Optimized effective potential model for the double perovskites $\text{Sr}_{2-x} \text{Y}_x \text{VMoO}_6$ and $\text{Sr}_{2-x} \text{Y}_x \text{VTcO}_6$

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Abstract

In an attempt to explore half-metallic properties of the double perovskites $\text{Sr}_{2-x} \text{Y}_x \text{VMoO}_6$ and $\text{Sr}_{2-x} \text{Y}_x \text{VTcO}_6$, we construct an effective low-energy model, which describes the behavior of the $t_{2g}$ states of these compounds. All parameters of such a model are derived rigorously on the basis of first-principles electronic structure calculations. In order to solve this model, we employ the optimized effective potential method and treat the correlation interactions in the random phase approximation. Although correlation interactions considerably reduce the intraatomic exchange splitting in comparison with the Hartree–Fock approach, this splitting still substantially exceeds the typical values obtained in the local-spin-density approximation (LSDA), which alters many predictions based on the LSDA. Our main results are summarized as follows. (i) All ferromagnetic states are expected to be half-metallic. However, their energies are generally higher than those of the ferrimagnetic ordering between V and Mo/Tc sites (except $\text{Sr}_2\text{VMoO}_6$). (ii) All ferrimagnetic states are metallic (except fully insulating $\text{Y}_2\text{VTcO}_6$) and no half-metallic antiferromagnetism has been found. (iii) Moreover, many of the ferrimagnetic structures appear to be unstable with respect to the spin-spiral alignment. Thus, the true magnetic ground state of these systems is expected to be more complex. In addition, we discuss several methodological issues related to nonuniqueness of the effective potential for the half-metallic and magnetic insulating states.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently double perovskites $\text{A}_{2-x}\text{A'}_x\text{BB'O}_6$, where A and A' are the di- and three-valent (typically alkali- or rare-earth) elements, respectively, and B (B') are the transition-metal elements, have attracted considerable attention [1], following experimental discoveries of the room-temperature ferromagnetism and the colossal-magnetoresistance effect in $\text{Sr}_2\text{FeMoO}_6$ [2], which make these materials promising in the field of spin electronics. The extraordinary properties of the double perovskites are frequently attributed to their half-metallic electronic structure, although the situation can be rather subtle [3]. Nevertheless, the first discoveries have sparked new research activity aiming at the systematic search for half-metallic double-perovskite materials. Many such predictions have been made on the basis of first-principles electronic structure calculations. Besides ferromagnetic compounds, particular attention was paid to the half-metallic antiferromagnets—the systems where the half-metallicity coexists with zero net magnetization [4, 5]. However, even apart from the technological issues, related to the defects in the double-perovskite structure, there are a number of fundamental problems, which call many predictions into question:

(i) Most of the calculations are based on the local-spin-density approximation (LSDA) or its refinement—the generalized gradient approximation—which have many limitations for the transition-metal oxides. In particular, all these theories employ the functional dependence of the exchange–correlation energy obtained in the limit of a homogeneous electron gas. However, many unique properties of the double perovskites are related to the alternation of two different transition-metal sites B...
and B', and in this sense the systems are essentially inhomogeneous. Thus, even though the double-perovskite compounds may be classified as itinerant electron magnets, it does not necessarily mean that their properties are well described within the LSDA.

(ii) In the vast majority of calculations, it is believed that the LSDA + U technique, which incorporates the physics of on-site Coulomb interactions [6, 7], can serve as a reasonable alternative to the LSDA and provide a superior description for the double perovskites. However, the LSDA + U scheme is ill-defined, particularly for the double perovskites: there are many uncertainties related to the values of the on-site Coulomb repulsion U at the sites B and B', which are frequently taken as adjustable parameters, the subspace of ‘localized orbitals’, and the double-counting term [8]. Moreover, the total energy in the LSDA + U is taken in the ad hoc form, which is valid only in the atomic limit and equivalent to some constrained density functional theory [7]. There is no guarantee that the same approximations will work for the itinerant electron systems. In such a situation, all predictions of the half-metallic behavior for the double perovskites should be taken very cautiously.

In this paper we will illustrate how these problems could be resolved by applying the optimized effective potential (OEP) method, and what the consequences on the electronic and magnetic properties of the double perovskites could be. The OEP method is formulated in the spirit of the Kohn–Sham density functional theory [9] by introducing an auxiliary one-electron problem, which is specified by some local effective potential and which is used in the search for the true spin density through the minimization of the total energy of the system [10–13]. In this work we will apply the OEP technique for the solution of the low-energy model, constructed for the double perovskites, where all the parameters are derived rigorously, on the basis of first-principles electronic structure calculations. Besides simplicity, such a model analysis typically allows one to concentrate directly on the microscopic picture, underlying the considered phenomena. For the first applications of the OEP model, it is more convenient to consider the t_{2g} systems, whose electronic and magnetic properties are predetermined by the behavior of the t_{2g} states of the sites B and B', located near the Fermi level. In this case, the effective potential is specified by only three parameters, which should be used for the minimization of the total energy.

The OEP method was introduced in 1976 by Talman and Shadwick [10], in an attempt to minimize the Hartree–Fock total energy for atoms in the spirit of the Kohn–Sham density functional theory without additional approximations for the exchange potential (besides spherical averaging). Since then, OEP has been regarded as one of the possible routes to go beyond the LSDA in the electronic structure calculations. The method was successfully applied for atoms and molecules [14], as well as for transition-metal monoxides [11–13]. In particular, it is very important that, unlike the conventional LSDA, OEP is able to reproduce the insulating ground state for the whole series of transition-metal monoxides MnO, FeO, CoO and NiO [13]. Nevertheless, the method is very computationally demanding, and so far most of the OEP calculations are limited by the so-called exact exchange (EXX) formulations, which is based on minimization of the Hartree–Fock energy and totally neglects the correlation interactions. However, EXX is known to be a very poor approximation for the itinerant electron systems, such as ferromagnetic transition metals Fe, Co and Ni [12]. Therefore, as was demonstrated by Kotani [12], the next important step was to combine EXX with the correlation energy in the random phase approximation (RPA). In the homogeneous electron gas limit, it would correspond to the well-known Barth–Hedin approximation for the exchange–correlation potential [15]. Nevertheless, the main difference of the EXX + RPA scheme [12] is that it does not employ the homogeneous electron gas picture. The EXX + RPA greatly improves the description for the transition metals as well as for the insulating MnO [12]. In our work, we will use the same strategy, but reformulated for the solution of the low-energy model. Being based on the previous calculations, we hope that this scheme will provide a reliable description for both metallic and insulating states of the double perovskites.

We select two prototypical examples Sr_{2−x}Y_xVMO_6 and Sr_{2−x}Y_xVTcO_6, crystallizing in the undistorted double-perovskite structure with the lattice parameters a = 7.846 Å and 7.899 Å, respectively. In fact, a = 7.846 Å is the experimental lattice parameter for SrLaVMO_6 [16], which is close to the theoretical values obtained in the first-principles calculations [17], and a = 7.899 Å is the theoretical lattice constant for La_xVTcO_6 [18]. Deviations from the ideal double-perovskite structure are expected to be small for these compounds [18] and were not considered here. The band-filling dependence, caused by the substitution of Sr by Y, was treated in the virtual crystal approximation. According to the electronic structure calculations in the local-density approximation (LDA), the basic difference between Sr_xVMO_6 and Sr_xVTcO_6 lies in the relative position of the V and Mo(Tc) states: in Sr_xVMO_6, the V and Mo states are separated in energy and form two nonoverlapping bands, while in Sr_xVTcO_6 these states form one common broad band (figure 1). Both Sr_{2−x}Y_xVMO_6 and Sr_{2−x}Y_xVTcO_6 (and other compounds iso-electronic to them) were intensively discussed in the literature in the context of half-metallic applications. For instance, SrLaVRuO_6, SrLaVMO_6 and La_xVTcO_6 were proposed to be the half-metallic antiferromagnets [16, 18–20]. On the other hand, metallic ferrimagnetic (i.e. non-spin-compensated) behavior was also suggested for SrLaVMO_6 [17, 21]. In general, such conclusions are sensitive to the values of the on-site Coulomb repulsion U, which are used in the calculations.

The rest of this paper is organized as follows. The method is discussed in section 2. In particular, in section 2.1 we briefly describe construction of the low-energy model for the double perovskites and in section 2.2 the basic idea of the OEP method. Results of the model OEP calculations are presented in section 3. In particular, the obtained electronic band structure is discussed in section 3.1, the screening of on-site interactions due to the correlation effects and its consequences on the properties of Sr_{2−x}Y_xVMO_6 and Sr_{2−x}Y_xVTcO_6 are...
was derived by using the downfolding method, and the details the reader is referred to the review article [22]. There the RPA method was discussed in the literature, and for by combining the constrained density functional theory with section 3.3. Finally, a brief summary of the work is given in and the stability of the ferrimagnetic states are discussed in section 4.

2. Method

2.1. Construction and parameters of the low-energy model

The first step of our approach is the construction of the effective low-energy model for the \( t_2g \) states of double perovskites:

\[
\hat{\mathcal{H}} = \sum_{ij} \sum_{\sigma} \sum_{m} t_{ij}^{m\sigma} c_{i\sigma m}^{\dagger} c_{j\sigma m} + \frac{1}{2} \sum_{i} \sum_{\sigma \sigma'} \sum_{m} U_{jj'\sigma\sigma'}^{m\sigma} c_{i\sigma m}^{\dagger} c_{i\sigma' m} c_{i\sigma' m} c_{i\sigma m},
\]

which is derived in the Wannier basis by starting from the LDA band structure. The Wannier functions are specified by the indices \( i, j \) or \( x, y, z \), and \( \sigma \) stands for the spin indices \( \uparrow \) or \( \downarrow \). The one-electron part \( t_{ij}^{m\sigma} \) of the model Hamiltonian was derived by using the downfolding method, and the Coulomb (and exchange) interactions \( U_{jj'\sigma\sigma'}^{m\sigma} \) were obtained by combining the constrained density functional theory with the RPA. The method was discussed in the literature, and for details the reader is referred to the review article [22]. There are three sets of parameters in the model Hamiltonian (1):

(i) The ‘charge transfer’ energies, or the energy splitting between ‘atomic’ \( t_2g \) levels of the V and Mo(Tc) sites, which are described by the site-diagonal part of \( t_{ij}^{m\sigma} \). The values of these parameters are \(-391 \) and \( 94 \) meV for the VMO and VTC compounds, respectively. Thus, as expected from the LDA band structure (figure 1), for the VMO compounds, the atomic V states are located lower in energy and are well separated from the Mo states, while for the VTC compounds, the situation is reversed and the splitting is considerably smaller.

(ii) The transfer integrals, which are described by the off-diagonal elements of \( t_{ij}^{m\sigma} \) with respect to the site indices. As expected, the strongest one is the d\( \delta \delta r \)-transfer integral between the nearest-neighbor V and Mo(Tc) sites, which is as large as \( 271 \) (\( 245 \)) meV. Other important parameters are the d\( \delta \delta r \)-transfer integrals between the next-nearest neighbors of the same atomic type. For the VMO compounds, these parameters are \(-72 \) and \(-116 \) meV in the V and Mo sublattice, respectively. For the VTC compounds, they are \(-73 \) and \(-113 \) meV in the V and Tc sublattice, respectively.

(iii) Intraatomic Coulomb and exchange interactions in the \( t_2g \) band, which are screened by all other states. At each site of the system, these interactions are fully specified by two Kanamori parameters [23]: the intraorbital Coulomb interaction \( U = U_{kmkm} \) and the exchange interaction \( J = U_{kmkm} \) for \( m \neq m' \). In the perfect cubic environment, the third Kanamori parameter \( U' = U_{kmkm'} \) (the interorbital Coulomb interaction) is related to \( U \) and \( J \) by the identity \( U' = 2JJ \). Other types of matrix elements of \( ||U_{kmkm'}|| \) are equal to zero. The band-filling dependence of \( U, U' \) and \( J \), as obtained in the virtual crystal approximation, is explained in figure 2. Generally, as the number of \( t_2g \) electrons increases, the effective Coulomb interactions also increase, reflecting the tendencies of the RPA screening [22]. On the other hand, the effective exchange interaction \( J \) is less sensitive to the band filling. The Coulomb repulsion \( U' \) is larger for the VMO compounds, due to the specific electronic structure of \( \text{Sr}_2\text{ TM}O_6 \) (figure 1): since the V band is separated and located in the lower part of the spectrum, it will be populated first in the process of band filling. It will effectively reduce the number of channels, available for the RPA screening of \( U' \), for example, due to the transitions from the occupied oxygen band to the unoccupied part of the V band [22]. Thus, \( U' \) will be less screened in the VMO compounds in comparison with the VTC ones, where the V and Tc states form one common band (figure 1).

2.2. Optimized effective potential method

In order to solve the model and to find the magnetic ground state of the double perovskites, we employ the OEP method. The model OEP approach works in the spirit of the Kohn–Sham density functional theory [9] on the double-perovskite lattice, where the kinetic energy

\[
E_{\text{kin}} = \sum_{\alpha} \sum_{\mathbf{k}} \sum_{n=1}^{\text{occ}} \frac{1}{\Omega_{\text{BZ}}} \int d\mathbf{k} \langle c_{\sigma\mathbf{k}} | \hat{H} | c_{\sigma\mathbf{k}} \rangle,
\]
the number of electrons
\[ n^{\tau} = \sum_{\sigma} \sum_{m} \sum_{n} \Omega_{BZ} \int \text{d}k \, \epsilon_{\sigma n k}^{\tau} \delta_{\sigma n k}, \]
and the spin magnetic moment
\[ m^{\tau} = \sum_{\sigma} \sum_{m} \sum_{n} \Omega_{BZ} \int \text{d}k \left( \epsilon_{\sigma n k}^{\tau} \right) = \sum_{\sigma} \sum_{m} \sum_{n} \Omega_{BZ} \int \text{d}k \left( c_{\sigma n k}^{\tau} c_{\sigma n k}^{\tau} \right), \]
at the site \( \tau \) are constructed from the one-electron orbitals \( c_{\sigma n k} \), which are obtained from the solution of the auxiliary one-electron problem:
\[ (\hat{t}_k + \hat{V}_{\text{eff}}^\tau) c_{\sigma n k} = \epsilon_{\sigma n k} c_{\sigma n k} \quad (2) \]
with the potential \( \hat{V}_{\text{eff}}^\tau \). In the above notations, \( \hat{t}_k \) is the Fourier image of \( \tilde{t}_{ij} = \| t_{ij}^{\tau} \| \), each eigenvector \( c_{\sigma n k} \) is specified by its components \( c_{\sigma n k}^{\tau} \), in the basis of three \( t_{ij}^{\tau} \) orbitals \( m = x y, z \), or \( x z \), or \( y z \) of the atomic type \( \tau = V \) or \( Mo(Tc) \), \( n \) is the band index and \( k \) is the position in the first Brillouin zone with the volume \( \Omega_{BZ} \).

The parameters of the effective potential \( \hat{V}_{\text{eff}}^\tau \), which is supposed to be ‘local’ (or diagonal with respect to the site indices), are obtained from the minimization of the total energy of the system:
\[ E = E_{\text{kin}} + E_{\text{C}} + E_{\text{X}} + E_{\text{corr}}, \quad (3) \]
where the Coulomb \( (E_{\text{C}}) \) and exchange \( (E_{\text{X}}) \) energies are given by
\[ E_{\text{C}} = \frac{1}{2} \sum_{\tau} \sum_{\sigma \sigma'} \sum_{m m'} \sum_{m'' m'''} U_{\eta \eta'}^{\tau m m' m''} n_{\sigma m}^{\eta \tau} n_{\sigma' m'}^{\eta' \tau}, \]
and
\[ E_{\text{X}} = -\frac{1}{2} \sum_{\tau} \sum_{\sigma \sigma'} \sum_{m m'} \sum_{m'' m'''} U_{\eta \eta'}^{\tau m m' m''} n_{\sigma m}^{\eta \tau} \epsilon_{\sigma' m'}^{\eta' \tau}, \]
respectively, in terms of the density matrix:
\[ n_{\sigma m}^{\eta \tau} = \sum_{n} \frac{1}{\Omega_{BZ}} \int \text{d}k \, \epsilon_{\sigma n k}^{\tau} \delta_{\sigma n k}. \]
The expression for the correlation energy, which is treated in the RPA, is given by [15, 24, 25]
\[ E_{\text{corr}} = -\frac{1}{4 \Omega_{BZ}} \int \text{d}q \text{Tr} \left[ \ln \left( 1 - \hat{P}^{\tau} (\omega, q) \hat{U} \right) \right] \times \left[ 1 - \hat{U} \hat{P}^{\tau} (\omega, q) \right] \hat{U}. \quad (4) \]
where \( \hat{U} \) are the diagonal matrices \( \| U_{\eta \eta'}^{\tau m m' m''} \| \) with respect to the site indices \( \tau \), \( \hat{P}^{\tau} = \| P_{\eta \eta'}^{\tau m m' m''} \| \) is the polarization in the imaginary frequency:
\[ P_{\eta \eta'}^{\tau m m' m''} (\omega, q) = \sum_{\sigma} \sum_{n} \frac{1}{\Omega_{BZ}} \int \text{d}k \left( \epsilon_{\sigma n k}^{\tau} \right) \delta_{\sigma n k}, \quad (5) \]
and matrix multiplication in (4) implies the convolution over two orbital indices: \( \left( \hat{U} \hat{P}^{\tau} \right)^{\eta \eta'}^{\tau m m' m''} = \sum_{\eta''} U_{\eta \eta''}^{\tau m m' m''} P_{\eta'' \eta'}^{\tau m m' m''}. \)

For the cubic systems (and neglecting the orbital polarization effects), the effective potential is specified by only three parameters: \( \hat{V}_{\text{eff}}^{V m} = -\Delta_{V}^{m} / 2 \), \( \hat{V}_{\text{eff}}^{Mo(Tc)} m = \Delta_{V}^{m} / 2 \), and \( \hat{V}_{\text{eff}}^{Mo(Tc)} m = \Delta_{V}^{m} / 2 \). In other words, \( \Delta_{V}^{m} \) and \( \Delta_{Mo(Tc)}^{m} \) is the exchange–correlation splitting between minority- and majority-spin states at the sites V and Mo(Tc), respectively, and \( \Delta_{V}^{m} \) is the ‘charge transfer energy’ between sites V and Mo(Tc). These parameters should be obtained from the minimization of the total energy (3). In practice, we calculate the total energy on some coarse mesh of these parameters, identify the minimum, then continue the calculations around the minimum by using a finer mesh, and so on, until reaching the necessary accuracy for the total energy minimum (typically less than 1 meV).

3. Results and discussions

3.1. Electronic structure and arbitrariness of the OEP procedure for half-metallic and insulating states

In the following, we consider two magnetic solutions: ferromagnetic \( \Delta_{V}^{m} = 0 \) and \( \Delta_{Mo(Tc)}^{m} = 0 \) and ferrimagnetic \( \Delta_{V}^{m} > 0 \), while \( \Delta_{Mo(Tc)}^{m} < 0 \), and find parameters of the effective potential by minimizing the total energy for each case. Total and partial densities of states for Sr_{2−x}Y_{x}VMoO_{6} obtained from the solution of the Kohn–Sham equations (2) with the optimized potential, are shown in figure 3. All ferromagnetic solutions are half-metallic: the Fermi level crosses the majority-spin band, while the minority-spin band is completely empty. In the case of Sr_{2}VMoO_{6} and SrYVMoO_{6}, there is a strong hybridization between V and Mo states, which form one broad majority-spin band. However, in Y_{x}VMoO_{6}.
Figure 3. Total and partial densities of states as obtained in the OEP model for the ferromagnetic (upper panel) and ferrimagnetic (lower panel) configurations of $\text{Sr}_{2-x}\text{Y}_x\text{VMoO}_6$. The Fermi level is at zero energy.

...the majority-spin band is split into the Mo and V subbands, which are separated by an energy gap. This behavior is related to the large on-site Coulomb repulsion $U$ in $\text{Y}_2\text{VMoO}_6$ (figure 2), which additionally shifts the V states towards higher energies. Any deviations from the half-metallic behavior and partial population of the minority-spin band increase the total energy of $\text{Sr}_{2-x}\text{Y}_x\text{VMoO}_6$ and make this state unstable.

The choice of parameters of the effective potential in the half-metallic regime is not unique. For example, any redistribution of the unoccupied minority-spin states does not affect the ground-state properties. Moreover, any change of $\Delta_{ct}^V$, $\Delta_{ct}^\text{Mo}$ and $\Delta_{ct}$, which does not deform the partially populated majority-spin band (apart from the constant shift), does not affect the ground-state properties either. Quantitatively, this means that the ground-state properties in the half-metallic regime are controlled by the single parameter $S = \Delta_{ct} + (\Delta_{ct}^V - \Delta_{ct}^\text{Mo})/2$. Any change of $\Delta_{ct}^V$, $\Delta_{ct}^\text{Mo}$ and $\Delta_{ct}$, which keeps $S$, does not affect the ground-state properties in the half-metallic regime.

All ferrimagnetic configurations of $\text{Sr}_{2-x}\text{Y}_x\text{VMoO}_6$ are metallic. In this case all three parameters of the effective potential are uniquely defined. The degree of spin polarization ($P$) in the ferrimagnetic state is sensitive to the concentration $x$ and the definition of the polarization itself [26]. For example, by using the densities of states shown in figure 3, one obtains $P = 0.3$, 0.1 and 0.2 for $x = 0$, 1 and 2, respectively. On the other hand, by using a more sophisticated Bloch–Boltzmann transport theory definition one can obtain $P = 0.1$, 0.1 and 0.5 for $x = 0$, 1 and 2, respectively. The experimental value of $P$ for $\text{SrLaVMoO}_6$, measured by the point-contact Andreev reflection technique, is about 0.5 [16]. Nevertheless, as we will see below, many of these ferrimagnetic states appear to be unstable and calculated spin polarization cannot be compared directly with the experimental data.

Similar behavior was obtained for $\text{Sr}_2\text{VTcO}_6$ and $\text{SrYVTcO}_6$, where again the half-metallic ferrimagnetic state competes with the normal metallic ferrimagnetic state (figure 4).

$\text{Y}_2\text{VTcO}_6$ requires special attention: it has six electrons in the $t_{2g}$ band. The system is insulating and all metallic configurations have higher energies. Therefore, in the ferrimagnetic state, the parameters $\Delta_{ct}^V$, $\Delta_{ct}^\text{Mo}$ and $\Delta_{ct}$ can be chosen in an arbitrary way. Indeed, any combination of these parameters (provided that the system remains insulating) yields the same number of electrons $n^\tau = 3$, spin magnetic moments $m^\tau = 3\mu_B$ and the total energy of the system. Since all majority-spin states are occupied and all minority-spin states are empty, the RPA correlation energy (4) is exactly equal to zero in this particular case. The arbitrariness with the choice of the effective potential also remains in the antiferromagnetic state of $\text{Y}_2\text{VTcO}_6$ (figure 5), although the number of parameters which can be chosen in an arbitrary way decreases. Indeed, the splitting between the V and Mo states with the same spin affects the ground-state properties. However, the bands with different spins can be rigidly shifted relative to each other: as long as the system remains in the insulating state, this shift will not affect the ground-state properties. Thus, the behavior of the antiferromagnetic $\text{Y}_2\text{VTcO}_6$ is defined by only two parameters: $\Delta_{ct}$ and $(\Delta_{ct}^V - \Delta_{ct}^\text{Mo})$, while the third parameter $(\Delta_{ct}^V + \Delta_{ct}^\text{Mo})$ can be arbitrary. Finally, we would like to emphasize that antiferromagnetic $\text{Y}_2\text{VTcO}_6$ becomes an insulator due to the large exchange...
splitting (both at the V and Tc sites) obtained in the OEP calculations. If the splitting were smaller, the majority-spin V and Tc bands would eventually merge and form some half-metallic antiferromagnetic state, which was indeed obtained in LSDA calculations for the isoelectronic La$_2$VTcO$_6$ [18]. Nevertheless, such a half-metallic antiferromagnetic state is probably an artifact of LSDA, and a more rigorous treatment of correlation effects will open the bandgap in both spin channels.

3.2. Screening and the effective Stoner model

Since the effective potential is local (or diagonal with respect to the site indices) and does not affect the orbital degrees of freedom, the OEP scheme has many similarities with the Stoner model of magnetism, where the strength of the intraatomic splitting $\Delta_\text{ex}$ between the minority- and majority-spin states is controlled by the effective parameter $I^\tau$: $\Delta_\text{ex}^\tau = I^\tau m^\tau$. Thus, using the intraatomic exchange–correlation splitting, obtained from the minimization of the total energy, and corresponding values of the spin magnetic moments in the ground state (figure 6), one can find the effective Stoner parameter $I^\tau_{\text{OEP}}$. All such considerations are valid only for the ferrimagnetic metallic state, where $\Delta_\text{ex}$ is uniquely defined. The results for Sr$_{2-x}$Y$_x$VMoO$_6$ are explained in figure 7. The effective Stoner parameters, derived from the OEP calculations, are of the order of 1.3–1.6 eV at the V sites and 1.0–1.1 eV at the Mo sites. Similar parameters were obtained for Sr$_{2-x}$Y$_x$VTcO$_6$: $I^\tau_{\text{OEP}}$ = 1.27 eV and $I^\tau_{\text{OEP}}^{\text{V}}$ = 1.06 eV in the case of Sr$_2$VTcO$_6$, and $I^\tau_{\text{OEP}}$ = 1.28 eV and $I^\tau_{\text{OEP}}^{\text{Tc}}$ = 1.18 eV in the case of SrYVTcO$_6$. All of them are systematically larger than the typical values of $I^\tau$ obtained in the LSDA (typically, $I^\tau_{\text{LSDA}}$ is close to 1 eV for the 3d elements and even smaller for the 4d and 5d elements [27]). This example clearly shows the importance of the rigorous treatment of the exchange–correlation interactions (beyond LSDA) in the physics of the double perovskites.

Another limiting case is the Hartree–Fock (HF) approximation, which neglects the correlation interactions and takes into account only the exchange term. Then, the corresponding Stoner parameter, describing the exchange splitting in the system of three t$_{2g}$-orbitals, is given by $I^\tau_{\text{HF}} = (U + 2J^\tau)/3$. They are also plotted in figure 7. The difference between $I^\tau_{\text{HF}}$ and $I^\tau_{\text{OEP}}$ is the measure of correlation interactions and their
Figure 6. Local spin magnetic moments at the V and Mo(Tc) sites, as obtained in the OEP model for Sr_{2-x}Y_xVMoO_6 (left) and Sr_{2-x}Y_xVTcO_6 (right).

Figure 7. Effective Stoner parameters for Sr_{2-x}Y_xVMoO_6 as derived in the OEP model for the ferrimagnetic state, in the HF approximation, and using only static values of Coulomb and exchange interactions, evaluated in the RPA. One can clearly see that I_{\tau}^{OEP} is reduced by about 10–20% in comparison with I_{\tau}^{HF}, which indicates the importance of correlation interactions.

Finally, it is instructive to consider the effect of the static screening alone. The corresponding on-site interactions in RPA are given by

$$\hat{U}_{\text{RPA}} = \frac{1}{\Omega_{\text{BZ}}} \int d\mathbf{q} [1 - \hat{U} (0, \mathbf{q})]^{-1} \hat{U},$$

which yield the parameter I_{\tau}^{RPA} = (U_{\tau}^{RPA} + 2J_{\tau}^{RPA})/3. Such a picture can be regarded as the static limit of the GW approximation [28, 29], where the frequency-dependent screened Coulomb interaction $U_{\text{RPA}}(\omega)$ is replaced by its static counterpart $U_{\text{RPA}} = U_{\text{RPA}}(0)$ [30]. Typically, it is sufficient to consider only site-diagonal contributions to $U_{\text{RPA}}$, because if $\hat{U}$ is site-diagonal, the off-diagonal contributions to $\hat{U}_{\text{RPA}}$ are expected to be small [31]. These results are also shown in figure 7. One can clearly see that the parameters I_{\tau}^{RPA} are overscreened and strongly underestimated in comparison with I_{\tau}^{OEP}. This indicates the importance of the dynamical screening effects in the OEP.

3.3. Total energy and stability of the ferrimagnetic state

The behavior of the total energy and of its partial contributions, as obtained in the OEP model, is explained in figure 8. For all considered compounds, except Sr_2VMoO_6, the ferrimagnetic configuration has lower energy. The tendencies toward ferrimagnetism increase with the band filling. The main factor stabilizing the ferrimagnetic state is the gain of the kinetic energy. The main factor destabilizing it is the loss of the exchange energy.

In order to investigate the local stability of the ferrimagnetic phase, we calculate the spin stiffness $D$, which is related to the second derivative of the total energy with respect to the spin-spiral vector $\mathbf{q}$ near the ferrimagnetic state:

$$E(\mathbf{q}) \approx E(\mathbf{q}_0) + D(\mathbf{q} - \mathbf{q}_0)^2,$$

where $\mathbf{q}_0 = (\pi/a, \pi/a, \pi/a)$ and $a$ is the cubic lattice parameter. More specifically, the numerical calculations of $E(\mathbf{q})$ were performed using the generalized Bloch approximation.
the exchange–correlation functional \[8\]. Thus, the range of
and can be proven by considering the rotational invariance of
the OEP approach allows one to improve the commonly
hand, the OEP approach allows one to improve the commonly
obtained model have been investigated on the basis of the

In summary, using first-principles electronic structure calcu-
lations, we have constructed an effective low-energy model
for the \(t_{2g}\) states of double perovskites \(\text{Sr}_{2-x}\text{Y}_x\text{VMO}_6\) and
\(\text{Sr}_{2-x}\text{Y}_x\text{VTCO}_6\). Then, the ground-state properties of the
obtained model have been investigated on the basis of the
OEP method, by treating correlation interactions in the RPA.
The reason for such a strategy was twofold. On the one
hand, the OEP approach allows one to improve the commonly
used LSDA for the double perovskites and to incorporate
the physics of electron correlations beyond the homogeneous
electron gas limit. On the other hand, since OEP is formulated
as the ground-state method, where all the parameters are
derived rigorously, from the minimization of the total energy of
the system, it gets rid of many ambiguities inherent in the
LSDA + \(U\) approach. In particular, although \(\text{Sr}_{2-x}\text{Y}_x\text{VMO}_6\),
\(\text{Sr}_{2-x}\text{Y}_x\text{VTCO}_6\) and other compounds isoelectronic to them
are frequently proposed to exhibit half-metallic ferromagnetic
or antiferromagnetic properties, the situation is probably not
so optimistic because of the electron correlation effects,
which affect the intraatomic exchange splitting and make it
substantially larger than in LSDA. Of course, this will revise
many predictions based on the LSDA. For example, \(\text{Y}_2\text{VTCO}_6\),
which was expected to be a half-metallic antiferromagnet,
appears to be an insulator. The behavior of other materials is even
more complicated. For most of them (except \(\text{Sr}_2\text{VMO}_6\)), the
half-metallic ferromagnetic state is energetically less favorable
than the (normal) metallic ferromagnetic state. Nevertheless,
this ferrimagnetic state appears to also be unstable with respect
to the spin-spiral alignment. Thus, the true magnetic ground
state of these compounds will be a spin-spiral or some more
complicated noncollinear magnetic arrangement.

Finally, we have argued that the effective potential (and
therefore the one-electron band structure itself) for the half-
metallic and insulating ferro- or antiferromagnetic state is not
uniquely defined. Generally, there is a bunch of parameters,
which yield the same total energy, occupation numbers and
spin magnetic moments at the transition-metal sites.

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