

Electronic structure and magnetism of SrFeO₃ and SrCoO₃

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The electronic-structure calculations of the perovskite oxides SrFeO₃ and SrCoO₃ in the nonmagnetic and magnetic phases are reported here. The calculations were performed with use of the self-consistent linear muffin-tin-orbital method within the atomic-sphere approximation. The calculations show strong hybridization between the Fe and Co 3*d* and O 2*p* orbitals and the conduction bands are found to arise from these hybridized orbitals as was predicted by Goodenough through his chemical approach. The O 2*s* bands lie deep below the conduction bands and the 2*p* bands of oxygen extends up to the Fermi level. The theoretically predicted magnetic moments are found to be in good agreement with the experimental observations.

I. INTRODUCTION

Since the advent of high- T_c systems, and especially after the discovery of potassium-doped BaBiO₃, which exhibits a maximum T_c of 30 K,¹ there has been renewed interest in the study of AMO_3 -type perovskite oxides. Apart from the above, these oxides exhibit a wide variation in their electrical, magnetic and other physicochemical properties with respect to the composition, temperature, etc. They also exhibit significant changes in their properties when the M or A cation is changed from one element to other.^{2,3} These motivated us to make a detailed study of these oxide systems.

In addition to the exhaustive collection of literature work done by Muller and Roy⁴ and the work of Galasso⁵ on these AMO_3 systems, the most important contribution comes from the work of Goodenough.² He has given a qualitative chemical description of these perovskite oxides in terms of the M -O overlap parameter and has classified a large number of these oxides according to their M -cation spin and the M -O overlap strength. As these perovskite oxides have the strong 180° M -O- M linkage, his chemical picture assumes that the MO_6 octahedra to be the most important factor in describing these systems. Even though the work of Goodenough shows overall good agreement with the experimental observations, it is only qualitative in nature. Hence it is desirable to have quantitative estimates of the various band parameters such as the Fermi energy, density of states at the Fermi energy, conduction-band width, etc., as they can be more useful in the understanding of their various properties. Further most of the above quantities can be compared with the experimental measurements. This led us to calculate the electronic structure of these compounds. In this paper we present the band structure

and the calculated electronic properties of the systems SrFeO₃ and SrCoO₃.

The paper contains five sections and a brief discussion about the method of calculating the band structure is given in Sec. II. Section III deals with the paramagnetic and antiferromagnetic (AF) band structure of SrFeO₃ and in Sec. IV the paramagnetic and ferromagnetic electronic structure calculations of SrCoO₃ are presented. The last section is devoted to the discussion of results and conclusions.

II. METHOD OF CALCULATION

We have used the self-consistent linear muffin-tin-orbital (LMTO) method^{6,7} within the atomic-sphere approximation (ASA) to calculate the band structures. Both the systems considered for the present investigation have close packed structures and they crystallize in the simple cubic structure with one molecule per cell.^{5,8} The positions of the basis are for Sr, (0.0,0.0,0.0); for M , (0.5,0.5,0.5); and for O, (0.5,0.5,0.0), (0.0,0.5,0.5), and (0.5,0.0,0.5). The lattice parameters and the atomic-sphere radii corresponding to the individual atoms are given in Table I. The sphere radii were judiciously chosen, subject to the constraint that the sum of the volumes of the individual atomic spheres is equal to the

TABLE I. Lattice parameters and atomic-sphere radii of SrMO₃ in a.u.

	Lattice parameter	Atomic-sphere radii		
		Sr	M	O
SrFeO ₃	7.311	3.469	2.471	2.298
SrCoO ₃	7.275	3.400	2.423	2.339

cell volume. The trial potential parameters were generated from the Herman-Skillman atomic charge densities⁹ renormalized to the specified atomic-sphere radii. The Madelung contribution to the potential was also included and the von Barth-Hedin exchange correlation was used in all the calculations. The electronic structure problem was solved self-consistently and the eigenvalues were calculated to an accuracy of 1 mRy.

As both the systems of our current interest possess magnetic order¹⁰ (SrFeO₃ has antiferromagnetic order while SrCoO₃ has ferromagnetic order) it became important to include the effect of the magnetic ordering in the calculations. Hence in the present work we have done the calculations in the paramagnetic phase for both the systems and in the AF phase for SrFeO₃ while in the ferromagnetic phase for SrCoO₃. In both the cases the orbitals 4*p* and 5*s* of Sr, 3*d* and 4*s* of Fe and Co, and 2*s* and 2*p* of O were treated as valence orbitals to obtain the energy bands. The results of our calculations are described in the following sections.

III. BAND STRUCTURE AND MAGNETISM OF SrFeO₃

A. Paramagnetic band structure of SrFeO₃

In the LMTO method, the self-consistent calculation of the energy band requires the self-consistent evaluation of the potential parameters. Hence to initiate the self-consistent iterations, the trial potential parameters ob-

tained from the Herman-Skillman charge densities were used. The arbitrary energies about which the trial potential parameters are calculated were suitably chosen so that the logarithmic derivative is negative. The calculated band structure and the density of states histogram are shown in Figs. 1 and 2. As seen from Fig. 1, the O 2*s* bands lie deeper below the conduction bands and are positioned at the bottom of the bands. The next three bands lying above the O 2*s* bands are due to the Sr 4*p* orbitals. The calculations predict a strong hybridization between the Fe 3*d* and O 2*p* orbitals and these hybridized orbitals form the conduction bands. As the 2*p* bands of oxygen extends up to the Fermi level, it gives the indication that O 2*p* orbitals are, comparatively, to be in the delocalized state. The conduction bandwidth is found to be 0.467 Ry and the density of states at the Fermi energy is 162.495 states/Ry f.u. The partial contributions to the density of states at the Fermi energy and the number of states are given in Table II.

B. Antiferromagnetic band structure of SrFeO₃

The experimental studies on this system shows that it exhibits AF ordering with a Néel temperature of 130 K.² Goodenough has attributed collective electron behavior to this system, further in his description of this system, he assumes that the Fe ion is in the *d*⁴ outer electron configuration. In order to have a quantitative and detailed understanding of the electronic structure and the

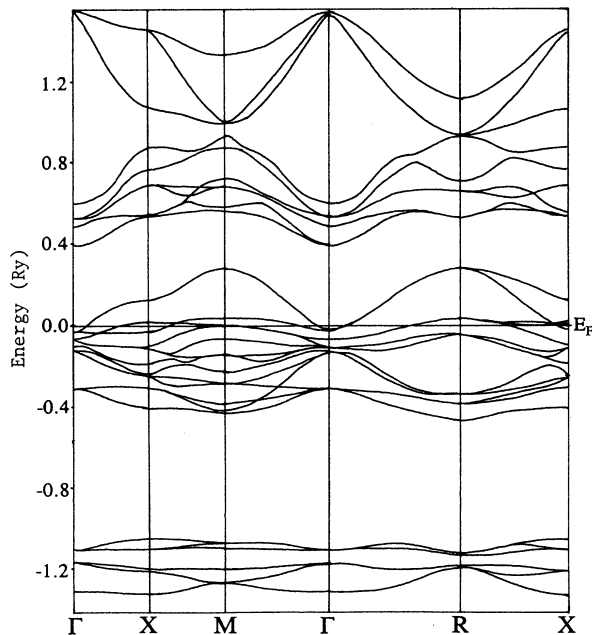


FIG. 1. Band structure of paramagnetic SrFeO₃.

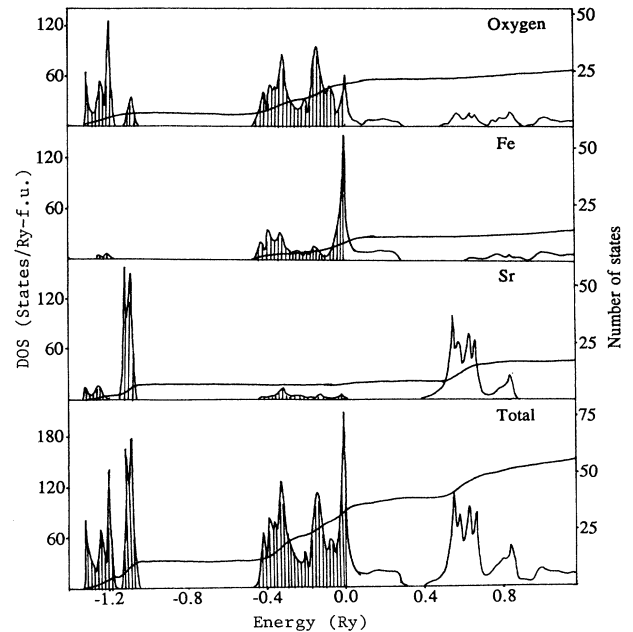


FIG. 2. Density of states of paramagnetic SrFeO₃.

TABLE II. Partial contributions of the density of states at the Fermi energy [$N(E_F)$] and the number of states (NOS) of paramagnetic SrFeO₃.

	$N(E_F)$ (states/Ry f.u.)			NOS (electrons per f.u.)		
	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>
Sr	0.993	0.494	3.285	0.256	6.190	0.931
Fe	0.073	0.316	112.737	0.382	0.642	6.040
O	0.428	41.824	2.343	5.503	13.721	0.334

spin states of the ions, we have done the AF electronic structure calculations on this system. As the AF structure of his oxide is of helical type structure, it became difficult to do the calculations in this helical magnetic structure. Hence a simple AF ordering as found in PbCrO₃ was used in the present calculation.¹¹ In this AF ordering, one Fe ion has AF coupling with all the six nearest-neighbor Fe ions. The magnetic unit cell is body centered tetragonal with lattice parameters of $a = \sqrt{2}a_0$, $c = 2a_0$, where a_0 is the lattice parameter of the perovskite cubic unit cell. The magnetic primitive cell contains ten atoms with two different Fe atoms with opposite spin orientations.

In order to initiate the AF calculations, we assumed a positive spin splitting at all atoms in one sublattice and the corresponding negative spin splittings at the other sublattice. The self-consistent potential parameters obtained from the paramagnetic calculations were used as the trial potential parameters. After the self-consistent iterations were over, local magnetic moments were found to exist at the Fe and O sites whereas there was a negli-

ble moment at the Sr site. The calculated values of the magnetic moments of Fe and O are, respectively, $2.567\mu_B$ and $0.011\mu_B$ whereas the experimental values^{10,12} are, respectively, $2.7\mu_B$ at the Fe site and $0.1\mu_B$ at the O site. Our theoretical value of the magnetic moment at the Fe site compares well with the experimental data whereas the magnetic moment at the O site is much less compared to the experimental value. But it should be noted here that the magnetic structure used in the calculation is not the exact one and further it has been found from the experimental observation that the magnetic moments of the Fe and O are not parallel and such a magnetic configuration cannot be incorporated in our present calculation. However the AF calculations have given a better description of the electronic structure of this system and have provided reasonable estimates of the magnetic moments of the individual atoms. The density of states at the Fermi energy is 28.365 states/Ry cell and it was found to have changed drastically from the value ob-

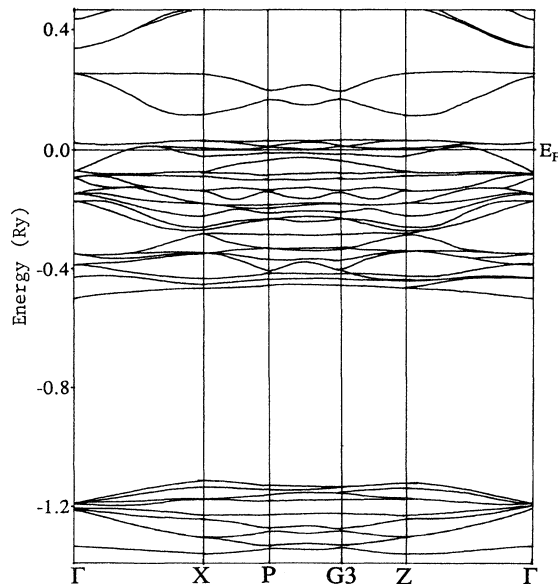


FIG. 3. Band structure of antiferromagnetic SrFeO₃.

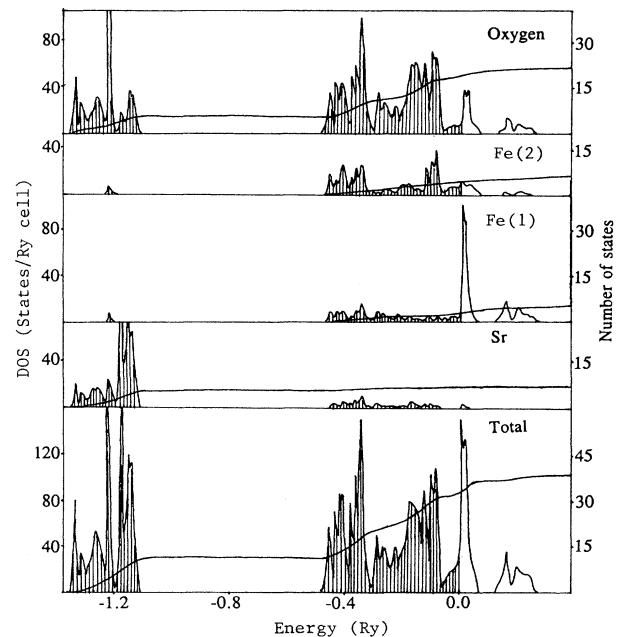


FIG. 4. Density of states of antiferromagnetic SrFeO₃.

tained for the paramagnetic calculations. The density of states given here represents the value calculated within the magnetic primitive cell which contains two formula units. The AF band structure and the density of states corresponding to the one spin direction are shown in Figs. 3 and 4. In Fig. 4 the Fe(1) and Fe(2) atoms represent the two different Fe atoms belonging to the two sublattices having opposite spin orientations. As the magnetic moments possessed by the oxygen and strontium species are negligible, their up-spin and down-spin densities of states are not distinguished. The density of states corresponding to the other spin direction can be obtained by interchanging the Fe(1) and Fe(2) density of states.

IV. BAND STRUCTURE AND MAGNETISM OF SrCoO₃

A. Paramagnetic band structure of SrCoO₃

As was done for SrFeO₃, the trial potential parameters obtained from the Herman-Skillman charge densities were used to initiate the self-consistent iterations. The calculations showed that the O 2s and Sr 4p orbitals to lie deeper below the conduction bands and the conduction bands are found to arise from the hybridization of the Co 3d and O 2p orbitals as was expected. The calculation has given a value of 0.463 Ry for the conduction bandwidth and the density of states at the Fermi energy is found to be 117.886 states/Ry f.u.

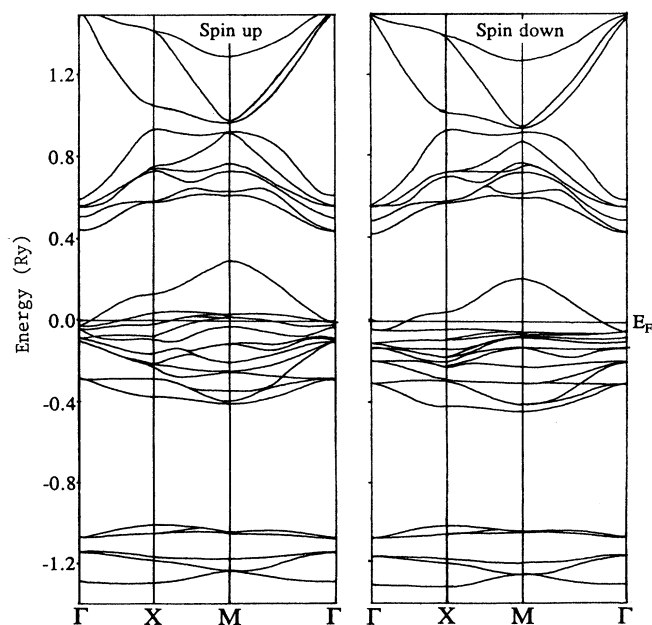


FIG. 5. Band structure of ferromagnetic SrCoO₃.

B. Ferromagnetic band structure of SrCoO₃

As the paramagnetic calculation is inadequate to describe this system since it has ferromagnetic ordering, we did the electronic structure calculations for the ferromagnetic phase. As was done for the AF calculation in SrFeO₃, the ferromagnetic calculations were initiated by assuming a finite magnetic moment at all atomic sites. Here again the self-consistent potential parameters obtained from the paramagnetic calculation were used as the trial potential parameters. After the self-consistency is achieved, local magnetic moments were found to exist at the Co and O sites whereas, there was a negligible moment at the strontium site. Our calculations have given a value of $1.691\mu_B$ and $0.190\mu_B$ for the magnetic moments at the Co and O sites, respectively. Our calculated values of the magnetic moments are found to be in fairly good agreement with the experimental work of Takeda *et al.*¹⁰ who have reported a magnetic moment of $1.25\mu_B$ at the Co site and $0.1\mu_B$ at the O site. The ferromagnetic calculations indicate that the magnetic moment at the oxygen site results from the O 2p orbitals and the exchange splitting of the O 2p level is 0.017 Ry. The density of states at the Fermi energy is 57.567 states/Ry f.u. and the conduction bandwidth is 0.479 Ry. As in the case of SrFeO₃, the value of the density of states at the Fermi energy obtained from the ferromagnetic calculations is very much different from the value obtained in the paramagnetic calculations. The calculated band structure and density of states corresponding to the up-spin and down-spin electrons are shown in Figs. 5 and 6. The electron distribution to the various subbands and the subband contribution to the density of states at the Fermi energy are given in Table III. As seen from the Table III, the density of states at the Fermi energy is mainly contributed by the Co and O atoms.

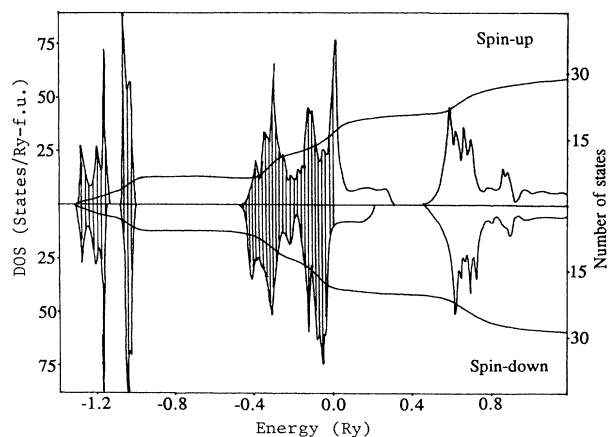


FIG. 6. Density of states of ferromagnetic SrCoO₃.

TABLE III. Partial contributions to the density of states at the Fermi energy [$N(E_F)$] and the number of states (NOS) of ferromagnetic SrCoO₃.

	$N(E_F)$ (states/Ry-f.u.)			NOS (electrons per f.u.)		
	<i>s</i>	<i>p</i>	<i>d</i>	<i>s</i>	<i>p</i>	<i>d</i>
			Spin-up			
Sr	0.241	0.163	0.996	0.115	3.076	0.417
Co	0.054	0.134	33.935	0.188	0.307	2.624
O	0.190	14.452	1.009	2.775	6.677	0.174
			Spin-down			
Sr	0.003	0.020	0.032	0.120	3.085	0.435
Co	0.089	0.296	2.537	0.201	0.318	4.283
O	0.116	2.991	0.305	2.794	7.191	0.218

V. DISCUSSION OF RESULTS AND CONCLUSION

The AF and ferromagnetic band-structure calculations on these oxides have provided a good description of the electronic structure and magnetic properties of these oxides. As expected in the case of perovskite oxides, the O $2p$ orbitals have strong hybridization with the Fe and Co $3d$ orbitals and these hybridized orbitals give rise to the conduction bands. Further these hybridized orbitals are found to dominate the electronic structure of these oxides and the density of states at the Fermi energy is mainly contributed by the Fe and Co and O atoms. This leads us to conclude that the Fe-O or Co-O bands are of primary importance in determining the properties of these oxides. This is in agreement with Goodenough's description of the perovskite oxides according to whom the M -O overlap strength is of the utmost importance in describing the perovskite oxides. However, as the conduction bands are found to arise mainly from the hybridization of the Fe or Co d orbitals and O $2p$ orbitals, our calculations indicate no evidence of Fe or Co ion to be in d^4 or d^5 outer electron configuration and the general features of the results of our calculation are in good agreement with the Goodenough's predictions.

In the case of SrCoO₃, the experimental estimates of the magnetic moments at the Co and O sites have been made and it is found that the magnetic moments of Co and O are parallel.¹⁰ The magnetic moments obtained from our ferromagnetic calculations are in good agreement with the experimental results. In the case of SrFeO₃, the experimental studies indicate that the magnetic moments of Fe and O are not parallel¹⁰ and this could not be incorporated in the calculations. This could be the reason for the observed difference in magnitude of

the magnetic moment at the O site between the theory and experiment. However the magnetic moment at the Fe site compares favorably well with the experimental value.

Soft-x-ray spectroscopy (SXS) of metals has been very helpful in the measurement of conduction bandwidth of several metals for the past few decades¹³ and band-structure results were in good agreement with the experimental measurements.¹⁴ In recent years the technique of photoelectron spectroscopy has emerged as one of the most important methods for obtaining information on the electronic structure of metals and alloys.¹⁵ Unfortunately such measurement have not been done on the compounds whose band structures are reported here. However XPS measurements have been performed on La-based compounds such as LaFeO₃, LaCoO₃, etc. We would like to stress at this stage that very little experimental data is available on perovskite oxide systems in general and there is lot of scope to perform various experiments to extract more useful information about these compounds. It should be stated that enough caution should be exercised when a comparison is made between the experimental measurement and the theoretical result as often these compounds are nonstoichiometric as prepared. For instance, SrFeO₃ when prepared under normal conditions is only SrFeO_{2.5}.⁴ From a theoretical point of view LMTO-ASA should work much better in these cases compared to layered perovskite compound such as La₂CuO₄ (Ref. 16) as the former is more closely packed.

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