Electronic structure of half-metallic double perovskites

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We present the self-interaction corrected local spin density (SIC-LSD) electronic structure and total energy calculations, leading also to valencies of the ground state configurations, for the half-metallic double perovskites such as Sr₂FeMoO₆, Ba₂FeMoO₆, Ca₂FeMoO₆, and Ca₂FeReO₆. We conclude that the Fe and Mo (or Re) spin magnetic moments are anti-parallel aligned, and the magnitude of the hybridization induced moment on Mo does not vary much between the different compounds. The hybridization spin magnetic moment on Re is of the order of -1.1 μ_B, while that on Mo is about -0.4 μ_B, independently of the alkaline earth element. Also the electronic structure of all the compounds studied is very similar, with a well defined gap in the majority spin component and metallic density of states for the minority spin component, with highly hybridized Fe, Mo (or Re), and oxygen bands.

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I. INTRODUCTION

The interest in double perovskites A₂B'B''O₆, with A being alkaline earth (AE) ion, and the transition metal sites (B-sites) alternately occupied by different cations B' and B'', has really taken off with the paper by Kobayashi et al. ¹ demonstrating a convincing half-metallic behaviour in Sr₂FeMoO₆. The calculated electronic structure of this compound shows a gap in the majority spin component, while for the minority spin component one observes strongly hybridized Fe 3d(t₂g), Mo 4d(t₂g), and O 2p states at the Fermi level. Their study has also established that the latter compound exhibits tunnelling magnetoresistance (TMR) at low applied magnetic field even at room temperature. The double perovskites were discovered in 1960s ²,³,⁴,⁵,⁶ and seem to be metallic and ferromagnetic for B' = Fe, and B'' = Mo or Re. Unlike the manganites, they are stoichiometric and have large Curie temperatures, Tₐ, which makes them very promising for technological applications. The Sr₂FeMoO₆ compound has Tₐ of about 450 K, but also Ba₂FeMoO₆ and Ca₂FeMoO₆ have been shown to have interesting TMR characteristics and high Tₐ. ²⁷ Although Sr₂FeReO₆ (see Ref. ⁸) shows similar TMR properties to those of Sr₂FeMoO₆, recent studies claim that the Ca-compound, Ca₂FeReO₆, unlike Ca₂FeMoO₆, may be insulating. ²⁸ It has been suggested that the magnetic temperature Tₐ, and whether the ground state is metallic or insulating, vary as A is changed from Ba to Sr to Ca. ¹³ Also mis-site disorder may have pronounced effect on the magnetic properties of these compounds.¹¹,¹²

Recent experiments have established in Sr₂FeMoO₆ an electronic structure and configuration of five localized majority electrons (high spin state) on Fe and one delocalized electron shared between Mo and the other sites. We aim to validate this electronic structure by a more systematic study involving two other alkaline earths, Ca and Ba, as well as Sr. The aspect of a delocalized Mo electron is investigated by replacing Mo by Re and investigating the amount of delocalized electrons shared between Re and the other sites.

In this paper we present an application of the self-interaction corrected local spin density (SIC-LSD) approximation to the double perovskites Ba₂FeMoO₆, Ca₂FeMoO₆, Sr₂FeMoO₆, and Ca₂FeReO₆. Specifically, we concentrate on the electronic and magnetic properties of these compounds and in particular the size and relative orientation of the spin moments of Fe and Mo (or Re). In all the compounds the SIC-LSD calculations find a spin moment of about -0.4 μ_B on the Mo and about -1.1 μ_B on Re, with an opposite orientation to the respective spin moments on Fe sites. In addition, we find these double perovskites to be half-metallic, with a well defined gap in the spin-up density of states, and strong hybridization at the Fermi energy between the spin-down Fe 3d, Mo 4d (or Re 5d), and O 2p states.

The earlier first-principles calculations performed for double perovskites had to be done with GGA and implement theoretical optimisation of oxygen positions to obtain the half-metallic groundstate. Other applications were done with the LDA+U which similarly to SIC-LSD provides better description of localized states in solids. The present study is the first SIC-LSD application to double perovskites. Its advantage is that it treats both localized and delocalized states on equal footing, and therefore should be well suited for describing the localized nature of Fe 3d electrons as well as the Fe valency.

The remainder of the paper is organized as follows. In the next section, we briefly present the theoretical background of the SIC-LSD approach. In section III, the technical and computational details regarding the application to double perovskites are elaborated upon. In section IV, we present total energy and density of states calculations. There we also compare magnetic moments and determine valency of Fe in the studied compounds. The paper is concluded in section V.
II. THEORY

The basis of the SIC-LSD formalism is a self-interaction free total energy functional, \( E^{\text{SIC}} \), obtained by subtracting from the LSD total energy functional, \( E^{\text{LSD}} \), a spurious self-interaction of each occupied electron state \( \psi_{\alpha} \), namely

\[
E^{\text{SIC}} = E^{\text{LSD}} - \sum_{\alpha} \delta^{\text{SIC}}_{\alpha}.
\]

Here \( \alpha \) numbers the occupied states and the self-interaction correction for the state \( \alpha \) is

\[
\delta^{\text{SIC}}_{\alpha} = U[n_{\alpha}] + E^{\text{LSD}}_{xc} \bar{n}_{\alpha},
\]

with \( U[n_{\alpha}] \) being the Hartree energy and \( E^{\text{LSD}}_{xc} \bar{n}_{\alpha} \) the LSD exchange-correlation energy for the corresponding charge density \( n_{\alpha} \) and spin density \( \bar{n}_{\alpha} \). It is the LSD approximation to the exact exchange-correlation energy functional which gives rise to the spurious self-interaction. The exact exchange-correlation energy \( E^{\text{xc}} \) has the property that for any single electron spin density, \( \bar{n}_{\alpha} \), it cancels exactly the Hartree energy, namely

\[
U[n_{\alpha}] + E^{\text{xc}}[\bar{n}_{\alpha}] = 0.
\]

In the LSD approximation this cancellation does not take place, and for truly localized states the correction (Eq. (2)) can be substantially different from zero. For extended states in periodic solids the self-interaction vanishes. Consequently, the SIC-LSD approach can be viewed as a genuine extension of LSD in the sense that the self-interaction correction is only finite for spatially localized states, while for Bloch-like single-particle states \( E^{\text{SIC}} \) is equal to \( E^{\text{LSD}} \). Thus, the LSD minimum is also a local minimum of \( E^{\text{SIC}} \).

It follows from minimization of Eq. (1) that within the SIC-LSD approach such localized electrons move in a different potential than the delocalized valence electrons which respond to the effective LSD potential. For example, in the case of the double perovskites, five (Fe\(^{3+}\)) or six (Fe\(^{2+}\)) Fe \( d \) electrons move in the SIC potential, while all other electrons feel only the effective LSD potential. Thus, by including an explicit energy contribution for an electron to localize, the ab-initio SIC-LSD describes both localized and delocalized electrons on an equal footing, leading to a greatly improved description of static Coulomb correlation effects over the LSD approximation. Assuming various atomic configurations, consisting of different numbers of localized states, one can explore the corresponding local minima of the SIC-LSD energy functional of Eq. (1), and determine the lowest energy solution and valency. The advantage of the SIC-LSD formalism is that for such systems as transition metal oxides or rare earth compounds the lowest energy solution will describe the situation where some single-electron states may not be of Bloch-like form. Regarding the valency, it is determined here as the integer number of electrons available for band formation, i.e.,

\[
N_{\text{val}} = Z - N_{\text{core}} - N_{\text{SIC}},
\]

where \( Z \) is the atomic number (26 for Fe), \( N_{\text{core}} \) is the number of core (and semi-core) electrons (18 for Fe), and \( N_{\text{SIC}} \) is the number of localized, i.e., self-interaction corrected, states (either five or six, respectively for Fe\(^{3+}\) and Fe\(^{2+}\)).

In the present work the SIC-LSD approach has been implemented within the linear muffin-tin-orbital (LMTO) band structure method in the tight-binding representation, where the electron wave functions are expanded in terms of the screened muffin-tin orbitals, and the minimization of \( E^{\text{SIC}} \) becomes a non-linear problem in the expansion coefficients. The atomic spheres approximation (ASA) has been used, according to which the polyhedral Wigner-Seitz cell is approximated by slightly overlapping atom centered spheres, with a total volume equal to the actual crystal volume.

III. CALCULATIONAL DETAILS

All the compounds studied here crystallize in ordered double perovskite structures. The simplest system is Ba\(_2\)FeMoO\(_6\) which occurs in the cubic structure, with the Fm\(_{3m}\) space group. The Sr\(_2\)FeMoO\(_6\) compound has the body-centered tetragonal \( bct \) structure, with the I\(_4/mmm\) space group. Replacing Sr by a smaller still Ca element results in a monoclinic structure for the Ca\(_2\)FeMoO\(_6\) and Ca\(_2\)FeReO\(_6\) compounds, with the P\(_{2}1/n\) space group. The experimental lattice parameters used in the calculations for the first three compounds have been taken from Refs. (9) and (10). For the NaMoO\(_3\) compounds two formula units (20 atoms) have been necessary. In addition, for a better space filling also eight empty spheres have been introduced in Re-compound. Concerning the linear muffin-tin basis functions, we have used 4\( s \), 4\( p \), and 3\( d \) partial waves on all Fe atoms, and treated them as low-waves, on the oxygens (2\( s \) and 2\( p \)) and Ca (4\( s \) and 3\( p \)) in addition to the \( s \) and \( p \) low partial waves, 3\( d \) partial waves have been treated as intermediate. On the empty spheres the 1\( s \)–waves have been considered as low- and the 2\( p \)'s as intermediate-waves. On the Ba (6\( s \), 5\( p \), and 5\( d \)), Sr (5\( s \), 4\( p \), and 4\( d \)), Mo (5\( s \), 5\( p \), and 4\( d \)), and Re (6\( s \), 6\( p \), and 5\( d \)) atoms, the \( s \), \( p \), and \( d \)–waves have been treated as low and the 4\( f \)–waves as intermediate. In all the cases, the SIC-LSD calculations have been started using the self-consistent LSD charge densities with the Perdew and Zunger exchange-correlation potential. Mostly the Fe 3\( d \) electrons have been treated as localized states (in some test calculations we have also treated Mo \( d \)'s as localized), meaning that they have been moving in the self-interaction corrected LSD potentials, while all other electrons have seen the effective LSD potential. In all the cases studied, we have allowed for a number of different configurations of SIC 3\( d \) states to find the ground state.
solution. Namely, treating five $3d$ electrons on the Fe's as localized, moving in the SIC-LSD effective potentials, meant that the Fe ions were trivalent. Similarly, for divalent Fe's, six $3d$ electrons on the Fe's were considered to be localized. By comparing total energies corresponding to different localized Fe $3d$ configurations we have been able to find the ground state configuration which for all the compounds has been that of Fe$^{3+}$. However, other configurations have been energetically close, with the Fe$^{2+}$ being insulating in all Mo-based compounds. Although, unlike in the work by Kobayashi et al. optimizing oxygen positions in Sr$_2$FeMoO$_6$ was not needed for obtaining half-metallic ground state, however in order to study its effect on the magnetic properties and to make contact with Ref. 1 for this compound we have also performed calculations for the scenario where the theoretically optimized positions of Ref. 1 have been implemented.

### IV. RESULTS AND DISCUSSION

The SIC-LSD spin-polarized total densities of states (DOS) per formula unit are presented in Fig. 1 for Ca$_2$FeReO$_6$, Ca$_2$FeMoO$_6$, Sr$_2$FeMoO$_6$, and Ba$_2$FeMoO$_6$ compounds. There we also show the O 2$p$ spin polarized densities of states. The spin polarized densities of states of Fe $3d$ and Mo $4d$ and Re $5d$ are given in Fig. 2, for all the different compounds. First thing to note is the similarity between the densities of states, independently of which alkaline earth compound is considered. For all compounds we see convincing half-metallic behaviour, with well defined gap at the Fermi energy in the majority spin channel, and strongly hybridized Fe $3d$, Mo $4d$ (or Re $5d$) and oxygen $2p$ states, in the other spin channel. The half-metallic character is reflected in the total spin magnetic moments that are all integer, as can be seen in Table I, where we summarize the total and species decomposed spin moments for all the compounds together with the respective volumes per formula unit. As can be seen in Fig. 1, the valence band consists predominantly of O $2p$ states, but contains a small admixture of Mo, Re- and Fe $d$–states. The unoccupied majority Re $d$ bands lie closer to the Fermi energy in comparison with the unoccupied majority Mo $d$ states in Ca$_2$FeMoO$_6$. We can also see that the unoccupied Mo $d$ states move closer to the Fermi energy as one traverses the series in the sequence Ca, Sr and Ba. However, the majority spin channel maintains a band gap for all these compounds. In the minority spin channel these systems are metallic with O $2p$, Mo $4d$ and Fe $3d$ states straddling the Fermi energy. These are the states which reduce the Fe magnetic moment from essentially $5 \mu_B$ to 3.87 $\mu_B$ (Ca$_2$FeReO$_6$), 3.76 $\mu_B$ (Ca$_2$FeMoO$_6$), 3.71 $\mu_B$ (Sr$_2$FeMoO$_6$) and 3.81 $\mu_B$ (Ba$_2$FeMoO$_6$) (see Table I). From these DOS one can also expect the oxygen to acquire a moment. This happens according to Table I and it is parallel to the Fe spin moment and is non-negligible at around 0.1 $\mu_B$. However it is the Mo and Re sites which are of interest. Substantial spin magnetic moments of -0.4 $\mu_B$ and -1.1 $\mu_B$ are found on the Mo and Re sites respectively. This results from the strong hybridization with Fe in the minority spin channel. This also explains the antiparallel alignment of these spin magnetic moments with respect to Fe.

The densities of states in the majority spin channels for these four compounds are insulating, since a fully occupied O $p$ band and five localized Fe $d$ states accomodate $23 \times 3+5=23$ valence electrons. Of the remaining 19 or 20 valence electrons for the Mo and Re compounds respectively, 18 fill up the minority O $p$ band. This leaves one or two electrons for the Mo and Re compounds to occupy the minority states which straddle the Fermi level, and have Fe $d$, Mo or Re $d$ and oxygen $p$ character. We have also considered a scenario of localising through the self-interaction correction one Fe (Mo) $d$ state in the minority spin channel describing Fe$^{5+}$ (Mo$^{5+}$) respectively. In this case the states straddling the Fermi energy which accomodate this one electron are pulled down below the bottom of the O $p$ valence bands and we also obtain an insulating state in the minority spin channel. However, these scenarios are energetically unfavourable by 70 mRy and 103 mRy for Mo$^{5+}$ and Fe$^{2+}$ respectively. Obviously the gain in localisation energy does not compensate the loss in hybridization energy.

It is interesting to see how little the magnetic properties of these compounds are affected by the size of the alkaline earth atom. There is hardly any variation in the size of the Fe and Mo or Re moments with the substantial change in volume of the compounds (see Table I). Also the reduction in the size of the Fe and Mo spin moments for Sr$_2$FeMoO$_6$, as a result of implementing theoretical optimization of oxygen positions, as given by Kobayashi et al. does not seem too important although brings the size of our calculated moments close to the values of Ref. 1. The reduced values are given in parenthesis in the fourth column of Table I. Concerning spin moments of the other species, the small changes cannot be resolved when rounded off to two digits after the decimal point.
Finally, we would like to comment on the valency of Fe and the ground state configuration for all the compounds. Regarding energetics, in all SIC-LSD calculations the Fe$^{3+}$ configuration has been most energetically favourable, followed by Fe$^{4+}$ (energetically unfavourable by 53, 61 and 83 mRy in Ba-, Sr- and Ca-compounds, respectively), and Fe$^{2+}$ solution, at least twice as unfavourable as the former configuration (specifically, by 103, 122 and 250 mRy). Moreover, treating also Mo $d$ states as localized has been energetically unfavourable, and the more states have been localized the more unfavourable solutions have been obtained.

V. CONCLUSIONS

In summary, the SIC-LSD approach has been applied to four different double perovskites, and in all cases the half-metallic ground state solutions have been obtained. This seems to be a rather generic result for double perovskites involving Fe with a filled majority d shell and transition metal ions which donate few, one (Mo) to two (Re), d electrons. This type of materials could therefore be a fruitful playground for the discovery of new spintronics materials. In particular, also the Ca$_2$FeReO$_6$ has been found to be half-metallic, and not insulating as indicated in Ref. 8. The electronic structure for all studied compounds appears to be very similar, with a gap in the majority spin component, and strongly hybridized bands at the Fermi level for the minority spin component. The spin magnetic moments induced by hybridization on the Mo sites have been of the similar magnitude, about -0.4 $\mu_B$, independently of the alkaline earth element, while that of Re is of the order of -1.1 $\mu_B$. These induced spin magnetic moments are antiparallel aligned with the Fe spin moment. Concerning the Fe valency, for all the compounds the trivalent configuration has been most favourable, followed by the tetravalent and divalent ones.

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FIG. 1: Spin polarized total and oxygen 2p densities of states per formula unit, for Ca$_2$FeReO$_6$ (top row, left), Ca$_2$FeMoO$_6$ (top row, right), Sr$_2$FeMoO$_6$ (bottom row, left), and Ba$_2$FeMoO$_6$ (bottom row, right).
FIG. 2: Spin polarized Fe \(3d\) and Re \(5d\) densities of states per formula unit in \(\text{Ca}_2\text{FeReO}_6\) (top row, left), and spin polarized Fe \(3d\) and Mo \(4d\) densities of states per formula unit in \(\text{Ca}_2\text{FeMoO}_6\) (top row, right), \(\text{Sr}_2\text{FeMoO}_6\) (bottom row, left), and \(\text{Ba}_2\text{FeMoO}_6\) (bottom row, right).