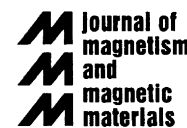




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## *Ab initio* study of cubic complex $\text{Bi}_2\text{CrCuO}_6$ perovskite

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### Abstract

We report a detailed calculation of the structural and electronic properties for the cubic complex  $\text{Bi}_2\text{CrCuO}_6$  perovskite material by density functional theory. The exchange-correlation potential was included through the generalized gradient approximation. From the adjusting of Murnaghan state equation to the energy as a function of volume data, we obtain an ideal lattice parameter of 7.763 Å. The density of states study was carried out considering the two spin polarizations. Results reveal that this material behaves as a conductor to the spin-down polarization and evidence a semiconductor tendency to the spin-up configuration. This tendency to the half-metallicity character is corroborated by the integer number of magnetic moment ( $3.0 \mu_B$ ), which is attributed to the Cr-spin-up orbital contribution. © 2008 Elsevier B.V. All rights reserved.

**Keywords:** Electronic structure; DFT; Complex perovskite

### 1. Introduction

Ceramic materials, which belong to the perovskite family, have been extensively investigated in the last decades. It is known that small structural distortions, vacancies and compositional modifications can induce a great variety of physical and chemical properties [1]. When the ideal perovskite formula  $\text{ABO}_3$  is changed to introduce two different types of cations on the octahedral site of the primitive perovskite unit cell, the cationic ordering leads to a cubic complex superstructure perovskite, which is identified by the  $\text{A}_2\text{BB}'\text{O}_6$  formula [2]. This circumstance permits to infer the possibility of producing new materials by the introduction of an alkaline earth ion A and B, B' transition metal ions. Depending on the magnetic or electric characteristics of B and B', it is relatively easy to create new perovskite systems with half-metallic properties [3], magnetoelectric response [4] or magnetic ordering [5], which offer technological perspectives in the recent spintronics industry [6].

The objective of this work is to study the structure and electronic properties of the newly proposed perovskite

material  $\text{Bi}_2\text{CrCuO}_6$  based on its cubic complex structure [7]. Inclusion of multivalent transition elements like Cr on the B site guarantees the magnetic response of the system. We expect that the presence of Cu on the B' site inserts a metallic contribution into the compound. At last, the presence of Bi, which has diamagnetic character and is a non-conventional metal [7], could be raising the location of exotic properties in the final material.

### 2. Calculation method

We use the Wien2k code [8], which is a program based on density functional theory (DFT) [9,10] and that allows to perform electronic structure calculations of crystalline solids. Wien2k works with the full-potential (linearized) augmented plane-wave (LAPW)+local orbital (lo) method, which is most accurate for electronic calculations. The exchange correlation potential can be treated using several approximations in the framework of local density approximation (LDA) and the generalized gradient approximation (GGA) [11]. By searching the energy minimum, we have optimized the unit cell volume. From this volume, the lattice parameter  $a$  was found. For calculation we used the muffin-tin radii (in Å): 1.3229, 0.9737, 0.9737 and 0.8679 for Bi, Cr, Cu and O, respectively. The utilized  $\text{RMT}^*K_{\text{max}}$  was 8.0. We used 120k-points over the irreducible Brillouin

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zone, and the maximum angular momentum inside the muffin-tin sphere was  $l = 10$ . Magnetic character of system was introduced by the spin polarization into the GGA. From energy–volume DFT calculations, we determined the optimal structure for the  $\text{Bi}_2\text{CrCuO}_6$  system, by using the  $\text{Fm}\bar{3}\text{m}$  (2 2 5) space group.

### 3. Results and discussion

Fig. 1 shows the energy as a function of volume. Each one of the squares constitutes an individual calculation and the line corresponds to a fitting with the Murnaghan state equation, which was carried out by using the concept of the least-square fitting method [12,13].

From the results of Fig. 1, we determine the minimum energy and calculate the lattice parameter  $a = 7.763 \text{ \AA}$ . Fig. 2 shows the density of states as a function of energy density of states (DOS) for the lattice constant obtained from the minimization of energy as a function of volume. Fermi level is the reference for energies. From Fig. 2a (total DOS), we observed an apparent metallicity for both up and down spin orientations through the Fermi level. However, the little value of the DOS spin-up after the Fermi level in Fig. 2a can fall inside the possible numeric error and, therefore, a tendency of the spin-up channel to show the semi-conducting behavior is possible. Then, we propose that  $\text{Bi}_2\text{CrCuO}_6$  perovskite material presents a half-metallic-like feature.

From Fig. 2b and c it is evident that the conductor character can be attributed to the spin-down channel of Cu, with a minor participation of the Cr-spin-down polarization. On the other hand, spin-up orientation of Cu has an apparent insulator behavior and spin-up polarization of Cr reveals the same tendency of Cu. Our calculation permitted to predict a magnetic moment of  $3.0 \mu_B$  for the  $\text{Bi}_2\text{CrCuO}_6$  material, which can be attributed to the Cr-spin-up contribution. Fig. 3 shows calculated

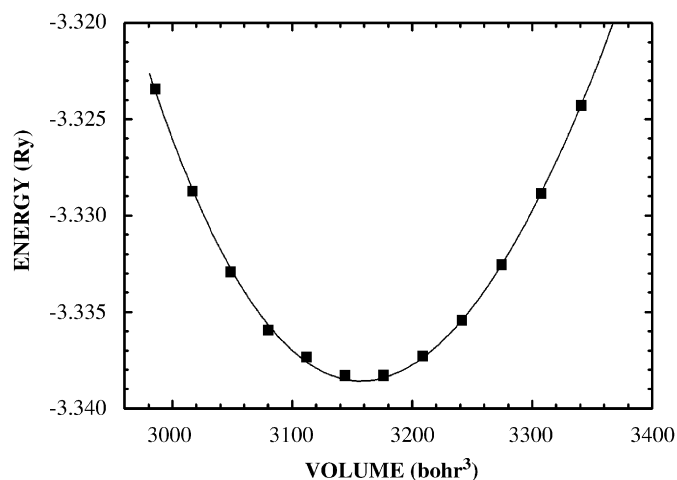


Fig. 1. Energy vs. volume. Squared points represent the calculated data of energy as a function of volume for the primitive cell of  $\text{Bi}_2\text{CrCuO}_6$ . Line is the fitting with the Murnaghan's state equation.

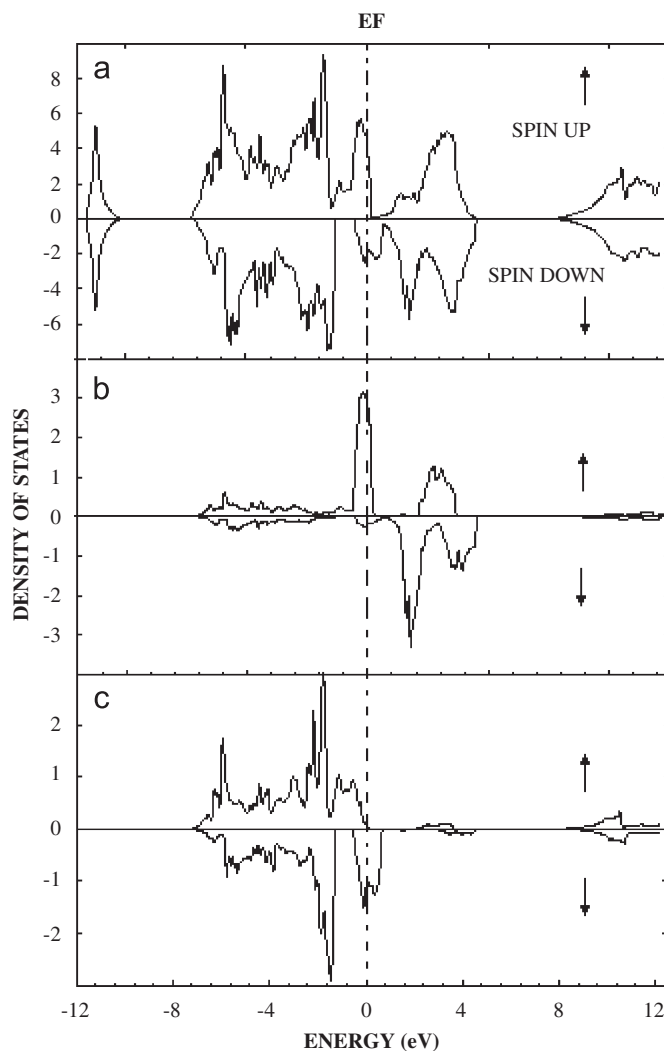


Fig. 2. Calculated total and partial (Cr, Cu) DOS of  $\text{Bi}_2\text{CrCuO}_6$  for up and down spin polarization. In the figure, positive DOS represents spin up and negative DOS spin down.

DOS for  $t_{2g}$  and  $e_g$  electrons in the up and down spin configurations for Cr and Cu elements. Undoubtedly, the orbital  $\text{Cr-}t_{2g}$  (spin-up) is directly responsible for the magnetic response of this system. The conductor character of material is particularly due to the spin-down contribution of  $\text{Cu-}e_g$  and  $\text{Cr-}e_g$  orbitals.

Additionally, we determine a strong exchange splitting between up and down spin orientations of  $\text{Cr-}t_{2g}$  orbital, with an energy gap of  $0.65 \text{ eV}$ , which goes from  $0.24 \text{ eV}$  up to  $0.89 \text{ eV}$ . The superposition of a partial DOS for localized  $\text{Cr-}t_{2g}$  and delocalized  $\text{Cr-}e_g$  levels, which characterize the splitting of crystalline field between  $t_{2g}$  and  $e_g$  states [14,15], was observed from  $-0.7$  up to  $0.1 \text{ eV}$ .

### 4. Conclusions

DFT calculations of lattice constant for the new  $\text{Bi}_2\text{CrCuO}_6$  perovskite were performed by considering the  $\text{Fm}\bar{3}\text{m}$  space group. The DFT calculations predict that the

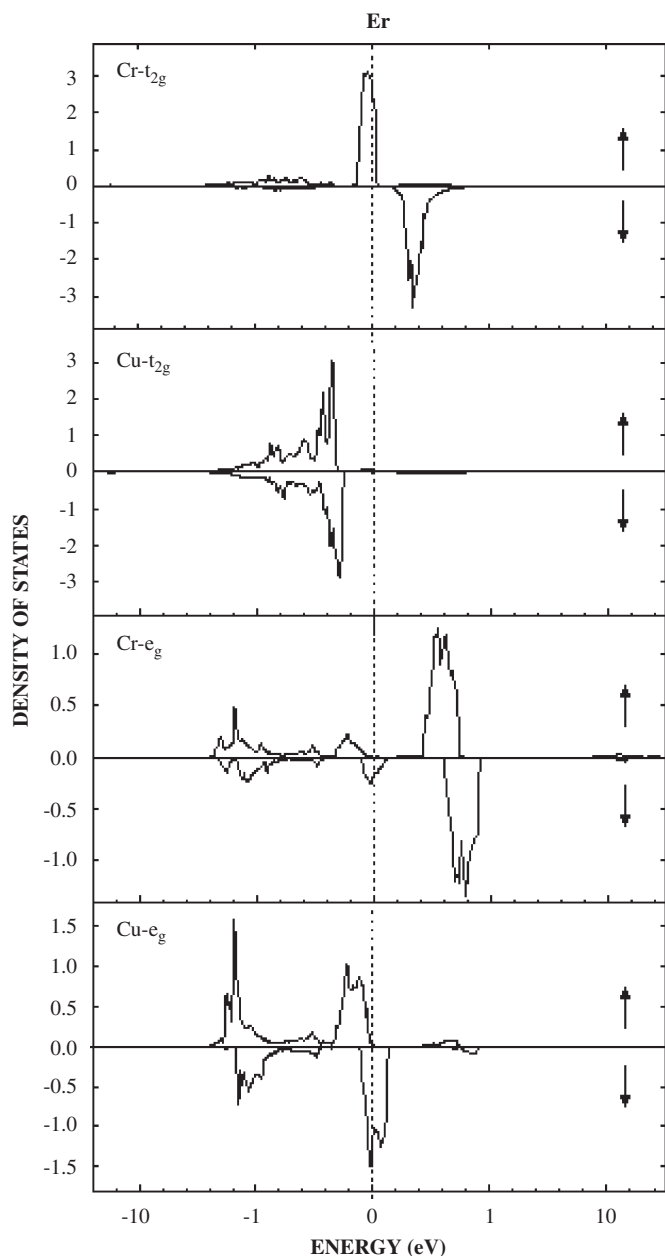


Fig. 3. Calculated contributions of  $t_{2g}$  and  $e_g$  electrons to the DOS for up and down spin polarization of  $\text{Bi}_2\text{CrCuO}_6$ . In the figure, positive DOS represents spin up and negative DOS spin down.

$\text{Bi}_2\text{CrCuO}_6$  material has a clear conductor feature for the spin-down channel. From calculated partial DOS, we determine that  $\text{Cu-}e_g$  orbital is directly responsible for the

metallic character. On the other hand, the spin-up configuration presents an apparent semiconductor behavior, evidencing an energy gap of 0.65 eV. These results and the integral number obtained for the magnetic moment are accepted as evidences of the possible half-metallic character of  $\text{Bi}_2\text{CrCuO}_6$  double-perovskite material.

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