\mathbf{q}| > 2|\mathbf{k}_F|$, electronic excitations are strongly impeded. This leads to a change of screening of metal ions by conduction electrons which in turn influences the phonon spectrum. A giant Kohn anomaly can occur if for a certain $\mathbf{G}_0$ the Fermi surface lies in a band gap with $2|\mathbf{k}_F| = |\mathbf{G}_0|$. As a consequence, $|\mathbf{q}| \approx 0$, i.e., the anomaly then happens at long-wavelength acoustic and optical phonons and can be very pronounced.

It has been shown that a giant Kohn anomaly strongly influences the elastic constant c_{44} in Cd [6], if the topology of the Fermi surface is changed. Such an electronic topologic transition (ETT) has been observed for Cd under high external pressure of 1.8 GPa via de Haas–van Alphen measurements [9]. In the present Letter we report ^{67}Zn Mössbauer studies as well as band-structure calculations for Zn metal at high external pressures up to ~16 GPa. We find that at reduced volume Zn metal exhibits an ETT which destroys the giant Kohn anomaly, thereby drastically changing low-energy phonons. We demonstrate that this ETT can be seen in a collapse of the Lamb-Mössbauer factor (LMF) and a change of the second-order Doppler shift (SOD) at a reduced volume [$(1 - V/V_0) \approx 0.085$] and 4.2 K. Our theoretical band-structure calculations confirm a change of the topology of the Fermi surface although at a slightly smaller reduced volume $(1 - V/V_0) \simeq 0.115$.

The experiments were carried out in transition geometry with a ^{67}Ga*Cu* source, which shows no hyperfine splitting in the emission line [4]. Pressure is applied to the ^{67}Zn metal foil (91.1 at.% ^{67}Zn) by a B_4C anvil cell for pressures up to 8.5 GPa and by a high-pressure cell with sintered diamonds for pressures up to 16 GPa. The absorber thickness corresponds to 0.32 and 0.16 g/cm^2 of ^{67}Zn metal in the B_4C and diamond anvil cells, respectively. The design of the B_4C cell has been described earlier [4], details of the sintered diamond cell will be presented in a forthcoming publication [10]. All measurements were performed at 4.2 K.

^{67}Zn Mössbauer transmission spectra recorded at 4.2 K an various pressures are shown in Fig. 1. Because of the quadrupole interaction, the spin-$\frac{5}{2}$ ground state of ^{67}Zn splits into three sublevels (the spin-$\frac{1}{2}$ excited state remains unchanged) which gives rise to three absorption lines. The spectra were fitted by a superposition of three independent Lorentzians. The LMF is derived from the total area under the three lines after correction for nonresonant background radiation. The volume dependence

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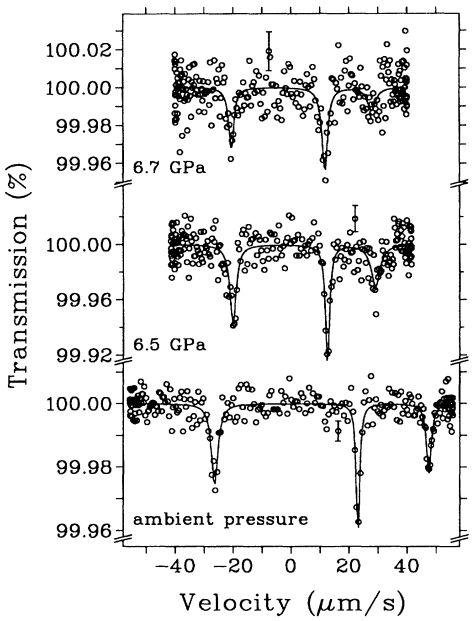

FIG. 1. ^{67}Zn Mössbauer spectra of ^{67}Zn metal at 4.2 K and various pressures. The source is ^{67}Ga in Cu also at 4.2 K.

of the LMF [11] is summarized in Fig. 2. We used compressibility data of Ref. [12] to convert pressure to volume changes. At first, the LMF drastically increases with reduced volume. At $(1 - V/V_0) = 0.085$, however, the LMF is sharply reduced by about a factor of 2. This sudden reduction has been observed twice (see Fig. 2), with two identical setups of B_4C high-pressure cells. Compressibility data [12] as well as our results on ^{67}Zn hyperfine interactions (e.g., there is no jump in the center shift, see below) prove that there is no crystallographic phase transition in Zn metal at this volume reduction. Since the LMF is weighing the phonon frequency distribution by $1/\omega$, the sharp drop indicates a drastic softening of low-frequency acoustic and optical phonons.

Experimental and theoretical investigations [5,6,13] show that the Fermi surface in Zn metal does not have occupied electronic states in the third Brillouin zone at the symmetry point L (no "butterflies"). The Fermi level E_F at the symmetry point L corresponding to the center of the Brillouin zone boundary (101) lies in a local band gap close to its upper edge [5]. A consequence of such an electronic structure is the formation of a giant Kohn anomaly within a small region of $\mathbf{q}$ vectors, $\Delta q \propto 2V_G/|\mathbf{G}|$, around $q = 0$ [6]. Here V_G is the Fourier component of the effective electron-ion interaction corresponding to the reciprocal lattice vector $\mathbf{G}$. It is important where E_F lies within the local band gap. Theoretical calculations [6] predict that if E_F lies in the upper (lower) part of the gap the giant Kohn anomaly results in an extra hardening (softening) of low-frequency acoustic phonons. Such an effect has been estimated to be substantial for the elastic constant c_{44} in Cd [6].

Our scalar-relativistic (spin-orbit coupling is neglected) linearized augmented plane wave (LAPW) calculations use the WIEN93 code [14] and show indeed that the electronic band structure of Zn metal changes considerably with reduced volume. It strongly influences hyperfine interactions (see below) as well as lattice dynamics. We had to use a $\mathbf{k}$ mesh of 12 000 points in the full Brillouin zone to obtain reliable results, explicitly including the symmetry point L.

With decreasing unit cell volume, the separation between the upper edge of the local band gap and E_F is reduced. This is depicted in Fig. 3. The extra hardening of low-frequency acoustic phonons due to the giant Kohn anomaly is felt by the steep initial rise of the LMF. Our calculations predict that the upper edge of the band gap reaches E_F at $(1 - V/V_0) \approx 0.115$. Here the topology

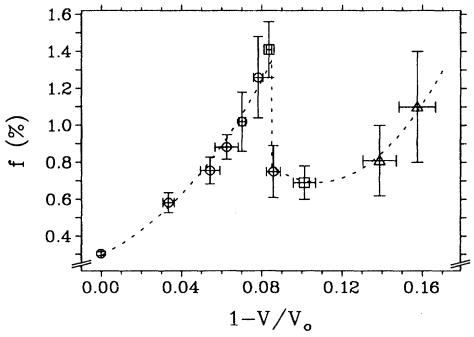

FIG. 2. Volume dependence of the Lamb-Mössbauer factor f. The sharp drop at $(1 - V/V_0) = 0.085$ was reproduced in two identical setups with B_4C cells (symbols □, ○). The results at the two highest pressures (△) were obtained in a sintered diamond cell. The lines through the data points are guides to the eye only.

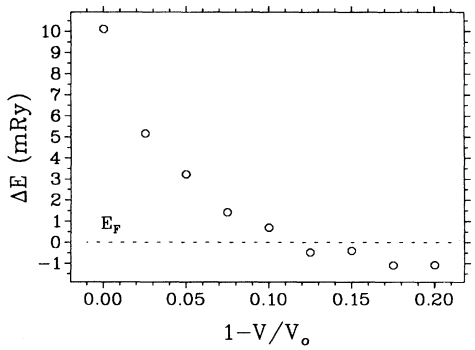

FIG. 3. Results of scalar-relativistic LAPW calculations for the energy separation, $\Delta E = E_L - E_F$, between the Fermi level E_F and the upper edge of the local band gap at the symmetry point L. At $(1 - V/V_0) = 0.115$, the upper edge crosses E_F and an electronic topological transition occurs.

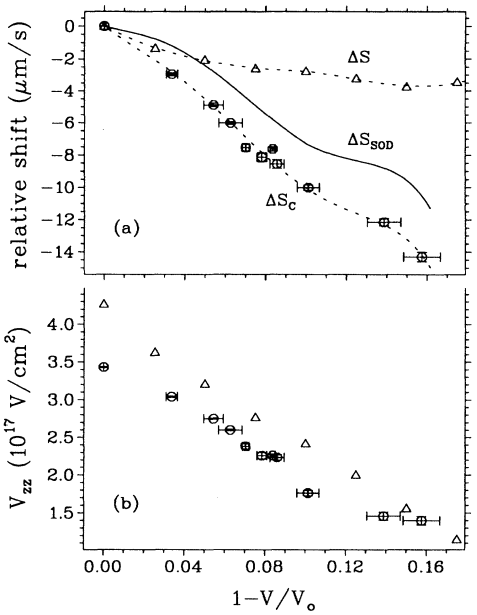

FIG. 4. (a) Volume dependence of the center shift ΔS_C (○), the second-order Doppler shift ΔS_{SOD} (continuous line), and the isomer shift ΔS (△). All shifts are given with respect to their values at ambient pressure ($V = V_0$). ΔS_C is experimentally determined, ΔS is derived from our LAPW calculations, and $\Delta S_{SOD} = \Delta S_C - \Delta S$. The lines are guides to the eye only. (b) Volume dependence of the main component V_{zz} of the electric field gradient tensor: experiment (○), LAPW calculation (△) using the structural parameters of Ref. [12]. The experimental error bars for V_{zz} reflect the statistical uncertainty. The total error of V_{zz} is ≈10%. It is predominately due to the relatively large uncertainty of the electric quadrupole moment of the ^{67}Zn nucleus.

of the Fermi surface suddenly changes: At the symmetry point L, states in the third Brillouin zone can now be occupied. This electronic topological transition (Lifshitz transition) is accompanied by a destruction of the giant Kohn anomaly ("usual" Kohn anomalies, however, at $q \neq 0$ are still present). The extra hardening is lost which in turn leads to a sudden drop of the LMF. The agreement between our theoretical (0.115) and experimental (0.085) values for $1 - V/V_0$ at which the ETT takes place is reasonable.

Another lattice-dynamical parameter expected to be influenced by the ETT is the second-order Doppler shift. In a Mössbauer measurement the experimentally determined center shift (S_C) is the sum of isomer shift (S) and second-order Doppler shift S_{SOD}. Contrary to many other Mössbauer isotopes where $|S_{SOD}| \ll |S|$, for the 93.31 keV transition in ^{67}Zn S_{SOD} can be comparable in size to S and can give valuable information on lattice dynamics. The change ΔS with reduced volume is given by $\Delta S = \alpha \Delta\rho(0)$, where for ^{67}Zn the calibration constant, $\alpha = [(27.3 \pm 2.7)\ \mu m/s]a_0^3$ [15], and $\Delta\rho(0)$ is the change of the s electron density at the ^{67}Zn nucleus with reduced volume. We have determined $\Delta\rho(0)$ from our band-structure calculations. Our results are summarized in Fig. 4(a), where all shifts are plotted with respect to their values at ambient pressure. When the unit-cell volume is compressed, at first the isomer shift S (s electron density $\rho(0)$ at the ^{67}Zn nucleus) is reduced and there might be a small kink in the critical volume region [$(1 - V/V_0) \approx 0.10$], although the influence of the ETT on the hyperfine interactions is not pronounced. The decrease of S up to $(1 - V/V_0) \simeq 0.15$, however, is surprising. Only above this value does S increase. A decrease of $\rho(0)$ with reduced volume is a rare case for pure elements. It has been observed for Sb [16] and β-Sn [17]. Our theoretical calculations show that in Zn metal this decrease is mainly due to the valence electrons, the contribution originating from the core electrons decreases only slightly. The main effect is a $s \rightarrow p$ transfer of valence electrons, especially between symmetry points Γ and M and between K and H. The L point, however, is hardly involved.

With reduced volume the binding forces between Zn atoms are increased and ΔS_{SOD} becomes more negative. At $(1 - V/V_0) \approx 0.09$, the curvature of the ΔS_{SOD} curve changes sign, ΔS_{SOD} flattens and finally sharply decreases beyond $(1 - V/V_0) \approx 0.14$. The change in curvature of ΔS_{SOD} occurs at about the same volume reduction where we observe the drop in the LMF (see Fig. 2) and again reflects the softening of phonon modes at the ETT. The influence on ΔS_{SOD}, however, is much less pronounced than on LMF. This is easily understood, since in the low-temperature limit the LMF weighs the phonon frequency distribution by ω^{-1} as compared to ω^{+1} in the case of SOD and is thus more sensitive to the low-frequency mode softening.

The question arises if the ETT is connected to an isostructural phase transition. This is probably the case in Cs metal where a fcc-fcc phase transition has been observed [18] when the unit cell volume has been enormously reduced [$(1 - V/V_0) \approx 0.57$] by high pressure. The experimental and theoretical situation is less clear for Zn metal. Older high-pressure x-ray data [19] indeed show an anomaly of the c/a ratio in the proper volume range [$0.06 < (1 - V/V_0) < 0.09$]. In more recent x-ray investigations [12], however, this anomaly has not been corroborated. On the other hand, theoretical total energy calculations [20] using the linear muffin tin orbital method do predict an anomalous behavior in the c/a ratio in the volume range [$0.08 < (1 - V/V_0) < 0.10$], where we observe the ETT. Such calculations, however, might be less reliable since they use the atomic sphere approximation. Our own total energy calculations do not find a significant c/a anomaly, but it should be mentioned that the theoretical c/a ratio is largely overestimated when using the standard local density approximation. To settle this question high-pressure x-ray measurements of higher precision

and at low temperature would be preferable, but we can also use our results for the EFG.

Figure 4(b) shows our experimental and theoretical results for the main component V_{zz} of the EFG tensor. The relatively large experimental error is due to the uncertainty of the nuclear quadrupole moment [4]. The ETT which occurs at $(1 - V/V_0) \approx 0.085$ does not seem to influence the EFG directly. The reason is that the ETT abruptly changes the dynamic screening of the conduction electrons, whereas the band structure and thus the static electronic structure is altered only marginally. Our calculations show that the EFG is decisively determined by the c/a ratio. There appears to be a change in curvature at $(1 - V/V_0) \approx 0.10$ in the experimental data and these results give a hint that the volume dependence of the c/a ratio might slightly change in the interesting volume region at low temperatures, but certainly much less than given in Ref. [19]. Thus the ETT may indeed also be reflected in a small, but anomalous change of the crystallographic structure. Although the overall agreement between experiment and theory is satisfactory, this change in curvature is not present in our theoretical results. This is probably due to the fact that our calculations rely on the room temperature structural data [12], whereas the ^{67}Zn Mössbauer experiments had to be performed at liquid-He temperatures where the lattice parameters may be slightly different.

In conclusion, our high-pressure Mössbauer data and scalar-relativistic LAPW calculations show that the conduction electrons decisively determine the lattice dynamics of Zn metal. An electronic topological transition which involves the L symmetry point causes the destruction of a giant Kohn anomaly and as a consequence drastically changes the lattice dynamics. It is demonstrated for the first time that such effects can be followed by Mössbauer spectroscopy. Whereas hyperfine interactions (isomer shift and electric field gradient) are affected very little at the ETT itself, the Lamb-Mössbauer factor changes abruptly. Our LAPW calculations do describe the electronic energy changes as well as isomer shifts and electric field gradients. However, first principles lattice-dynamic models are highly desirable to reproduce quantitatively the sudden changes observed for the LMF at the ETT.

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