Pseudo-half-metallicity in the double perovskite Sr_2CrReO_6 from density-functional calculations

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The electronic structure of the spintronic material Sr_2CrReO_6 is studied by means of full-potential linear muffin-tin orbital method. Scalar relativistic calculations predict Sr_2CrReO_6 to be half-metallic with a magnetic moment of 1 μ_B. When spin–orbit coupling is included, the half-metallic gap closes into a pseudo-gap, and an unquenched rhenium orbital moment appears, resulting in a significant increase of the total magnetic moment to 1.28 μ_B. This moment is significantly larger than the experimental moment of 0.9 μ_B. A possible explanation of this discrepancy is that the anti-site disorder in Sr_2CrReO_6 is significantly larger than hitherto assumed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1855418]

The family of magnetic oxides with an ordered double perovskite structure are complex materials with high technological potential in the area of spin electronics. Double perovskites have the general formula $A_2BB'O_6$, where A can be an alkali metal such as strontium, calcium, or barium, or a lanthanide, and B and B′ are transition metals. Each transition metal site is surrounded by an oxygen octahedron (sometimes heavily distorted), and the A atoms are situated in the holes produced by eight adjacent oxygen octahedra.

In 1998, it was discovered that one such double perovskite, Sr_2FeMoO_6, possesses intrinsic tunneling-type magnetoresistance at room temperature—until then only observed in the mixed-valent manganese oxides[1]—making it a hot candidate material for spin-electronics applications.[2] The physical origin of the magnetoresistance in Sr_2FeMoO_6 and in the mixed-valent manganese oxides is half-metallicity, i.e., the material is an insulator in one of the spin channels, but a metal in the other. This leads to a complete spin polarization at the Fermi level, which in turn results in strongly spin-dependent scattering of the charge carriers and thus a possibility to influence the resistance using relatively weak magnetic fields. Prerequisites for realizing high-performance devices using these materials are that the half-metallicity to a high degree is preserved at ambient temperature, and that high quality thin films of the material can be grown.

In this letter, we investigate the electronic structure of the double perovskite Sr_2CrReO_6 using density functional theory. This system is particularly interesting since it exhibits the hitherto largest Curie temperature T_C of all known double perovskites, 635 K,[3] which is a couple of hundred kelvin higher or more than for Sr_2FeMoO_6 (Ref. 4) as well as for the mixed-valent manganese oxides. Sr_2CrReO_6 is a metallic ferromagnet with a saturation magnetic moment of around 0.9 μ_B per formula unit. At room temperature, the moment is only slightly reduced to around 0.8 μ_B, and high quality thin films of Sr_2CrReO_6 can be produced in quite a large temperature window.[3,5] Thus, this material appears to satisfy important technological criteria. The measured saturation moment is quite well reproduced by a simple ionic picture of the Sr_2CrReO_6 system, although this model takes neither hybridization nor orbital moments into account. In the ionic model, the Cr ions, situated on the B sites, have a $3d^3$ configuration, leading to a moment of 3 μ_B antiferromagnetically coupled to the neighboring Re ions on the B′ sites, with configuration $5d^2$ or 2 μ_B per atom. In total, this gives a saturation spin moment of 1 μ_B per formula unit in the case of perfect ordering.

The present density-functional calculations were performed using an all-electron full potential linear muffin-tin orbital method (FP-LMTO), which has been described in detail elsewhere.[6] In this method, space is divided into nonoverlapping muffin-tin spheres surrounding the atoms, and an interstitial region. Most important, this method assumes no shape approximation of the potential, wave functions, or charge density. Spin–orbit coupling was included in our calculations. The spherical-harmonic expansion of the potential was performed up to $l_{max}=6$, and we used a double basis so that each orbital is described using two different kinetic energies in the interstitial region. Furthermore, we included several pseudo-core orbitals in order to further increase accuracy. Thus, the basis set consisted of the Sr (4*s* 5*s* 4*p* 5*p* 4*d*), Cr (4*s* 3*p* 4*p* 3*d*), Re (6*s* 5*p* 6*p* 5*d*), and O (2*s* 2*p*) LMTOs. We performed our calculations using the experimentally determined structure and atomic positions, i.e., the tetragonal structure with space group symmetry $I4/mmm$, with cell parameters $a=b=5.52$ Å, and $c=7.82$ Å.[3] The radii of the muffin-tin spheres were $2.68a_0$ for Sr, $2.0a_0$ for Cr, $1.98a_0$ for Re, and $1.6a_0$ for O, respectively. The direction of the spin magnetic moment was chosen to be along the *c* axis. The integration in reciprocal space was performed using 376 *k*-points in the irreducible Brillouin zone (BZ), corresponding to 2744 points in the full BZ for our self-consistent ground-state calculation. We tried both the local spin density approximation[7] and the generalized gradient approximation (GGA)[8] to the exchange–correlation functional. In the following, we will concentrate on our GGA results with the spin–orbit coupling included.

Our calculations reveal two important features of the electronic structure of Sr_2CrReO_6. First, our calculated total magnetic moment J_z, i.e., the sum of the spin and orbital

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TABLE I. Calculated spin and orbital d magnetic moments in μ_B/atom for Sr_2CrReO_6, with and without spin–orbit coupling (SO) included, and for different choices of the exchange–correlation functional. The total moment includes also the small spin and orbital moments present in non-d orbitals, and the spin moment in the interstitial region.

	Spin		Orbital		
	Cr	Re	Cr	Re	Total
LSDA	2.00	−0.75			1.00
LSDA+SO	2.02	−0.69	−0.029	0.17	1.31
GGA	2.24	−0.90			1.00
GGA+SO	2.25	−0.85	−0.030	0.18	1.28
Ionic picture	3	−2			1

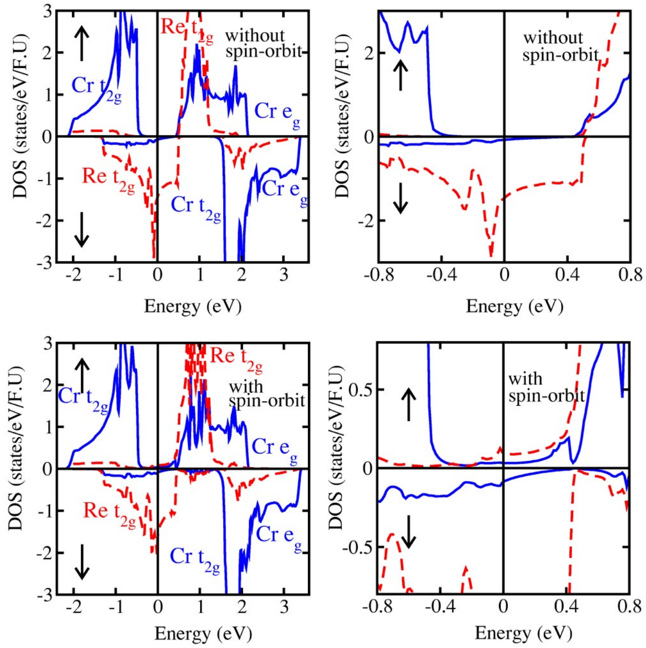

FIG. 1. (Color online) Orbital-resolved density of states (DOS) for Sr_2CrReO_6, without spin–orbit coupling (top row), and with spin–orbit coupling (bottom row). In the left-most panels the DOS is shown in an extended energy region and the symmetries of the peaks are indicated, whereas the right-most panels show a more detailed view of the DOS around the Fermi level.

moments, at perfect ordering of the Cr and Re atoms, is about 1.28 μ_B per formula unit when spin–orbit coupling is included, i.e., a 28% larger magnetic moment than the one predicted by the ionic picture. (See Table I.) Second, we find that Sr_2CrReO_6 is in fact not a perfect half metal. Let us discuss the magnetic moment first. When spin–orbit coupling is neglected, we find the total spin moment to be precisely 1 μ_B. With spin–orbit coupling included, the spin moment increases to 1.1 μ_B. Our calculated spin and orbital Cr and Re d moments are listed in Table I. Note that a large part of the spin moment is delocalized into the interstitial region, and therefore the individual d spin moments of the individual Cr and Re atoms inside their respective muffin-tin spheres in Table I appear small compared to the ionic values.

We find a Re 5d orbital moment of around 0.18 μ_B and a total orbital moment of also 0.18 μ_B, calculated by summing up the orbital moments in all muffin-tin spheres. Both Cr and Re have less than half-filled d shells, and therefore the orbital moment is antiparallel to the spin moment for both species. Since the Cr and Re spin moments couple in antiparallel, the net result is that the total orbital moment, dominated by the Re orbital moment, is parallel to the total spin moment which, in turn, is dominated by the Cr spin moment. Consequently, the orbital moment has the effect of further increasing the total magnetic moment in this system.

Thus, when spin–orbit coupling is taken into account, our total predicted magnetic moment becomes significantly larger than what experimental studies indicate, and also larger than what the ionic model of Sr_2CrReO_6 suggests.[9] Evidently, the spin–orbit effect is very important in this compound, which is hardly surprising since even in the case of elemental Re metal, the spin–orbit coupling is necessary in order to reproduce the experimentally observed band structure and Fermi surface.[10] What is surprising on the contrary is that the experimentally found moment is so close to the ionic value. A possible explanation for this paradox is that the anti-site disorder might be significantly larger in this system than previously assumed. One way to resolve this issue would be to determine the individual atomic spin and orbital moments in this system experimentally by performing, e.g., x-ray magnetic circular dichroism experiments.

We now turn to the question of half-metallicity in Sr_2CrReO_6, at perfect ordering. In our scalar-relativistic calculations, we indeed find a gap of 0.7 eV in the majority spin channel (see the top panel of Fig. 1), but when spin–orbit coupling is included, the band gap disappears and turns into a pseudo-gap with a low but finite density of states (DOS), see the bottom panel of Fig. 1. The carriers at the Fermi level remain highly polarized; $D(\downarrow)/D(\uparrow)\sim 13$, where $D(\downarrow)$ and $D(\uparrow)$ is the density of states at the Fermi level for minority and majority spin, respectively, instead of infinity as would be the case for a perfect half metal. As a first hint as to why the gap disappears, we note that in Re metal, the spin–orbit parameter $\zeta(r)$ of the t_{2g} states in the spin–orbit Hamiltonian $\hat{H}_{SO}=\zeta(r)\hat{\mathbf{l}}\cdot\hat{\mathbf{s}}$ is around 0.4 eV,[10] a number that decreases to approximately 0.3 eV in the double perovskite due to covalency.[11] Thus, the half-metallic gap and the spin–orbit parameter are of the same order, which makes it plausible that the spin–orbit splitting is capable of washing away the gap.

In order to understand in some more detail why the half-metallicity is destroyed, we analyze the density of states of this system, and work out why the spin–orbit coupling affects the DOS in this particular way. The basic critical ingredients in the DOS are the d states of the Cr and Re atoms, which in turn are split into t_{2g} and e_g states by the crystal field produced by the oxygen octahedra, with the t_{2g} states having lower energy and place for three electrons per spin channel, whereas the e_g states are higher in energy and have place for two electrons per spin channel. In the absence of spin–orbit coupling, the t_{2g} and e_g states are eigenstates to the Hamiltonian and do not hybridize with each other. Similarly, the spin channels do not hybridize with each other. (To be exact, the slight distortion of the oxygen octahedra introduces some very small extra splitting. We will however neglect this in the following.) In the scalar-relativistic DOS, the threefold degenerate Cr t_{2g} states of the majority spin channel are filled. Therefore, the Fermi level ends up in the crystal-field gap between the Cr t_{2g} and e_g states. A similar situation is seen in Sr_2CrWO_6.[12,13] Due to the antiferromagnetic coupling of Cr and Re, it is the minority spin channel in

Re which is the occupied one, and it contains two electrons. This means that the Re minority spin t_{2g} states are only filled to about two-thirds, resulting in a high DOS at the Fermi level in the minority spin channel. Due to hybridization, also the minority spin Cr t_{2g} states obtain a small occupation. In the majority spin channel, the Re d states are essentially empty; hybridization with the majority Cr t_{2g} states results nevertheless in a finite, small occupation. When spin–orbit coupling is included, the e_g and t_{2g} states are no longer eigenstates to the Hamiltonian, and they will therefore mix, as will the spin states. As a result, the high Re t_{2g} DOS at the Fermi level in the minority spin channel induces states in the majority spin channel. Since the spin–orbit parameter and the gap are both of the order of a few tenths of an electron volt, the result is that the half-metallic gap closes and the Cr t_{2g} and e_g peaks become connected. The induced pseudo-gap states have Re t_{2g} Cr e_g, as well as Cr t_{2g} character.

In summary, we have analyzed the electronic structure of the double perovskite Sr_2CrReO_6. The effect of spin–orbit coupling results in a rather large Re orbital moment and as a result, a total magnetic moment of 1.28 μ_B, whereas our predicted scalar-relativistic spin-only moment is precisely 1.0 μ_B. Furthermore, the large spin–orbit coupling in Re produces a nonvanishing DOS at the Fermi level in the majority spin channel, destroying the half-metallicity even at perfect ordering of the Cr and Re sites.

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