First Principles Linear Response Calculations of Lattice Dynamics for CuCl

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CuCl is known to exhibit large anharmonic effects and possibly a complicated multiwell Born-Oppenheimer surface reminiscent of the instabilities in perovskite ferroelectrics and cuprate superconductors. However, we have determined its phonon dispersion from first principles calculations and find it to agree well with low temperature experimental results. The calculations were carried out using a linear response formalism based on the linearized augmented plane wave method. Born effective charges are within 10% of experiment and the dielectric constant ϵ_∞ is about 30% larger than the experimental value. This level of agreement is comparable to that attained in simpler semiconductors.

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There is considerable evidence that the many anomalous properties of CuCl result from its strong anharmonic interactions. The phonon spectra show unusual features such as a double-peak structure of the long wavelength optic modes [1–9] and the disappearance of many observable phonon peaks in neutron scattering measurements upon heating to as low as room temperature [9]. Two competing models of the phonon anomaly near the zone center have emerged. Krauzman *et al.* [2] and Kanellis *et al.* [10] described the extra modes near the zone center as arising from anharmonic coupling between the TO(Γ) mode and a two-phonon continuum. The off-center model of Vardeny, Livescu, and Brafman [7,11] assumes the existence of four equivalent secondary minima for the Cu^+ cation lying along the [111] directions in addition to its ideal lattice site. This gives rise to the extra observed modes and can explain other vibrational anomalies observed by Raman scattering, infrared, and phonon-polariton measurements. The off-center model has recently received theoretical support from local density functional approximation (LDA) total energy calculations of Wei, Zhang, and Zunger [12] who found a secondary relative minimum along the [111] directions outside the trigonal face for the Cu^+ cation in CuCl and CuBr. This double-well energy surface is reminiscent of that found in perovskite structure ferroelectrics and some high-temperature cuprate superconductors, except there the displaced site corresponds to the global energy minimum [13,14]. It is thus of great interest to map out the Born-Oppenheimer surface of CuCl near the ideal zinc blende structure.

Linear response calculations are performed using the recently developed LAPW (linearized augmented plane wave) linear response method [15]. This method is similar to the LDA linear response method of Baroni and coworkers [16–18] except that the use of LAPW basis functions greatly facilitates the treatment of localized valence wave functions such as those derived from the Cu $3d$ orbitals. In this method, the dynamical matrix is calculated at each q point from the first order forces, and the frequencies are obtained by standard matrix diagonalization. Kerker type [19] pseudopotentials were used to avoid dealing with core states. The resulting nonlocal d pseudopotential is very "hard," but since the LAPW method employs a dual representation of the wave functions, charge density, and potential, such very strong potentials are easily handled. The calculations were performed at the experimental lattice constant 5.41 Å [20], which is only slightly bigger than the calculated value 5.33 Å, using the Wigner interpolation formula [21] for the exchange-correlation potential. The muffin-tin radii are 2.14 a.u. for Cu and 2.09 a.u. for Cl. A kinetic energy cutoff of 20.5 Ry was used, yielding approximately 300 LAPW basis functions at each k point and convergence of the calculated phonon frequencies to better than 0.05 THz. When calculating the dynamical matrices, a (4 4 4) special k-point [22] mesh was used for the Brillouin zone (BZ) integration, which yields 2 k points in the irreducible BZ wedge for the unperturbed lattice. The calculated bulk modulus is 0.655 Mbar, in excellent agreement with the experimental value of 0.654 Mbar [23] derived from inelastic neutron scattering at liquid helium temperature [9].

Since CuCl is a polar semiconductor, the long-range Coulomb interaction contributes to the macroscopic electric field for LO phonons. At finite wave vectors q such contributions are automatically included in the linear response calculations. In the long-wavelength limit $q=0$, it is more convenient to separate the matrix of force constants into two terms [18,24,25]. One term is analytic in q, corresponding to the response to a zone-center phonon with no macroscopic electric field, and this is just the force constant matrix calculated for the TO mode. The other (nonanalytic) term is related to the Born effective charge tensor and the high-frequency dielectric tensor. In the cubic zinc-blende structure the relationship between the angular frequencies of the TO and LO modes at the Γ point simplifies to

$$\omega_L^2=\omega_T^2+\omega_p^2, \tag{1}$$

where

$$\omega_p=\sqrt{4\pi e^2 Z^{*2}/\epsilon_\infty \mu v} \tag{2}$$

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TABLE I. Calculated CuCl Born effective charges and dielectric constant.

No. of k points	ϵ_∞	Z^*(Cu)	Z^*(Cl)
	This calculation		
2	4.75	0.16	−1.26
10	4.65	1.28	−1.11
28	4.65	0.94	−1.11
	Press and Ellis[a]		
	...	1.30	
	Experiment		
	3.61[b]	$[1.13_{TO(\gamma)}, 0.93_{TO(\beta)}]$[c]	

[a]Reference [27].
[b]Reference [26].
[c]Extracted estimates from Ref. [11] and see the discussion in text.

is defined in terms of the volume of the primitive cell v, the reduced mass μ of the Cu and Cl atoms, the calculated Born effective charge Z^*, and the calculated high-frequency dielectric constant ϵ_∞. Two separate linear response calculations [15] determine ϵ_∞ and Z^*.

Table I summarizes our calculated results for Born effective charges and the high-frequency dielectric constant for three different k-point samplings in the irreducible BZ together with the values extracted from experimental measurements as discussed below [11,26]. The LDA cluster calculation of Press and Ellis [27] is also given. The effective charges must obey the acoustic sum rule, which in the case of CuCl requires the values of Z^*(Cu) and Z^*(Cl) to be equal in magnitude but of opposite sign. As discussed in Ref. [18], inadequate k-point sampling can result in violations of this rule. As seen in Table I, Z^*(Cl) is converged, but Z^*(Cu) is still not converged at the largest 28 k-point set that was used. Using Eqs. (1) and (2), we took Z^*(Cl) to determine the theoretical frequency of the longitudinal optic mode at Γ given in Table II. The LDA is known to systematically overestimate ϵ_∞ in general [17,18], and the calculated ϵ_∞ is about 30% too large, consistent with this tendency.

In conventional semiconductors, the experimental effective charges for zinc-blende diatomic crystals are readily determined from Eqs. (1) and (2) using the measured values of ϵ_∞ and ω_L and ω_T at the Γ point. The anomalous features of the phonon spectrum of CuCl at the Γ point, however, complicate the analysis here, because four optic modes are observed (see the review in Ref. [11]). In decreasing frequency, they are [11] LO(γ), TO(γ), LO(β), and TO(β), and their values are given in Table II. The additional $q=0$ modes are labeled by Vardeny and Brafman and Livescu [7,11] as β-TO(β) and LO(β), and arise in their model from the off-center cation sublattice. By contrast, Hennion *et al.* [5] invoke the mechanism of strong anharmonic coupling between TO(Γ) mode and a two-phonon continuum to explain the inelastic neutron scattering data of the TO phonons in

TABLE II. Calculated and experimental phonon frequencies for CuCl in THz.

	Calculation (2 k points)	Experiment	
TO(Γ)	5.05	4.83[a]	4.65 (β)[b]
		5.11[a]	5.22 (γ)[b]
LO(Γ)	6.21	6.20 ± 0.16[c]	5.00 (β)[b]
			6.24 (γ)[b]
TA(X)	1.37	1.16 ± 0.12[c]	
LA(X)	3.78	3.69 ± 0.20[c]	
TO(X)	6.58	6.55 ± 0.12[c]	
LO(X)	7.16	7.00 ± 0.12[c]	
TA(L)	1.05	1.00 ± 0.12[c]	
LA(L)	3.47	3.40 ± 0.14[c]	
TO(L)	5.78	5.70 ± 0.10[c]	
LO(L)	7.47	7.34 ± 0.16[c]	
$q=[\frac{1}{4}00]^{2\pi/a}$			
TA	0.80	0.74[d]	
LA	1.66	1.8[d]	
TO	5.32	5.21[d]	
LO	6.38	6.43[d]	
$q=[\frac{1}{4}\frac{1}{4}0]^{2\pi/a}$			
	0.64	0.66[d]	
	1.10	1.05[d]	
	2.29	2.22[d]	
	5.24	5.21[d]	
	5.54	5.47[d]	
	6.56	6.64[d]	

[a]Frequencies resolved from neutron scattering data at 5 K by Ref. [5].
[b]From Ref. [11].
[c]Inelastic neutron scattering measurements at 4.2 K from Ref. [9].
[d]Interpolated from Ref. [9].

CuCl at 5 K. They resolved the anomalous line shape into two frequencies of 5.11 and 4.83 THz. A direct comparison with the anomalous modes at Γ is not possible, since our calculations assume the validity of the harmonic and Born-Oppenheimer approximations and are performed for distortions about the ideal structure. Table II indicates that the calculated TO(Γ) frequency falls between the two experimental TO peaks. The theoretical LO frequency is in good agreement with the highest frequency mode in the spectrum at Γ, which lies well above the troublesome frequency range (4.2–5.4 THz) and is identified [1–11] as a normal LO mode. The LO(β) mode is very weak, lying between the two strong TO lines. It is thus unclear how to extract experimental values of Z^*. Without adopting any particular model of the anomalous modes, we estimate "experimental" values Z^* using the experimental frequencies [11] of the zone center optical modes given in Table II that are determined [11] by a combination of polariton dispersion measurements and fitting to the infrared reflectivity at 2 K. These frequencies are nearly identical to the values measured by Raman scattering at liquid helium temperature

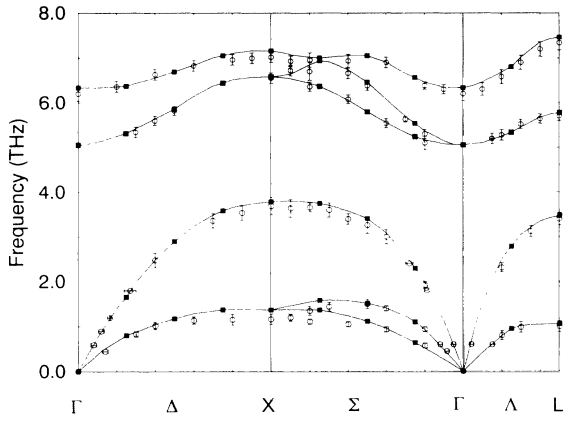

FIG. 1. Phonon dispersion curves of CuCl. Filled square symbols give the calculated results. The solid line is an interpolation through the filled squares. Open circles are measurements at 4.2 K (Ref. [9]).

[3,4]. We extract two estimates of the experimental effective charges using the highest frequency mode LO(γ) together with (i) the TO(γ) and (ii) the TO(β) modes and these are so labeled in Table I. The calculated Z^*(Cl) is close to the extracted experimental effective charge determined by the γ branch modes [LO(γ) and TO(γ)]. In the off-center model, the γ branch modes arise from Cu ions at the ideal structure sites [11], and the frequency of this mode might be expected to be similar to our calculated value based on the ideal structure.

The calculated phonon frequencies along symmetry lines, $\Delta[\xi 00]$, $\Sigma[\xi\xi 0]$, and $\Lambda[\xi\xi\xi]$, are shown in Fig. 1, together with the inelastic neutron scattering experimental data obtained at 4.2 K by Prevot, Hennion, and Dorner [9]. None of the calculated modes is unstable (imaginary frequencies), which shows that the zinc-blende structure is at least a local minimum. Table II gives the numerical values at high symmetry points. Typical experimental accuracy is about 0.1 THz. From Fig. 1 and Table II, we see that the majority of the calculated frequencies fall within the limits of experimental errors. In the past two decades, complete phonon dispersion curves of CuCl have been calculated only with empirical models [28]. Kremer and Weyrich [23,29] reported full-potential LMTO calculations of TO(Γ) and X point phonon frequencies of CuCl and other semiconductors. For CuCl, the frequency of TO(Γ) they determined is 4.68 THz, 7% smaller than ours, and their frequencies of X point are in greater disagreement with experiment. The present calculation is the first self-consistent LDA linear response calculation of the complete phonon dispersions for a semiconductor in which the effects of localized d electrons are fully considered. The agreement between the calculated and the experimental frequencies of optic phonons is generally better than that of the low lying acoustic phonons near the X point, where the calculated frequencies appear to be systematically too high. Giannozzi *et al.* [18] found that using more k points improved the agreement in the acoustic region for Si and GaAs. We performed calculations for the X-point phonons using 10 k points. The disagreement is a bit worse in this case with the frequencies of LO(X), TO(X), and LA(X) increasing by 0.02–0.03 THz, and TA(X) by $\sim$0.1 THz compared to the 2-k-point calculation.

Carabatos *et al.* [30] reported earlier neutron scattering measurements of phonon spectra at room temperature which differ significantly from the results in Fig. 1. They find that the optic branches cross each other in the Δ and Λ directions and that the highest acoustic branch disperses higher up, close to the optic modes in the Σ direction. These discrepancies are probably due to a combination of sample quality [9] and the fact that the measurements were performed at room temperature. Our calculations are in agreement with the finding of Prevot, Hennion, and Dorner [9] that there is no crossing of the optic branches in Δ and Λ directions and that there is a large gap between the highest acoustic branch and optic branches in the Σ direction.

Besides the anomalous modes at Γ, the agreement between theory and experiment elsewhere in the Brillouin zone is as good as in less problematic materials such as GaAs. Our theoretical LDA linear response calculations performed for the ideal zinc-blende structure have not addressed, of course, the source of these observed anomalies. Despite the anomalous properties of CuCl and the presence of large anharmonic interactions, its low-temperature phonon dispersion is accurately predicted by LDA calculations. A similar conclusion was reached in the high-T_c superconductors La_2CuO_4 [31] and $YBa_2Cu_3O_7$ [32,33] where LDA calculated frequencies are generally in good agreement with experiment despite perhaps even greater anharmonicity.

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