Lattice dielectric response of $CdCu_3Ti_4O_{12}$ and of $CaCu_3Ti_4O_{12}$ from first principles

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Structural, vibrational, and lattice dielectric properties of $CdCu_3Ti_4O_{12}$ are studied using density-functional theory within the local spin-density approximation, and the results are compared with those computed previously for $CaCu_3Ti_4O_{12}$. Replacing Ca with Cd is found to leave many calculated quantities largely unaltered, although significant differences do emerge in zone-center optical phonon frequencies and mode effective charges. The computed phonon frequencies of $CdCu_3Ti_4O_{12}$ are found to be in excellent agreement with experiment, and the computed lattice contribution to the intrinsic static dielectric constant (~60) also agrees exceptionally well with a recent optical absorption experiment. These results provide further support for a picture in which the lattice dielectric response is essentially conventional, suggesting an extrinsic origin for the anomalous low-frequency dielectric response recently observed in both materials.

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The complex perovskite compound $CaCu_3Ti_4O_{12}$ (CCTO) has recently attracted considerable attention in view of its anomalously large dielectric response. Low-frequency studies uncovered dielectric constants near 16,000 for ceramics[1,2] and 80,000 for single-crystal samples[3] that are *nearly constant* over a wide temperature range (~100-600 K). Moreover, above a critical frequency that ranges between ~10 Hz and 1 MHz depending on temperature, the dielectric constant drops to a rather ordinary value of ~100, typical of conventional perovskite insulators[4] where contributions from zone-center infrared-active phonons can easily result in values of this magnitude. Detailed measurements of the dynamic susceptibility indicated that the low-temperature crossover is characteristic of an activated Debye-type relaxation process.[3]

In a previous first-principles study of CCTO,[5] we calculated the lattice contribution to the dielectric constant, and found it to be in order-of-magnitude agreement with the measured far-infrared value[3] and drastically lower than the static value. Thus, while the dielectric response in the infrared range is essentially well understood, the origin of the enormous low-frequency response and its dynamic behavior remain perplexing. An extrinsic mechanism, i.e., one associated with defects, domain boundaries, or other crystalline deficiencies, was initially proposed by Subramanian *et al.*[1] These authors reported twinning in CCTO samples and suggested that internal capacitive barrier layers, formed by domain boundaries, might explain the unusual dielectric response. A similar explanation has been proposed by another group.[6] We discussed some of these issues in Ref. 5 and, in the absence of direct evidence for intrinsic lattice or electronic origins, we concluded that extrinsic effects were the likely source of the unusual low-frequency behavior. A subsequent report by Lunkenheimer *et al.*[7] discussed a scenario in which barrier layers associated with poor metallic contacts are responsible for the Debye relaxation. Further discussion of extrinsic mechanisms will be given elsewhere.[8]

While the enormous low-frequency response is the primary puzzle in this material, two other aspects of the response at higher frequencies are also currently enigmatic. First, the oscillator strength of one low frequency IR-active mode has been observed to *increase* strongly with decreasing temperature. And second, one IR-active mode, at somewhat higher frequency, is not observed at all, although it is expected by symmetry and has been predicted to possess a non-vanishing oscillator strength.[5,9] It is not clear whether there could be any connection between these IR anomalies and the enormous low-frequency response, but in any case, further experimental and theoretical scrutiny of the infrared phonon spectrum would clearly be of significant physical interest.[3]

In this report, we extend our previous work on CCTO by carrying out a parallel study on the closely related material $CdCu_3Ti_4O_{12}$ (CdCTO).[1,9] A recent experimental study of ceramic CdCTO samples[9] has revealed that CdCTO also has a temperature-independent anomalous response over a wide range and shows a similar Debye crossover between low- and high-frequency regimes. While the magnitude of this response (ϵ ~400 for ceramic samples) is considerable, it is nonetheless significantly lower than in CCTO, which is somewhat surprising since Cd and Ca are chemically so similar. (Anomalies also appear in the low-frequency IR-active mode oscillator strengths of CdCTO.) After calculating ground-state and dielectric properties of CdCTO, we compare with recent experiments and with the corresponding quantities for CCTO. The results obtained for both materials are similar, typical of ordinary perovskite oxides, and in excellent agreement with recent optical experiments.[3,9] Our results indicate no significant fundamental differences in the intrinsic properties of these two materials and thus provide support for an extrinsic origin of their substantial

TABLE I. Comparison of calculated and measured structural parameters of CCTO and CdCTO. Both have the space group $Im3$ (point group T_h); the Wyckoff positions are Ca/Cd$(0,0,0)$, Cu$(1/2,0,0)$, Ti$(1/4,1/4,1/4)$, O$(x,y,0)$. See Ref. 15 for further details.

	Structural parameter	LSDA	Exp
$CaCu_3Ti_4O_{12}$	a (Å)	7.324	7.384[a]
	O(x)	0.303	0.303
	O(y)	0.175	0.179
$CdCu_3Ti_4O_{12}$	a (Å)	7.324	7.384[b]
	O(x)	0.306	
	O(y)	0.176	

[a]35 K (a=7.391 Å at 298 K).
[b]298 K.

low-frequency responses.

Our first-principles study of CdCTO employs density-functional theory within the local spin-density approximation (LSDA), as implemented within the Vienna *ab-initio* Simulations Package (VASP).[10,11] VASP utilizes a plane-wave basis and Vanderbilt ultrasoft pseudopotentials.[12] All pseudopotentials include non-linear core corrections.[13] For Ca and Ti, these potentials treat the highest occupied p shell electrons explicitly as valence; for Cu, we also consider electrons in the $3d$ and $4s$ shells self-consistently; and for Cd, the $4d$ and $5s$ shells are included explicitly. The ions are relaxed towards equilibrium until the Hellmann-Feynman forces are less than 10^{-3} eV/Å. Brillouin-zone integrations are performed with a Gaussian broadening of 0.1 eV during all relaxations. A 37 Ry plane-wave cut-off and a $2\times2\times2$ Monkhorst-Pack **k**-point mesh (equivalent to a $4\times4\times4$ mesh for a single 5-atom perovskite unit cell) results in good convergence of all properties reported here.

Neutron-diffraction measurements[1] suggest that, as with CCTO, CdCTO crystallizes in a lattice with a 20-atom body-centered cubic primitive cell[14] having space and point groups $Im3$ and T_h, respectively. Since the $Im3$ space group is centrosymmetric, the spontaneous polarization necessarily vanishes by symmetry. To accommodate the observed antiferromagnetic (AFM) spin arrangement, all calculations are performed using a doubled 40-atom simple-cubic unit cell containing eight perovskite 5-atom units, of which 3/4 have Cu on the A site and 1/4 have Ca or Cd on the A site. (Each Cu–Cu nearest-neighbor pair has antiparallel spins.)

Structural parameters resulting from the relaxation appear in Table I. Replacing Ca with Cd leaves the lattice constant virtually unchanged,[15] and the internal parameters also remain essentially the same. Only minor structural changes would be expected, given the similar nominal valence (+2) and ionic radii of Ca and Cd (1.48 and 1.45 Å, respectively[16]). Unfortunately we are unaware of any experimental refinements of the internal structural parameters of CdCTO, and thus direct comparison of our computed oxygen positions with experiment is not possible. As for the lattice parameters, however, our LSDA results are consistent with the near-negligible difference (<0.1%) between the lattice constants measured for CCTO and CdCTO (7.391 and 7.384 Å at 298 K, respectively). (The CCT0 lattice constant at 35 K is smaller and, coincidentally, 7.384 Å; a low-temperature lattice constant for CdCTO has yet to be measured.) Lattice constants computed within the generalized gradient approximation[17] (GGA) are calculated to be about 1.2% larger than experiment for both CCTO and CdCTO. All results presented below were computed within the LSDA without gradient corrections.

The computed electronic structure (at $T=0$) is quite similar for both materials; replacing Ca with Cd evidently has little effect on electronic and magnetic properties. CdCTO is found to possess an antiferromagnetic (AFM) insulating ground state, and its single-particle density of states (DOS) closely corresponds to that of CCTO near the band edges (see Figs. 2 and 3 in Ref. 5). Although the Cd ion has a nominal valence of +2, its electronic configuration includes a filled $4d$ shell, which results in a well-localized set of d bands located about 8 eV below the valence band maximum. As with CCTO, the gap and magnetic moment of CdCTO originate from a splitting of hybridized Cu($3d$)-O($2p$) σ-antibonding states. The magnetic moment of each CuO_4 plaquette, estimated from spin densities, is $\sim0.84\,\mu_B$, and the (indirect) band gap is computed to be about 0.19 eV. To our knowledge, experimental values for the optical gap remain unavailable. However, the observed gap will undoubtedly be strongly underestimated by our calculations, as was found for CCTO, owing to the well-known limitations of the LSDA.

The lattice contribution to the dielectric constant that we computed for CCTO ($\sim$40) was roughly a factor of two smaller than the value measured by far-infrared spectroscopy.[3] We now perform a similar calculation for CdCTO and carefully examine any differences between the materials.

The static *lattice* dielectric response can be approximated (neglecting anharmonicity) as the zero-frequency response of a system of classical Lorentz oscillators, i.e.,

$$\epsilon_{\rm ph} = {\Omega_0}^2 \sum_\lambda \frac{{Z^*_\lambda}^2}{{\omega_\lambda}^2}\,, \tag{1}$$

where ω_λ and Z^*_λ are respectively the IR-active mode frequencies and mode dynamical charges, and ${\Omega_0}^2 = 4\pi e^2/m_0 V$ is a characteristic frequency having the interpretation of a plasma frequency of a gas of objects of mass m_0=1 amu, charge e, and density V^{-1} (V is the 20-atom primitive cell volume).

The lattice dielectric constant $\epsilon_{\rm ph}$ is obtained by first calculating the frequency and mode effective charges of each zone-center IR-active phonon, and then inserting these quantities into Eq. (1). Since CdCTO and CCTO possess the same structure, their zone-center phonons are computed and analyzed as in our previous study.[5] As

TABLE II. Comparison of calculated mode frequencies ω_λ, effective charges Z^*_λ, and oscillator strengths $S_\lambda = \Omega_0^2\, Z^{*2}_\lambda/\omega^2_\lambda$ of IR-active T_u modes with the experimental values (at T = 295 K) of Homes *et al.* (Refs. 3,9). See Ref. 18 for further details.

$CaCu_3Ti_4O_{12}$				$CdCu_3Ti_4O_{12}$			
ω (cm^{-1})		S_λ		ω (cm^{-1})		S_λ	
LSDA	Exper.	LSDA	Exper.	LSDA	Exper.	LSDA	Exper.
125	122.3	4.6	14.3	72	74	15.1	22.8
135	140.8	9.3	15.9	125	121	7.3	11.3
158	160.8	7.5	6.92	148	155	0.4	7.9
199	198.9	2.7	5.25	170	167	11.8	4.3
261	253.9	12.5	13.8	238	239	12.6	7.9
310	307.6	1.0	0.68	303	295	2.4	2.8
385	382.1	0.5	1.96	385	385	0.7	1.6
416	421.0	5.5	1.72	405	422	2.4	1.4
471		1.5		461	469	4.2	0.3
494	504.2	0.6	0.78	499	494	0.4	1.1
547	552.4	0.4	0.62	545	550	0.3	0.7

discussed there, of the six irreducible representations allowed by the T_h point group, only the T_u modes display IR activity. After obtaining symmetry-adapted modes of T_u symmetry, IR-active phonon frequencies and corresponding eigenvectors are calculated using the frozen-phonon method, as described in detail elsewhere.[5] The results appear in Table II, where we also compare with corresponding theoretical results for CCTO[18] and with recent experimental data. As was the case for CCTO, all CdCTO IR-active modes are found to be stable ($\omega^2 > 0$) and their computed frequencies agree very well with experiment.[9]

Given that Ca and Cd are isoelectronic, and that CCTO and CdCTO possess similar structural and electronic properties, we may expect their phonon frequencies and eigenvectors to be similar as well, especially for modes that do not involve Ca or Cd. To investigate this and related issues, we find it useful to sort the zone-center mode frequencies from lowest to highest in frequency, and then project each CCTO eigenvector onto the corresponding one of CdCTO. For all but the lowest four modes, the projections result in values > 0.9, reflecting a close correspondence between the character of their eigenmodes. However, the third- and fourth-lowest eigenvectors (the 148 and 170 cm^{-1} modes of CdCTO and the 158 and 199 cm^{-1} modes of CCTO) are substantially mixed by replacement of Ca with Cd, and possess considerably different eigenvectors. Further, the frequencies of the lowest two modes reverse order on going to the Cd from the Ca material: the 72 cm^{-1} mode of CdCTO shares nearly the same eigenvector with the 141 cm^{-1} mode in CCTO, and we observe a close correspondence between the 125 cm^{-1} modes of CdCTO and CCTO. The latter two are dominated by Cu-O motion, and thus are unaffected by the replacement of Ca with Cd. We note here that peculiar changes in oscillator strengths with

TABLE III. Comparison of calculated Born effective charge tensors Z^* (in a Cartesian basis) for CCTO and CdCTO. Atoms are at Wyckoff positions given in the caption of Table I.

	$CaCu_3Ti_4O_{12}$			$CdCu_3Ti_4O_{12}$		
Ca/Cd	2.46	0	0	2.47	0	0
	0	2.46	0	0	2.47	0
	0	0	2.46	0	0	2.47
Cu	2.06	0	0	2.09	0	0
	0	1.85	0	0	1.87	0
	0	0	1.21	0	0	1.10
Ti	6.98	−0.13	0.06	6.91	−0.18	0.03
	0.06	6.98	−0.13	0.03	6.91	−0.18
	−0.13	0.06	6.98	−0.18	0.03	6.91
O	−1.92	0.54	0	−1.94	0.54	0
	0.22	−1.94	0	0.25	−1.91	0
	0	0	−5.01	0	0	−4.94

temperature are observed to occur for this mode in both materials,[9] indirect confirmation of their similar character.

The conspicuous reduction in frequency of the 135 cm^{-1} mode in CCTO to 72 cm^{-1} in CdCTO originates from both inertial and chemical effects. The masses of Ca and Cd are 112.4 and 40.1 amu respectively; on this basis alone, the frequency could decline at most by a ratio of $\sqrt{M_{\rm Ca}/M_{\rm Cd}}$=0.597. Since Ca/Cu motion accounts for only 38% of the eigenvector character, the inertial shift must actually be considerably smaller, and thus cannot account for the calculated frequencies. Indeed, we carried out a test calculation in which the Ca mass was replaced by that of Cd while retaining the force-constant matrix of CCTO. Rediagonalizing the dynamical matrix, we observe that the lowest four frequencies change to 102, 126, 155, and 186 cm^{-1}, respectively (the other seven remain almost unchanged). Thus, the mass effect alone would only be able to explain a decrease from 135 cm^{-1} to 102 cm^{-1}, i.e., a downward shift of about 24%. This is much less than the reduction observed experimentally (48%) or theoretically (47%). The remainder of the shift is associated with an appreciable softening ($\sim$ 40%) of the force constants of this mode. Evidently this softening is connected with chemical differences between the two atoms, e.g., the $4d$ shell present in Cd but absent in Ca.

In our previous work,[5] we calculated the mode effective charges $Z^*_\lambda = V\Delta P_z/u_0$ for each z-polarized IR-active mode of CCTO using the Berry-phase formalism.[19] (Here $\Delta P_z = P_z(\mathbf{u}_{eq} - u_0\mathbf{u}_\lambda) - P_z(\mathbf{u}_{eq})$, $\mathbf{u}_{eq}$ is the equilibrium configuration of ions, and $\mathbf{u}_\lambda$ is the eigenvector of mode λ and u_0 is its amplitude.) We repeat the process for CdCTO and obtain the mode effective charges; the corresponding oscillator strengths are compared with experiment in Table II. As we found for CCTO, the individual oscillator strengths disagree with experimental values for some of the modes. Remarkably, however, the mode that was absent from the CCTO spectrum reappears in the case of the CdCTO spectrum (Ref. 9), albeit with an oscillator strength of only 0.3; for both materials this mode is primarily composed of O ($\sim$ 80%) and Ti ($\sim$ 15%) displacements.

From the mode effective charges we now estimate the lattice contribution to the static lattice dielectric constant by summing over our calculated oscillator strengths, i.e., $\epsilon_{\rm ph} = \Omega_0^2 \sum_\lambda Z_\lambda^{*2}/\omega_\lambda^2 = \sum_\lambda S_\lambda$. Using the eigenmodes and their effective charges in Table II, we obtain $\epsilon_{\rm ph}$ =57.6, in excellent agreement with the experimental value at room temperature ($\epsilon_{\rm ph}$ =62.1) but somewhat less that the low temperature value ($\epsilon_{\rm ph}$ =106 at 10 K), where an anomalous increase in the oscillator strength has been observed.[3] Compared with value of $\sim$45 computed for CCTO, that obtained for CdCTO is $\sim$50% larger, a consequence of the lowest-frequency IR phonon in CdCTO having a lower frequency and larger effective charge than the corresponding mode in CCTO. Thus, despite differences in computed oscillator strengths for these modes, their combined contribution to the dielectric constant is remarkably close to that observed experimentally. Since the computed frequencies agree much better with experiment than the oscillator strengths, the agreement for $\epsilon_{\rm ph}$ implies some degree of error cancellation in the latter.

To complete our comparative study of these two materials, we also compute their atomic effective charge tensors. This is done in practice by starting with the mode effective charges and then using the corresponding mode eigenvectors to transform back to an atomic displacement basis. (The results for CCTO were not reported in Ref. 5 and are given for the first time here.) As can be seen from Table III, the atomic effective charge tensors are virtually identical for both materials,[20] and thus the same discussion applies to both. The Ca and Cd cations have diagonal and isotropic effective charge tensors of almost identical magnitude, +2.46 and +2.47 respectively. Thus, while the force constants are quite sensitive to the different underlying atomic shell structure of the Ca and Cd ions, the effective charge is not, suggesting that there is little dynamical charge transfer between this cation and its oxygen neighbors. For Cu, the two components associated with displacements parallel to the CuO_4 plaquettes are close to the nominal valence (+2), while the third component corresponding to normal displacements is considerably smaller. Except for the presence of some small off-diagonal components permitted by symmetry, the results for Ti and O are strongly reminiscent of other perovskites: we find that Z^* for Ti has a large positive anomalous component (relative to the nominal +4), and correspondingly each oxygen has a negative anomalous component (relative to the nominal -2) for displacements toward the nearest-neighbor Ti. Indeed, the atomic effective charges computed for Ca, Cd, Ti, and O are all entirely consistent with those computed in other perovskite insulators such as $BaTiO_3$[21,22] or $CaTiO_3$,[23] all of which possess rather typical lattice dielectric constants of $\epsilon_{\rm ph} \sim$ 10-100.

In summary, our first-principles calculations indicate that both CCTO and CdCTO possess similar *intrinsic* structural, vibrational, and dielectric properties. Our computations of the lattice contributions $\epsilon_{\rm ph}(0)$ to the static dielectric constant are in good order-of-magnitude agreement with the values measured experimentally in the far-infrared range for both CdCTO and CCTO, but are drastically smaller than the enormous values measured at frequencies below the Debye cutoff range. The latter discrepancy reinforces the conclusion that some extrinsic mechanism is likely to be responsible for the large dielectric constant present in both materials.[8] Several important issues remain to be resolved by experiment, such as the connection between internal sample morphology and the large response, and the origin of the anomalous behavior of the oscillator strengths of the Cu-O mode at low frequency observed in both materials.

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