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On the Bonding Nature of Electron States for the Fe-Mo Double Perovskite

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Abstract. The electronic transport as well as the effect of an external magnetic field has been investigated on manganese-based materials, spinels and perovskites. Potential applications of double perovskites go from magnetic sensors to electrodes in solid-oxide fuel cells; besides the practical interests, it is known that small changes in composition modify radically the physical properties of double perovskites. We have studied the Sr_2FeMoO_6 double perovskite compound (SFMO) using first-principles density functional theory. The calculations were done within the generalized gradient approximation (GGA) scheme with the Perdew-Burke-Ernzerhof (PBE) functional. We have made a detailed analysis of each electronic state and the charge density maps around the Fermi level. For the electronic properties of SFMO it was used a primitive cell, for which we found the characteristic half-metallic behavior density of states composed by e_g and t_{2g} electrons from Fe and Mo atoms. Those peaks were tagged as bonding or antibonding around the Fermi level at both, valence and conduction bands.

Keywords: Double perovskites; Ferromagnetism; Colossal magnetoresistance
PACS: 71.15.Mb; 71.30.+h; 72.25.-b; 71.23.-k

INTRODUCTION

Attention on double perovskites was renewed after the report done by Kobayashi *et al* [1] on the Sr_2FeMoO_6 compound, which shows a large low-field tunneling type magnetoresistance at room temperature. From the multiple experimental studies on SFMO, such as neutron diffraction [2], nuclear magnetic resonance [3], electron spin resonance [4], X-ray absorption, ultraviolet photoelectron and electron energy-loss spectroscopies [5] among others, it is known that this double perovskite is a half-metallic ferromagnetic oxide which has a complete spin polarization and substantial low-field magnetoresistance.

In Sr_2FeMO_6 (M=Mo,W) the metal-insulator transition depends on the number of conduction electrons and also on the energy level difference of the Fe and M *d* electrons [6, 7]. It is found that the formation of Fe-O-Mo-O-Fe chains is the essential factor for the half-metallic ferromagnetism [8].

In this paper, we report a Density Functional Theory study of the electronic structure of SFMO. We found that bonding-antibonding splitting in band structure

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produces richer electron states than those reported in literature, *i.e.*, in alpha states the bonding and antibonding *d* states of Fe are fully contained in the valence band, whereas in the beta states former are in the valence band and the latter are in the conduction band.

COMPUTATIONAL METHODS

The electronic properties of SFMO were studied within the density functional theory (DFT) framework. The generalized gradient approximated (GGA) Perdew-Burke-Ernzerhof (PBE) functional [9] was used, within the CASTEP code, as implemented in the Materials Studio software suite; all run parameters were set to fine quality. To study the electronic properties of SFMO, we calculated the electron density of states (DOS) for a primitive cell [2], and visualized the electronic clouds of the DOS peaks.

RESULTS AND DISCUSSIONS

Our DOS confirmed that SFMO is a half-metallic compound (Fig. 1): for the up spin channel (alpha electrons) there are an energy gap of almost 1 eV meanwhile the down spin channel (beta electrons) behaves as a conductor. As reported by other groups [10, 11], we found in the alpha channel a t_{2g} character for the *d* states of Mo above the Fermi level (E_F) and the valence band contain Fe and Mo e_g contributions. In the beta channel there are t_{2g} contributions from Fe and Mo atoms around the E_F. However these states present a bonding-antibonding unfolding as detailed below.

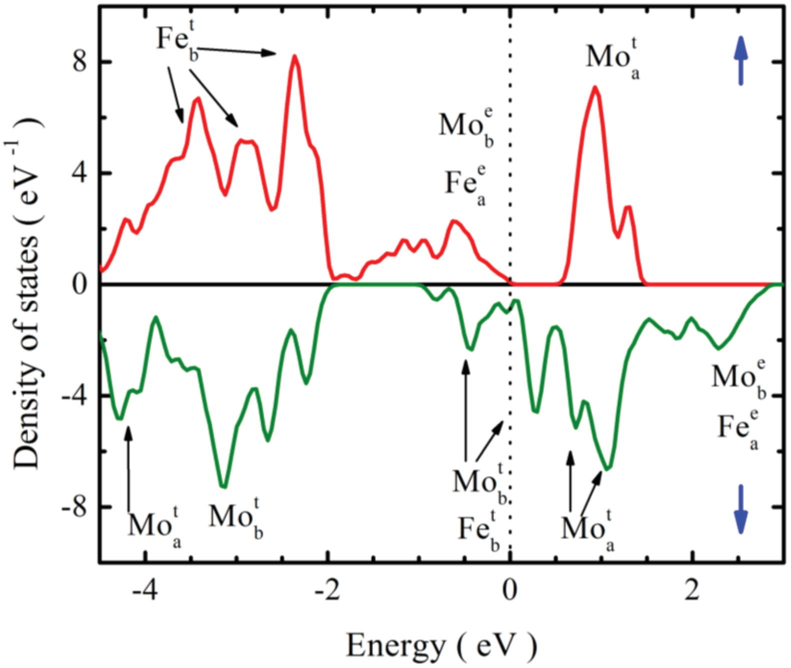

FIGURE 1. (Color online) Density of states of Sr_2FeMoO_6 around the Fermi level (vertical dotted line) for up and down spin channels (blue right side arrows). The orbital symmetry labels are included for iron (Fe) and molybdenum (Mo) contributions. Every label was tagged through the use of subscripts as bonding (b) or antibonding (a) and by superscripts as t_{2g} (t) or e_g (e).

Between -8 eV and 3 eV the density of states for both spin channels was made up mostly of O *p* states and Fe and Mo mixed *d* states, being of t_{2g} or e_g character (not all shown in this paper). In the up spin channel, there are e_g and t_{2g} bonding states contributions of Mo and e_g bonding states of Fe for energies between -7 eV and -6 eV. For energies in the interval [-6 eV, -2 eV] the main contribution comes from Fe atoms with e_g and t_{2g} bonding states. Below the E_F there is a mixed contribution from Mo e_g bonding states and antibonding e_g Fe states, that has not been reported in literature. Around 1 eV, the main contribution to the conduction band comes from Mo through t_{2g} antibonding states. For the down spin channel the behavior is different, the main contribution comes from Mo states; we found e_g and t_{2g} bonding states below -4 eV, where there are t_{2g} antibonding states which reduce their contribution until near -2 eV. For this spin channel, around the Fermi level, we found mixed contribution from Fe and Mo t_{2g} bonding states, until 1 eV where the antibonding t_{2g} Mo states are the relevant, before Fe (antibonding) and Mo (bonding) e_g states mix between 2 and 3 eV.

At higher energies, there are almost no differences between the corresponding *DOS* to the up and down spin channels. The main contribution comes from the Mo e_g antibonding states in the range from 3.5 to 6 eV. Around 7 eV, there are Mo t_{2g} antibonding states. The Fe states become relevant until the energy rise to around 12 eV, as antibonding t_{2g} states.

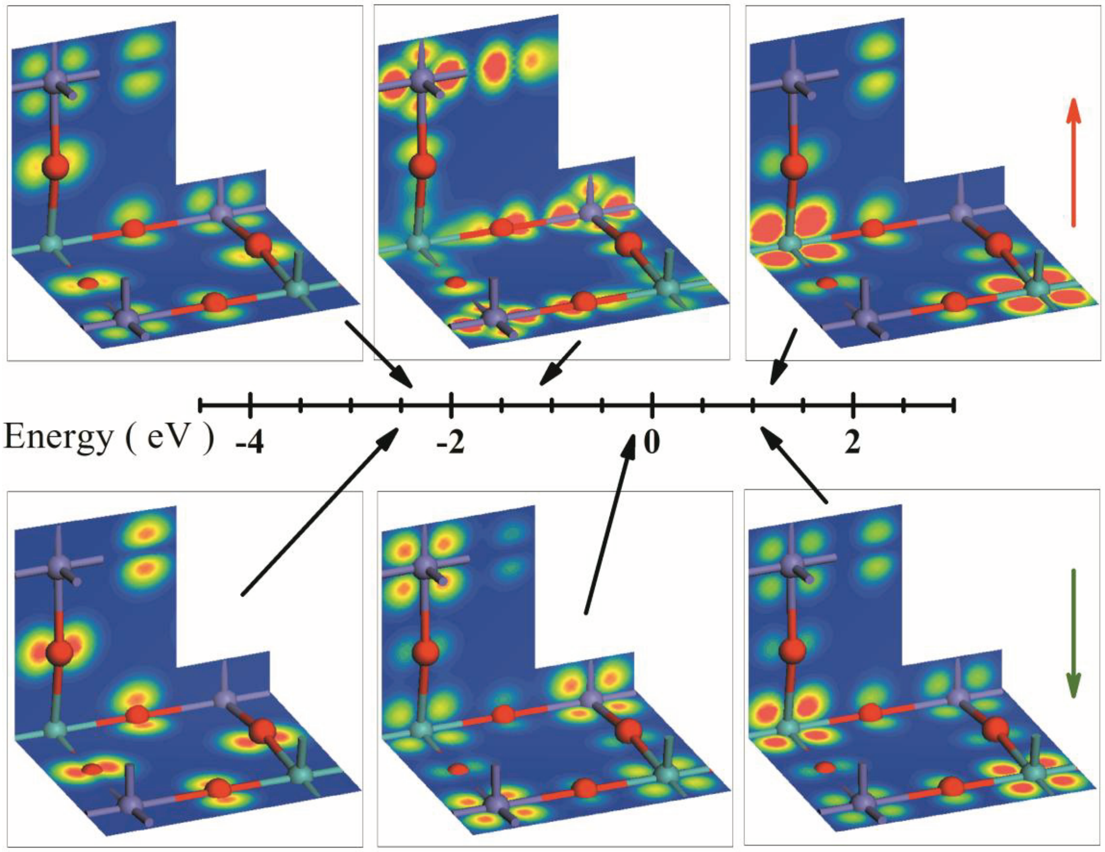

FIGURE 2. (Color online) Electron density maps around the Fermi level of Sr_2FeMoO_6 for up and down spin channels (vertical arrows at right). The black arrows show the center of the energy interval corresponding to every figure: -2.3, -1.2 and 1.1 eV for spin up; -2.3, 0.1 and 1.1 eV for spin down. Different atoms in the compound are shown in colors: Fe in purple, O in red, Mo in blue.

Below the E_F the charge is concentrated around the Fe atoms independently of the spin state (Fig. 2). While the down spin channel has bonding contributions from Fe and Mo, on the up spin channel the Fe states are antibonding. At the same time all the accessible states, above the E_F for the down spin channel, are built up by bonding states from the Mo atoms, as well as from Fe atoms too. Although the down spin band is continuous through the E_F and has contributions from the t_{2g} Fe and Mo states, the role of these atoms change in crossing E_F respect to the charge density.

It is worthy to mention that in reference [12] it was found similar bonding-antibonding splitting from d states for single clusters of FeO_6 and MoO_6, and that the half-metallic behavior is related to the non-zero spin at Fe site.

CONCLUSIONS

From our calculations, it is clear that SFMO is a half-metallic material for which, around the Fermi level, the states was made up by hybridizations of oxygen p states and iron or molybdenum d states, as reported by other groups. However, the t_{2g} or e_g character of those d states is not the only factor which determines the electronic behavior of this double perovskite; *i.e.*, the bonding-antibonding unfolding shown by the Fe and Mo d states is crucial to define the way that the accessible states are occupied, and then the half-metallic character of this material.

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