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Study on optical and dielectric properties of $CaCu_3Ti_4O_{12}$ by first-principles calculation

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ABSTRACT

The electronic and optical properties of the high-dielectric-constant material $CaCu_3Ti_4O_{12}$ (CCTO) are studied using density-functional theory within the generalized gradient approximation. The calculated electronic structure shows that CCTO is of a charge-transfer character. The optical functions are calculated and the optical spectra are given where all the peaks are assigned with a remarkable absorption peak around 3.5 eV, which is attributed to the charge-transfer transitions from O 2p to Cu 3d states. A discussion is made for the optical infrared anomalies in CCTO.

1. Introduction

Perovskite material $CaCu_3Ti_4O_{12}$ (CCTO) has attracted considerable attention due to its intriguing behaviors in dielectric, electrical, optical and magnetic properties [1–14]. The colossal dielectric constant of order 10^4 in CCTO is nearly temperature-independent above 100 K, and shows Debye-like frequency dependence [1,2]. Similar dielectric behaviors are also observed in single-crystal and thin-film samples [3–6]. Additionally, a remarkably strong nonlinear current–voltage characteristic is found in CCTO [9]. The unique dielectric and electrical properties are attributed to extrinsic factors, such as twin domains, dislocations and grain boundaries [1,2,7–9,15], and several extrinsic models were provided for explaining the dielectric response of CCTO [1,2,7–9,15,16]. Recent infrared measurements show that the oscillator strength of one infrared low-frequency mode at about 122 cm^{-1} is dramatically increased with decreasing temperature, which implies a strong temperature-dependent charge-transfer effect in CCTO [3,10]. However, the infrared anomalies have not been well understood.

Several *ab initio* calculations have been performed to investigate the ground-state properties of CCTO [14,17–20]. The structural and electronic properties of CCTO were first calculated within the local spin-density approximation (LSDA) [17,18] and within LSDA under high pressure [19]. The electronic and magnetic properties of CCTO were also investigated within LSDA and within the generalized gradient approximation (GGA) [14,20]. Unfortunately, all of these theoretical studies did not well interpret the anomalous behaviors in CCTO.

Our previous work gave the fundamental electronic properties of the ground-state CCTO [20]. This work is involved in studying the optical properties relative to the calculated optical function. We employ charge-transfer mechanism to elucidate correlation between the electronic structures and unusual infrared and dielectric properties of CCTO.

2. Method of calculation

Calculations are done using the full-potential linearized augmented plane-wave method within the GGA exchange-correlation functional of PBE96 via the WIEN2k code [21–23]. Detailed description of the crystal structure and the computational method of electronic structure were given elsewhere [20]. It should be noted that in order to obtain the low-temperature magnetic structure, the spins of the two distinct magnetic CuO_4 complexes are initiated in the antiferromagnetic fashion (see Fig. 1). In the optical study, dipole matrix elements are computed on a dense mesh of 340 k-points in the irreducible Brillouin zone. The interband contribution to the imaginary part $\varepsilon_2(\omega)$ of the dielectric constant $\varepsilon(\omega)$ is calculated separately for each spin channel in the random-phase approximation, and corrected in the scissors approximation to increase the underestimated energy gap E_{gap}. The total imaginary

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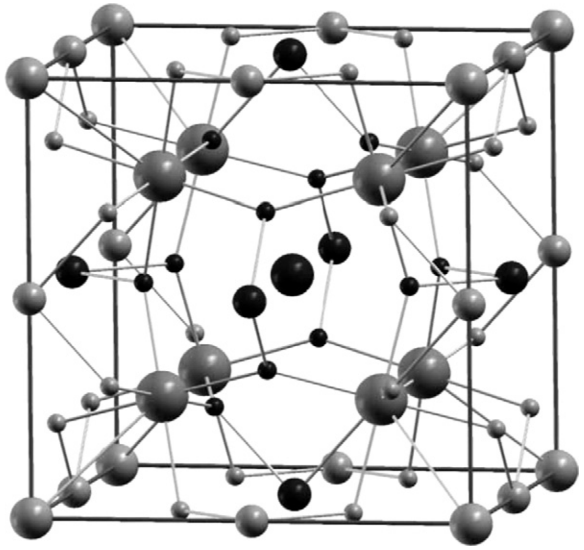

Fig. 1. Antiferromagnetic spin structure of CCTO containing two crystallographic units. The eight largest atoms inside the cell are Ti, non-spin-polarized by symmetry. The large, middle and small gray (black) solid circles stand for atoms are Ca1 (Ca2), Cu1 (Cu2) and O1 (O2), respectively. The atom denoted by gray has the opposite spin to the black ones.

part is then the sum of the two spin contributions. Kramers–Kronig relation is used to obtain the corresponding real part $\varepsilon_1(\omega)$. Other optical functions, such as the refractive index $n(\omega)$, extinction coefficient $k(\omega)$, real part of the optical conductivity $\sigma_1(\omega)$, absorption coefficient $I(\omega)$, reflectivity $R(\omega)$ and energy-loss function $L(\omega)$, are derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ [24].

3. Results and discussion

Fig. 2 shows the total density of states (DOS) and the site-projected partial DOS (PDOS) in the energy range from −22 to 10 eV. Symmetry demands both the total DOS and the Ti PDOS are identical for spin-up and spin-down channels. PDOS of Ca2, Cu2 and O2 have the opposite spin to those of Ca1, Cu1 and O1, respectively (they are not shown). A sharp peak at −20.2 eV is predominantly composed of Ca 3p states. Peak around −17.5 eV is dominated by O 2s states. O 2p and Cu 3d states strongly hybridize in the energy range from −7 to 1 eV with some mixing of Ti 3d state. In particular, there are two distinct energy-isolated structures in the −0.5 to 1 eV range, which was clearly illustrated in the inset. For the spin-up (spin-down) channel, the structure below the Fermi level is mainly derived from the Cu1 (Cu2) d_{xy} and O1 (O2) p_σ states, and the other above the Fermi level primarily from the Cu2 (Cu1) d_{xy} and O2 (O1) p_σ states. The Ca atom is fully ionized with its 3d states showing a peak around 7 eV.

Table 1 gives the calculated E_{gap} under various lattice parameters and different theoretical approaches. The calculated E_{gap} by LSDA is about 0.2 eV, including our calculation results by LSDA listed in column 5 in Table 1, whereas the experimental value E_{gap} is larger than 3 eV [10]. All the calculated band gaps by LSDA are greatly underestimated. Our calculated E_{gap} by GGA is equal to 0.51 eV, closer to the experimental result, where the lattice parameter taken is from a recent experiment data on single-crystal CCTO [25]. It is generally believed that the structural optimization (lattice parameter and internal structural parameters) is necessary only when the residual forces on atoms are large or when the physical quantities are very sensitive to atom positions. For example, He et al. [17,18] and Fagan et al. [19] relaxed the lattice parameters of CCTO in order to well study the structural properties. If taking experimental parameters for calculation, the residual force effects on O atoms have been taking into account during experimental measurement. That is why many authors used experimental parameters to calculate the electronic, magnetic and optical properties without doing structural optimization [e.g. 14,20]. In the case of CCTO we used the experimental structural parameters which are already considered residual force effects on O atoms, which is very small (see below). The following is the residual forces on O atoms in the WIEN2K.

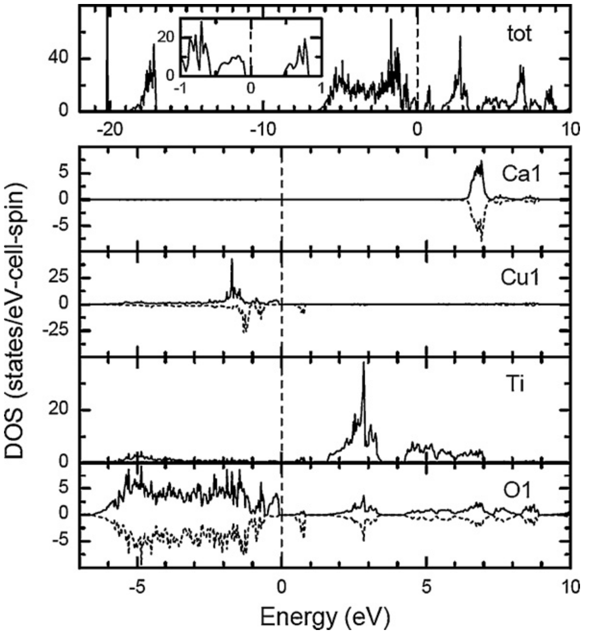

Fig. 2. Total density of states (DOS) and site-projected partial density of states (DOS) of Ca1, Cu1, Ti, and O1 (states/eV cell spin). The solid and dashed curves denote spin-up and spin-down densities, respectively. The vertical dashed line indicates the Fermi level. The inset is a magnified view of the total DOS near the Fermi level.

Total force in mRy/a.u. = |*F*|		F_x	F_y	F_z
FOR01: 1. Atom	0.000	0.000	0.000	0.000
FOR02: 2. Atom	0.000	0.000	0.000	0.000
FOR03: 3. Atom	0.000	0.000	0.000	0.000
FOR04: 4. Atom	0.000	0.000	0.000	0.000
FOR05: 5. Atom	0.045	0.000	0.000	0.045
FOR06: 6. Atom	4.142	−3.030	2.824	0.000
FOR07: 7. Atom	4.168	−3.047	2.843	0.000

In Table 1 we can compare clearly the calculated gap energy by using both the calculated and experimental lattice parameters

Table 1
Calculated band gaps (E_{gap}) of CCTO under various lattice parameters (a) and different theoretical approaches

		By LSDA [17,18]	By LSDA [14]	By LSDA [19]	By LSDA [20]	By GGA [20]
a (Å)	Exp		7.3843 [1]		7.4037 [25]	7.4037 [25]
	Cal	7.290		7.398		
E_{gap} (eV)	0.19	0.18	0.2	0.23	0.51	