

Comment on “Ground State Structural Anomalies in Cuprous Halides: CuCl”

The Raman spectrum of CuCl in the TO-phonon regime is anomalous, consisting of a sharp [TO(γ), ~ 172 cm $^{-1}$] and a broad [TO(β), ~ 154 cm $^{-1}$] line even at low temperatures (2 K). Two interpretations have been offered: In one, the *anharmonic decay* of the TO phonon into two acoustic phonons leads to a *Fermi resonance* [1–3]; in another, a substantial fraction of Cu atoms are located on *off-center sites* [4]. In a recent Letter, Park and Chadi [5] adhere to the latter interpretation, claiming that CuCl shows “two sets of TO phonon peaks” and attributing the narrow line TO(γ) to the regular zone center phonon “of the ‘normal’ zinc blende lattice”. From their total energy calculations, they obtain a new defect (Cu $_4$), and they note that “the stability of the Cu $_4$ defect is consistent with the temperature dependence of the intensity of the anomalous TO(β) mode” and explicitly associate the two with each other.

Optical zone center phonon frequencies are—in the harmonic approximation—proportional to the inverse square root of the reduced mass μ . Raman spectra of CuCl with different isotopic composition are shown in Fig. 1. While the LO phonon shifts according to the changes in μ [6], the TO(γ) peak strongly deviates from this behavior, and therefore cannot be attributed to a zinc blende Γ -point phonon. Comparing $^{65}\text{CuCl}$ with $^{63}\text{CuCl}$, TO(γ) shifts by 2.3 ± 0.2 cm $^{-1}$, i.e., much more than the shift of 1.0 cm $^{-1}$ expected from the change in μ , while TO(β) shifts by 0.9 ± 0.4 cm $^{-1}$ close to the reduced mass behavior. In fact, the large TO(γ) shift is close to the value expected from a *pure* Cu vibration [LA(X) + TA(X), 2.7 cm $^{-1}$] [6,7]. If the TO(β) mode were due to off-center sites solely occupied by copper atoms, it would seem reasonable—though not

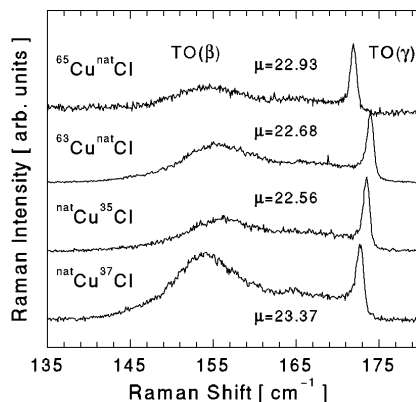


FIG. 1. Raman spectra of CuCl at 10 K ($^{\text{nat}}\text{Cu} = ^{63.6}\text{Cu}$, $^{\text{nat}}\text{Cl} = ^{35.5}\text{Cl}$).

compulsory—to expect the full copper isotope effect, which clearly does not occur. Going from Cu ^{37}Cl to Cu ^{35}Cl , TO(γ) shifts by 0.8 ± 0.2 cm $^{-1}$, much less than anticipated from the change in μ (~ 3.0 cm $^{-1}$). Chlorine substitution results in a large shift for TO(β) (~ 2.5 cm $^{-1}$, again close to the change in μ), rendering its association with Cu $_4$ related modes improbable. These shifts and the anomalous line shape can be very well explained in the framework of the Fermi resonance model (FRM) [1,3,6,7]. Although we cannot exclude the existence of the estimated 20% of off-center Cu atoms [5], we do not see any evidence for them in the Raman spectra, and there is no necessity to invoke a second set of optical phonons.

The Letter [5] also states that the Cu $_4$ center concentration “should gradually increase with pressure”, and that “this may account for the experimental observation that the elastic constants (EC) of CuCl decrease with pressure”. It has to be pointed out that the EC of ZnSe show a similar behavior and that there is a trend from EC increasing with pressure to decreasing ones in the series Ge, GaAs, ZnSe, and CuCl [8].

To explain the decreasing intensity of the TO(β) mode with increasing pressure, the authors [5] invoke another lattice instability having C_{2v} symmetry. In the FRM this effect is a direct consequence of the TO(Γ) phonon emerging from the two-phonon continuum with increasing pressure [2] due to different Grüneisen parameters for acoustic and optical phonons [8] across the Brillouin zone.

If double potential wells do exist, they may be described for single occupancy by a strongly anharmonic single well and thus relate, indirectly, to the preferred FRM.

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