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First Principles Investigations on the Electronic and Magnetic Properties of $La_4Ba_2Cu_2O_{10}$

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Abstract

Electronic and magnetic properties of $La_4Ba_2Cu_2O_{10}$ had been studied *by first-principles density functional theory (DFT). Based on the DFT calculation* $La_4Ba_2Cu_2O_{10}$ *is found to have a ferromagnetic (FM) ground state. The material undergo charge-transfer type insulator to Mott-Hubbard type insulator transition which happens due to strong correlation in La-4f and Cu-3d states. Our results show that the 3d electrons of Cu hybridize strongly with O-2p states near the Fermi level giving rise to the insulating state of* $La_4Ba_2Cu_2O_{10}$. *Our study suggests that the enhanced magnetic moment is a result of itinerant exchange rather than the exchange interaction involving individual ions of Cu atoms. The total magnetic moment calculated in the present studies is 2* μ_B *per unit cell for* $La_4Ba_2Cu_2O_{10}$.

Keywords*: Density functional theory, lanthanide cuprates, electron-correlation effects, ferromagnetic Mott-insulator*.

1. Introduction

The discovery of superconductivity in ceramic materials has been a strong race to understand the mechanism of superconductivity in CuO materials, in particular how magnetism influences its behavior. It has been found that at very low doping, cuprates show the long range order of antiferromagnet, doping breaks up the antiferromagnetic order and becomes an insulator. Only with doping fraction between about 0.1 and 0.2, they become superconductors [*Bednortz and Muller*, 1986; *Freeman and Xu*, 1987]. The understanding which has emerged is that copper oxide layers provide the path for currents. These copper oxide layers are separated by layers of other atoms which serve as spacers and charge reservoirs [*Matthias,* 1954; *Mizuno et al.,* 1990]. *S*ince the discovery of high temperature superconductors, many new materials have been invented. Precise physical and chemical work on high temperature superconductors has made tremendous progress in the theoretical and experimental study of physical properties and carrier state characterizations [*Yahua et al.,* 2015; *Ghimire et al.,* 2011, 2015; *Rai et al.,* 2015]. Since the discovery of first transition metal oxide has obvious benefits of room temperature superconductors, which conduct electricity without resistance, may include lossless power generator, transformers and transmission lines, powerful supercomputers and even superfast magnetically levitated trains. Needless to say the discovery of room temperature superconductors

would revolutionize the way we use and generate power. Cuprates are the king of super conductors [*Amin et al.,* 2011; *Wannier,* 1937]. Although no theory on the mechanism of high temperature superconductivity has gained acceptance, the observation of high temperature superconductivity in this class of layered materials has led to a phenomenological understanding that superconductivity depends on the two dimensional conducting planes with weak interplane coupling. The compound $Ln_4Ba_2Cu_2O_{10}$ (where Ln=Lanthanide) is a ceramic material which is a new class lanthanide high temperature superconductors obtained by substituting barium atoms into the lattice of lanthanum copper oxide in a solid solution [*Paukov,*1991; *Good Enough*, 1958].

The overall feature of the specific heat in $La_4Ba_2Cu_2O_{10}$ agrees to that of the mean field approximation with 1/2 spin system and is more 3-dimensional than that of 2-dimensional Cu ferromagnet K_2CuF_4. The measured magnetizations on the single crystals and the estimated anisotropy suggest the Heisenberg system with Ising-like anisotropy due to the comparably large interlayer coupling. In the system of Nd substitution for La, the ferromagnetic transition is not observed because Nd ions having the *f*-spins may disturb the exchange interaction between interlayer Cu^{2+} ions. The study of magnetic properties of $(La_{1-x}R_x)_4Ba_2Cu_2O_{10}$ for R=Nd, Sm, Gd and Eu, of which the end material $La_4Ba_2Cu_2O_{10}$ is known as a rather exceptional ferromagnet among the known copper-oxide insulators. It was found that the average ionic radius *r* of the elements at the La site determines the solubility limit of R elements. When *r* is larger than ~1.11 Å, the compound has the $La_4Ba_2Cu_2O_{10}$ type structure, while for smaller *r,* the Y_2BaCuO_5 type structure is formed [*Vaughey et al.*, 1991; *Khomskii and Kugel,* 1973; *Perdew et al.*, 1996]. The magnetic behavior of the compounds depended on the R element, even a rather small amount of Nd altered the ferromagnetic ground state to an antiferromagnetic one, with a possible spin-glass state in between [*Jongh and Miedema,*1974; *Ghimire et. al.* 2011; 2015; *Rai et al,* 2015]. For R=Sm and Gd, the experimental results suggest a similar change of ferromagnetism to antiferromagnetism, but a ferrimagnet [*Ghimire et al.*, 2015] like behavior was observed for intermediate compositions. On the other hand, ferromagnetism resided up to the solubility limit for R=Eu. The application of high pressure upto 8.0 GPa hardly affected the magnetism of $La_4Ba_2Cu_2O_{10.}$ This result, as well as the results of Rietveld analysis of R-substituted $(La_{1-x}R_x)_4Ba_2Cu_2O_{10}$, indicate that the reduction of ferromagnetism with the increase in x is not attributable to the structural change induced by the substitution, the chemical pressure effect.

Few investigation were done theoritically to study the properties of $La_4Ba_2Cu_2O_{10}$ using Hubbard model by Mizuno et al., they observed that most of the half-filled cuprates shows antiferromagnetic property in ground state while some of the cuprates possesses ferromagnetic behavior [*Meinert,* 2013]. Similarly the isostructural $Nd_4Ba_2Cu_2O_{10}$ are found to allign antiferromagnetically below 7.5 K but the half-filled Cu-d orbitals in $La_4Ba_2Cu_2O_{10}$ are found to align ferromagnetically below 5 K [*Wei et. al.,* 2002]. This type of unusual insulating FM phase possesses a great challenge to our quantitative

theoretical understanding of microscopic mechanism involved in real materials. There are few attempts done for quantitative processes to study the intriguing behavior of $La_4Ba_2Cu_2O_{10}$. The description of Hubbard like model is found to lack the identity of destructive interference of hoping paths which suppress AF coupling and give a small FM coupling along z axis in a narrow parameter range as assumed by Good enough et al. [*Marzari and Vanderbilt*, 1997]. Furthermore the assumption of FM coupling between the nearest neighbors in the plane is apparently in contradiction to the AF order in $Nd_4Ba_2Cu_2O_{10}$ [*Subramanian,* 1988].

In order to resolve this problem theoretically quantum magnetism model was introduced with adjustable parameters. Though this approach is intuitive and computationally manageable but this lack to describe the quantitative detail of the complex interaction that occurs in real materials and also lack to describe the spin spin coupling in magnetic orbit. A very good attempt was made by [*Wei et al.,* 2002 and *Ford*, 2005] to resolve the problem of microscopic mechanism of the unusual insulating ferromagnetism in $La_4Ba_2Cu_2O_{10}$. They experimented that the dominant mechanism turns out to be intersite FM direct exchange that is currently ignored in the macroscopic studies of this system [*Smirnov and Usvyat,* 2001]. This process occurring mainly at the La and O sites overwhelms the weak tendency towards AF order via Hubbard type super exchange [*Jonker and Van Santen,*1950; *Wu et al*.,1987; *Sun and In-Hwan Oh,* 1996]. On the other hand, on $Nd_4Ba_2Cu_2O_{10}$ crucial dominant direct exchange unlike the nearest neighbor as assumed by Hubbard but with sites above or below them. This generates the proper in plane order. Finally, the role of the chemical effect is introduced with numerical simulation of $La_4Ba_2Cu_2O_{10}$ under pressure which suggests an intriguing pressure induced FM to AF transition [*Castano et al.,* 2003; *Slater,* 1960].

2. Crystal Structure and Computational Details

The compound $La_4Ba_2Cu_2O_{10}$ is tetragonal with space group P_4/mbm. In this compound ten and eight coordinate cation sites (2b and 4g) are selectively occupied by Ba^{2+} and Ln^{3+} respectively, and no oxygen deficiency is observed in this compound [*Subramanian,* 1988]. The compound consists of five independent and eighteen total atoms in a unit cell.

The electronic and magnetic properties of $La_4Ba_2Cu_2O_{10}$ are studied by using full-potential linearized augmented plane wave (FP-LAPW) method based on density functional theory (DFT) as implemented in the WIEN2k code [*Blaha*, 2001]. The core states are treated fully relativistically while the semi-core and valence states are treated semi-relativistically. The standard generalized-gradient approximation (GGA) exchange correlation potential within the PBE-scheme [*Anisimov et al*., 1997] were used with Coulomb interaction U due to strong electron-electron interaction in La and Cu ions. The results shown here is with U_{La}=6 eV and U_{Cu}=5 eV respectively. We have chosen the muffin-tin (MT) radii for La, Ba, Cu, and O to be 2.34, 1.92, 1.99 and 1.77 a.u. respectively. Integrations in reciprocal space were performed

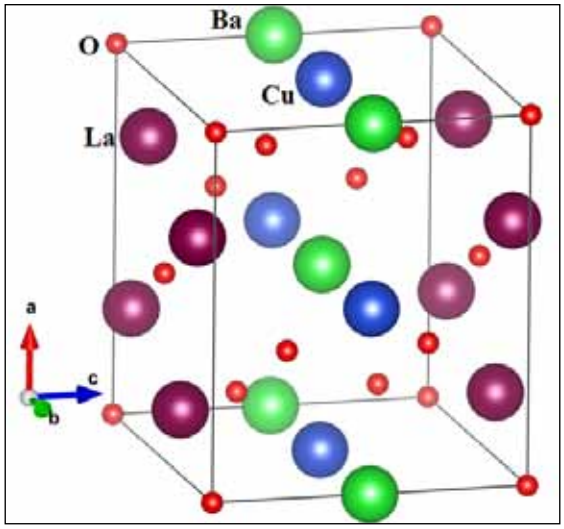

Figure 1. Crystal structure of $La_4Ba_2Cu_2O_{10}$ (oxygen atoms are co-ordinated to Cu-atoms).

using 108 spatial *k*-points in the irreducible wedge of the Brillouin zone.

3. Results and Discussions

$La_4Ba_2Cu_2O_{10}$ belongs to tetragonal cuprates family where La at A-site provides charge to the system and nominally take the charge state +3 with $4f^0$ configuration, lying in the conduction region above the Fermi level (E_F). The transition element Cu nominally takes the charge state +2 with $3d^9$ configuration where nine out of ten *d* orbits are occupied lying in the valence region, while the remaining un-occupied state lie in the conduction region due to large crystal field from oxygen ions.

For the ground state investigations of $La_4Ba_2Cu_2O_{10}$ we first consider the non-magnetic calculations with the standard GGA method. This provides a reference for studying the magnetic phases. From the partial density of states (DOS) for non-magnetic phase as shown in Fig. 2, the Cu-d states lying at the top of the valence band has a sharp peak indicating localized states which is an indication of the unstable ground state. As observed from Fig. 1, Ba states has no impact on the electronic states as they lie deep in the core region whereas the Cu-3d and O-2p states hybridize strongly in the valence region indicative of the possibility of magnetic ground state. La-4f states on

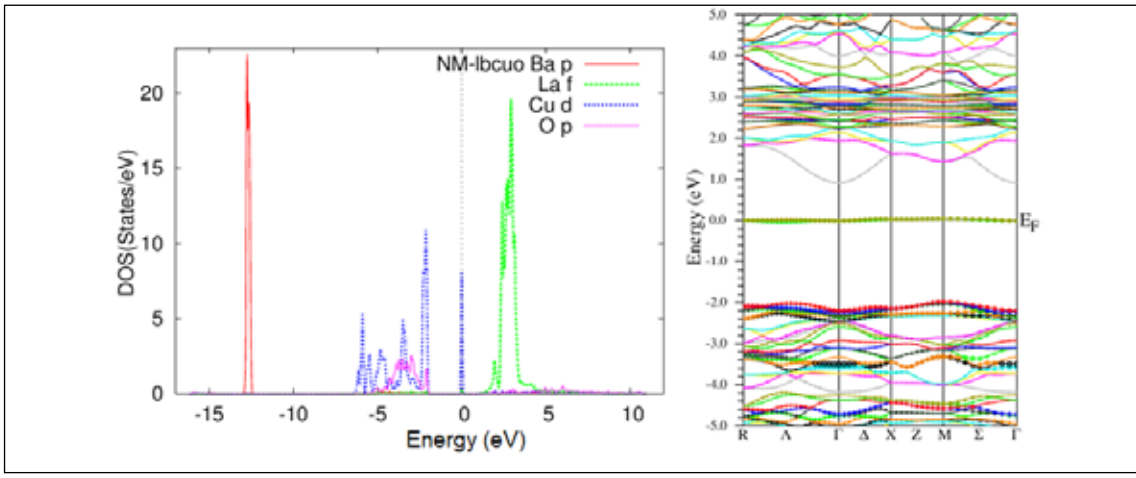

Figure 2. Partial density of states (DOS) and band structure for non-magnetic phase of $La_4Ba_2Cu_2O_{10}$ within GGA

the other hand lies in the conduction region with no contribution to the electronic states. Furthermore, the material $La_4Ba_2Cu_2O_{10}$ is found to be a charge-transfer type insulator.

In order to know the experimental ground state we calculated the total energies for nonmagnetic (NM), ferromagnetic (FM) and different phase of antiferromagnetic (AFM) configurations. Our calculation shows that FM configuration is the stable ground state consistent with the experimental prediction with total energy of ~1.5 eV less than the NM and ~10 meV less than the AFM's configurations.

To understand the electronic properties of $La_4Ba_2Cu_2O_{10}$ we carry out the DOS and band structure calculations for the FM phase as shown in Fig. 3 and Fig. 4. Since La and Cu are strongly correlated, GGA+U scheme was considered. According to our first-principles DFT calculations, the material $La_4Ba_2Cu_2O_{10}$ is found to be Mott insulator (see Fig. 3) with an energy gap of approx. 2.1 eV at the Fermi level (E_F). The gap is formed between the Cu-d and La-4f states in spin-up while that between Cu-d states in spin-down channels.

From the total and partial (La-4f, Cu-5d, O-2p) DOS shown in Fig. 3 and the band structure in Fig. 4 for spin-up and spin-down channels, it is observed that the empty La-4*f* states lies above E_F for both spin-channels in the conduction region. The Cu-3*d* states are found to play key role in dictating the electronic properties of $La_4Ba_2Cu_2O_{10}$. They are found to hybridize strongly with the O-2p states in both spin channels. Their hybridization occurs mostly in the valence region near E_F and in the conduction region. We observe that Cu-d (i. e., especially d_{eg}) states are fully occupied in spin-up channels and thus lies in the valence region whereas in spin-down channel, only one out of two d_{eg} states are occupied while the remaining states being empty lies in the conduction region hybridizing with O-2p and La-4f states. Charge transfer effect is prominent between Cu-3d and O-2p states due to strong hybridization. We observe that there is large exchange splitting

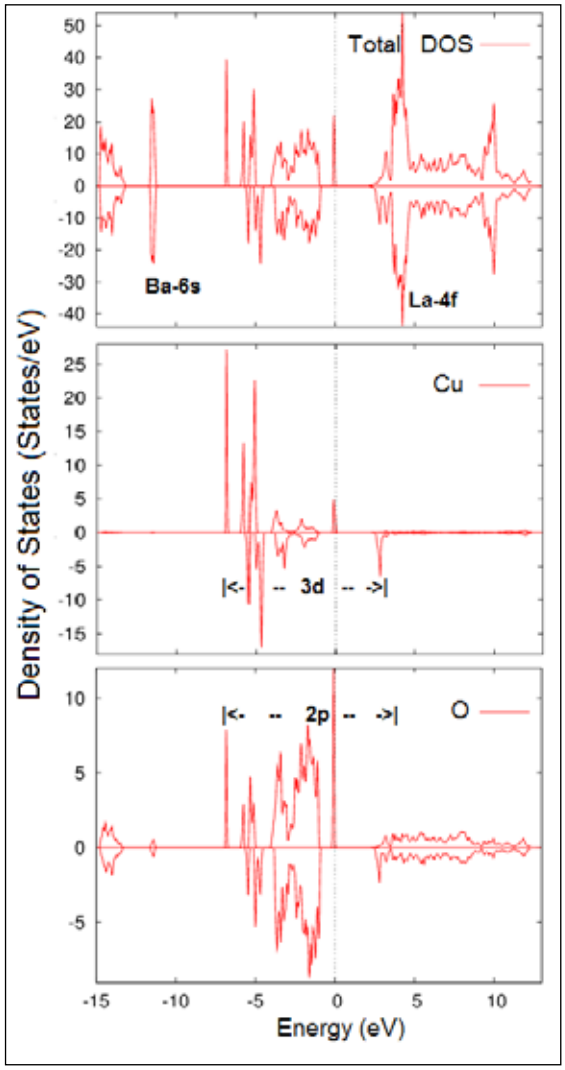

Figure 3. Total and partial density of states (DOS) of $La_4Ba_2Cu_2O_{10}$ for the ferromagnetic ground state.

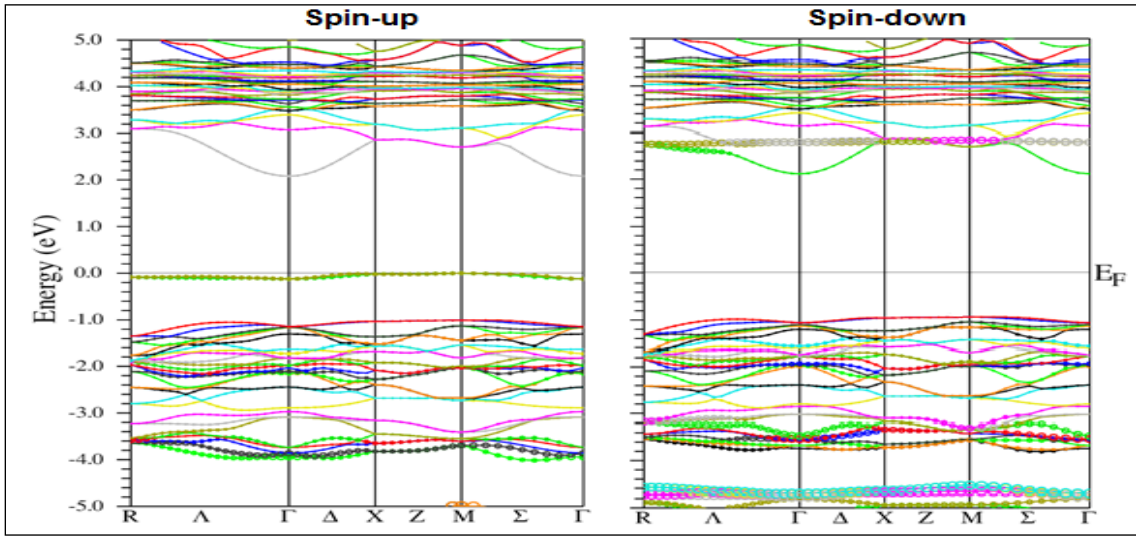

Figure 4. Band structures of $La_4Ba_2Cu_2O_{10}$ for spin-up (left) and spin-down (right) channels.

between Cu-3d states between the spin-up and spin-down states whereas for La-4f there is no exchange splitting due to vacant orbitals. Exchange splitting energy of Cu-3d is found to be ~4 eV which contributes to ferromagnetic behavior in $La_4Ba_2Cu_2O_{10}$.

From the band structure calculations shown in Fig. 4, the fat band appearing suggest the contributions from Cu-3d states while the contributions to conduction region are dominantly from the La-4f states with partial contributions from Cu-d states in spin-down channel. As observed clearly, $La_4Ba_2Cu_2O_{10}$ Cu-3d states fully occupy the valence region for spin-up as well as spin-down channels. The band structure plot depicts $La_4Ba_2Cu_2O_{10}$ to be an indirect band Mott-Hubbard type insulator with a band gap of 2.1 eV. From first-principles calculations, we obtain the magnetic moment of $\mu \approx 0.7\mu_B$ per Cu atom, and $\mu \approx 0.1\mu_B$ per O atoms, respectively, with a total magnetic moment of $\mu_{tot} = 2.0\mu_B$ per formula unit in $La_4Ba_2Cu_2O_{10}$.

4. Conclusions

Based on the first-principles density functional calculations, we predict $La_4Ba_2Cu_2O_{10}$ to be a ferromagnetic insulator consistent with the experiment. Our study suggests that the magnetic moment is a result of itinerant exchange and the exchange interaction involving individual Cu ions.

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