Spin-orbit coupling induced Mott transition in Ca$_{2-x}$Sr$_x$RuO$_4$ (0$\leq x\leq$ 0.2)

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We propose a new mechanism for the paramagnetic metal-insulator transition in the layered perovskite Ca$_{2-x}$Sr$_x$RuO$_4$ (0$\leq x\leq$0.2). The LDA+$U$ approach including spin-orbit coupling is used to calculate the electronic structures. In Ca$_2$RuO$_4$, we show that the spin-orbit effect is strongly enhanced by the Coulomb repulsion, which leads to an insulating phase. When Ca is substituted by Sr, the effective spin-orbit splitting is reduced due to the increasing bandwidth of the degenerate $d_{xy}$ and $d_{yz}$ orbitals. For $x=0.2$, the compound is found to be metallic. We show that these results are in good agreement with the experimental phase diagram.

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The layered perovskite Ca$_{2-x}$Sr$_x$RuO$_4$ (CSRO) has been intensely studied during recent years since this series of compounds exhibits a variety of interesting physical properties as a function of the Sr concentration $x$.\cite{1,2,3} Sr$_2$RuO$_4$ is a $p$-wave superconductor\cite{4} with a K$_2$NiF$_4$-type structure. The substitution of Ca for Sr causes the RuO$_6$ octahedra to rotate, and start to tilt at $x=0.5$.\cite{5} Following with the structure distortion, CSRO undergoes a series of phase transition from a paramagnetic metal ($0.5<x<2$) to a magnetic metal ($0.2<x<0.5$), and finally to a Mott insulator ($0<x<0.2$).\cite{6} It is unusual that in the Mott insulating regime the metal-insulator transition temperature ($T_M$) is higher than the Néel temperature ($T_N$) of the antiferromagnetic (AFM) phase, which shows that a paramagnetic (PM) insulating phase exists between these transition temperatures.\cite{5,7,8} For pure Ca$_2$RuO$_4$, the PM insulating regime extends from $T_N=110$ K to $T_M=357$ K.\cite{9,10,11} This property makes Ca$_{2-x}$Sr$_x$RuO$_4$ ($0<x<0.2$) different from other AFM Mott insulators.

Recently, Qi et al.\cite{12} found that the substitution of the lighter Cr for the heavier Ru strongly depresses $T_M$ in Ca$_{2-y}$Cr$_y$RuO$_4$ ($0<y<0.13$), which implies a possible influence of the relativistic spin-orbit (SO) coupling on the Mott transition as pointed out by the authors. It is well known that SO coupling plays an important role in 5$d$ transition-metal oxides. For example, Kim et al.\cite{13} found that Sr$_2$IrO$_4$ is a $J_{eff}=1/2$ Mott insulator, and they showed that the unusual insulating metal state can be explained by the combined effect of the SO coupling and Coulomb interaction. In the 5$d$ oxides, the importance of SO coupling is under debate. Mizokawa et al.\cite{14} observed strong SO coupling in Ca$_2$RuO$_4$ from their photoemission experiment. Based this finding, they argued that the strong SO coupling in Ca$_2$RuO$_4$ would cause a complex electronic configuration. Theoretical studies revealed strong SO effects in Sr$_2$RuO$_4$ and Sr$_2$RhO$_4$\cite{15,16} which seemingly support the photoemission experiment. However, Fang et al.\cite{17,18} reported an LDA+$U$ study of Ca$_2$RuO$_4$. They found the AFM state has a rather simple configuration $xy^\dagger z^\dagger y z^\dagger$ without much influence of the SO coupling. These seemingly inconsistent viewpoints raise a question: what role does the SO coupling play in CSRO?

In this paper we present electronic structure calculations for Ca$_{2-x}$Sr$_x$RuO$_4$ using the LDA+$U$ method including the SO coupling. We show the combination of the SO coupling and Coulomb repulsion opens a band gap in PM Ca$_2$RuO$_4$. The appearance of the Mott insulating phase is strongly dependent on the tilting of the RuO$_6$ octahedra, which naturally explains the PM Mott transition in the experimental phase diagram. On the other hand, we find SO has much less influence on the AFM order. We show that these phenomena can be explained by a simple formalism.

All the calculations in this work were performed with the full-potential linear augmented plane wave (FLAPW) within the local-density approximation (LDA), as implemented in package WIEN2K.\cite{19} Two experimental structures were considered in this work. For Ca$_2$RuO$_4$, we used the structure at 180 K, with the space group Pnma, lattice constant $a=5.394$, $b=5.600$, and $c=11.765$ Å.\cite{20,21} For Ca$_{1.8}$Sr$_{0.2}$RuO$_4$, we used the experimental structure at 10 K, but the substitution of Sr for Ca is only taken into account via the structural changes. Ca$_{1.8}$Sr$_{0.2}$RuO$_4$ also has the space group Pbca, lattice constant $a=5.394$, $b=5.600$, and $c=11.765$ Å.\cite{20,21} For the AFM state, we considered the 'A-centered' mode.\cite{22} The LDA+$U$ calculations were performed with $U=3.0$ eV, which is similar to the value used by Fang et al.\cite{17,18} We will show that this U value can reproduce the measured band gap in Ca$_2$RuO$_4$.

In Fig. 1 we present our theoretical band structures for paramagnetic Ca$_2$RuO$_4$ using different approximations. The LDA band structure is well known\cite{20,21}: the bands crossing the Fermi level are from Ru $t_{2g}$ orbitals, containing four $d$ electrons. Our LDA band structure shown in Fig. 1a is consistent with the previous study.\cite{20} The inclusion of the SO coupling (Fig. 1b) only shows some slight changes on the band structure. This is not surprising since the SO coupling constant $\zeta$ in Ca$_2$RuO$_4$ is presumably similar to the one in Sr$_2$RuO$_4$, where it is only about 93 meV.\cite{15} The inclusion of Coulomb interaction (Fig. 1c) also shows little influence on the band structure since U does not break the orbital symmetry in the paramagnetic state. Surprisingly, the combined inter-
action of the SO coupling and Coulomb repulsion gives a very different band structure compared to the LDA, LDA+SO or LDA+U results. The LDA+U+SO band structure shows an insulating phase with a gap about 0.2 eV wide. The band gap obtained from the chosen U is in good agreement with the experimental data.\cite{22}

Similar combined effect of the SO coupling and U has been found in Sr$_2$RuO$_4$ since the $xy$ orbital is also involved. \Fig{2} presents the partial density of states (PDOS) for the Ru-$d$ orbitals calculated by LDA+U+SO. Here we present the PDOS for the $\chi_{\pm 3/2}$ and $\chi_{\pm 1/2}$ orbitals instead of $xz$ and $yz$. The PDOS shows that the unoccupied $t_{2g}$ bands (0.2-0.9 eV) are dominanted by the $\chi_{\pm 3/2}$ states while the $\chi_{\pm 1/2}$ states are nearly fully occupied. The well separated $\chi_{\pm 3/2}$ and $\chi_{\pm 1/2}$ states indicate a large effective spin-orbit splitting in Ca$_2$RuO$_4$. Therefore, a simple explanation for the PM Mott transition is that the Coulomb-enhanced spin-orbit splitting opens a gap between the $\chi_{\pm 3/2}$ and $\chi_{\pm 1/2}$ bands, leading to an insulating phase with two holes residing on the $\chi_{\pm 3/2}$ orbitals. In this explanation, the $xy$ state is assumed to be fully occupied. However, in the experimental structure, the $xy$, $xz$ and $yz$ orbitals hybridize with each other due to the structural distortion. As may be seen, the weight of the $xy$ state in the unoccupied $t_{2g}$ bands is not small as shown in \Fig{2}. The relative hole population shown in \Fig{2} is $xy/\chi_{\pm 1/2}=19:13:68$, while this ratio is 21:39:5:39.5 within LDA approximation. This shows that the inclusion of SO and U hardly changes the occupancy of the $xy$ orbital. We may conclude that the band gap is mainly due to the splitting of $\chi_{\pm 3/2}$ and $\chi_{\pm 1/2}$ orbitals although the $xy$ orbital is also involved in the Mott transition.

Experimental research has found that the Mott transition in CSRO is accompanied by an structural phase transition from the high temperature $L$-Pbca phase to the low temperature $S$-Pbca phase,\cite{31} where L (S) indicates a long (short) c-axis. The phase transition temperature $T_S$ is a function of Sr concentration $x$, which decreases from 357 K at $x = 0$ to 0 K at $x \sim 0.2$.\cite{11} For $x \geq 0.2$, CSRO is metallic and only has the $L$-Pbca phase. As indicated by Friedt et al.,\cite{35} the structural transition from the $L$-Pbca to $S$-Pbca phase is characterized by an increase in the tilting angle of RuO$_6$ octahedra. We will show that the tilting angle of RuO$_6$ plays an important role in the Mott transition. To illuminate the
the LDA+SO interaction is taken into account. This is confirmed by Eq. (1), we get
\[ \frac{\chi_3}{x^{3/2}} \approx \frac{\chi_2}{x^{2/2}} \text{ for } \text{Ca}_{1.8}\text{Sr}_{0.2}\text{RuO}_4, \]
and \( \text{Ca}_2\text{RuO}_4 \). As may be seen, the occupancy difference between the
\( \chi \) states is larger in \( \text{Ca}_{1.8}\text{Sr}_{0.2}\text{RuO}_4 \) than in \( \text{Ca}_2\text{RuO}_4 \). The stronger orbital dependence could
be understood within this picture. Cr has a much smaller atomic SO constant than
Ru due to its smaller mass. And therefore the substitution of Cr for Ru will reduce the SO splitting, leading to
the observed decrease of \( T_{N} \).

As mentioned above, Fang et al. found that SO coupling has no much influence on the electronic configuration. They however pointed out that the photoemission measurement was done above the Neel temperature, while they applied the LDA+U method to the low temperature AFM state. To clarify if the SO coupling is less important in AFM state, we apply the LDA+U and LDA+U+SO calculation to AFM \( \text{Ca}_2\text{RuO}_4 \). Our LDA+U calculation gives a magnetic moment of \( m_{\text{Ru}}=1.25 \mu_B \), which is consistent with Fang et al.’s calculation, while SO reduces the moment to
1.21 $\mu_B$, showing a weak SO effect. The AFM PDOS for Ca$_2$RuO$_4$ are presented in Fig. 4. In contrast to the PM state, Fig. 4 shows that there is no Coulomb-enhanced SO splitting in the AFM state. The relative weak SO splitting in the PM state can be explained by Eq. (1). The LDA+$U$ calculation produces an insulating phase for PM Ca$_2$RuO$_4$ at $T_N$. This finding is consistent with the photoemission experiment, and also explains the recent experiment on Ca$_2$Ru$_{1-x}$Cr$_x$O$_4$. We show that the SO induced Mott transition in CSRO is driven by the change of the $xz/yz$ bandwidth. For $x = 0.2$, the compound is found to be metallic. On the other hand, we find that SO coupling has much less influence on the AFM state, which is in agreement with the previous LDA+$U$ study. The above picture shows that SO coupling plays a very subtle role in the correlated systems. The interplay of SO coupling, electron correlation and crystal structure distortion would cause very rich physical phenomena.

In summary, we have applied LDA+$U$+SO calculations to CSRO. We find the Coulomb enhanced SO splitting produces an insulating phase in PM Ca$_2$RuO$_4$. This finding is consistent with the photoemission experiment, and also explains the recent experiment on Ca$_2$Ru$_{1-x}$Cr$_x$O$_4$. The SO splitting produces an insulating phase in PM Ca$_2$RuO$_4$. The relative weak SO splitting in the PM state is enhanced. If the enhanced splitting is large enough, it will lead to an insulating phase. The PM-AFM transition at $T_N$ can be regarded as the competition of the Coulomb-enhanced SO splitting and the Coulomb-enhanced exchange splitting. In the AFM state, the SO enhancement is quenched by the large exchange splitting, which causes the very different electronic configuration from the PM state.

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