

Electronic structure of half-metallic double perovskitesZ. Szotek,¹ W. M. Temmerman,¹ A. Svane,² L. Petit,² and H. Winter³¹ *Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, Cheshire, United Kingdom*² *Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark*³ *INFP, Forschungszentrum Karlsruhe GmbH, Postfach 3640, D-76021 Karlsruhe, Germany*

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We present the self-interaction corrected local spin density (SIC-LSD) electronic structure and total energy calculations, leading also to Fe valencies of the ground state configurations, for the double perovskites such as $\text{Sr}_2\text{FeMoO}_6$, $\text{Ba}_2\text{FeMoO}_6$, $\text{Ca}_2\text{FeMoO}_6$, and $\text{Ca}_2\text{FeReO}_6$. 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 $-1.1\mu_B$, while that on Mo is about $-0.4\mu_B$, 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. All insulating solutions found for $\text{Ca}_2\text{FeReO}_6$ are energetically unfavorable with respect to the calculated half-metallic ground state.

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I. INTRODUCTION

The interest in double perovskites $A_2B'B''O_6$, with A being an 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 behavior in $\text{Sr}_2\text{FeMoO}_6$. 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 $3d(t_{2g})$, Mo $4d(t_{2g})$, 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 1960's (Refs. 2–6) and seem to be metallic and ferromagnetic for $B' = \text{Fe}$, and $B'' = \text{Mo}$ or Re. Unlike the manganites, they are stoichiometric and have large Curie temperatures T_c which makes them very promising for technological applications. The $\text{Sr}_2\text{FeMoO}_6$ compound has T_c of about 450 K, but also $\text{Ba}_2\text{FeMoO}_6$ and $\text{Ca}_2\text{FeMoO}_6$ have been shown to have interesting TMR characteristics and high T_c 's.⁷ Although $\text{Sr}_2\text{FeReO}_6$ (see Ref. 8) shows similar TMR properties to those of $\text{Sr}_2\text{FeMoO}_6$, recent studies claim that the Ca compound $\text{Ca}_2\text{FeReO}_6$, unlike $\text{Ca}_2\text{FeMoO}_6$, may be insulating.⁹ It has been suggested that the magnetic temperature T_c , and whether the ground state is metallic or insulating, vary as A is changed from Ba to Sr to Ca.¹⁰ Also mis-site disorder may have pronounced effect on the magnetic properties of these compounds.^{11,12}

Recent experiments¹³ have established in $\text{Sr}_2\text{FeMoO}_6$ 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 inspecting the amount of delocal-

ized 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 $\text{Ba}_2\text{FeMoO}_6$, $\text{Ca}_2\text{FeMoO}_6$, $\text{Sr}_2\text{FeMoO}_6$, and $\text{Ca}_2\text{FeReO}_6$. 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 $-0.4\mu_B$ on the Mo and about $-1.1\mu_B$ 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 optimization of oxygen positions to obtain the half-metallic ground state.^{1,14} Other applications were done with LSD and LDA+U.^{15,16} The latter, similarly to SIC-LSD, provides better description of localized states in solids, however, is rather dependent on the value of the on-site Coulomb interaction U , which is treated as adjustable parameter. 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, without adjustable parameters. The method is well suited to study the localized nature of Fe $3d$ electrons, and in particular, allows to determine the Fe valency in these compounds.

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 Sec. III, the technical and computational details regarding the application to double perovskites are elaborated upon. In Sec. IV, we present total energy and density of states calculations. There we also compare magnetic moments and determine the ground state valency

of Fe in the studied compounds. The paper is concluded in Sec. V.

II. THEORY

The basis of the SIC-LSD formalism is a self-interaction free total energy functional E^{SIC} obtained by subtracting from the LSD total energy functional E^{LSD} a spurious self-interaction of each occupied electron state ψ_α ,¹⁷ namely,

$$E^{\text{SIC}} = E^{\text{LSD}} - \sum_{\alpha}^{\text{occ}} \delta_{\alpha}^{\text{SIC}}. \quad (1)$$

Here α numbers the occupied states and the self-interaction correction for the state α is

$$\delta_{\alpha}^{\text{SIC}} = U[n_{\alpha}] + E_{\text{xc}}^{\text{LSD}}[\bar{n}_{\alpha}], \quad (2)$$

with $U[n_{\alpha}]$ being the Hartree energy and $E_{\text{xc}}^{\text{LSD}}[\bar{n}_{\alpha}]$ the LSD exchange-correlation energy for the corresponding charge density n_{α} and spin density \bar{n}_{α} . 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_{xc} has the property that for any single electron spin density \bar{n}_{α} , it cancels exactly the Hartree energy, namely,

$$U[n_{\alpha}] + E_{\text{xc}}[\bar{n}_{\alpha}] = 0. \quad (3)$$

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^{SIC} is equal to E^{LSD} . Thus, the LSD minimum is also a local minimum of E^{SIC} . A question arises, whether there exist other competitive minima, corresponding to a finite number of localized states, which could benefit from the self-interaction term without loosing too much band formation energy. This usually will be the case for rather well localized electrons such as the $3d$ electrons in transition metal oxides^{18,19} or the $4f$ electrons in rare earth compounds.²⁰ 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 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, and determination of valency.

In order to make the connection between valency and localization more explicit it is useful to define the nominal valency²⁰ as

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

where Z is the atomic number (26 for Fe), N_{core} is the number of core (and semicore) electrons (18 for Fe), and N_{SIC} is the number of localized, i.e., self-interaction corrected, states (either five or six, respectively for Fe^{3+} and Fe^{2+}). Thus, in this formulation the valency is equal to the integer number of electrons available for band formation. The localized electrons do not participate in bonding.

To find the valency we assume various atomic configurations, consisting of different numbers of localized states, and minimize the SIC-LSD energy functional of Eq. (1) with respect to the number of localized electrons. The SIC-LSD formalism is governed by the energetics due to the fact that for each orbital the SIC differentiates between the energy gain due to hybridization of the orbital with the valence bands and the energy gain upon localization of the orbital. Whichever wins determines if the orbital is part of the valence band or not and in this manner also leads to the evaluation of the valency of elements involved. The SIC depends on the choice of orbitals and its value can differ substantially as a result of this. Therefore, one has to be guided by the energetics in defining the most optimally localized orbitals to determine the absolute energy minimum of the SIC-LSD energy functional. 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. As mentioned, for double perovskites these would be the Fe $3d$ states, but not the O $2p$ or Mo $4d$ and Re $5d$ states since, as we shall see later, treating them as localized states is energetically unfavorable.

In the present work the SIC-LSD approach has been implemented²¹ within the linear muffin-tin-orbital (LMTO) band structure method²² in the tight-binding representation,²³ where the electron wave functions are expanded in terms of the screened muffin-tin orbitals, and the minimization of E^{SIC} becomes a nonlinear 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 $\text{Ba}_2\text{FeMoO}_6$ which occurs in the cubic structure, with the $Fm\bar{3}m$ space group. The $\text{Sr}_2\text{FeMoO}_6$ compound has the body-centered tetragonal bct structure, with the $I4/mmm$ space group. Replacing Sr by a smaller still Ca element results in a monoclinic structure for the $\text{Ca}_2\text{FeMoO}_6$ and $\text{Ca}_2\text{FeReO}_6$ compounds, with the $P2_1/n$ space group. The experimental lattice parameters used in the calculations for the first three compounds have been taken from Refs. 7 and 1, and for the last compound from Ref. 9. For the Ca 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

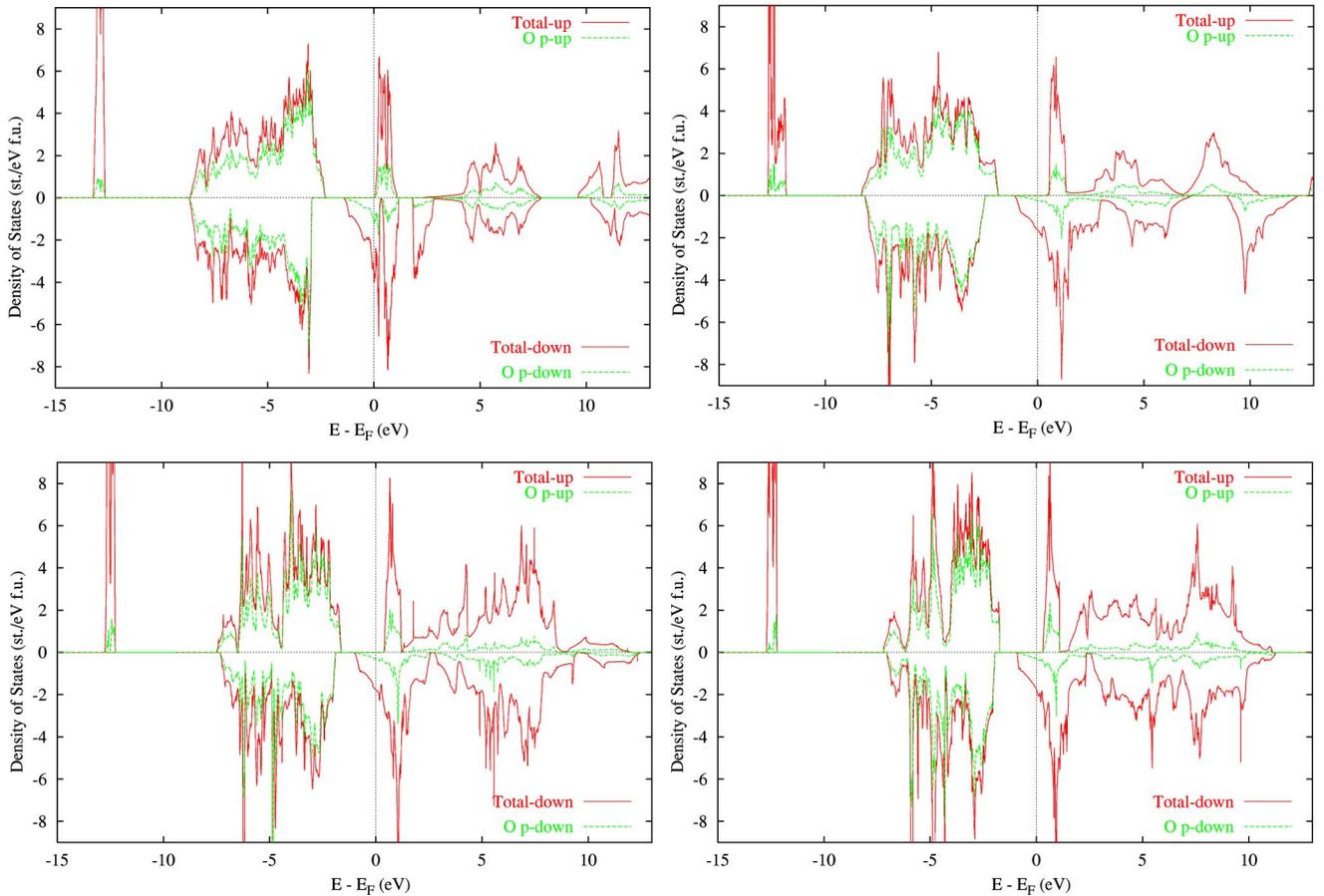


FIG. 1. (Color online) Spin polarized total and oxygen $2p$ densities of states per formula unit for $\text{Ca}_2\text{FeReO}_6$ (top row, left), $\text{Ca}_2\text{FeMoO}_6$ (top row, right), $\text{Sr}_2\text{FeMoO}_6$ (bottom row, left), and $\text{Ba}_2\text{FeMoO}_6$ (bottom row, right).

muffin-tin basis functions, we have used $4s$, $4p$, and $3d$ partial waves on all Fe atoms, and treated them as low waves, on the oxygens ($2s$ and $2p$) and Ca ($4s$ and $3p$) in addition to the s and p low partial waves, $3d$ partial waves have been treated as intermediate.²⁴ On the empty spheres the $1s$ waves have been considered as low- and the $2p$'s as intermediate waves. On the Ba ($6s$, $5p$, and $5d$), Sr ($5s$, $4p$, and $4d$), Mo ($5s$, $5p$, and $4d$), and Re ($6s$, $6p$, and $5d$) atoms, the s , p , and d waves have been treated as low and the $4f$ 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.¹⁷ Mostly the Fe $3d$ electrons have been treated as localized states, meaning that they have been moving in the self-interaction corrected LSD potentials, while all other electrons have seen the effective LSD potential. However for $\text{Sr}_2\text{FeMoO}_6$ and $\text{Ca}_2\text{FeReO}_6$ we have also studied a number of scenarios where in addition Mo $4d$'s and Re $5d$'s, respectively, have been treated as localized states. In all the cases studied, we have allowed for a number of different configurations of SIC d states to find the ground state solution. By comparing total energies corresponding to different localized configurations we have been able to establish that the ground state Fe configuration 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 when treating Mo $4d$'s as itinerant states. Although, unlike in the work by Kobayashi *et al.*,¹ optimizing oxygen positions in $\text{Sr}_2\text{FeMoO}_6$ 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.¹³

IV. RESULTS AND DISCUSSION

The SIC-LSD spin-polarized, ground state, total densities of states (DOS) per formula unit are presented in Fig. 1 for $\text{Ca}_2\text{FeReO}_6$, $\text{Ca}_2\text{FeMoO}_6$, $\text{Sr}_2\text{FeMoO}_6$, and $\text{Ba}_2\text{FeMoO}_6$ compounds. There we also show the O $2p$ 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, including $\text{Ca}_2\text{FeReO}_6$, we see convincing half-metallic behavior, 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

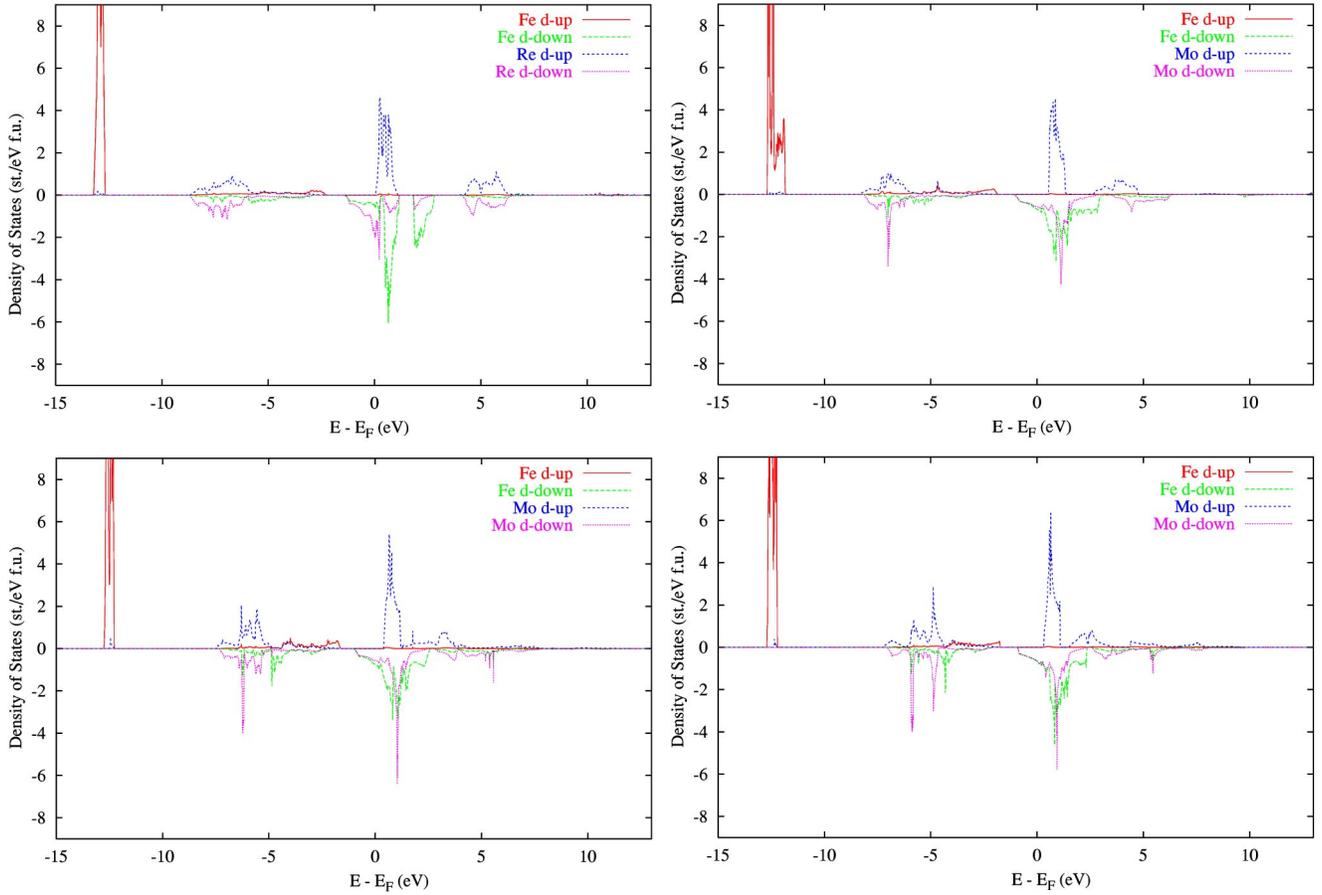


FIG. 2. (Color online) Spin polarized Fe 3*d* and Re 5*d* densities of states per formula unit in $\text{Ca}_2\text{FeReO}_6$ (top row, left), and spin polarized Fe 3*d* and Mo 4*d* densities of states per formula unit in $\text{Ca}_2\text{FeMoO}_6$ (top row, right), $\text{Sr}_2\text{FeMoO}_6$ (bottom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

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 2*p* 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

TABLE I. Total and species decomposed spin magnetic moments (in μ_B) as calculated self-consistently within SIC-LSD band structure method. In the last row the respective volumes per formula unit are quoted [in (atomic units)³].

Moment	$\text{Ca}_2\text{FeReO}_6$	$\text{Ca}_2\text{FeMoO}_6$	$\text{Sr}_2\text{FeMoO}_6$	$\text{Ba}_2\text{FeMoO}_6$
M_{total}	3.00	4.00	4.00 (4.00)	4.00
M_{Fe}	3.87	3.76	3.71 (3.65)	3.81
M_{Mo}		-0.40	-0.43 (-0.35)	-0.41
M_{Re}	-1.12			
M_{AE}	-0.02	0.01	0.02 (0.02)	0.02
M_{O1}	0.02	0.10	0.11 (0.11)	0.09
M_{O2}	0.01	0.11	0.11 (0.11)	
M_{O3}	0.11	0.11		
Volume	773.8	777.5	830.2	884.0

$\text{Ca}_2\text{FeMoO}_6$. 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 2*p*, Mo 4*d* and Fe 3*d* states straddling the Fermi energy. These are the states which reduce the Fe magnetic moment from essentially $5\mu_B$ to $3.87\mu_B$ ($\text{Ca}_2\text{FeReO}_6$), $3.76\mu_B$ ($\text{Ca}_2\text{FeMoO}_6$), $3.71\mu_B$ ($\text{Sr}_2\text{FeMoO}_6$), and $3.81\mu_B$ ($\text{Ba}_2\text{FeMoO}_6$) (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. Regarding comparison with the LDA+U work,^{15,16} for the relevant compounds, our results are in good agreement with Ref. 15. The agreement with the results of Ref. 16 is less satisfactory, as their considerably larger magnetic moments arise due to introduction of $U = 1.0$ eV for Mo 4*d* and Re 5*d* states. Our calculations for

Mo compounds find all scenarios with localized Mo $4d$ states to be energetically unfavorable with respect to treating them as itinerant. The situation is similar in the Re compounds.

The densities of states in the majority spin channels of these four compounds are insulating, since a fully occupied O p band and five localized Fe d states accommodate 23 ($6 \times 3 + 5 = 23$) 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 localizing through the self-interaction correction one Fe (Mo) d state in the minority spin channel describing Fe^{2+} (Mo^{5+}), respectively. In this case the states straddling the Fermi energy which accommodate 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 unfavorable by 70 mRy and 103 mRy for Mo^{5+} and Fe^{2+} , respectively. Obviously the gain in localization 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 $\text{Sr}_2\text{FeMoO}_6$, as a result of implementing theoretical optimization of oxygen positions, as given by Kobayashi *et al.*,¹ 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 for the Mo compounds, in all SIC-LSD calculations the Fe^{3+} configuration has been most energetically favorable, followed by Fe^{4+} (energetically unfavorable by 53, 61, and 42 mRy per formula unit in Ba, Sr, and Ca compounds, respectively), and Fe^{2+} configuration, at least twice as unfavorable as the former configuration (specifically, by 103, 122, and 125 mRy per formula unit). Moreover, treating also Mo d states as localized has been energetically unfavorable, and the more states have been localized the more unfavourable solutions have been obtained. In short, we obtain the nominal valencies of Fe^{3+} and Mo^{6+} in the ground state.

For $\text{Ca}_2\text{FeReO}_6$, as seen in Fig. 1, the ground state predicted by the SIC-LSD method is a convincing half-metal, with the nominal Fe valency of $3+$. In this case, the Re $5d$ states are described as itinerant states. It is important to note that we have identified three insulating solutions, corresponding to cases where six Fe $3d(\text{Fe}^{2+})$ and one Re $5d(\text{Re}^{6+})$ electrons have been treated as localized. In the first of them, apart from five majority Fe $3d$ electrons, also

the minority Fe $3d$ electron and minority Re $5d$ electron, both with the character of the yz spherical harmonic, have been described as localized states. In the second case, the minority Fe and Re electrons, both with the character of the zx spherical harmonic, have been treated as localized states, and in the third scenario the minority Fe and Re electrons, both with the character of the x^2-y^2 spherical harmonic, have been localized. However, all of these insulating solutions have been energetically unfavorable respectively by about 235, 220, and 195 mRy per formula unit, as compared to the ground state configuration with Fe^{3+} and all Re $5d$'s itinerant. Moreover, these insulating states, with $\text{Fe}^{2+}/\text{Re}^{6+}$ ionic configuration, are in contradiction to the experimental evidence,⁹ stating firmly that in this compound Fe occurs in a trivalent configuration.

Maintaining $\text{Fe}^{3+}/\text{Re}^{5+}$ ionic configuration we have also explored a number of scenarios where all majority Fe d electrons and two minority Re $5d$ electrons have been localized. However, all except two scenarios have given rise to half-metallic states, but unfavorable with respect to the ground state by about 255–395 mRy per formula unit, depending on the symmetry of the two minority Re electrons. The first of the two exceptions refers to the case where two minority Re $5d$ electrons with the characters of the spherical harmonics zx and x^2-y^2 have been described as localized, while in the second case two minority Re $5d$ electrons with the characters of the spherical harmonics yz and zx have been considered. The first scenario has given rise to an insulating state, however, unfavorable energetically by about 140 mRy per formula unit with respect to the ground state. The second scenario has delivered a nearly insulating state with zero DOS in one spin component and DOS of about 0.1 (states/spin eV formula unit) in the other spin component. Unfortunately, this state has also been unfavorable energetically by about 170 mRy per formula unit, with respect to the ground state.

Treating all five Fe majority d electrons and one minority Re d electron as localized has also led to half-metallic and not insulating solutions, unfavorable by 60–205 mRy with respect to the calculated ground state, depending on the symmetry of the one localized minority Re d electron. Therefore, we conclude that without invoking other circumstances, perhaps such as mis-site disorder, it is not possible to realize an insulating ground state for $\text{Ca}_2\text{FeReO}_6$ within the SIC-LSD description. The implementation of mis-site disorder would, however, be computationally very demanding as large super-cells would need to be utilized.

V. CONCLUSIONS

In summary, the *ab initio* 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 filled majority d shell, filled O p band, and Mo and Re transition metal ions which see their minority d bands occupied by one (Mo) to two (Re) electrons. This type of compounds could therefore be a fruitful playground for the discovery of new spintronics materials. In particular, also the $\text{Ca}_2\text{FeReO}_6$ has been found to be half-

metallic, and not insulating as indicated in Ref. 9. The insulating states found for $\text{Ca}_2\text{FeReO}_6$ when treating six Fe $3d$ electrons (Fe^{2+}) and one Re $5d$ electron (Re^{6+}) as localized, have been unfavorable by about 195–235 mRy/formula unit. Also, the insulating and nearly insulating states, obtained for the cases where five majority Fe $3d(\text{Fe}^{3+})$ electrons and two minority Re $5d(\text{Re}^{5+})$ electrons have been treated as localized, have been unfavorable, respectively by 140 and 170 mRy per formula unit with respect to the calculated half-metallic ground state of this compound.

The calculated ground state 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 favorable, followed by the tetravalent and divalent ones. Note that this is the only *ab initio* determination of Fe valency in these double perovskites.

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