

## ***Ab initio* study of ferromagnetic $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ <sup>†</sup>**

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**Abstract.** We study structure and magnetic properties of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  (LBCO) using *ab initio* density functional theory (DFT) method based on pseudopotentials and a plane-wave basis. We find the cubic structure of LBCO is ferromagnetic and lower in energy than the nonmagnetic rhombohedral structure. Through the calculation of  $\Gamma$ -point phonons of LBCO in the cubic structure, we determine its structural instabilities and find that they correspond to the structural phase transition accompanying a para-ferromagnetic transition observed recently.

**Keywords.** Ferromagnet; lanthanum barium cobalt oxide; phase transition; phonons.

### **1. Introduction**

Transition metal (TM) oxides constitute a group of compounds with a wide range of properties,<sup>1,2</sup> arising from electron correlations of *d*-electrons of the TM and their hybridisation with *p*-electrons of oxygen. Mixed oxides (for example, ternary) exhibit even richer variety of properties. Nature of their ground state is highly diverse, ranging from superconducting, various magnetic, charge and orbital orderings to ferroelectric. As a function of temperature or concentration of substitutional atoms, they show interesting transitions to different phases or states, adding to the richness of their properties and continue to be fundamentally interesting.<sup>3</sup>

$\text{LaCoO}_3$  (LCO), a member of the perovskite family of oxides, shows interesting semiconductor to metal and magnetic to nonmagnetic transitions and its electronic structure has been extensively studied experimentally<sup>4–6</sup> and theoretically.<sup>7,8</sup> Hole-doping of LCO by substitution of a divalent atom ( $\text{A}_x\text{La}_{1-x}\text{CO}_3$ ) results in several changes in its properties. Electronic spectroscopy study of the substitution of Sr for La, for example, showed a transition to a metallic state at the concentration of  $x=0.2$ .<sup>6</sup> Substitution of Ba was found to make LCO ferromagnetic at  $x=0.2$  and transform it from rhombohedral to cubic structure at  $x=0.4$ .<sup>10</sup>

Recently, a structural transition from the cubic to tetragonal structure was found to accompany a para-ferromagnetic transition in  $\text{LBCO}$ <sup>9</sup> as a function of temperature. In variance to most of the earlier studies, Fauth *et al*<sup>9</sup> reported an ideal cubic perovskite structure at RT and attributed the structural transition to Jahn–Teller distortion favoured by the intermediate spin-state. An independent confirmation of these results possibly from a theoretical calculation is desirable.

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<sup>†</sup>Dedicated to Professor C N R Rao on his 70th birthday

In the present work, we study atomic and electronic structure and magnetic properties of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$  (LBCO) using methods of DFT. A similar method has been used earlier in the study of  $\text{LaMO}_3$ <sup>7</sup> ( $M = \text{Mn, Fe, Ni and Co}$ ) compounds with good success and we compare their results for LCO with ours to benchmark our method. We investigate the structural instabilities of LBCO and interpret our results in relation to the recent experimental observation of a structural transition in LBCO.<sup>9</sup>

## 2. Computational methods

Computational methods based on the density functional theory (DFT)<sup>11,12</sup> have played an important role in understanding ground state properties of materials. TM oxides with the TM in the  $d^0$  state have been extensively studied using these methods. These include binary oxides, ferroelectrics, and many ceramics. The electron correlation in these materials, due to lack of  $d$ -electrons, are weak and fairly well approximated by the commonly used functional forms (such as local density approximation (LDA) or local spin density approximation (LSDA))<sup>13</sup> of the DFT.

TM oxides the TM in a  $d^n$  state often have strong correlation effects limiting the accuracy of their studies using DFT methods. In this case, use of models (for example, Hubbard model) with accurate treatment of correlation effects based on many body theory is common. There is an ongoing effort in combining the strengths of both methodologies and using them together<sup>14</sup> to understand these highly complex materials. DFT methods provide an important starting point in such studies and can be used for these complex materials to extract valuable microscopic information.<sup>15</sup>

*Ab initio* density functional theory calculations in this work were performed using the ‘ABINIT’ package.<sup>16</sup> We used optimised pseudopotentials<sup>17</sup> for La and Co, and extended norm-conserving pseudopotentials<sup>18</sup> for Ba and O. For high accuracy, we have included the semi-core states in the valence of La, Co and Ba, corresponding to 11, 17, 12 valence electrons per atom respectively and used an energy cutoff of 120 Ry on the plane wave basis used to represent the Kohn-Sham wavefunctions (this typically corresponds to using 16000 plane waves per wavefunction of a 10-atoms unit cell).

We use a local spin density approximation (LSDA)<sup>19</sup> for the exchange correlation functional. This approximation has been successfully used for many materials including  $\text{LaCoO}_3$ ,<sup>7</sup>  $\text{BiFeO}_3$ .<sup>20</sup> While we are aware of its limitations in obtaining accurate electronic structure of strongly correlated systems<sup>8</sup> such as one studied here, we use it here mainly to understand structural and some simple aspects of magnetic properties.

Due to nontrivial features in the electronic structure at the Fermi level, we need to use a fine  $k$ -point sampling of the Brillouin Zone in estimating integral quantities such as density of states, magnetization. A  $5 \times 5 \times 5$  mesh with a Fermi–Dirac broadening of 0.005 eV is used in the calculations of total energies and optimisation of structure using Hellman–Feynman forces and stresses. A  $10 \times 10 \times 10$  mesh was used the calculation of the density of states. We have checked convergence with respect to both the  $k$ -point sampling and energy cutoff.

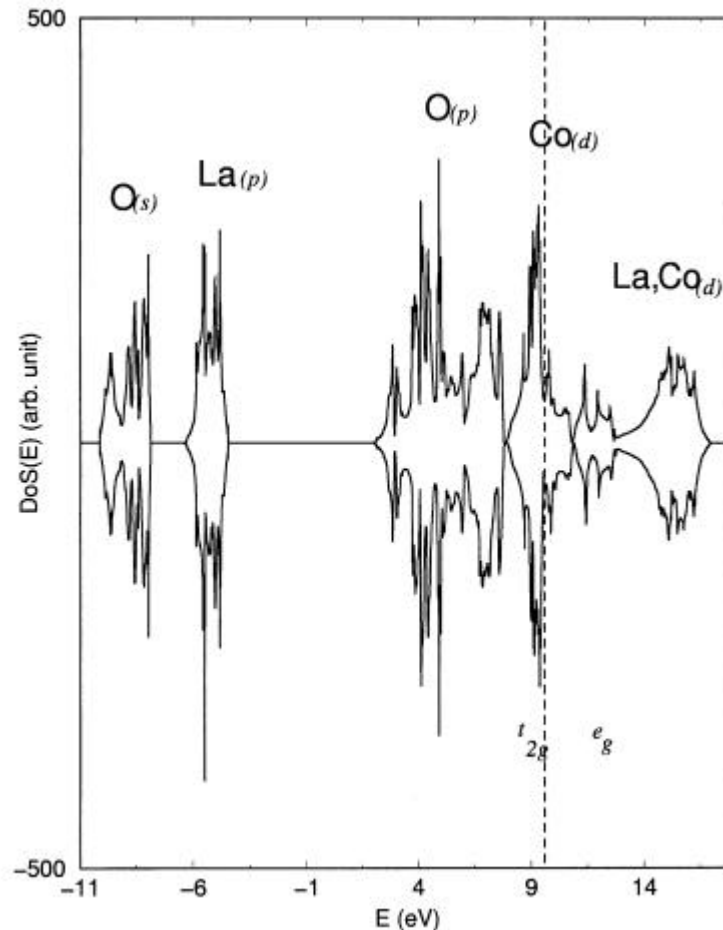
Phonon frequencies and eigenmodes have been obtained by calculating the dynamical matrix using DFT linear response.<sup>21</sup> Due to the intensive computational effort involved, we have used a  $3 \times 3 \times 3$   $k$ -point mesh for the BZ sampling. This is expected to give a reasonably accurate idea about the structural instabilities.

### 3. Results

#### 3.1 Crystal structure

There are three structural parameters ( $a$ ,  $\mathbf{a}$  and  $x$ ) for crystals with space group  $R\bar{3}c$  symmetry, which is the experimentally observed symmetry of LCO crystals. Maintaining the space group  $R\bar{3}c$  symmetry, we determine the equilibrium structure through minimization of total energy with respect to the internal parameter  $x$  and unit cell volume keeping  $\mathbf{a}$  fixed at the experimental value. We find  $a = 5.31 \text{ \AA}$  and  $x = 0.198$  in good agreement with the experimental<sup>10</sup> values of  $a = 5.39 \text{ \AA}$  and  $x = 0.2$ , discrepancy being typical of LDA calculations and is similar to that in the LAPW calculations for LCO.<sup>7</sup>

The crystallographic data of LBCO at RT was found<sup>9</sup> to be consistent with the cubic perovskite structure (S.G.  $Pm\bar{3}m$ ), but the same data could also be refined with a rhombohedral (S.G.  $R\bar{3}c$ ) and low-temperature tetragonal (S.G.  $P4/mmm$ ) structures with out much improvement in the quality of fit. We choose to work with structures of

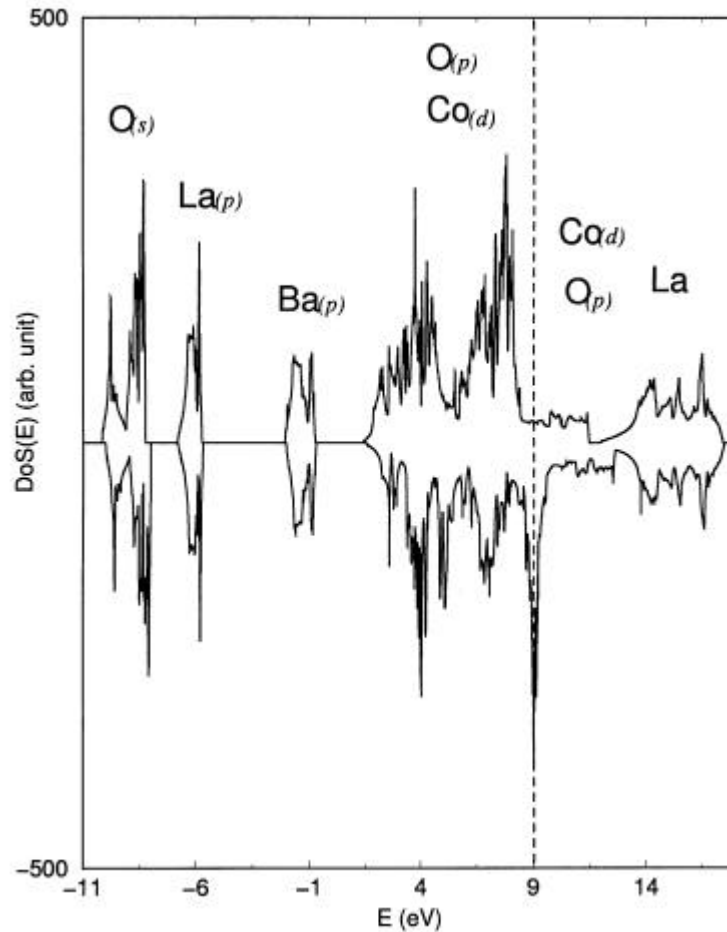


**Figure 1.** Electron density of states of  $\text{LaCoO}_3$  as a function of energy. Positive and negative values of the density correspond to spin up and down respectively.

$Pm\bar{3}m$  symmetry, due to its simplicity and for investigation of its symmetry-lowering structural instabilities. While Ba and La are disordered and occupy the A-site randomly in experimental samples, we pick an ordered configuration, where the La and Ba occupy the A-site alternately along (111) direction, for use in our calculations. This results in the choice of unit cell very similar to that of the  $R\bar{3}c$  structure, but with oxygen atoms at the (6*d*) Wyckoff position, in stead of (6*e*). We find the lattice parameter  $a = 3.81 \text{ \AA}$  within the LDA errors of experimental value of  $3.8843 \text{ \AA}$ .

### 3.2 Electronic structure and magnetic properties

While LCO is observed to be semiconducting, our calculations yield it to be semi-metallic with its Fermi energy falling in the pseudo-gap, as shown in figure 1. This is not too surprising as it is well-known that the LDA underestimates the band gap and at times finds systems with narrow gaps to be metallic. A similar result was obtained in the earlier



**Figure 2.** Electron density of states of  $\text{La}_{0.5}\text{Ba}_{0.5}\text{O}_3$  as a function of energy. Positive and negative values of the density correspond to spin up and down respectively.

DFT-LSDA work on LCO,<sup>7</sup> where the band gap was quoted to be  $-0.2$  eV and LCO as semi-metallic. The orbital content of electronic states has been obtained through projection of electron eigenfunctions on spherical harmonics centred at different atoms. The states near  $\epsilon_F$  are predominantly of Co  $d$ -type and are mixed with  $p$ -states of oxygen slightly lower in energy. The states below the  $p$ -bands of oxygen are the semi-core states of cations or  $s$ -states of oxygen. We label only the dominant orbital character of different bands in figures here.

The  $p$ -type conducting property of LCO inferred from Mossbauer studies<sup>5</sup> is consistent with our result that the Fermi energy is near the top of the Co  $d$ -subbands. It is clear from figure 1 that the density of states of electrons with both spins is almost the same, except for a few minute differences near the Fermi level. This results in a vanishing (0.06 Bohr magneton/formula unit) magnetization, consistent with the non-magnetic nature of LCO found experimentally<sup>10</sup> and in the earlier calculation.<sup>7</sup>

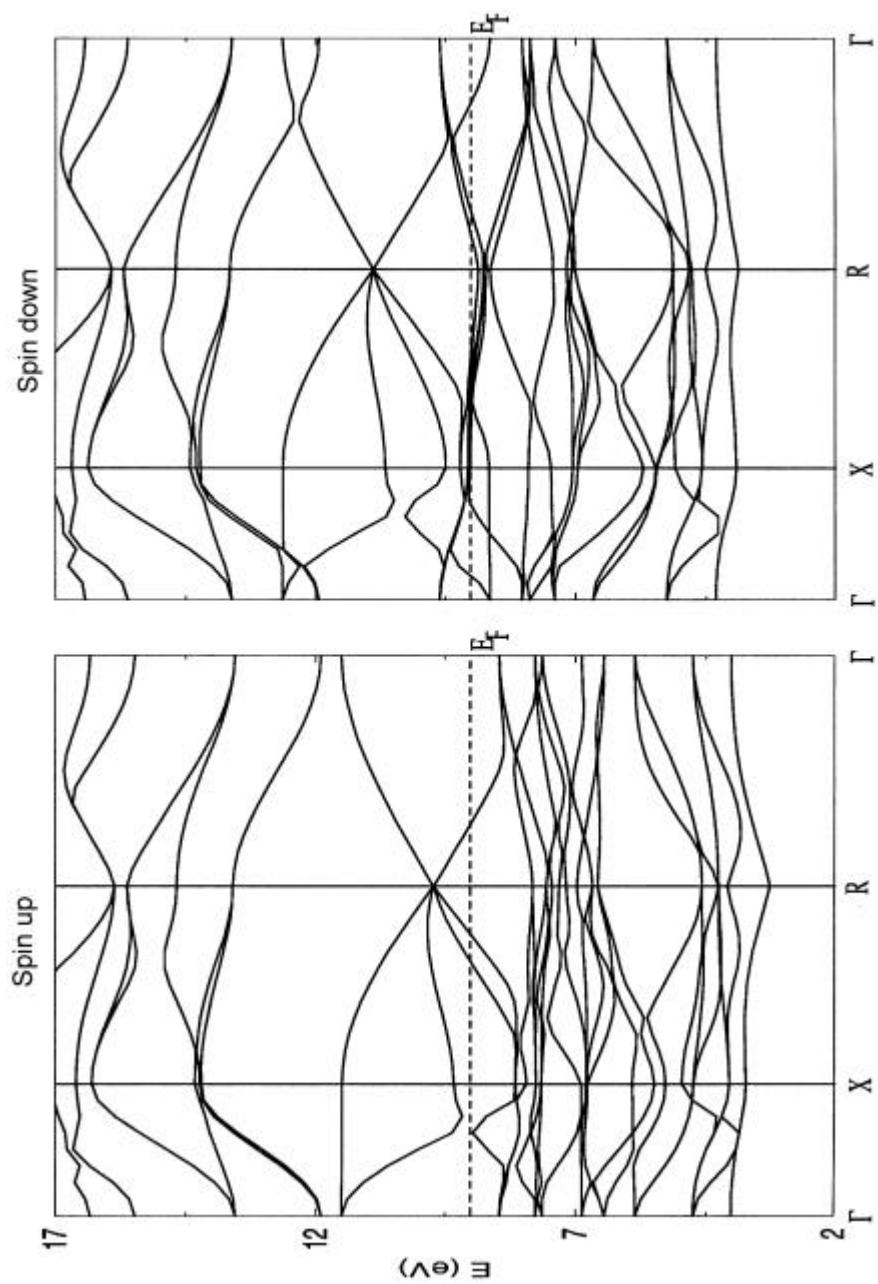
Density of electronic states of LBCO in the cubic structure, as shown in figure 2, shows it to be metallic, with a small (large) density of states for up (down) spin electrons at the Fermi level. In comparison with LCO, we find a much stronger hybridisation between  $p$ -states of oxygen and  $d$ -states of cobalt, with most of the states in the range of 6 eV below the Fermi level having mixed character. There is no clear separation between Co and O bands for up spin electrons as a function of energy. Strong hybridisation observed here is consistent with the intermediate or low spin configuration.<sup>9</sup> The semicore  $p$ -states of Ba appear close to the O- $p$  bands, and are slightly broadened due to weak hybridisation with oxygen.

In figure 3, we show electron band-structure for LBCO in the energy range of about 7 eV on both sides of the Fermi energy  $\epsilon_F$ . The bands that are relatively flat and crowded in the narrow range of energy typically correspond to the  $d$ -states of Co (as found through projection of some of these states on to spherical harmonics). It is quite clear that these are present about 2 eV below  $\epsilon_F$  for up-spin and at  $\epsilon_F$  for down-spin electrons, making LBCO almost half-metallic. The bands above  $\epsilon_F$  are widely dispersed and arise from mixing with  $d$ -states of La and other states.

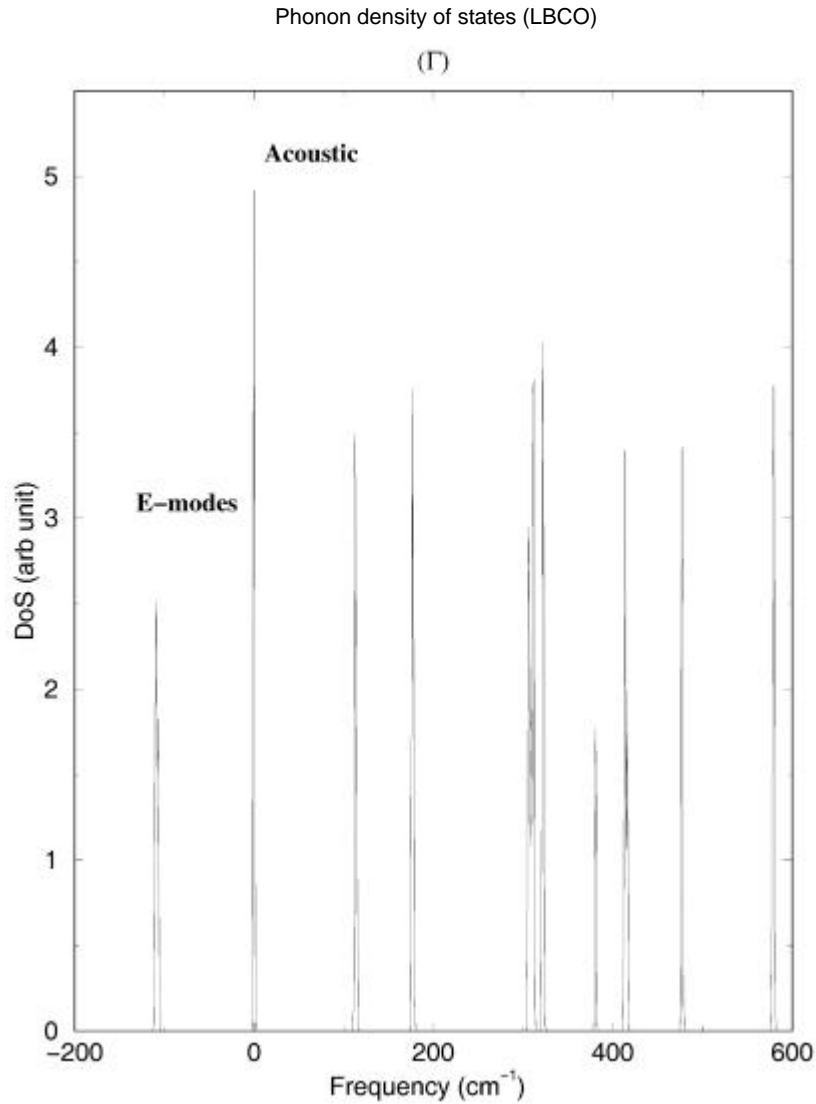
There is a marked difference between the density of states of electrons with up and down spin, giving rise to a nonzero magnetization. Our estimate of the magnetization is 1.9  $\mu_B$  per formula unit, in excellent agreement with the value (1.9  $\mu_B$  per formula unit) obtained experimentally<sup>9</sup> at 0 K. We note that the calculated value is for the cubic phase at 0 K. For LBCO in the  $R\bar{3}c$  structure with parameters same as that of LCO, we find a nonmagnetic ground state that is a couple of eV higher in energy than the cubic structure. This partially confirms the claim in (ref 9) regarding the cubic structure of LBCO at RT.

### 3.3 Phonons: LBCO

To explore possible structural distortions that will lower energy and preserve ferromagnetism, we focus on phonons of the ferromagnetic LBCO in cubic structure. We calculated a  $(30 \times 30)$  dynamical matrix at the  $\Gamma$  point (for the cell with two formula units) using DFT linear response, eigenvalues and eigenvectors of which  $(30 \times 30)$  give phonon frequencies and eigenmodes. Density of phonons at  $\Gamma$  point as a function of frequency is displayed in figure 4, we point out that all the observable long-wavelength modes are included in it.



**Figure 3.** Electronic structure of LBCO along high symmetry lines in the Brillouin zone (only the states near the Fermi energy  $e_F$  are shown).



**Figure 4.** Density of states of  $\Gamma$  point phonons of LBCO as a function of frequency ( $\omega$ ). Negative values are used to denote unstable modes with imaginary  $\omega$ .

We find two unstable modes with frequencies of about  $110i \text{ cm}^{-1}$  and one at  $\omega = 104i \text{ cm}^{-1}$ . As the unit cell of LBCO is obtained by doubling the unit cell of cubic perovskite along (111) direction and replacing one of the La with Ba, there is mixing between the modes at  $\Gamma$  and  $R$  ( $\frac{P}{a}(111)$  points of the cubic lattice. Further examination of the strongest unstable modes reveals predominantly  $E$ -mode like character, which corresponds to elongation of the oxygen octahedron or the  $R'_{12}$  mode of the cubic perovskite.<sup>22</sup> This is exactly what has been reported in ref. (9). We also find a component of rotational modes ( $R_{25}$ ) of oxygen octahedron in the unstable mode-eigenvectors.

#### 4. Conclusions

The structural and magnetization properties of LBCO derived from *ab initio* DFT calculations agree quite well with experimental observations. We find that the ferromagnetic cubic LBCO is structurally unstable at low temperatures and should have a lower symmetry structure obtained by elongation of oxygen octahedra. This is consistent with the recent experimental report<sup>9</sup> of the structural phase transition in LBCO.

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