Modern Physics Letters B, Vol. 6, No. 2 (1992) 103–112

ELECTRONIC STRUCTURE OF THE PEROVSKITE OXIDES $SrCrO_3$ AND $PbCrO_3$

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Received 15 January 1992

The electronic structure calculations of the perovskite oxides $SrCrO_3$ and $PbCrO_3$ performed both in the paramagnetic and antiferromagnetic phases are reported here. The calculations were carried out using the Linear Muffin Tin Orbital method within the Atomic Sphere Approximation. The quantitative results obtained are found to give a good description of the electronic states of $SrCrO_3$ and are in agreement with the Goodenough's qualitative chemical picture. However, it is not able to predict the semiconducting gap in $PbCrO_3$ which is an antiferromagnetic semiconductor. But the value of the theoretically calculated magnetic moment at the Cr site in $PbCrO_3$ is found to be in good agreement with the experimentally observed value. The calculations show strong hybridisation between the Cr-3*d* and O-2*p* orbitals and the density of states at the Fermi energy has major contributions from these hybridised orbitals.

1. Introduction

The study of the perovskite related oxide systems gained momentum especially after the discovery of the high temperature superconductors. The identification of isotropic potassium doped $BaBiO_3$ having a fairly high superconducting transition temperature gave added importance to the study of these oxides.[1] In all the perovskite related oxides such as A_2MO_4 and AMO_3, the MO_6 octahedra formed by the M–O bonds are believed to be important in understanding their properties.[2] In the present work, we have focused our attention on the cubic perovskite oxides (AMO_3) alone and in these oxides, the MO_6 octahedron is formed by the strong 180° M–O–M linkage that exists between the M and O atoms.[2,3] The characteristics of the bands arising out of the M–O–M bond depend on the nature of the M–cation and hence, changing the M–cation from one element to another will have a large influence on the M–O–M bands and hence their properties. For instance, one can consider the example of the insulator $SrTiO_3$ going to the metallic state when the M–cation is changed from Ti to V or Cr.[3–5] Even though the bands arising from the M–O–M linkage are more important in describing these oxides, there are typical cases where the change of the A-cation also drastically affects the properties. The two oxides, viz., $SrCrO_3$ and $PbCrO_3$ which we are considering for the present investigation fall under this category. $SrCrO_3$ is metallic[5] whereas $PbCrO_3$ is a

semiconductor.[2] It has also been found that the magnetic properties are different as $SrCrO_3$ is Pauli paramagnetic whereas $PbCrO_3$ is an antiferromagnet.[6] In these systems, the M–O–M linkage remains the same and obviously the significant changes in their properties are due to the A-cation. The Cr ion which was in the nonmagnetic state in $SrCrO_3$ becomes a magnetic ion in $PbCrO_3$ coupled antiferromagnetically with the nearest neighbor Cr ions.

Goodenough[2] has described these oxides by considering the Cr ion to be in the d^2 outer electron configuration. Further, he has accounted for the transition from the collective electron Pauli paramagnetism to the band antiferromagnetism caused by the change of the A-cation from Sr to Pb through the M–O overlap parameter. In order to have quantitative estimates of the various band parameters which are important in the understanding of the properties of these oxides, we were motivated to do the rigorous electronic structure calculations of these oxides. Concerning the calculation of the electronic structure, one can expect a satisfactory description of the electronic structure of $SrCrO_3$ as it is a Pauli paramagnetic metal. But in the case of $PbCrO_3$ which possesses band antiferromagnetism the question as to whether an electronic structure calculation based on the local density approximation can be successful in describing its electronic states arises. However, in order to have a better understanding of the interesting aspects of these oxides and to see the extent of validity of the local density approximation in these oxides, we have done the electronic structure calculations of these two systems. In this paper we present the results of our electronic structure calculations and also discuss some comparisons of our observation with Goodenough's predictions.

The paper contains five sections in which a brief discussion of the method of calculation is given in Sec. 2. Section 3 deals with the paramagnetic band structure of $SrCrO_3$ and in Sec. 4 the paramagnetic and antiferromagnetic band structure calculations of $PbCrO_3$ are represented. The last section is devoted to the discussion of results and conclusion.

2. Structural Parameters and the Method of Calculation

Both the oxides considered in the present investigation crystallise in the cubic structure with one formula unit per primitive cell.[6,7] The lattice parameters are respectively 3.818 Å for $SrCrO_3$ and 4.00 Å for $PbCrO_3$. $PbCrO_3$ exhibits antiferromagnetic (AF) order below 100 K and its AF structure is quite simple in which one Cr ion has AF coupling with all the six nearest neighbor Cr ions.[2,6] The magnetic unit cell was constructed out of the perovskite cell and it is found to have the bct symmetry. The lattice parameters of the magnetic cell are respectively $a = b = \sqrt{2}a_0$ and $c = 2a_0$. The magnetic primitive cell contains ten atoms with two different Cr atoms having opposite spin orientations. The Linear Muffin Tin Orbital method within the Atomic Sphere Approximation (LMTO-ASA)[8,9] was used to calculate the band structure. The Atomic Wigner-Seitz sphere radii of the individual atoms were judiciously chosen subject to the constraint that the sum of the volumes

of the individual spheres is equal to the cell volume. The calculated values of the Wigner-Seitz radii are given in Table 1. The trial potential parameters were obtained from the Herman-Skillman atomic charge densities renormalised to the specified Wigner-Seitz radius. The Madelung contribution to the potential was also included and the Barth-Hedin exchange correlation scheme was used in all the calculations. The self-consistent iterations were continued till an accuracy of 1 mRy was achieved in the eigen values. In all the cases, the orbitals $4p$, $5s$ of Sr, $6s$, $6p$ of Pb, $3d$, $4s$ of Cr and $2s$, $2p$ of O were treated as valence orbitals.

Table 1. Wigner–Seitz sphere radii of the constituent atoms of $SrCrO_3$ and $PbCrO_3$ in a.u.

$SrCrO_3$			$PbCrO_3$		
Sr	Cr	O	Pb	Cr	O
3.468	2.410	2.224	3.603	2.521	2.378

As one of the systems ($PbCrO_3$) considered in the present investigation possesses AF order, it was necessary to do the AF electronic structure calculation for this system. Hence in the present work, we have done the calculations in the paramagnetic phase for $SrCrO_3$ while both in the paramagnetic as well as in the AF phase for $PbCrO_3$. The results of our calculations are described in the following sections.

3. Paramagnetic Band Structure of $SrCrO_3$

With the use of the trial potential parameters obtained from the Herman-Skillman atomic charge densities, the self-consistent iterations were continued till an accuracy of 1 mRy was achieved in the eigen values. The eigen values were calculated at 84 k-points uniformly distributed in the irreducible wedge of the simple cubic Brillouin zone. The calculated band structure and the corresponding density of states are shown in Figs. 1 and 2. The band structure resembles that of $SrTiO_3$ and a small gap between the t_{2g} and e_g manifolds of the Cr-$3d$ orbitals is observed.[10] The conduction band has the major contribution coming from the Cr-$3d(t_{2g})$ orbitals and the conduction band width is 0.087 Ry. The density of states at the Fermi energy ($N(E_F)$) is 45.751 states/Ry-FU. The calculations have indicated that the conduction band contains 2 electrons per primitive cell. Even though there is a strong overlap between the Cr-$3d$ and O-$2p$ orbitals, the O-$2p$ orbitals are found to be comparatively in the localised state as in the case of $SrTiO_3$. The low-lying six bands are due to the O-$2s$ and Sr-$4p$ orbitals respectively. The electron distribution to the various sub-bands (number of states (NOS)) and the partial contribution to the density of states at the Fermi energy are given in Table 2. The results of our calculations have indicated that the charge states of the Sr, Cr, and O spheres are respectively 0.433^+, 1.284^+, and 0.573^-.

Experimental studies on this system have shown that it is a Pauli paramagnetic metal[5] having a resistivity value of the order of 10^{-5} Ωcm. Goodenough has des-

cribed this system by considering the outer electron configuration of Cr ion to be in the d^2 state (Cr ion is considered to be in the 4^+ state) and this is in agreement with what has been observed from the band structure calculations as described below. The nine bands that lie immediately below the conduction bands are mainly due to the strong hybridisation of the O-2p orbitals with the Cr-3d orbitals and these bands are found to be similar to the valence band in $SrTiO_3$. As these nine bands are separated from the conduction bands by a small gap, it gives the indication that the conduction bands are mainly due to the d^2 electrons of Cr.

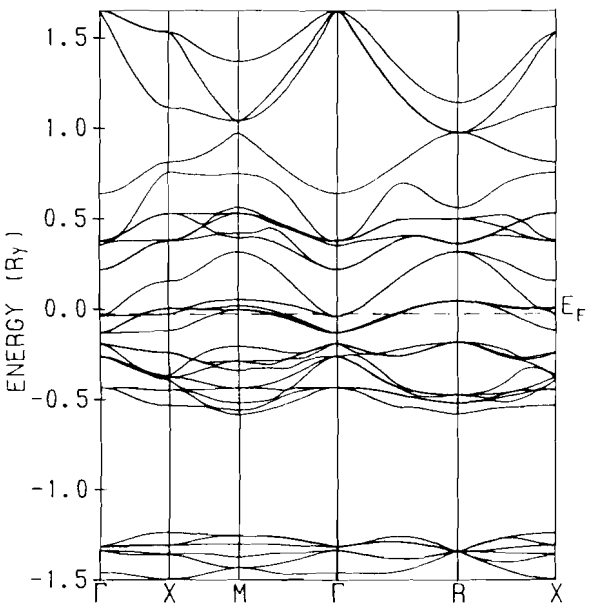

Fig. 1. Band structure of $SrCrO_3$.

Table 2. Electron distribution to the sub-bands and the sub-band contribution to the density of states at E_F of $SrCrO_3$.

	NOS (electrons/FU)			$N(E_F)$ (states/Ry-FU)		
	Sr	Cr	O	Sr	Cr	O
s	0.277	0.337	5.494	0.093	0.017	0.151
p	6.225	0.591	13.981	0.049	0.032	7.272
d	0.969	3.807	0.316	0.675	33.182	1.980

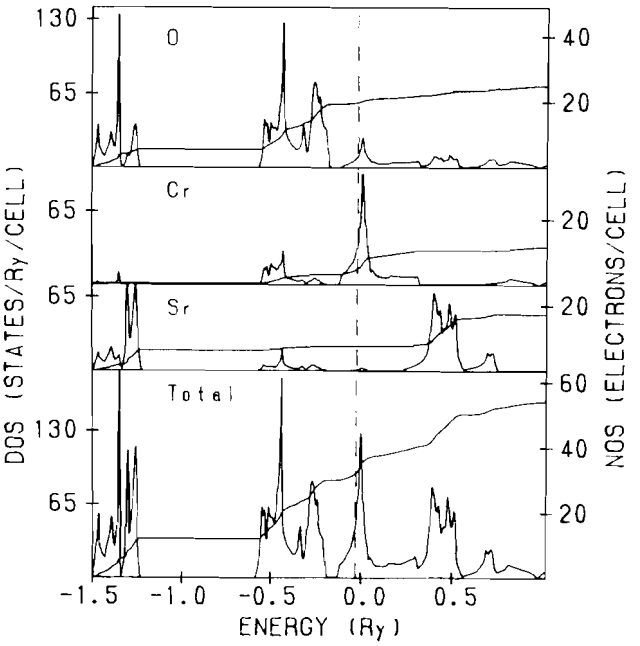

Fig. 2. Density of states of $SrCrO_3$.

The value of the $N(E_F)$ obtained was used to calculate the Pauli paramagnetic susceptibility (χ_p) and the electronic specific heat coefficient (γ). They are expressed as

$$\chi_p = \mu_B^2 N(E_F), \tag{1}$$

$$\gamma = (\pi^2/3) k_B^2 N(E_F). \tag{2}$$

The calculated value of the Pauli susceptibility of $SrCrO_3$ is 1.084×10^{-4} emu/mole whereas the experimental value[5] is 7.50×10^{-4} emu/mole. The enhancement in the experimental susceptibility value from the theoretically calculated value is due to the Stoner enhancement factor and the Stoner enhanced susceptibility is given by the relation[11]

$$\chi_p^e = \chi_p/(1 - N_0(E))\langle V\rangle \tag{3}$$

where $N_0(E)$ is the density of states per spin at the Fermi energy and $\langle V\rangle$ denotes the angular average of the potential energy of interaction between the electrons. The factor $1/(1 - N_0(E))\langle V\rangle$ is called the Stoner enhancement factor. In other words, the ratio $\chi_p^{expt}/\chi_p^{cal}$ represents the Stoner enhancement factor. In the case of $SrCrO_3$ the enhancement factor is found to be 6.911. The value of γ of this system is found to be 7.93 mJ/K^2-mole. As there is no experimental measurement of γ is available for this compound, our calculated value could not be compared with the experimental results.

4. Band Structure and Magnetism of $PbCrO_3$

4.1. *Paramagnetic band structure of $PbCrO_3$*

As was done for the case of $SrCrO_3$, the paramagnetic band structure calculation was carried out for this system starting from the trial potential parameters obtained from the Herman-Skillman atomic charge densities. Even though the calculation is found to give a good overall description of the band structure of this compound, it is not successful enough in predicting the semiconducting gap of this system. As expected, the calculation shows strong hybridisation between the Cr-3*d* and O-2*p* orbitals and these hybridised orbitals give the major contribution to the conduction bands. Unlike the case of $SrCrO_3$, the conduction bands have contributions from the Pb-6*s* orbitals too and this Pb-6*s* orbital is found to lie at the bottom of the conduction bands.

4.2. *Antiferromagnetic band structure of $PbCrO_3$*

As this system possess AF ordering,[6] it was felt that it is important to include the effect of the magnetic ordering on the electronic structure of this oxide. Further, as the paramagnetic calculations are unable to account for the semiconducting gap of this oxide, it necessitated us to do the AF electronic structure calculations in order to see the extent of the validity of the local density approximation in this system and to see whether an AF calculation will be able to open up the semiconducting gap. Hence we have carried out the calculations taking into consideration the AF ordering. In order to initiate the AF calculations, we assumed positive spin splittings 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 completion of the self-consistent calculation, local magnetic moments were found to exist at the Cr sites while the magnetic moments at the Pb and O sites were negligible. Even though the AF calculation has provided a better description of the electronic structure of this system, unfortunately, it is not able to account for the semiconducting gap of this oxide. However the value of the magnetic moment at the Cr site obtained from our calculations is reasonably in good agreement with the experimental results. Our calculations have given a value of 1.414 μ_B whereas the experimental work of Roth *et al.*[6] gives a value of 1.732 μ_B. The density of states at the Fermi energy is found to be 55.558 states/Ry-Fu. The band structure and the density of states corresponding to one spin direction are shown in Figs. 3 and 4. In Figure 4, the Cr-I and Cr-II atoms represent the two different Cr atoms belonging to the two different sublattices having opposite spin orientations. As the magnetic moments of Pb and O are negligible, their up-spin and down-spin densities of states are not distinguished. The electron distribution to the different sub-bands are given in Table 3. From Table 3 it may be seen that the charge states of the Pb, Cr, and O spheres are respectively 0.577^+, 1.208^+ and 0.595^-.

Table 3. Electron distribution to the various sub-bands in the antiferromagnetic $PbCrO_3$.

	NOS (electrons/FU)					
	spin-up			spin-down		
	Pb	Cr	O	Pb	Cr	O
s	0.966	0.165	2.807	0.966	0.174	2.808
p	0.490	0.277	6.923	0.491	0.293	6.938
d	0.254	1.244	0.154	0.254	2.638	0.154

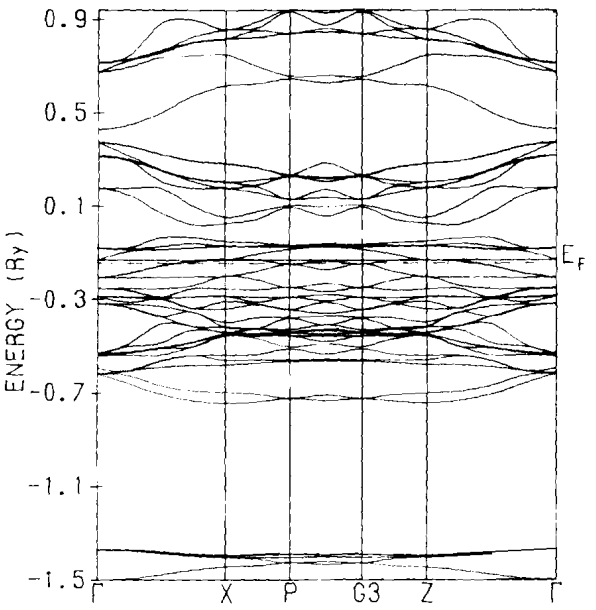

Fig. 3. Band structure of $PbCrO_3$.

5. Discussion of Results and Conclusions

The band structure of $SrCrO_3$ is found to be similar to that of $SrTiO_3$ except for the shift in the Fermi energy. The shift in the Fermi energy has been caused by the addition of two more electrons to the conduction band. Our earlier calculations[12] on the perovskite oxides $SrFeO_3$ and $SrCoO_3$ did not show the existence of the gap between the t_{2g} and e_g manifolds of the Fe/Co *d*-orbitals whereas in the case of $SrCrO_3$ such a gap is found to exist as in the case of $SrTiO_3$. As the cluster of nine bands that lie immediately below the conduction bands in this system is found to be similar to that of $SrTiO_3$, it may be inferred that, the conduction bands should

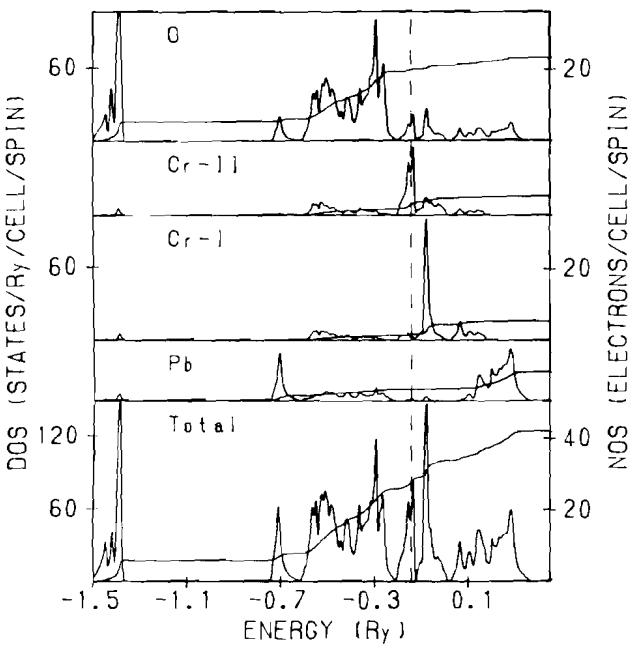

Fig. 4. Density of states of $PbCrO_3$.

be mainly due to the d^2 electrons of Cr. Furthermore, it has been observed that the cluster of nine bands are mainly due to the strong M–O–M linkage. Hence this shows that the O-2p orbitals are comparatively in the localised state as found in $SrTiO_3$. In the case of $PbCrO_3$, the strongly hybridised M–O bands extend upto the Fermi energy and hence the conduction bands of this sytem is found to contain 22 electrons per primitive cell. But in the case of $SrCrO_3$, our calculations have predicted only 2 electrons per primitive cell. Unlike the case of $SrCrO_3$, the conduction band of $PbCrO_3$ has additional contribution from the Pb-6s orbitals too and the small gap between the t_{2g} and e_g manifolds of the Cr-3d orbitals present in the case of $SrCrO_3$ is not obtained in the case of $PbCrO_3$. This gives no evidence of Cr ion in $PbCrO_3$ to be in the d^2 outer electron configuration. However the general features of our calculations agree well with the Goodenough's chemical picture and have predicted strong hybridisation between the Cr-3d and O-2p orbitals.

The AF electronic structure calculation of $PbCrO_3$ has predicted the existence of a local magnetic moment at the Cr site and has provided a better description of the electronic structure of this oxide. However, as in the case of La_2CuO_4,[13] the calculation is not able to predict the existence of the semiconducting gap in this system. This have made us to believe that localisation in this oxide is of Mott's type where the calculations based on the local density approximation is not successful. But it may be noted that the magnetic moment predicted by our

calculations compares fairly well with the experimental result. Another quantity that may be compared with the experimental results directly is the density of states histogram. However, because of the lack of the photoemission studies on this system, comparison could not be made.

Even though the M–O hybridisation in both the systems are similar, there arises differences in their A–O hybridisation. In the case of $SrCrO_3$, the O-2p orbitals have hybridisation with the Sr-5s orbitals whereas in the case of $PbCrO_3$, in addition to the hybridisation of the O-2p orbitals with the Pb-6p orbitals, it has hybridisation with the pb-6s orbitals too. Hence it can be expected that the strength of A–O hybridisation will be stronger in the case of $PbCrO_3$ and hence the shift of the O-2p bands due to the hybridisation will be larger for $PbCrO_3$. It has been found from our calculations that the centre of the O-2p band in $PbCrO_3$ lies about 0.034 Ry below than that of $SrCrO_3$.

The exchange splitting of the Cr-3d orbitals in $PbCrO_3$ was obtained from the AF calculation and its value is 0.078 Ry. As the exchange-splitting (Δ) is related to the Stoner integral (I) and the magnetic moment (m) by the relation[14]

$$I = \Delta/m \tag{4}$$

the value of the Stoner-I was calculated using the values of Δ and m and it is found to have a value of 0.056 Ry. The Stoner-I was used to get a rough estimate of the onsite repulsion between the d-electrons (U) which is about five times the value of Stoner-I. The value of U thus calculated is 0.28 Ry (3.808 eV). It may be mentioned here that the value of U calculated for the antiferromagnetic[15] $YBa_2Cu_3O_6$ is about 6.5 eV and because the calculated value of U for this system is fairly large as in the case of $YBa_2Cu_3O_6$, it suggests that this system may belong to the category of strongly correlated systems.

Acknowledgements

All the authors from Anna University acknowledge the financial support from UGC, India.

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