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Pressure-induced phonon instabilities in copper chloride

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The phonon spectra of zinc-blende CuCl are studied as a function of pressure using density functional linear-response theory. A pressure-induced soft transverse-acoustic-phonon mode is identified. At 2.6 GPa, the TA phonon mode softens at the *X* point, initiating the phase transition from the zinc-blende structure CuCl-II to a cubic structure CuCl-IV. The previously proposed off-center displacement model and the Fermi resonance model for Raman anomalies are examined. This study suggests that the anomaly in the Raman spectrum results from Fermi resonance.

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Copper chloride is a highly ionic I-VII semiconductor that has the zinc-blende (ZB) structure at ambient conditions. It exhibits unusual physical properties, such as a large negative thermal expansion at low temperatures, large mean-square displacements of Cu atoms at low temperature, and a high ionic conductivity at elevated temperatures. Consequently, this material has recently attracted considerable interest from experimentalists and theoreticians.

Another highly unusual feature of the copper chloride is the double-peak structure of the transverse-optic (TO) phonon in the Raman spectrum. Two different explanations have been suggested for the anomalous TO structure. The Fermi resonance model (FRM) assumes an anharmonic coupling of the TO phonon to resonant acoustic two-phonon states, and results in a shift and broadening of the TO mode and a transfer of oscillator strength to two-phonon scattering.[1,2] Recent Raman experimental reports for the effect of isotopic composition on the lattice dynamics[3] and the pressure-induced disappearance of the anomalous TO mode in ZB CuCl lent support to the FRM.[4] In the off-center model (OCM), Cu ions are assumed to occupy off-center positions along [111] antibonding directions[5,6] resulting in a contribution of localized vibrations to the Raman spectrum. There are several recent *ab initio* studies supporting the OCM.[7–9] Therefore the FRM and the OCM interpretations of the Raman anomaly in ZB CuCl are still a matter of intense debate.[10]

Phase transitions in CuCl under pressure have also been investigated extensively, both by experiment and theory. These studies have been motivated by claims of possible high-temperature superconductivity[11–14] and the observation of several consecutive phase transitions.[15] In addition, a phase transition from the ZB structure CuCl-II to an unknown structure CuCl-IIa, accompanied by a sharp drop in resistivity,[13,16] has been recently reconfirmed by Raman measurements.[17] The physical mechanism driving the structural phase transition of CuCl-II via an intermediate low-resistivity phase, CuCl-IIa, to the cubic structure CuCl-IV remains unclear. Consequently, *ab initio* investigations of the pressure-induced behavior and the lattice dynamics of ZB CuCl are desirable. These calculations can also serve as prototypes for other ZB semiconductors and their pressure-induced behavior.

Phonon band structures are calculated using the pseudopotential plane-wave density-functional linear-response method.[18] The generalized gradient approximation of the exchange-correlation functional is used in the calculations.[19] The Troullier-Martins[20] norm-conserving scheme is used to generate the pseudopotentials for Cu and Cl. The *d* orbital contributions of copper are included in the calculations. Particular attention was paid to generate a reliable hard copper pseudopotential. The kinetic-energy cutoff E_{cutoff} was chosen as 86 Ry in order to ensure convergence of the calculated phonon frequencies to within 0.02 THz. A $4\times4\times4$ k mesh in the first Brillouin zone was used in the phonon calculations. The theoretical equilibrium lattice constant, determined by fitting the total energy as a function of volume to the Murnaghan[21] equation of state, is 5.384 Å, 0.7% less than the experimental value of 5.42 Å.[15] The calculated bulk modulus is 0.58 Mbar and is in reasonable agreement with the fitted experimental value of 0.65 Mbar[22] and the theoretical values in the range 0.55–0.66 Mbar.[9,23,24]

Figure 1 compares the calculated phonon dispersions at the experimental lattice constant of 5.42 Å with the experimental neutron inelastic scattering data at zero pressure.[23,25] There is excellent agreement between the present *ab initio* phonon calculation and the experimental results, in particular for the acoustic modes. The calculations reproduce the well-known and interesting feature of phonon-dispersion curves in semiconductors with the diamond and ZB-type structures—low-energy and the very flat dispersion curves away from the zone center for the transverse-acoustic-phonon branches. The one-phonon density of states (DOS) is also shown in Fig. 1 and this agrees well with shell-model calculations.[2,25] Therefore the present *ab initio* calculations accurately predict the phonon frequencies at zero pressure.

For calculations of pressure dependences, the equilibrium reference volume V_0 is taken as 19.5 $Å^3$/atom at the theoretical lattice constant 5.384 Å. The calculated phonon dispersion curves of CuCl and one-phonon DOS at different volumes are shown in Figure 2. With decreasing volume, the TO, longitudinal-optical (LO), and longitudinal-acoustic (LA) phonon modes shift to higher frequency, while the transverse-acoustic (TA) mode decreases, indicating a negative Grüneisen parameter $\gamma_j(q) = -\partial \ln \omega_j(q)/\partial \ln V$ for mode j at zone boundary points (X and L), where q is wave vector, ω is frequency, and V is volume. This behavior is responsible for the negative thermal expansion in copper chloride at low temperature.[26] At a volume of $0.958V_0$, the

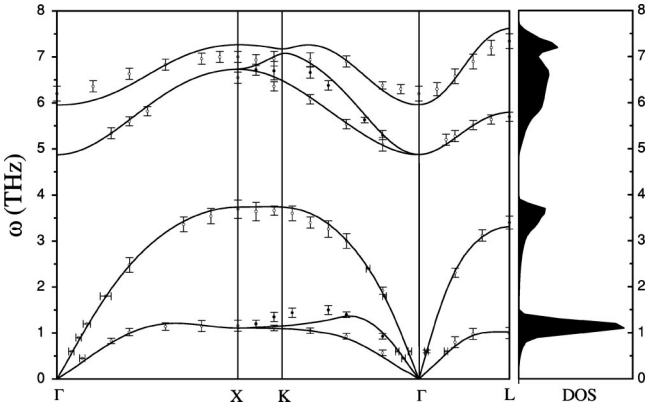

FIG. 1. The calculated phonon frequencies (solid lines) and DOS of zinc-blende CuCl at the experimental lattice constants, along with the experimental phonon-dispersion data (symbols) (Ref. 25).

phonon of the TA mode at the X point becomes imaginary, indicated also by the dramatic change in the one-phonon DOS near zero frequency, signaling a structural instability in the zinc-blende phase of copper chloride. The predicted transition pressure from CuCl-II to CuCl-IIa ($\sim$2.6 GPa obtained from Fig. 4) is somewhat less than the experimental transition pressure ($\sim$3.3 GPa) at $T=5$ K.[17] The origin of this difference may be attributed to the underestimation of the calculated bulk modulus and the neglect of temperature effects. The pressure-induced TA mode softening at X point may first drive the insulator phase (CuCl-II) to a low-resistivity phase (CuCl-IIa), increasing the screening of non-central long-range forces needed to stabilize the crystal

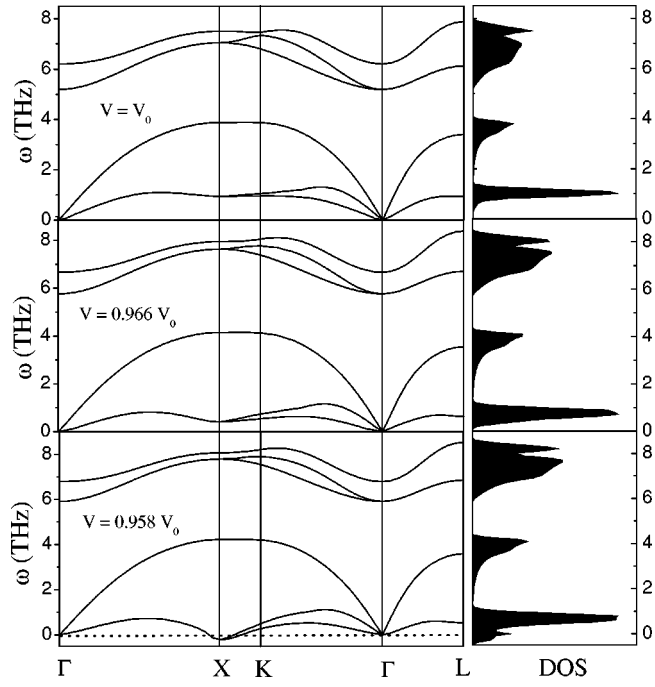

FIG. 2. Calculated phonon frequencies and DOS of zinc-blende CuCl at different volumes.

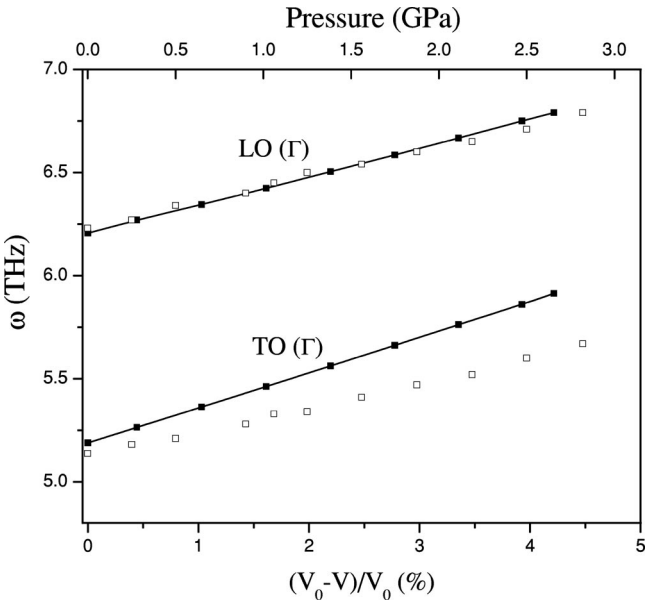

FIG. 3. Calculated (solid square) phonon frequencies for TO and LO modes of natural CuCl at Γ, and experimental (open square) Raman shift (Ref. 4) of $Cu^{65}Cl$ with volume (bottom labels) and pressure (top labels). Solid lines through the calculated data points are linear fits.

against short-wavelength shear distortions[27] finally resulting in a structural transformation from CuCl-II to CuCl-IV when the long range forces are weakened enough due to stronger screening effects.[28]

Figure 3 shows the comparison of the calculated pressure dependence for optical modes at the Γ point in natural isotope abundance CuCl with the Raman experimental results[4] for $Cu^{65}Cl$. The agreement between theory and experiment for the LO mode is excellent, but is less satisfactory for the TO mode at higher pressure. If we correct for the isotope effect from Cu^{65} ions, the agreement between theory and experiment in the TO mode improves slightly by $\sim$0.018 THz.[3] It should be noted that the TO-LO splitting decreases in the calculations with increasing pressure, in agreement with the results for other ZB-type semiconductors.[29] There are less detailed reports for pressure dependence of transverse-acoustic-phonon modes of ZB-type semiconductors in the literature,[30] which characterize the anomalous pressure-induced behavior of zinc-blende-type semiconductors. The calculated results on TA phonon modes at X and L points with pressure, together with the calculation of germanium with the diamond structure[30] are shown in Fig. 4. The two calculations give similar trends for the pressure-induced behavior for both TA (X) and TA (L) modes. The TA (X) frequency in this calculation decreases to zero at $(V_0-V)/V_0=4\%$, whereas the TA (L) energy has decreased to 60% of its ambient pressure value, in comparison to the calculated values of 18% and 40% for germanium, respectively. A squared phonon frequency ω^2 for TA at X point with pressure P is also plotted (not shown). A perfect linear relation between ω^2 and P was obtained. Such behavior is predicted in the Landau theory of pressure-induced soft-mode phase transitions.[31]

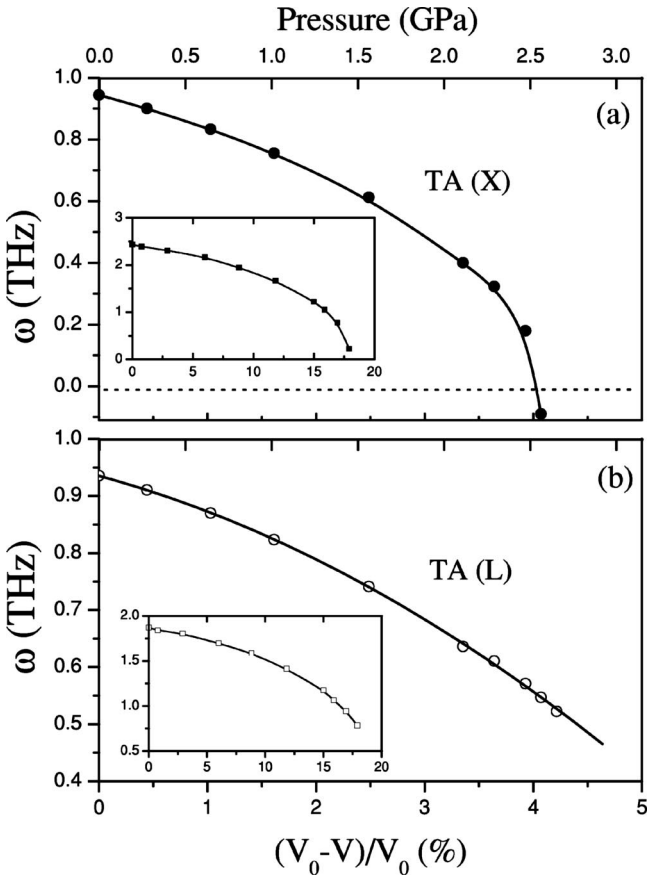

FIG. 4. Main figure: TA (*X*) (a) and TA (*L*) (b) frequencies as a function of volume (bottom labels) and pressure (top labels). Insets: the results for diamond-type germanium taken from Ref. 30. Symbols are the calculated data. Solid line through the calculated data points represent fitted curves using a *B* spline (a) and a second-order polynomial (b), respectively.

To contribute to the debate of the FRM and OCM in understanding the anomalous Raman TO spectra at low temperature, we calculated the total energies for a series of Cu atomic displacements along the [111] direction for collective movement in a two-atom primitive cell and for movement of one Cu atom in an eight-atom supercell, respectively. The calculated results are shown in Fig. 5. There is no second energy minimum in the calculation using the two-atom cell. This is in agreement with the linear muffin-bin orbital (LMTO) calculation of Kremer and Weyrich.[22] In contrast, a second energy minimum is found when the Cu atoms are displaced by $\sim$1.54 Å in the calculation of an eight-atom supercell. This result is similar to that of Wei *et al.*[7] The theoretical results may be in apparent contradiction with that of a recent *ab initio* molecular-dynamics study[9] which shows, at room temperature, that the Cu atoms can occupy both the fcc and off-center sites. We note that the energy barrier is $\sim$0.176 eV corresponding to an activation temperature of $\sim$ 2000 K (Fig. 5). Furthermore, the experimental isotropic thermal parameter for Cu atoms, B_{Cu}, is 2.99 Å^2 at $T=300$ K.[15] From the relation between thermal parameter and the mean-square amplitude ($\overline{\mu_{Cu}^2}$) of atomic vibration,[32]

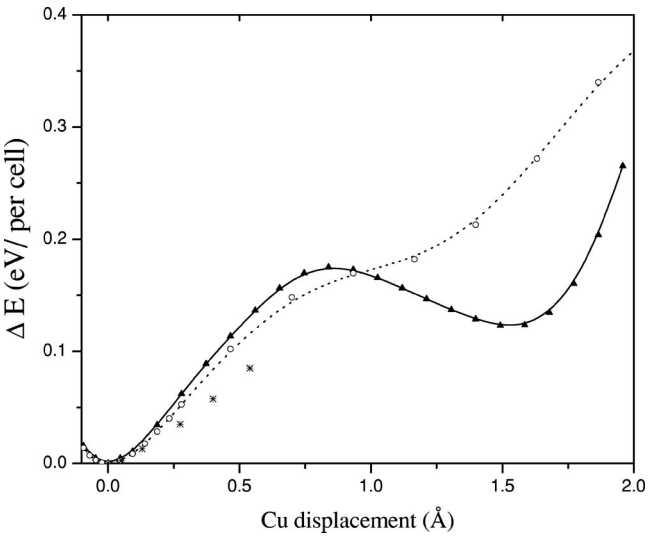

FIG. 5. The change in total energy as a function of [111] Cu atomic displacement for collective movement in two-atom primitive cell (open circle) and one Cu atom movement along the antibonding direction in an eight-atom supercell (solid triangle), respectively, together with the LMTO calculation (star).[22] The solid and dashed lines represent the *B*-spline fits of calculated data.

$$B_{Cu}=8\pi^2\overline{\mu_{Cu}^2}, \tag{1}$$

the approximate value of $\overline{\mu_{Cu}}$ is 0.195 Å. This is much less than the critical atomic displacement value, 0.84 Å, for the second energy minimum, corresponding to the largest energy barrier as shown in Fig. 5. The present phonon calculations, based on a harmonic approximation, also agree well with the experimental phonon dispersions in ZB CuCl. Harmonic vibrations are expected to dominate the lattice dynamics of CuCl. Therefore, Cu atoms vibrate harmonically around the ideal ZB lattice sites with an amplitude of $\sim$0.195 Å at room temperature (even smaller at lower temperature). This suggests that the consideration of the ideal ZB structure for CuCl is sufficient to account for the Raman anomaly at low temperature as proposed by Cardona *et al.*[10] In fact, one cannot easily understand the Raman TO anomaly in the case where the ideal ZB structure of CuCl is not maintained. If Cu atoms are displaced along the [111] direction, the ideal ZB structure of CuCl is destroyed and both the phonon-dispersion curves and Raman spectrum will be altered significantly. Finally, if the Cu atoms were in a dynamical equilibrium between the ideal fcc sites and the off-center sites, one would expect the existence of low-frequency modes and the Raman spectrum would be much more complex. From the above discussion, there is no strong evidence supporting the suggestion that Cu atoms should occupy off-center positions.

From the variation of phonon dispersions with pressure shown in Fig. 2, it is calculated that the TO and LA phonons shift to higher frequencies at high pressure, while the TA phonon branch goes down to lower frequencies with pressure. The TO mode therefore moves out of the range required for coupling with TA+LA modes at high pressure. This re-

sult is in agreement with the report of Ulrich *et al*. that the anomalous Raman mode disappears at high pressure,[4] which is in accord with the FRM.

In summary, the phonon-dispersion curves of ZB CuCl were studied as a function of pressure using density-functional linear-response theory. The pressure-induced soft transverse-acoustic-phonon mode is identified. At 2.6 GPa, the TA phonon mode at *X* point softens to zero frequency, contributing to the phase transition from CuCl-II to CuCl-IV. The calculations suggest that Cu atoms will not occupy off-center positions at room temperature or lower. The present *ab initio* calculations of phonon-dispersion curves provide a detailed characterization of the pressure-induced behavior of phonons of ZB CuCl. They can likely be used as a prototype for pressure-response studies of the lattice dynamics of other ZB semiconductors.

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