Electronic structure of Ca$_2$RuO$_4$: A comparison with the electronic structures of other ruthenates

L. M. Woods

Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200 and Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6032

(Received 14 April 2000)

Density-functional calculations are used to study the electronic and magnetic structures of Ca$_2$RuO$_4$. It is found that the magnetic and structural degrees of freedom are strongly coupled. It is also found that the electronic structure near the Fermi level is described by the antibonding Ru 4$d$ and O 2$p$ bands as is the case for other 4$d$ Ruddlesden-Popper materials. The distortion of the lattice has a pronounced effect on the magnetic ordering and localization of the carriers. The calculations give a good estimate of the magnetic moment and they indicate that there is a magnetic instability in this compound.

I. INTRODUCTION

It was discovered that Sr$_2$RuO$_4$ has superconductivity at a modest temperature of about 1 K. This compound is a perovskite ruthenium oxide and a representative of the Ruddlesden-Popper family, (Sr,Ca)$_{n+1}$Ru$_n$O$_{3n+1}$ with $n=1$. These materials exhibit a rich variety of magnetic phases. There is a strong resemblance in the structure to the cuprate compounds, the role of the RuO$_2$ plane is analogous to the role of the CuO$_2$ plane in the cuprates. The mechanism of superconductivity in Sr$_2$RuO$_4$ is widely studied. It was suggested that Sr$_2$RuO$_4$ is a possible candidate of a superconductor. The assumption is that the triplet pairing is induced by ferromagnetic fluctuations. Since SrRuO$_3$ is a strong ferromagnet, ferromagnetic fluctuations should be present in Sr$_2$RuO$_4$. It was calculated that Sr$_2$RuO$_4$ has a tendency of ferromagnetism. The importance of the electronic correlation effects are the subject of an ongoing discussion in the literature. Reference 4 claims that correlation effects are not qualitatively important and many properties can be explained with the traditional density-functional theory. Reference 5 presents LDA + $U$ electronic structure calculations. They find that the correlation effects are not large, but they need to be included in describing the features of the electronic structure. Also a simple tight-binding model with an analytical expression for the band dispersion near the Fermi level is introduced. The results can be used in the calculation of physical quantities that depend on the explicit form of the band structure.

Another representative of the Ruddlesden-Popper (RP) group has been synthesized—Ca$_2$RuO$_4$ (CRO). The reported measurements in these papers are quite different. The authors from Ref. 8 perform powder x-ray diffraction. Their results for the crystal structure and the lattice constants differ from the reported data in Ref. 9. The most complete work on this compound is found in Ref. 10, where it is measured that CRO possesses several crystal-structure phases that depend on temperature and oxygen content. Their results were confirmed by Ref. 11, where the same experimental technique is used—powder neutron diffraction. The measurements show that unlike Sr$_2$RuO$_4$ which has flat RuO$_2$ planes, CRO has distorted (tilted and rotated) RuO$_2$ planes. It also has two different insulating antiferromagnetic phases and a phase that is a nonspinpolarized metal. The short Ru-O distances indicate a significant transition-metal oxygen hybridization near the Fermi surface. The resistivity measurements show that one of the structural phases is an insulator over the entire temperature region. The other structural phase is an insulator below about 150 K and after that it becomes a metal.

Calculating the electronic structure of this material is the first step towards understanding its rich variety of physical and magnetic properties. To our knowledge this is the first detailed electronic structure calculation on this compound presented in the literature, although some results of a similar calculation were reported in Ref. 12. In order to address some of the aspects of the problem, we have calculated the self-consistent electronic structure of Ca$_2$RuO$_4$ in the framework of density-functional theory (DFT) using a relativistic linearized augmented plane-wave (LAPW) method. Density-functional theory is used to determine the ground-state total energy and electron density of states of many materials. However, it does not guarantee that excitations will be reproduced correctly. Failure of this theory is widely observed as an underestimating of the measured band gaps of most materials, especially 3$d$ materials. Nevertheless, we can obtain useful qualitative information about the electronic structure of Ca$_2$RuO$_4$.

The paper is organized as follows. In Sec. II we give details of the method of the calculation. In Sec. III the results for the different phases for the band structure and the density of states are presented. Section IV is devoted to conclusions.

II. CALCULATION METHOD

All members of the RP series are materials with open 4$d$ shells. A very important feature of the $d$ orbitals is that they are concentrated closer to the nucleus than the $s$ and $p$ orbitals. For example, 3$s$, 3$p$, and 3$d$ have the same energy, but for angular momentum $l=0,1$ the orbital is more extended into space than the one with $l=2$. Thus, the $d$ states are less influenced by the neighboring atoms. In many compounds
with open $d$ shells the Coulomb energy $U$ between two $d$ electrons on the same site is large, which means that the $d$ electrons are localized and the correlation effects become important. The $4d$ states suggest weaker localization and correlation effects, since they are more extended than the $3d$ states.

On the other hand, the Ca substitution for the Sr in Sr$_2$RuO$_4$ is the reason for the tilt and rotation of the RuO$_6$ octahedra, because the ionic radius of the Ca atom is smaller than the ionic radius of the Ru atom (compare $R_{Ca}=0.99$ Å with $R_{Ru}=1.18$ Å). However, the shape of the octahedron is distorted differently in the different structural phases. The distortion will diminish the matrix elements between the $d$ states and the states on the adjacent atoms. Thus, there are two competing processes: (i) the extension of the $4d$ orbital due to the larger quantum number compared to the $3d$ orbitals will make the correlation effects less important, and (ii) the distortion of the lattice due to smaller ionic radius will act towards localization and make the correlation effects more important. Therefore, the question if the ruthenates can be described by the conventional band theory, or by a strong-correlation theory, is still open.

For a system with strong correlation effects, as is the case for layered cuprates, the conventional local-density approximation (LDA) does not describe properly the antiferromagnetism in the compounds. The LDA either fails to reproduce the magnetic instability, or underestimates the magnetic moments and band gaps.

So far, the reported electronic structure calculations using the LDA for the $4d$ materials show that LDA is suitable for their description. The ferromagnetism for SrRuO$_3$ and its total magnetization predicted by the calculation and measured by experiment agree; the antiferromagnetism for Sr$_2$RuYO$_8$ and its magnetic moment are reproduced in agreement with experiment; Sr$_2$RuO$_4$ and CaRuO$_3$ are predicted correctly to be paramagnets. Thus, we want to see how the LSDA method will describe the parameters and magnetic ordering of Ca$_2$RuO$_4$.

In our calculations we utilize the full-potential linearized augmented plane-wave method in the wien97 code. This is an application of the density-functional theory. The Kohn-Sham equations are solved with a basis of linearized augmented plane waves. For the exchange and correlation potential the local spin-density parametrization (LSDA) of the exchange-correlation energy by Perdew and Wang is used. As usual, the core electrons are treated relativistically, while the valence electrons are treated with a scalar relativistic procedure.

Three sets of data are presented--non-spin-polarized and with a ferromagnetic and antiferromagnetic orderings. The calculations were done for all reported structural phases in Refs. 10 and 11. The atomic sphere radii were chosen to be $R=1.8$ Å for the Ru, Ca, and O atoms. For the Ru atoms the states up to $3d$ are taken as core states, for the Ca atoms the core states are up to $2p$, and for the O atoms the $1s$ orbital is considered as a core state. The plane-wave cutoff is $K_{M}K_{MAX}=8.0$ and we used 168 $k$ points in the irreducible wedge of the Brillouin zone. The results did not change with the increase of the $k$ points. The experimental values for the lattice constants and positions of the atoms were used.

### III. ELECTRONIC STRUCTURE

#### A. Structural model

There are two phases with respect to the long-axis $c$-S-CRO (short $c$) and excess oxygen O-CRO (long $c$). The crystal structure of Sr$_2$RuO$_4$ is that of K$_2$NiF$_4$. It is demonstrated that in Ca$_2$RuO$_4$ in both phases the ideal K$_2$NiF$_4$ is severely distorted—the RuO$_6$ octahedra are rotated and tilted. The octahedra remain rigid which is related to the covalency of the Ru-O bond.

It is found that for S-CRO the lattice constants are changing with temperature, but the space group stays the same—Pbca. The Pbca symmetry group is responsible for the splitting in Ru-O(1) bond distances. For the same reason there are four Ca-O(1) distances [compare to one Sr-O(1) distance] and five Ca-O(2) distances [compare to two Sr-O(2) distances]. The Pbca space group has four formula units per unit cell. One of the units (Ru) has four equivalent atoms, the other three [Ca, O(1), and O(2)] each has eight equivalent atoms. Thus, it is obvious that this is a very demanding calculation.

The angle of the rotation of the octahedron is rather large—$\phi=11.8^\circ$ and it is temperature independent. The bond angle from $\theta=180^\circ$ [Ru-O(1)-Ru] for Sr$_2$RuO$_4$ is reduced to $\theta=151^\circ$ at 11 K. The tilting angle increases from $11.2^\circ$ at room temperature to $12.7^\circ$ at $T=11$ K. The magnetic structure is very interesting—below $T=110$ K the antiferromagnetism is A-centered, that is the Ru at (0 0.5 0.5) is equivalent to the one at the origin. After $T=110$ K the antiferromagnetism is B centered, the Ru at (0 0.5 0.5) is equivalent to the one at the origin.

The other crystal phase O-CRO is more stable with temperature. Below $T=150$ K the space group is the same Pbca, with the same rotational angle as in S-CRO and the material is a B-centered antiferromagnet. Above $T=150$ K the space group changes from Pbca to $P_{2_{1}/c}$ and O-CRO becomes a paramagnet. The monoclinic angle in $P_{2_{1}/c}$ always stays very close to $90^\circ$. $P_{2_{1}/c}$ is also a subgroup of Pbca, and the Ca, Ru, and O sites are split. Thus, there are now eight formula units per unit cell. This is the reason for the increase of free parameters in this structure. In the $P_{2_{1}/c}$ phase the tilt is highly suppressed, which is compensated by a larger rotation angle. The most important structural parameter for this Ru layered compounds is the distance of the in-plane Ru-O bond. The structure of the Ru-O coordinates is similar to the metallic S$_2$RuO$_4$. Thus, one would expect that the electronic properties of the $P_{2_{1}/c}$ phase would be similar to the electronic properties of S$_2$RuO$_4$.

#### B. Band structure

We calculated the band structure of S-CRO and O-CRO with no magnetic ordering first. We find that even though the lattice constants are changing with temperature for the Pbca symmetry group there are practically no changes in the band structure. However, when compared with the $P_{2_{1}/c}$ space group there are some differences. The band structure for the two symmetries are shown in Figs. 1(a) and 1(b). The crystal field splits the Ru $d$ orbitals into three $t_{2g}$ and two $e_{g}$ orbitals. The valency of the Ru is four, so the $d$ band has four
electrons which are located on the $t_{2g}$ levels. The flat bands around the Fermi level are mainly $t_{2g}$ with some admixture of O $2p$ bands due to the hybridization. The paramagnetic calculation predicts that a metallic state arises for both phases.

The bands crossing $E_F$ are antibonding and they are due to the Ru $t_{2g}$ and the in-plane O $2p$. The unoccupied $e_g$ bands are located above the $t_{2g}$ bands and they are separated by about 1 eV. The bands lying under $-2$ eV are the bonding states of the Ru $d$ and O $p$ orbitals, and the nonbonding states of $p$. One notes that the bands from R-$\Gamma$ are almost symmetrical to the bands from the M-$\Gamma$ portion of the Brillouin zone.

The bandwidth in this Ru $d$ materials comes from the Ru-O-Ru interaction and it depends on the bonding angle $\phi$. The bandwidth $w$ is proportional to $\cos^2 \phi$. The bond angle in Sr$_2$RuO$_4$ is close to 180°, so $w$ is maximum. Electronic structure calculations predict that the bandwidth is about 3.1 eV. In Ca$_2$RuO$_4$ due to the tilt and rotation of the octahedra the bond angle $\phi$ is reduced to 151°, and the bandwidth should be reduced by approximately 0.74 eV and it should become 2.36 eV. From Figs. 1(a) and 1(b) one estimates that $w \approx 2.5$ eV. Thus, the distortion of the lattice due to rotation and tilt of the octahedra has a pronounced effect of decreasing of the bandwidth, which means that the electrons should become more localized in comparison with Sr$_2$RuO$_4$.

The electronic structure calculations with ferromagnetic ordering for the S-CRO produced an exchange splitting near the Fermi level between spin-up and spin-down states. For the case of the S-CRO phase at 11 K (Ref. 10) the exchange splitting is calculated to be in the order of 0.8 eV. The band structures for the different parameters at the different temperatures$^{10}$ practically did not change. The magnetic moments that we have obtained are the following: the Ru atom has a moment of about $1.08 \mu_B$, O(1) has a moment of $0.11 \mu_B$, and O(2) has a moment of $0.12 \mu_B$. The oxygen contribution is largely due to the strongly hybridized bands near $E_F$. Similar values are obtained for the ferromagnetic (FM) calculations with the other reported data in Ref. 10.

Finally, a third set of calculations were done, a calculation with an antiferromagnetic (AFM) ordering for the appropriate phases. We found that the AFM and the FM cases are almost degenerate in energy. In fact, the AFM case is about 1 meV lower in energy than the energy of the FM case. Thus, this is an indication of a close competition between the two magnetic orderings. A similar conclusion was found in the electronic structure calculation reported in Ref. 12.

It was found experimentally$^{10}$ that the S-CRO phase has two coexisting magnetic modes. The ordered moment of the first mode (A centered) saturates when an onset of the second one (B centered) is observed with a magnetic moment. The A-centered mode is considered the main contribution to the AFM ordering. In O-CRO only the B-centered mode is the dominant one. It is determined experimentally$^{10}$ that the magnetic moment is $1.3 \mu_B$, which is smaller than the ideal $2 \mu_B$ expected for Ru. We have performed AFM calculations for all structural phases that are reported to be AFM and we find similar results. The magnetic moment for the Ru atom is calculated to be about $1 \mu_B$ and the magnetic moment for oxygen is about $0.12 \mu_B$. Again, the contribution from the

---

FIG. 1. (a) The band structure of S-CRO with space group $Pbca$. (b) The band structure of O-CRO with space group $P_{21/3c}$. 

---
oxygen is largely due to the hybridization. The AFM phases are measured to be insulators with an optical gap of about 0.2 eV. The band structure is given in Fig. 2 and it is similar to the band structure of the non-spin-polarized S-CRO, except that the bands around $E_F$ become even more flat, especially in the $R$-$\Gamma$ and $M$-$\Gamma$ directions. The LSDA calculation could not open the experimentally observed gap, thus, the AFM S-SRO calculated by LSDA is still a metal. The calculation also suggests that there is a magnetic instability and it gives a good estimation of the magnetic moment.

C. Density of states (DOS)

We present the calculated projected density of states (DOS) for the experimental structure for the three sets of magnetic ordering—in Fig. 3 the DOS for the paramagnetic $Pbca$ phase is shown, in Fig. 4 the DOS for the paramagnetic $P2_1/c$ is shown, in Fig. 5 the DOS for the FM $Pbca$ is shown, and finally the DOS for the AFM $Pbca$ is also given in Fig. 6.

The lattice constants change with temperature, but as it was the case for the band structure, only minor changes are found within the same structural and magnetic phases. The major differences are in the non-spin-polarized calculations between the $Pbca$ and $P2_1/c$ phases. Notice that in the latter symmetry the number of atoms is doubled. The partial density of the Ru atoms is very similar, the same is true for the Ca atoms. O I is similar to O III, and O II is similar to O IV. One of the main features is that the DOS is piled up near the Fermi level, although the peak structure for $P2_1/c$ at the Fermi level is somewhat broadened compared to the one for the $Pbca$. It looks like there is a tendency of splitting near $E_F$ from Fig. 4. The DOS for the $Pbca$, Fig. 3, is 29.4 states/eV, and for the $P2_1/c$, Fig. 4, the DOS is 21.4 states/eV; both numbers are indications of relatively high DOS. The hybridization between the Ru and O atoms is significant for both structural phases.

For the FM ordering the DOS for the spin down is 10.9 states/eV and 1.1 states/eV for spin up, which add up to 12 states/eV—Fig. 5. This is more than twice smaller than the nonmagnetic case. The DOS of the two spin channels in the FM are similar in shape; the same is true for the AFM—Fig. 6, except for the Ru atom, where for spin down a sharp peak appears at $E_F$, while for spin up the peak is relatively small. As was the case for the non-spin-polarized calculation, a significant hybridization is also present between the in-plane Ru and O atoms in both orderings—FM and AFM. The LSDA calculation did not produce a gap between the two spins in the AFM case.
All main features of the DOS for the different structural and magnetic phases are similar. The DOS between $-2\,\text{eV}$ and $-8\,\text{eV}$ reflects the bonding between Ru $d$ and O $p$, and it is mainly of O $2p$ character. In the interval of $4-6\,\text{eV}$ the peaks are entirely due to the Ca contribution. The antibonding states of the Ru and O orbitals are just located around $E_F$.

A very important fact for the electronic structure of Ca$_2$RuO$_4$ is the tilting of the RuO$_6$ octahedra. There is no tilting in Sr$_2$RuO$_4$ and calculations show$^{16}$ that there is a peak at the Fermi level in the DOS. In the $P_{2_1}/c$ structural phase, which has a similar Ru-O coordination as the one of Sr$_2$RuO$_4$, it has a moderate tilting. It looks like the peak tends toward splitting. In the $Pbca$ phase the tilting is even more enhanced and the peak seems to be suppressed. A similar tendency was noticed when comparing Sr/CaRuO$_3$ and Sr$_2$YRuO$_6$. The tilting is also the reason for the reduction of the bond angle. As was discussed in the previous section, this leads to higher hybridization between Ru and O, which narrows the bands.

The presence of a strong hybridization between the Ru 4$d$ and O 2$p$ states leads to a strong coupling between the structural and magnetic degrees of freedom, and this is characteristic for the RP materials. The covalency of the Ru-O bond requires some of the magnetic moments of the Ru atom to be located on the O atom. Usually, the effect of the oxygen will

FIG. 4. Total and partial electronic DOS of non-spin-polarized O-CRO with space group $P_{2_1}/c$.

FIG. 5. The total DOS of spin down and spin up for S-CRO with ferromagnetic ordering. The solid line is for spin up and the dotted line is for spin down.

Sr$_2$YRuO$_6$. The tilting is also the reason for the reduction of the bond angle. As was discussed in the previous section, this leads to higher hybridization between Ru and O, which narrows the bands.

The presence of a strong hybridization between the Ru 4$d$ and O 2$p$ states leads to a strong coupling between the structural and magnetic degrees of freedom, and this is characteristic for the RP materials. The covalency of the Ru-O bond requires some of the magnetic moments of the Ru atom to be located on the O atom. Usually, the effect of the oxygen will

FIG. 6. (a) The total DOS of spin up (solid line) and spin down (dotted line) of the Ru atom of S-CRO with antiferromagnetically ordering. (b) The total DOS of spin up (solid line) and spin down (dotted line) of the O atom.
cause ferromagnetic ordering inside the layer. Thus, the magnetic fluctuations in the layered ruthenates would have ferromagnetic character in the plane. An example is Sr$_2$RuO$_6$. The case with the Ca$_2$RuO$_6$ is different. The $P_{2_1/c}$ phase has a similar Ru-O coordination as Sr$_2$RuO$_6$ and one expects and finds many similarities in the electronic structure. For the other phase $Pbca$ another factor comes into play—the tilting of the octahedra becomes significant and the compound is antiferromagnetic. Thus, it seems that the existing of tilting and AFM ordering are coupled, and the tilting works towards the destabilization of the FM state and the appearance of antiferromagnetism, where the oxygen atoms are positioned between Ru atoms with opposite spins. According to Ref. 12 the effect of nesting is the cause for the AFM transition. The nesting can be increased by a reduction of the hopping between the nearest neighbors. The tilting is directly connected to the reduction of the bonding angle in the Ru-O plane. This leads to a decrease of the bandwidth and hopping.

IV. CONCLUSIONS

We have presented band-structure calculations for the Ruddlesden-Popper representative Ca$_2$RuO$_4$ using the LSDA method. The expectation is that since the $4d$ orbitals are more extended and less localized DFT should be able to give a reasonable description. Recent theoretical results in the literature seem to support the above conclusion. Satisfactory electronic structure calculations were done for Sr$_2$CaRuO$_5$, Sr$_2$RuO$_4$, and Sr$_2$YRuO$_6$. Thus, the notion is that DFT could work in this case also.

We find that the structural phase $P_{2_1/c}$, which is a paramagnetic metal, is fairly well described by LSDA. For the other structural phase $Pbca$ which is an AFM insulator, LSDA predicts that there is an AFM ordering, but the material is still a metal. LSDA also predicts that there is a competition between the FM and AFM state in the $Pbca$ phase. The calculated magnetic moments for the different structures are in good agreement with the measured ones.

The calculated electronic structure shows many similarities with the electronic structures of other members of the RP group. There is a strong hybridization effect at the Fermi level, which is shown on the band structure and the DOS. The flat bands around $E_F$ are due to the antibonding between Ru and O. Below $-2$ eV the bonding between Ru and O is noticed. The electronic properties are mainly affected by the layered structure. The FM and the AFM cases are almost degenerate by energy, which suggests that there is a magnetic instability.

It is interesting to see that the electronic structure is composed in segments. Around the Fermi level only the Ru $4d$ and O $2p$ orbitals contribute. There is no direct contribution from the Sr or Ca, but yet their influence is strong. The substitution of Sr with Ca changes significantly the energy and DOS bands around $E_F$. The structural distortion due to a smaller radius of the Ca atom is significant. The effect of tilting of the RuO$_6$ octahedra can alter the magnetic ordering of the ground state. Although in the ruthenates the layer itself is FM ordered, here one finds an AFM transition when there is a significant tilting, which is responsible for the reduction of the bandwidth and the hopping. Thus, this compound is an example of how structural and magnetic degrees of freedom can influence each other.

ACKNOWLEDGMENTS

The author is grateful to Professor Gerald Mahan for reading this manuscript and Dr. David Mandrus and his group for sharing their experimental data about the compound. The author also would like to thank Dr. Cristian Halloy from the Joint Institute for Computational Science and Gerald Woods for their help in using the SP2 facility at The University of Tennessee.