

Half-metallic behavior and electronic structure of $\text{Sr}_2\text{CrMoO}_6$ magnetic system

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Abstract

Complex perovskite materials with the $\text{A}_2\text{BB}'\text{O}_6$ formula have been recently studied because of their peculiar magnetic and electronic properties. The origin of magnetism in the double perovskite $\text{Sr}_2\text{FeMoO}_6$ brought these properties again into discussion. Recently, a new interaction mechanism was proposed for cases in which the hybridization of 3d and 2p levels of Mo with the 3d Fe levels is responsible for the half-metallic behavior in the $\text{Sr}_2\text{FeMoO}_6$ material. We report on LAPW ab initio calculations within the generalized gradient approximation (GGA) to density functional theory (DFT) for another double perovskite, namely, $\text{Sr}_2\text{CrMoO}_6$. Our results show that this is also a half-metallic system. We correlate our results with an extension of the recent model proposed by Sarma to explain the conduction mechanism in this compound.

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1. Introduction

Double perovskites with formula $\text{A}_2\text{BB}'\text{O}_6$, where A represents an alkaline earth, B and B' are metal transition magnetic and nonmagnetic ions and O is the oxygen, have been known for many years [1] but recently the study of these materials has increased due to the various technological applications in the design of magnetic memories or tunnel junctions and other magnetic devices in the spintronics area [2]. Properties such as colossal magnetoresistance [3], half-metallicity [4], high magnetic ordering temperature [5] and magnetodielectricity [6], make these materials ideal for the production of devices which can operate at room temperature. However, not only the technological potential of these oxides attract the attention of the scientific community but also their many exotic electrical and magnetic properties interesting in themselves.

In 1998 Kobayashi et al. [4] reported considerable magnetoresistance behavior and a high magnetic transition temperature in a $\text{Sr}_2\text{FeMoO}_6$ compound; these are important properties for the operation of devices at room temperature. Since then, many other compounds have been proposed, changing the metallic/magnetic ions on the B and B' sites [7] or partially replacing the divalent alkaline earth ions on the A site by trivalent rare earth ions such as La [8], for the purpose of obtaining these amazing properties.

In order to observe low-field magnetoresistive effects in other compounds, the series $\text{Sr}_2\text{CrB}'\text{O}_6$ has recently been studied [7]. The compound $\text{Sr}_2\text{CrReO}_6$ presented the highest Curie temperature known with $T_c = 635$ K, increasing importantly the T_c reported for the $\text{Sr}_2\text{FeMoO}_6$ material [4]. In the particular case of the Sr_2CrWO_6 , bulk, thin film samples have been made, which revealed ferrimagnetism with T_c up to 458 K [8,9]. The strong influence of the low magnetic field in these oxides might be related to the high degree of spin polarization of the charge carriers, but the origin of magnetism in these systems is still being studied.

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Recently, different models have been proposed to explain the transport mechanism in these compounds. When following the simple manganites one is tempted to use the double-exchange mechanism to explain the ferromagnetic and half-metallic behavior in these materials. But, due to the large distance between the magnetic ions, close to 8 Å, a much weaker ferromagnetic interaction is expected in this model. That is why the generalized double-exchange or kinetic energy driven exchange (SFTK) model proposed by Sarma [10] and more extensively developed by Fang–Terakura–Kanamori [11], has met with wider acceptance. In this model kinetic energy is obtained from the hybridization of the t_{2g} states in the non-magnetic site, with the t_{2g} states in the magnetic site and the hopping of the electrons occurring between the minority spin electrons from the non-magnetic site (into the empty minority spin bands of the magnetic ion) [9]. This means that a magnetic moment at the non-magnetic site is generated.

In this work, we studied the $\text{Sr}_2\text{CrMoO}_6$ system and will correlate our electronic structure results for this case with the SFTK model.

2. Calculation method

The calculation of band and electronic structure for the complex perovskite $\text{Sr}_2\text{CrMoO}_6$ may be seen as the result of solving a multiple body problem of ions and electrons. To study the electronic structure in this compound we have performed the calculations by employing the FP-LAPW method, in the framework of DFT and implemented in the WIEN2K code [10].

The FP-LAPW consists in the calculation of solutions for the Kohn–Sham equations (from DFT) for ground state density, total energy, and eigenvalues of a crystal, by introducing a basis set for two different regions in the unit cell. In one of these regions an expansion of radial functions times spherical harmonics is employed, in the other region a plane wave expansion is used. According to the linear variation method the solutions are expanded in this combined basis set.

In the calculations reported here, we use a $R_{\text{MT}}K_{\text{max}} = 8$ parameter, which determines matrix size (convergence), where K_{max} is the plane wave cut-off and R_{MT} is the smallest of all atomic sphere radii.

The exchange and correlation effects were treated by using the generalized gradient approximation (GGA) [11]. This potential considers the difference between the electronic densities for the two distinct spin orientations from the beginning. The density of states is calculated by the histogram method and the position of the Fermi level is found by integrating consistent calculations, which are considered to be convergent when the total energies of two successive iterations agree to within 10^{-4} Ry. We adjusted the Fermi energy to zero. The integrals over the irreducible Brillouin zone are performed up to 47 k-points.

3. Results and discussion

The tolerance factor (f) determines theoretically the perovskite structure by means of the ionic radii of each element in the compound. Their expression is

$$f = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}, \quad (1)$$

where r_B is the average ionic radius for the ions on the B and B' sites, r_A is the ionic radii for the ion on the A site and r_O is the ionic radii of the oxygen. When $f < 1$ the bond angles B–O–B are different from the ideal 180° . In consequence, the ideal cubic structure becomes rhombohedral or orthorhombic. When $f > 1$ a hexagonal structure is formed.

In order to obtain the most accurate results, we have determined the optimal lattice parameters corresponding to the minimal energy value. This is the total energy as the function of volume. For the $\text{Sr}_2\text{CrMoO}_6$ compounds total energy was calculated by fittings with the equation state of Murnaghan. Figs. 1 and 2 show total energy as a function of volume for the $\text{Sr}_2\text{CrMoO}_6$ complex perovskite.

Some structural information is presented in Table 1. Calculations were performed by using the tolerance factor and choosing the cubic crystallographic structure Fm3m. The optimal lattice parameter obtained by this procedure ($a = 7.84$ Å) is in agreement with the experimental value.

The total density of states for both spin orientations is shown in Fig. 1. We have plotted the behavior between -8 and 8 eV where the main features occur. For the spin down polarization at the top we use a continuous line and a broken line for the spin up polarization at the bottom. We observe the half-metallic nature, the spin-down channel has a conducting behavior and the spin-up channel evidences an isolated feature with a gap of 0.92 eV.

In Fig. 3 we show partial states corresponding to Cr-d in a continuous bold line and Mo-d states in a broken line. In

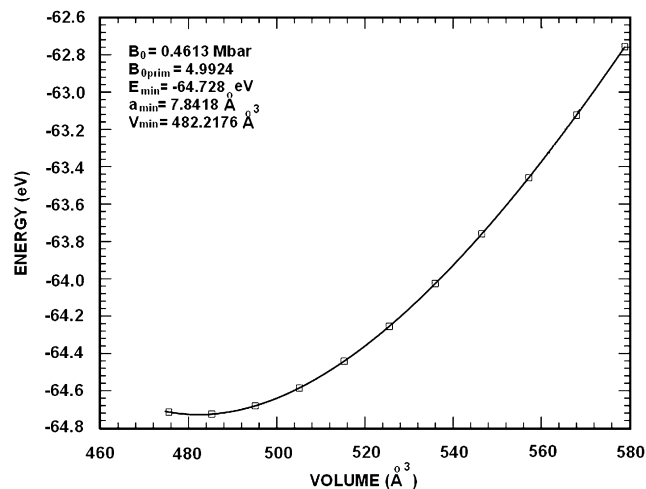


Fig. 1. Total energy (in eV per unit of formula) as a function of atomic volume (in \AA^3) for $\text{Sr}_2\text{CrMoO}_6$, by considering the Fm3m group.

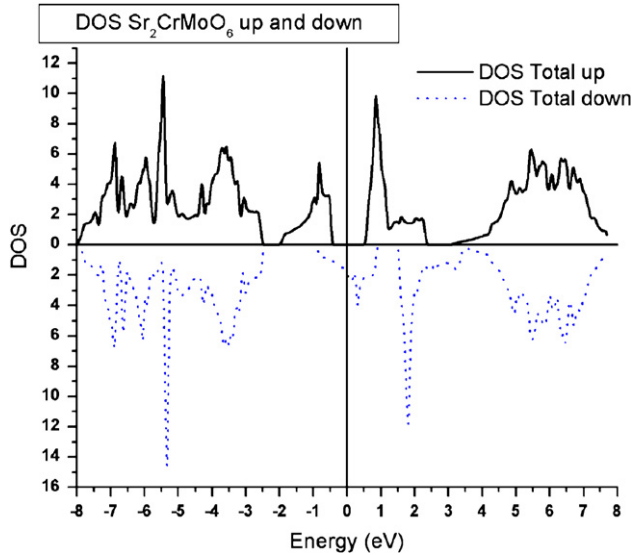


Fig. 2. Density of states for both up (bottom) and down (top) spin polarizations in $\text{Sr}_2\text{CrMoO}_6$.

Table 1
Structural parameters for the system [7]

Compound	$\text{Sr}_2\text{CrMoO}_6$
Tolerance factor	1.009
Crystallographic structure	Fm3m
Experimental lattice parameter	$a = 7.84 \text{ \AA}$
Theoretical lattice parameter	$a = 7.84 \text{ \AA}$

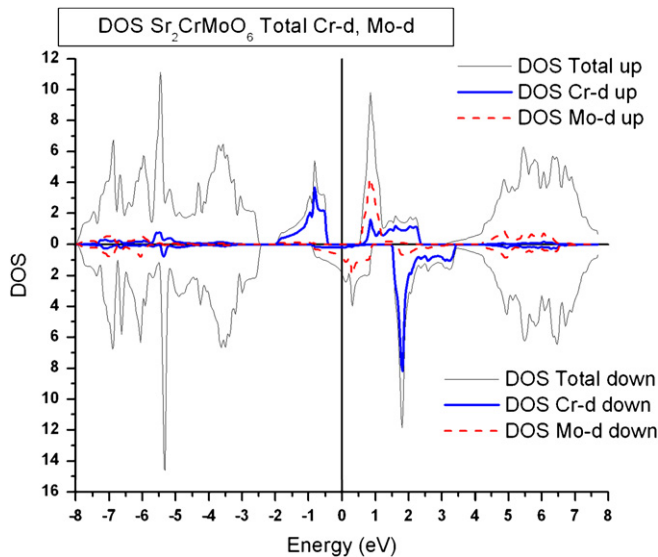


Fig. 3. Partial density of states for Cr-d and Mo-d states for both up (bottom) and down (top) spin polarizations in $\text{Sr}_2\text{CrMoO}_6$.

order to discuss the conduction mechanisms we have also calculated partial densities for Cr-d and Mo-d states.

For the down spin we clearly observe that Mo-4d states contribute to the conducting behavior. The Cr-d states are also present but in a very scant proportion. On the other

hand, the contribution to the occupied states is mainly from the Cr-d. The conduction band is mainly occupied by Mo-d down states and there are practically no Cr-d states around the Fermi level. The occupied states are chiefly Cr-d down states 0.39 eV below the Fermi level. As we all know, the presence of oxygen atoms around the Cr and Mo sites results in a splitting of the d levels into t_{2g} and e_g orbital, the last ones with higher energy. Partial DOS for Cr and Mo e_g and t_{2g} states for both spin orientations are shown in Figs. 4 and 5, the t_{2g} states in continuous bold line and the e_g states in broken line for both figures.

The Cr-d DOS in the spin-down channel shows that the energy spans from the 1.5 to 2.27 eV and from the 1.97 to 3.41 eV. This means that the crystal field split is very small, almost inexistent; for the spin-up channel the crystal split is

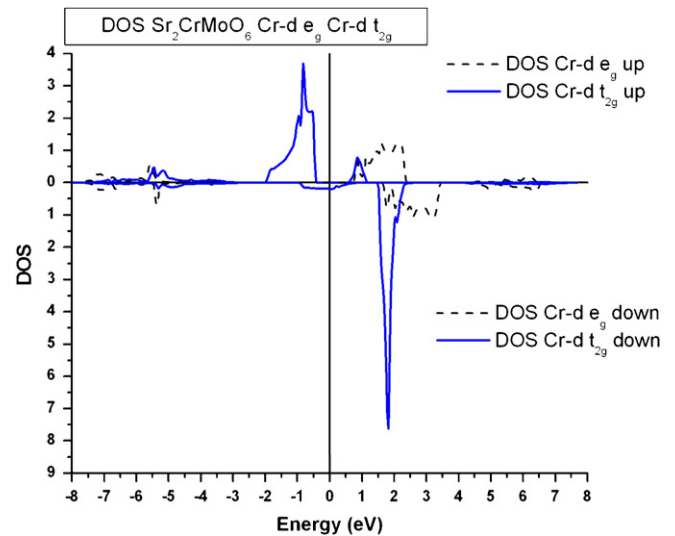


Fig. 4. Partial density of states for Cr-d e_g and Cr-d t_{2g} states for both up (bottom) and down (top) spin polarizations in $\text{Sr}_2\text{CrMoO}_6$.

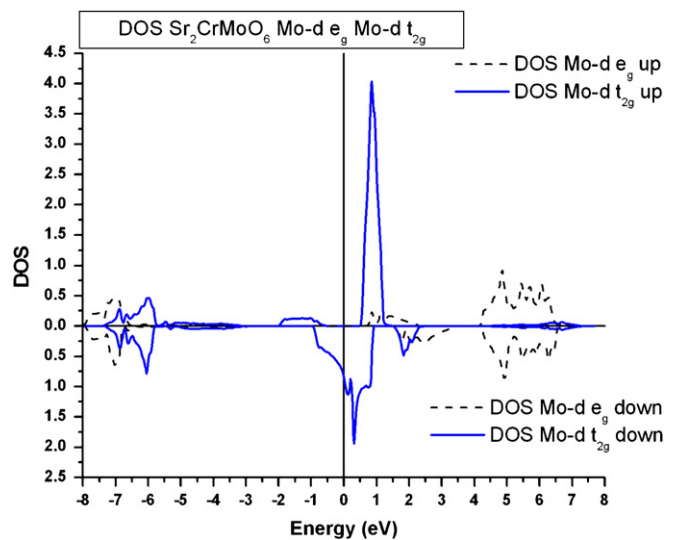


Fig. 5. Partial density of states for Mo-d e_g and Mo-d t_{2g} states for both up (bottom) and down (top) spin polarizations in $\text{Sr}_2\text{CrMoO}_6$.

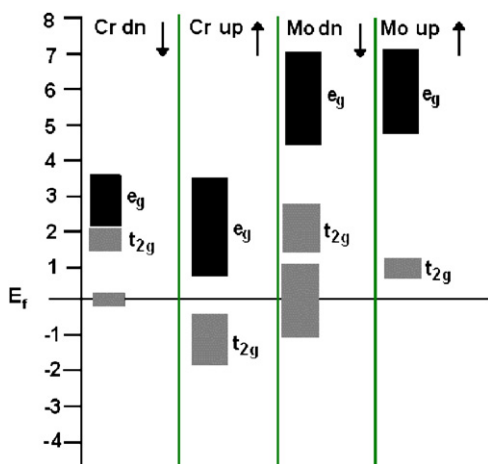


Fig. 6. Qualitative scheme of crystalline field splitting and exchange splitting as function of energy for: (a) Cr states, (b) Mo states.

smaller. On the other hand, the exchange splitting for Cr-d is more pronounced for t_{2g} states than for e_g . The gap between the t_{2g} up and down states is close to 3 eV.

In Fig. 5, we clearly observe the superposition of partial density of states for localized Mo-d- t_{2g} and delocalized Mo- d_{eg} levels, which characterize the splitting of crystalline field between t_{2g} and e_g states, and the exchange splitting between t_{2g} up and t_{2g} down levels and between e_g up and e_g down levels. There are gaps of 5.11 and 4.57 eV between the e_g and t_{2g} states for down and up directions respectively. We can observe that the e_g states appear only at high energies. The exchange splitting in this case is the opposite of the magnetic Cr ion, for Mo there is a small exchange splitting of 0.5 eV.

The results may be resumed by means of the qualitative scheme in Fig. 6. Here we can observe the exchange and crystal field splitting for Cr-d states down and up and Mo-d states down and up as well. This sketch is in agreement with the scheme proposed by Sarma to explain ferromagnetism in the double perovskite Sr_2FeMoO_6 . In this model the hopping interactions permit the hybridization of Mo-d t_{2g} and Fe d t_{2g} states and shift the bare energy levels in a special way. The Mo t_{2g} spin up states are pushed up, and the Mo t_{2g} spin down states are pushed down, polarizing the Fermi level. The itinerant electrons in the Mo t_{2g} spin-down band cause the kinetic energy gain via double exchange type interaction. When

applying the mechanism it is important that the conduction band be placed within the energy gap formed by the large exchange splitting of the localized electrons at the transition metal site just as we sketched in Fig. 6.

4. Conclusions

We performed several ab initio calculations over the Sr_2CrMoO_6 double perovskite. Our results revealed an insulator feature for the spin-up orientation and a conductor for the other, as may be expected of half-metallic materials. Analysis of electronic structure by DOS calculations, for both spin orientations, based on the DFT-LAPW method, allowed us to infer that the t_{2g} spin down states are responsible for the conductivity feature chiefly for Mo-4d states. On the other hand, the insulate behavior of the spin up configuration can be due to the e_g states. The distribution of energy, determined from the partial densities of states, was compared with the distribution of energy proposed by the SFTK model.

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