Short communication

Fe—Mo double perovskite: From small clusters to bulk material

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ABSTRACT

To understand the differences in behaviour between up- and down-spin electrons observed in the half-metallic Sr_2FeMoO_6 double perovskite, the density of states (DOS) was studied for the $(FeO_6)^{-4}$ and $(MoO_6)^{-6}$ octahedral clusters using first-principles density functional theory within the generalised gradient approximation (GGA) scheme and the Perdew–Burke–Ernzerhof (PBE) functional. Our results reveal that half-metallic character is present, even starting from an isolated $(FeO_6)^{-4}$ cluster, and is a consequence of spin decoupling of antibonding hybridisations between iron t_{2g} states and oxygen p states (t_{2g}^a states), i.e., t_{2g}^a states lie below the Highest Occupied Molecular Orbital (HOMO) in the up-spin channel, whereas they lie above the HOMO level in the down-spin channel. The spin-induced shifting between up-spin and down-spin DOS situates the HOMO in such a way that the molecular orbitals oxygen p states (p bands) are fully spin-paired by octet electrons. Thus, the down-spin channel has metallic character because the HOMO lies just at the p bands, and the up-spin channel is semiconducting because the HOMO falls within the energy gap between the t_{2g}^a and e_g^a bands. Finally, the $(MoO_6)^{-6}$ octahedron does not inhibit the perovskite half-metallic character since this cluster has a zero total spin.

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1. Introduction

The physical properties of the Sr_2FeMO_6 double perovskite materials (M = Mo, Re, Ru, W) range from a half-metallic ferromagnetic to an antiferromagnetic insulator, depending on M [1–3]. In particular, when the M cation is Mo or W and the Fe/M relative content changes, as in $Sr_2Fe_{1−x}M_{1+x}O_6$, it is possible to observe transitions between different electrical and magnetic behaviours [4–6]. The single structures $SrFeO_3$ and $SrMoO_3$ have been studied by different groups because the magnetic properties of iron break the symmetry between up-spin (alpha) and down-spin (beta) electrons [7,8].

The half-metallic behaviour shown by the double perovskite Sr_2FeMoO_6 makes this material a good candidate for use in spintronic devices. However, the performance of all these types of materials can be compromised by antisite disorder, non-stoichiometry and other defects [9]. Hence, in seeking to control their physical properties, we are looking for the critical size at which bulk-like behaviour is clearly displayed. It is known that the metal-insulator transition in Sr_2FeMO_6 (M = Mo, W) depends on

the number of conduction electrons and on the energy level difference of the Fe and M d electrons, and it is argued that the formation of Fe—O—Mo—O—Fe chains are essential for half-metallic ferromagnetism. To find the critical size at which the half-metallic behaviour appears and to gather insights about its origin, we report herein our calculations of the electronic properties of single octahedral clusters excised from the experimental bulk Sr_2FeMoO_6.

2. Models and computational methods

By using the Materials Studio (MS) software [10], a tetragonal Sr_2FeMoO_6 cell was drawn, as reported by experimental groups [11–15], i.e., taking the space group $I4/m$, lattice parameters $a = 5.5704$ and $c = 7.8983$ and atomic positions as in reference [15]. Then, the clusters of FeO_6 and MoO_6 were excised from this unoptimised experimental cell (Fig. 1). Unrestricted-spin, density-functional-theory, single-point energy calculations were performed using the DMol3 module of MS on both the cell and the clusters in the generalised gradient approximation within the Perdew–Burke–Ernzerhof functional [16] with a spin value of $2\hbar$ and fine-accuracy run options. The electronic structure of the two clusters was studied by means of the density of states, whose composition was analysed from energy levels of isolated Fe, Mo and O atoms. Each cluster and single-atom DOS was computed by

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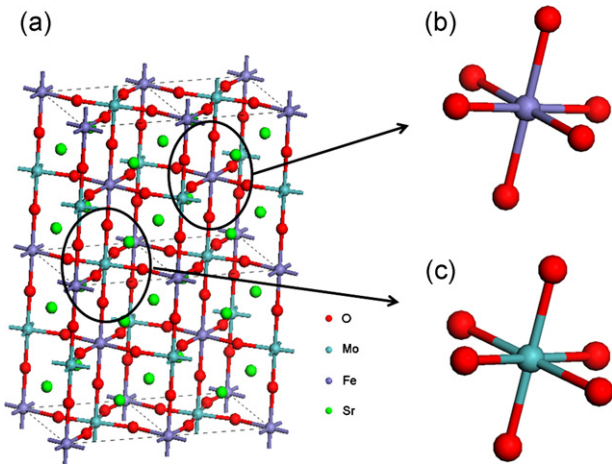 E-mail address: ecarvajalq@ipn.mx (E. Carvajal).

Figure 1. (a) Supercell for the bulk Sr_2FeMoO_6 double perovskite, from which were excised the octahedral arrangements (b) FeO_6 and (c) MoO_6.

Gaussian peaks centred at energy eigenvalues E_i (which were extracted from the output DMol3 files) using the following equation:

$$DOS(E) = (\sqrt{2\pi}\sigma)^{-1} \sum_i \exp\left[\frac{-(E - E_i)^2}{2\sigma^2}\right],$$

whereas the Gaussian-broadened DOS for the crystal structure was automatically given by the DMol3 analysis tool. DOS units are $(eV)^{-1}$, and we assigned a 0.05 eV value to σ.

3. Results and discussions

The typical half-metallic behaviour of Sr_2FeMoO_6, resulting from exchange splitting from a total spin of $2\hbar$ in the primitive cell, is revealed by means of the energy gap at alpha DOS and the conducting band at beta DOS (Fig. 2), as obtained by DMol3. The energy gap is almost 1 eV, which is in agreement with previous reports [17–20]. Explanations for the electronic structure via the dispersion relation $E(k)$ and the DOS of the bulk material have been extensively reported since the discovery in 1998 of its room-temperature magnetoresistance [21]. In our paper, this bulk DOS is taken as the reference for comparison of the DOS results of the cluster. To understand the origin of exchange splitting in this perovskite, we have started by analysing the electronic states of
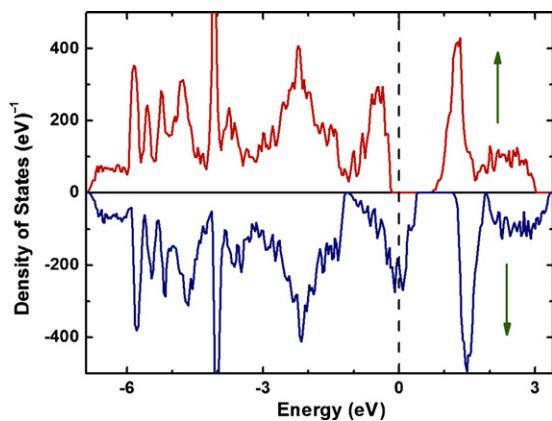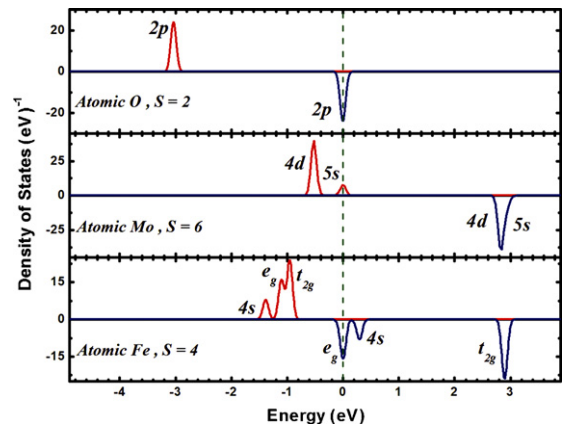

Figure 3. Density of states for isolated O, Mo and Fe atoms together with their spin. The Fermi level is indicated by a green, vertical, dashed line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

single, neutral transition-metal atoms and then those of Mo- and Fe-centred octahedral clusters.

As is well known, isolated, atomic Fe has 8 valence electrons that are distributed into one s and five d states, i.e., the total spin is $4\hbar$. Usually, spin pairing is considered to take place fully in s states and partially in d states (we will refer to this as the "s–d scenario"). However, our DFT calculation reveals that the s level is not closed, but rather all spin pairing occurs at d levels instead (Fig. 3). Because the d levels are composed of both doubly degenerate states, e_g, and triple degenerate states, t_{2g}, the four, spin-paired electrons are most likely to be in e_g states, and so these d sub-levels are closed (spin-paired) to minimise the total energy (Fig. 4). We will refer to this situation as the "e_g scenario". The latter scenario leads to a lower total energy of the Fe atom compared to the former scenario because in the t_{2g} scenario of the Fe s and t_{2g} electrons spins are unpaired, whereas in the s–d scenario there is a mixing of both paired and unpaired electrons within Fe d states, i.e., none of the e_g or t_{2g} states are clearly reinforced, which is important in forming directional bonds.

The electronic states of isolated Mo atoms are very similar to the Fe case (Fig. 3). Because Mo has 2 fewer valence electrons than Fe, pairing in e_g states is lost, and the total spin is $6\hbar$ (Fig. 4). In that case, all of the valence d states of Mo have the same energy because they are equally occupied, in contrast to Fe d states.

The above results for Fe and Mo spins suggest that when these transition-metal atoms are surrounded by an octahedral coordination of 6 oxygen atoms, as occurs in perovskites, Fe valence

Figure 2. Density of states for bulk Sr_2FeMoO_6 double perovskite. The Fermi level is indicated by a black, vertical, dotted line and the spin channels by the green, vertical arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
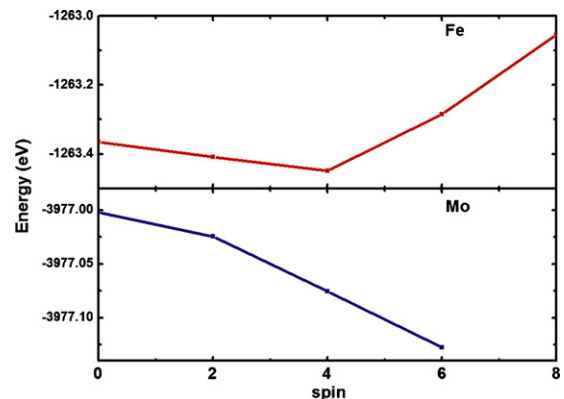

Figure 4. Total electron energy as function of spin for neutral, atomic Fe and Mo. Fe has 8 valence electrons, and Mo has 6.
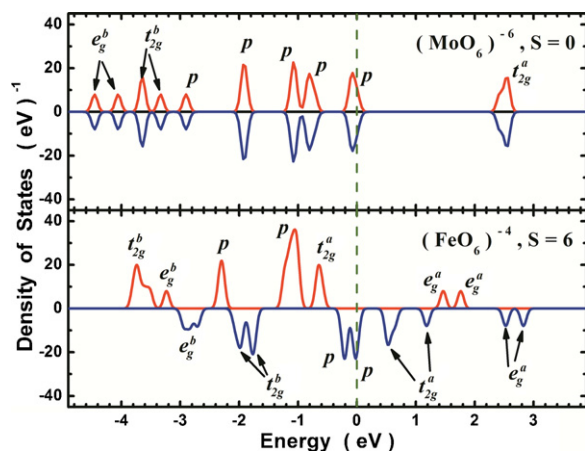
Figure 5. Density of states for charged MoO_6 and FeO_6 clusters. Also, their charge and spin values are included. The Fermi level is indicated by a green, vertical, dashed line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

electrons do not pair fully, but those of Mo do because only 4 bonds are sufficient to spin-pair the Fe electrons, which are spread over all bonds anyway in the octahedral coordination. In other words, while bonds in this coordination allocates a maximum of 12 electrons, in the Fe-based cluster there are only 10 electrons to share (1 per oxygen atom and 4 that are spin-unpaired at Fe). We estimate that Fe—O bonds must have a bond order of 0.833, which is lower than the expected bond order of 1 (*i.e.*, single character) for the Mo—O bonds.

Our DFT calculations reveal that the $(MoO_6)^{-6}$ cluster, in which a charge of $-6e$ is necessary to fulfil the octet rule, has a minimum total energy when the total spin equals zero, which means that the DOS is symmetric under alpha and beta spin channels (Fig. 5). That octahedron, which comes from the bulk perovskite, is distorted and has four, longer Mo—O bonds and two, shorter ones with lengths of 1.978 Å and 1.907 Å, respectively. Their corresponding, calculated, bond orders in the Mayer formalism are 1.059 and 1.121, respectively, in agreement with the above estimate. As expected, the Mayer bond order is greater for shorter bond lengths.

In turn, the $(FeO_6)^{-4}$ cluster has two, longer Fe—O bonds and four, shorter ones that measure 2.045 Å and 1.978 Å, respectively, and their corresponding Mayer bond orders are 0.746 and 0.812, again in some agreement with the estimate. The lowest total energy occurs for a spin value of $6\hbar$, which breaks the DOS symmetry between alpha and beta channels (Fig. 5).

An inspection of the molecular orbitals in the valence range of $(FeO_6)^{-4}$, between $-4\,eV$ and $0\,eV$, reveals that there are mainly three types of molecular orbitals (Fig. 5), which are combinations of the atomic orbitals present in single atoms (Fig. 3): (a) hybridisation among oxygen p states only, labelled p molecular orbitals (MO), (b) hybridisation among oxygen p states and iron e_g states via bonding, labelled e_g^b, and (c) bonding or antibonding hybridisation among oxygen p states and iron t_{2g}, denoted t_{2g}^b and t_{2g}^a, respectively. Notice that for the beta spin channel of $(FeO_6)^{-4}$ and the two spin channels of $(MoO_6)^{-6}$, the e_g^b DOS peak is at a lower energy than t_{2g}^b peak. Ligand-field theory (LFT) predicts that octahedral coordination around a transition metal atom situates the t_{2g} atomic states at lower energies than the e_g states. However, LFT arguments are insufficient to describe the nature of the electronic structure because they are based only on electrostatic repulsion among the negative charges of ligands and the electron cloud of the metal site, ignoring the formation of bonding or antibonding molecular combinations [22]. Thus, it would not necessarily be expected

that the energy-level order among t_{2g} and e_g orbitals must originate from LFT.

A comparison between the alpha and beta DOS in the $(FeO_6)^{-4}$ cluster reveals that not all of that states are spin-paired (Fig. 5), *i.e.*, the t_{2g}^a MOs are the source of the non-zero total spin because they are below the HOMO energy in the alpha channel, whereas in the beta channel the states are unoccupied (above HOMO). The p MOs, because they come only from oxygen atoms, are non-bonding. Thus, the two, p DOS peaks in each spin channel are located in the middle of the energy region of the bonding–antibonding splitting of e_g and t_{2g} states. Spin-induced shifting between the alpha and beta DOS causes the p MOs to lie just at the HOMO level in the beta channel, which then acquires a metallic character because the p MOs must all be occupied by octet electrons around oxygen atoms. The alpha channel, however, is semiconducting because this HOMO falls in the energy gap between its t_{2g}^a and e_g^a states. It is worth mentioning that near the HOMO level, or equivalently the Fermi level, the alpha and beta DOS for $(FeO_6)^{-4}$ resemble that of the Sr_2FeMoO_6 bulk (Fig. 2), *i.e.*, the origin of the half-metallic behaviour could be similar for both the cluster and the bulk systems. The presence of Mo in the bulk does not alter this physical origin because of its null spin in the octahedral coordination.

4. Conclusions

To understand the origin of half-metallic behaviour in the Sr_2FeMoO_6 double perovskite, we have determined, using Density Functional Theory, the total spin that minimises the electronic energy for single, transition-metal atoms and small clusters of isolated, oxygen octahedra centred around either a Fe or Mo atom. We have found that satisfying e_g states is critical for the total spin because, in the isolated Fe case, all of the spin-paired, valence electrons are in these states, thus leaving all if the t_{2g} states unpaired, along with the s states, to give a spin of $4\hbar$, which is mismatched with the octahedral oxygen coordination. On the contrary, the Mo atom has a spin of $6\hbar$, which is well suited to this coordination. Then, the $(FeO_6)^{-4}$ cluster has a non-zero spin due to the spin-unpaired band that is formed by t_{2g}^a molecular orbitals, which are below the HOMO level in the alpha channel and above the HOMO level in the beta channel. Consequently, although the $(FeO_6)^{-4}$ cluster has the required electrons to satisfy the octet rule, the bond strengths of this cluster are weak in comparison to the $(MoO_6)^{-6}$ cluster. In $(FeO_6)^{-4}$, the semiconducting and metallic characters of alpha and beta electrons, respectively, are due to the adjustment of spin-induced shifting between the alpha and beta DOS in such a way that the HOMO level in the beta channel falls just at the energy of the molecular orbitals composed solely of oxygen p atomic orbitals, which are occupied by octet electrons, and in turn, in the alpha channel, this HOMO level falls within the energy gap between t_{2g}^a and e_g^a molecular orbitals.

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