Orbital-dependent phase control in $Ca_{2-x}Sr_xRuO_4$ ($0 \leqslant x \leqslant 0.5$)

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We present first-principles studies on the orbital states of the layered perovskites $Ca_{2-x}Sr_xRuO_4$. The crossover from antiferromagnetic (AF) Mott insulator for $x<0.2$ to nearly ferromagnetic (FM) metal at $x=0.5$ is characterized by the systematic change of the xy orbital occupation. For the AF side ($x<0.2$), we present firm evidence for the xy ferro-orbital ordering. It is found that the degeneracy of t_{2g} (or e_g) states is lifted robustly due to the two-dimensional crystal structure, even without the Jahn-Teller distortion of RuO_6. This effect dominates, and the cooperative occupation of xy orbital is concluded. In contrast to recent proposals, the resulting electronic structure explains well both the observed x-ray-absorption spectra and the double-peak structure of optical conductivity. For the FM side ($x=0.5$), however, the xy orbital with half filling opens a pseudo-gap in the FM state and contributes to the spin $S=1/2$ moment (rather than $S=1$ for $x=0.0$ case) dominantly, while yz,zx states are itinerant with very small spin polarization, explaining the recent neutron data consistently.

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I. INTRODUCTION

The spin and orbital structures in $Ca_{2-x}Sr_xRuO_4$ ($0 \leqslant x \leqslant 0.5$) attract much attention recently as a model system of t_{2g} electrons. It is an antiferromagnetic (AF) Mott insulator for $x<0.2$, but nearly ferromagnetic (FM) metal at $x=0.5$.[1–3] There are four electrons occupying t_{2g} states per Ru^{4+}, while e_g states are empty. The isovalent substitution of Sr for Ca does not change the number of electrons, but modifies the crystal structure systematically[3] due to their different ionic radii. The key issue here is the orbital degree of freedom, which couples with lattice and magnetism strongly. Extensive experimental[4–8] and theoretical[9–12] studies have been done for this issue, while the present understanding of this compound is quite controversial.

First, for the AF side ($x=0.0$), the preferential occupation of the xy orbital was predicted by earlier calculations.[9,10] However the O 1*s* x-ray-absorption spectroscopy (XAS) study reported the occupation of about 0.5 holes in the xy orbital.[4] In addition to this, the photoemission experiment suggested strong spin-orbit coupling (SOC), leading to the proposal of complex t_{2g} orbitals.[4] The presence of 0.5 holes in the xy orbital also led Hotta and Dagotto[12] to propose the ''antiferro-orbital ordering'' (AFO) with 2×2 periodicity of RuO_6 in the plane. The recent experiment on optical conductivity was interpreted in terms of this orbital pattern.[5] However, the lattice distortion corresponding to the AFO (i.e., the 2×2 structure) is not observed experimentally, and the orbital pattern of AFO is not consistent with the recent resonant x-ray scattering experiment,[6] in which no superlattice peak was observed. Second, for the nearly FM side ($x=0.5$), the fitting of the Curie-Weiss-type susceptibility suggested $S=1/2$ spin moment,[2] in sharp contrast with the high-spin ($S=1$) state for $x=0.0$. A similar picture may hold also for $x=0.2$.[7] The recent polarized neutron-diffraction studies for $x=0.5$ (Ref. 8) suggested dominant magnetization distribution on the xy orbital rather than the theoretically suggested yz/zx orbitals.[10] Therefore it is an important and challenging issue to determine the orbital state of $Ca_{2-x}Sr_xRuO_4$ explaining consistently the available experiments, which we undertake in this paper.

We show that the crossover of magnetic properties with increasing doping x is characterized by the systematic change in the xy orbital occupation. For the AF side ($x<0.2$), we conclude that the predicted ferro-orbital (FO) ordering with dominant xy occupation explains well (a) the XAS spectra and (b) the double-peak structure of the optical conductivity. We further point out that the stabilization of the xy state is quite robust, and mostly due to the two-dimensional (2D) crystal field, which has not been considered seriously so far. In contrast to the AF side, for $x=0.5$, the electronic structure is characterized with the yz/zx states with small moment and the xy orbital with half filling, which opens a pseudo-gap in the FM state and contributes to the $S=1/2$ moment dominantly. This picture, which is in strong contradiction to the previous proposal,[10] explains the neutron data[8] consistently.

II. CALCULATION METHOD

The calculations were done with the first-principles plane-wave pseudopotential method. In our previous work,[9] the effects of structural distortions were emphasized by taking into account important distortions mostly, however here we use the experimental structures to compare the calculated results with the measured spectra. Five experimental structures are considered, i.e., $x=0.0$ at 11 K and 295 K, $x=0.1$, 0.2, and 0.5 at 10 K.[3] Two kinds of magnetic states,

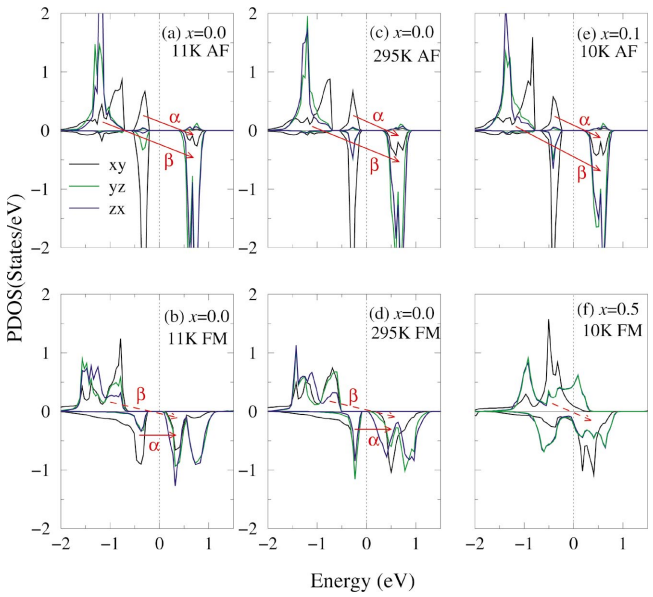

FIG. 1. (Color) The calculated PDOS of Ru-4d-t_{2g} orbitals for various states. The solid red arrows indicate the main optical transition paths, while the dashed red arrow shows the transition which is significantly suppressed. Note the transitions indicated here mean that from the states at one Ru^{4+} site to the corresponding states at nearest-neighboring Ru^{4+} site.

FM and staggered AF states, are considered for each structure. In the previous work,[9] the local spin-density approximation (LSDA) was adopted for the entire range. The validity of LSDA for predicting the stable magnetic state of ruthenates was demonstrated.[13] However for Ca_2RuO_4, though LSDA can predict the stability of AF magnetic order, the band gap does not open.[9,11] As we aim to analyze the optical conductivity also, a proper reproduction of the band gap is important. Therefore, we employ the LDA+U scheme[14,15] for the insulating region ($0 \leqslant x < 0.2$) with $U_{\text{eff}} = 2.5$ eV to reproduce the band gap of Ca_2RuO_4. The LSDA was employed for other region of x. The details of other aspects of the calculation were described in the previous paper.[9] For the studies of XAS spectra and optical conductivity, the interband transitions are calculated from the converged Kohn-Sham wave functions and eigenvalues, by using the core compensation form of pseudo-wave functions (see Ref. 16 for technical details).

III. RESULTS AND DISCUSSION

A. Ca_2RuO_4 ($x=0$)

We start with Ca_2RuO_4 at 10 K. Our calculations predict the AF ground state with energy gain about 28.2 meV with respect to the FM state. The mechanism for stabilizing the AF state was analyzed in our previous paper[9] in terms of lattice distortion, flattening, rotation, and tilting of RuO_6. The projected density of states (PDOS) in Fig. 1(a) suggests that the present situation may correspond to the localized spin picture of $S=1$, where the xy states are fully occupied and the yz/zx orbitals are half filled. In reality, as the Ru 4d orbitals are extended, inter-site hybridization modifies the picture quantitatively. For example, the occupation numbers (in LDA+U) are given as follows: $n^{\uparrow}_{xy}=0.86$, $n^{\uparrow}_{yz/zx}=0.87$, $n^{\downarrow}_{xy}=0.79$ and $n^{\downarrow}_{yz/zx}=0.28$, with up and down arrows indicating the spins [see Figs. 1(a) and 2(a)]. The cooperative occupation of the xy orbital for all Ru sites forms the FO ordering. These occupation numbers give $1.25\mu_B$ as the magnetic moment of a Ru atom M_{Ru_total}, which agrees well with the experimental value of $1.3\mu_B$.[3] As for the spin polarization of oxygen, the in-plane oxygen atoms have no net polarization due to symmetry while the apical oxygen atoms are strongly polarized (about 0.1 $m\mu_B$) due to the strong p-d hybridization because the yz/zx orbitals which extend toward apical oxygen contribute dominantly to the Ru spin polarization. The corresponding values in LSDA for the above orbital population are $n^{\uparrow}_{xy}=0.80$, $n^{\uparrow}_{yz/zx}=0.82$, $n^{\downarrow}_{xy}=0.71$, and $n^{\downarrow}_{yz/zx}=0.40$. Therefore, the basic feature of the orbital population remains the same in LSDA, though the

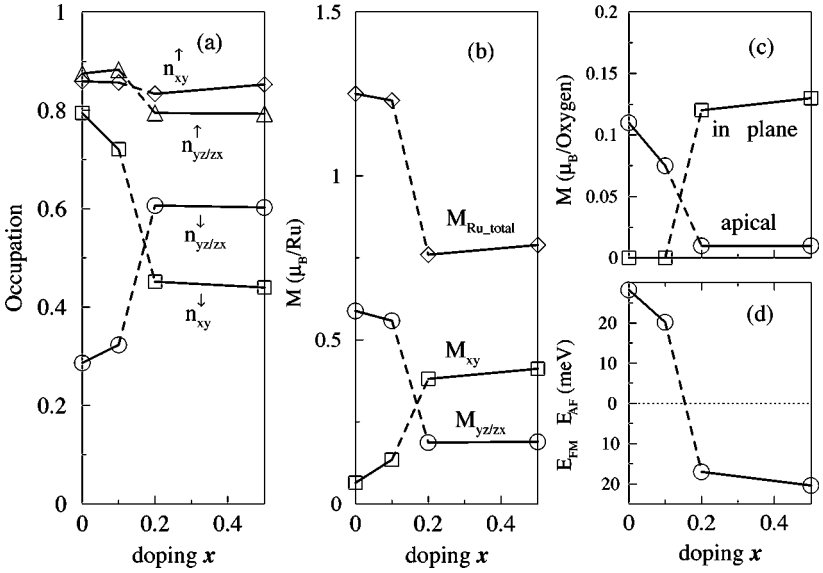

FIG. 2. The calculated (a) orbital occupation numbers and (b) magnetic moments for the ground state of $Ca_{2-x}Sr_xRuO_4$ with different doping x. M_{xy} ($M_{yz/zx}$) denotes the magnetic moment associated with the xy (yz/zx) orbital and $M_{Ru\_total}=M_{xy}+2.0M_{yz/zx}$. The absolute value of magnetic moments from oxygens are shown in (c) (see text for further explanations). The panel (d) shows the total energy difference between the FM and AF states. The AF side ($x=0.0,0.1$) is connected with the FM side ($x=0.2,0.5$) by dashed lines.

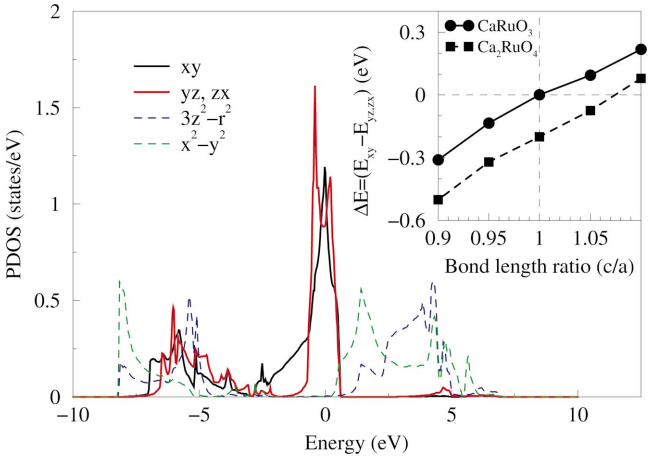

FIG. 3. (Color) The projected density of states of tetragonal Ca_2RuO_4 without the JT distortion in the NM state. The inset shows the calculated energy-level splitting between the xy and the yz,zx states for $CaRuO_3$ and Ca_2RuO_4 with tetragonal Jahn-Teller distortion, which is defined as the bond-length ratios (Ru-O bond length along the c axis vs that in the ab plane).

orbital polarization and the spin polarization are reduced compared with those in LDA+U. For example, LSDA gives $0.93\mu_B$ as M_{Ru_total}. The reduction in these polarizations is due to the stronger intersite hybridization caused by the vanishing band gap in LSDA. Therefore, we believe that the results obtained by LDA+U which adjusts the effective Coulomb repulsion U_{eff} to reproduce the band gap should be quantitatively more reliable than those by LSDA. The present results for the electronic structure are consistent with the previous calculations.[10,11]

As for the orbital character, there are three factors mainly contributing to the stabilization of the xy orbital.

(1) The energy-level splitting due to 2D crystal field in the layered structures [in contrast to its 3D counterpart, where the t_{2g} (or e_g) states are degenerate]: Fig. 3 (main panel) shows the calculated PDOS for the nonmagnetic (NM) state of Ca_2RuO_4 without the Jahn-Teller (JT) distortion (i.e., three Ru-O bonds having equal length). In the inset of Fig. 3, we show the calculated energy difference between the xy and the yz,zx bands as a function of the tetragonal JT distortion, by calculating the center of gravity for each band. Clearly, even for the hypothetical tetragonal Ca_2RuO_4 without JT distortion, the xy orbital is lower in energy than the yz and zx orbitals by about 0.2 eV as estimated by our calculation. This lowering of xy state energy is added to that due to the tetragonal distortion as demonstrated in the almost uniform downward shift of the dashed line (Ca_2RuO_4) from the solid line ($CaRuO_3$) in the inset of Fig. 3. As a first approximation, the origin of the energy-level splitting is attributed to the following geometrical aspect in the second neighbor configurations. In Ca_2RuO_4, Ru-O-Ru in the ab plane is replaced with Ru-O-Ca along the c axis. Two factors coming from this geometrical aspect contribute to the energy-level splitting. First, the electrostatic potential due to the reduced positive charge of the second neighbor Ca^{2+} along the c axis will raise the energies of those orbitals extending along the c axis, such as the yz and zx (or $3z^2-r^2$) states. This can be seen in Fig. 3 from the global upward shift of yz,zx bands and their oxygen bonding counterparts relative to those of the xy state. Second, due to the absence of Ru-O bond at one side of the apical oxygen along the c axis, the remaining Ru-O bonds are strengthened. This will further push up yz and zx states, which are the antibonding parts of the $2p$-$4d$ hybridization.

(2) The compressive JT distortion: The xy state is further lowered by about 0.06 eV (see inset of Fig. 3) due to the 2% shrinkage of the apical Ru-O bond length observed for Ca_2RuO_4 at 10 K.

(3) The orbital-dependent hybridization: In the AF state, the intersite hybridization between the occupied orbitals and the unoccupied ones, which is the origin of the superexchange, will push up the unoccupied yz/zx states, and again enhance the splitting between xy and yz/zx in minority spin by about 0.07 eV from our calculations. This effect does not exist in the FM state, and will explain the reduced occupation of xy orbital in the FM solution even for $x=0.0$ [see Fig. 1(b)].

As the results, $n_{xy}^{\downarrow}$ reads 0.79, 0.72, and 0.67 for the cases corresponding to ($x=0.0$, 11 K, AF), ($x=0.1$, 10 K, AF, where JT distortion is nearly vanishing), and ($x=0.0$, 11 K, FM), respectively. It is clear that the xy occupation is dominantly determined by the energy-level splitting due to the 2D structure, which is comparable with the typical band width of t_{2g} states. The existence of such 2D crystal field is common for all the layered perovskites, while it has not been considered seriously so far. This effect, which is not taken into account in the analysis by Hotta and Dagotto,[12] will certainly suppress the stability of their proposed AFO state for Ca_2RuO_4.

We also performed self-consistent calculations by including the SOC using the relativistic fully separable pseudopotentials[17] in the framework of noncollinear magnetism. We found that the obtained orbital occupations are almost identical to those for the case without SOC in the AF ground state of Ca_2RuO_4. This is consistent with above discussions in the sense that the crystal field is strong enough to quench the orbital moment and stabilize the real orbital xy. Note that the photoemission measurement[4] was done at 150 K which is above the Néel temperature where the degree of orbital polarization is reduced.

The electronic structures obtained in the present work can account well also for the observed XAS (Ref. 4) for Ca_2RuO_4 though the number of holes in the xy state is not exactly 0.5 (the estimated number of holes is between 0.2 and 0.3 from our calculations for the AF ground state). There are two important aspects in the experimental analysis. One is the distribution of holes among t_{2g} states and the other is its variation from the low-temperature AF phase to the high-temperature paramagnetic (PM) phase. Such information was derived from the observed relative intensity of two XAS peaks (A and B) as a function of light incidence angle θ. The peaks A and B correspond to the $1s$-$2p$ transition at the apical and the in-plane oxygen, respectively. In the single electron transition limit, we obtain the XAS spectra from the converged Kohn-Sham eigenstates by calculating the matrix elements of the optical transition.[18] For the low-temperature

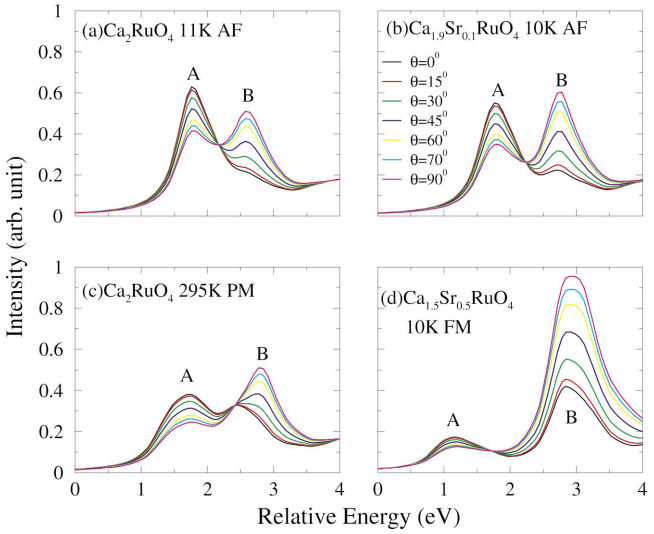

FIG. 4. (Color) The calculated relative intensity of two XAS peaks (*A* and *B* located at 528.5 and 529.5 eV experimentally) as a function of light incidence angle θ.

AF phase, the calculation is straightforward. However, we have to introduce an approximate treatment for simulating the XAS in the high-temperature PM state. Here we use the following simplest approximation in the cluster expansion technique for treating the alloy problem,[19] assuming that a magnetic state can be regarded as an alloy with two constituents, up spin state and down spin state. As the simplest approximation, we use a dimer for the cluster. Then the XAS of paramagnetic state can be approximated simply as an average of XAS of FM and AF states. (If we use a larger cluster, other magnetic orders have to be taken into account and the short-range order effect can be included.) As shown in Figs. 4(a) and 4(c), our calculated XAS at 11 K and 295 K can be well compared with the experimental spectra taken at 90 K and 300 K (Fig. 3 of Ref. 4). At elevated temperature, which tends to suppress the compressive JT distortion and to enhance the spin disordering (increasing FM component in spin configurations), the $n_{xy}^{\downarrow}$ will decrease as obtained in our calculations for the 295 K structure [see Figs. 1(c) and 1(d)], being consistent with the experimental tendency.

Recently, the anisotropic optical conductivities in Ca_2RuO_4 were measured by Lee *et al.*[5] and Jung *et al.*[20] For the $\mathbf{E}//a$ spectra (see Fig. 5), two peak structures (called α and β at about 1.0 eV, and 2.0 eV respectively) are related to the $4d$-$4d$ transitions (the strong peak at 3.0 eV is due to the p-d charge transfer). By increasing the temperature, spectral weight transfer from the strong peak β to the weak peak α is observed and simultaneously the gap is reduced. We calculate[16] the optical conductivities by using the Kubo formula,[21] and all transition matrix elements are calculated from first principles.[16] As shown in Fig. 5, the experimental results can be well explained by our calculations, and the corresponding transition paths are indicated in Fig. 1 by red arrows. Again we use the simple average of FM and AF solutions to simulate the PM state at 295 K. For the low-temperature AF state, the peak β at 2.0 eV is mostly due to the transition from the occupied majority spin yz (zx) state

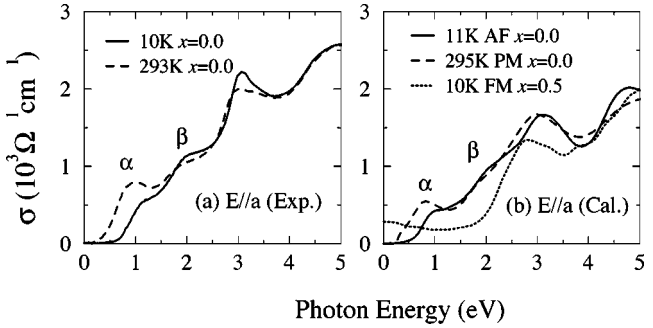

FIG. 5. The (a) experimental (Ref. 20) and (b) calculated optical conductivities. The interband transitions are calculated by using the Kubo formula. The simple average of FM and AF solutions is used to simulate the PM state at 295 K.

at one Ru^{4+} site to the unoccupied minority spin yz (zx) state at the neighboring Ru^{4+} site. In the simple energy-level picture (i.e, the occupation number of each orbital is regarded as integers, either 0 or 1), it is easy to understand the origin of peak β (which corresponds to transition shown in Fig. 1(c) of Ref. 5 with energy $U+J$), but not that of α. This argument has been used by Lee *et al.*[5] against the FO ordering. So they pursue the proposal for the AFO state,[12] which has been shown in the above discussions not to be favored. However, our calculation clearly shows the existence of peak α at about 1.0 eV, which is due to the nonvanishing transition matrix element between xy and yz/zx states, and crucially depends on the orthorhombic distortion and the admixture of xy and yz/zx states of Ru-$4d$. One of the strong contributions to α is the transition from the occupied majority spin xy state at one Ru^{4+} site to the unoccupied minority spin xy component mixed into the yz,zx states at the neighboring Ru^{4+} site [see Fig. 1(a)]. Therefore, the double-peak structure is just the natural consequence of strong hybridization. The peak β should be strong at the low-temperature AF phase and sensitive to the magnetic ordering. Actually, this transition should be suppressed in the FM configuration [as shown in Fig. 1(d)], because of the flipping of the spin. The peak α is weak at low-temperature AF state, and should be sensitive to the occupation number of xy orbital. The less n_{xy} is, the stronger the transition is. Actually, this transition is much enhanced in the FM configuration as shown in Fig. 1(d). Therefore, with the increasing temperature, the enhancement of peak α can be understood by the increasing apical Ru-O bond length and the increasing FM components in the spin configuration, both of which will suppress the xy occupation, while the reduction of peak β is mostly due to the spin disordering. The reduction of the gap at elevated temperature can be understood in terms of reduction in the AF long-range order.

B. $Ca_{2-x}Sr_xRuO_4$

Above results present firm evidence for the xy FO ordering for $x=0.0$. Now going from $x=0.0$ to 0.1, we see quantitative change of the electronic states [Figs. 1(e) and 2], while the ordering pattern does not change qualitatively. The elongation of the Ru-O bond along the c axis[3] (going from

$x=0.0$ to 0.1) tends to suppress the occupation of xy orbital and to destroy the AF order. As a result, we see from Fig. 2 the followings: (1) the energy gain of AF state with respect to the FM state reduces, being consistent with the reduced Néel temperature T_N observed experimentally; (2) the reduction of ordered moments; (3) electron transfer in the minority spin channel from the xy orbital ($n^{\downarrow}_{xy}$) to the yz/zx orbitals ($n^{\downarrow}_{yz/zx}$); and (4) redistribution of magnetization from the yz/zx orbitals ($M_{yz/zx}$) to the xy orbital (M_{xy}). The reduction of $n^{\downarrow}_{xy}$ is also visible from the calculated XAS spectra [shown in Fig. 4(b)], where the relative intensity of two peaks (A and B) is just between those of Figs. 4(a) and 4(c).

However for $x=0.5$, where RuO_6 is quite elongated and has only strong rotation around the c axis without tilting, the situation is completely different [Figs. 1(f) and 2]. These structural modifications produce basically two important changes in the electronic structure compared with the case of Ca_2RuO_4: (1) reduction in $n^{\downarrow}_{xy}$ due to the elongation; and (2) broadening of the yz/zx bands due to the absence of tilting. Nevertheless, the existence of RuO_6 rotation keeps the xy band narrow.[22] This will contribute to the high density of states at the Fermi level of nonmagnetic solution, leading to the Stoner-type FM instability. Since this instability mostly comes from the xy state, we observe from the FM solution [Fig. 1(f)] that the xy states are strongly spin polarized, opening a pseudogap and contributing to the magnetization dominantly (Fig. 2). On the other hand, yz/zx bands are quite broad, and are located around the Fermi level with much reduced spin polarization compared with the case of $x=0.0$. In contrast to the $S=1$ picture with the magnetic moment supported by the yz/zx orbitals for the $x=0$ case (Ca_2RuO_4), the present case may correspond to the $S=1/2$ picture where the xy orbital contributes to the magnetic moment. This picture accounts well for the observations by the Curie-Weiss fitting with $S=1/2$ of susceptibility[2] and the polarized neutron[8] showing the spatial magnetic moment distribution of the xy character. The large spin polarization for the in-plane oxygen atoms and the negligibly small one for the apical oxygen atoms [Fig. 2(c)] are the results coming from the xy orbital origin of the Ru magnetic moment and are consistent with the experiment.[8]

In contrast to the present study, the proposal in Ref. 10, which claims the contribution of yz/zx states to the magnetization, was obtained by neglecting the RuO_6 rotation, which is an important ingredient for obtaining our orbital-dependent picture. In their treatment,[10] an elaborate LDA +DMFT (dynamical mean-field theory) scheme was used, but high-symmetry structure of Sr_2RuO_4 was assumed. Then the effects of doping are simulated by increasing the size of U, instead of changing the bandwidth. However, we pointed out in our calculation that the strong RuO_6 rotation will reduce the band width of xy significantly, but not that of yz,zx bands. This difference produces the main source of the discrepancy discussed above. The characteristic results of our picture for $x=0.5$ are the much suppressed (enhanced) peak A (B) in the XPS spectra [Fig. 4(d)] and the structureless optical spectra below the charge-transfer peak [Fig. 5(b)]. These predictions should be confirmed by further experiments.

Our picture for $x=0.5$ was obtained by the LSDA calculations which tends to overestimate the FM stability. Experimentally no FM long-range order has been observed, while the significant enhancement of susceptibility down to 2 K (Ref. 2) clearly suggested the existence of strong FM correlation (at least for short range). Actually, the recent experiments down to 0.3 K (Ref. 7) suggested the existence of weak FM component (cluster glass) at this doping. This may suggest that some magnetic orders may be energetically in near degeneracy with FM state. At present we do not have any clear idea about what magnetic orders they may be and the problem is left for future studies.

Finally, we discuss only briefly the case for the critical point $x=0.2$. 10 K is already above the metal-insulator transition temperature[3] in this case, and the system crystallizes in the L-$Pbca$ phase with a long apical Ru-O bond, suggesting the adjacency to the metallic side ($x=0.5$). However, in contrast to the case of $x=0.5$, the tilting of RuO_6 still exists to reduce the width of yz/zx bands as well at $x=0.2$. This aspect tends to stabilize the insulating AF state. If we adopt LSDA, the former aspect is emphasized to make the case of $x=0.2$ very similar to the case of $x=0.5$ as can be seen in Fig. 2. On the other hand, the LDA+U method with $U_{\mathrm{eff}}=2.5$ eV emphasizes the latter aspect to bring the AF state very close to the FM state with the energy difference given by $E_{\mathrm{FM}}-E_{\mathrm{AF}}=-3$ meV. Note, however, that the similar LDA+U calculation for $x=0.5$ enhances the stability of the FM state with respect to the AF state and doubles the energy difference in Fig. 2(d). These calculations, though not conclusive, clearly suggest that the system with $x=0.2$ may be in the critical situation.

IV. CONCLUDING REMARKS

We have presented a systematic picture for the orbital states in $Ca_{2-x}Sr_xRuO_4$ ($0\leqslant x\leqslant 0.5$). For the AF side ($x<0.2$), we conclude that the orbital ordering is of the FO type with the dominant xy occupation and that the yz/zx orbitals contribute to the magnetic moment. The electronic structure corresponds basically to $S=1$ in the localized spin picture. However, strong intersite hybridization due to extended Ru $4d$ orbitals significantly modifies the magnetic moment distribution and the present calculation agrees well with the experiments. For $x=0.5$, our LSDA calculation predicts the system to be ferromagnetic and the narrow xy band with half filling may correspond to an $S=1/2$ localized spin picture. Experimentally the system shows strong tendency toward ferromagnetism but remains paramagnetic for $x=0.5$ even down to very low temperature. Only below 0.3 K, the existence of cluster glass phase with weak FM component was observed. The LSDA calculation seems to overestimate the stability of ferromagnetism in other cases also. This problem is left for future studies. However, the present result for the character of the spin-density distribution is consistent with the neutron data. We emphasized that the structural modifications such as rotation, tilting, and flat-

tening of RuO_6 octahedron have to be fully taken into account in order to describe properly the systematic variation of the orbital states. Our results can explain other existing experiments, for example, XAS and optical conductivity, quite consistently. Furthermore, we made predictions for these experiments for the $x=0.5$ compound, which await experimental tests.

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