Pressure-induced dimerization and molecular orbitals formation in Na₂RuO₃ with strong correlation-enhanced spin-orbit coupling effect

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Introduction

The competition between spin-orbit coupling (SOC), Coulomb correlations together with Hund's coupling interactions has given rise to a rich set of emergent phenomena and exotic quantum states in 4d/5d transition metals compounds [1,2].

The tetravalent ruthenates Na₂RuO₃ feature with a nearly ideal honeycomb lattice and weaker SOC strength relative to iridates, provides a new playground to explore unusual physics emerging from the intricate interplay of electron correlations, SOC and Hund's Coupling. However, The conflicting experimental results raise a question of whether a spinorbital-entangled state can provide a suitable description for the nonmagnetic insulating behavior of the ordered phase Na₂RuO₃ [3,4].

In the present work, we revisit the electronic structure of the ordered phase Na₂RuO₃ under ambient conditions by explicitly considering the Coulomb interactions and SOC, provide strong theory evidence for its J_{eff} nonmagnetic insulating description and explore the



evolution of the honeycomb lattice and electronic structure as a function of applied pressure.

(a) Conventional cell of the ordered phase Na_2RuO_3 with honeycomb-ordered $[Na_{1/3}Ru_{2/3}]O_2$ slabs. (b) Schematic diagram of the hexagonal ab plane of the honeycomb Na₂RuO_{3.}

J_{eff} nonmagnetic insulating ground state



Comparison of the projected DOS of the 4d state of Ru ions at ambient pressure: (a) GGA, (b) GGA + U, (c) GGA + SOC and (d) GGA + SOC + U.



(a) The evolutions of total DOS of Ru 4d states as a function of SOC strength within GGA+SOC calculations (b) the changes of band gaps as a function of SOC strength as well as Coulomb interaction U within GGA+SOC+U calculations.

The opening of the nonmagnetic insulating gap in Na₂RuO₃ can be attributed to the enhancement of SOC by correlation effects. We find that just enhance the SOC strength up to two times indeed can open the insulating gap of Na₂RuO₃ without considering the electronic correlation U (FIG. (a)). In addition, the band gap value further increases linearly along with increasing SOC strength once the gap has been opened, which is consistent with the anticipation that the charge gap is proportional to the SOC strength $(3\lambda/2)$. On the other hand, the electronic structure still keeps a metallic characteristic by GGA + U calculations with an impossibly huge U of 5 eV. Especially, the slope of band gap vs SOC strength increases obviously from 0.143 (U = 0 eV) to 0.216 (U = 3 eV) along with the Coulomb interaction U increasing from 0 eV to 3 eV, which implies the effective SOC strength λ has been enhanced.

Individual SOC or *U* has relatively small influences on the dispersion of the band structures, however, an insulating gap of ~0.6 eV has been opened up around the Fermi level in case SOC together with U are considered simultaneously.

We demonstrate that SOC plays a crucial role in driving the system to a J_{eff} state, while U further amplifies the effect of SOC. The correlation-induced enhancement of SOC effect by a factor of about two has been predicted theoretically [5,6] and demonstrated experimentally for Sr₂RuO₄ [7].

Structural dimerization under hydrostatic pressure



Evolutions of the crystal structure of Na2RuO3: (a) lattice constants, (b) unit cell volume and the β angle, (c) Ru-Ru bond lengths, (d) hexagon interior angles.

When the pressure increases to 17.5 GPa, a significant change in lattice parameters is observed, indicating a structural transition occurring between 15 and 17.5 GPa. Simultaneously, two parallel Ru-Ru bonds undergo a sharp contraction, forming dimers.



DOS of the 4*d* state of Ru for dimerized Na_2RuO_3

the degeneracy of the Ru t_{2g} states in the vicinity of the Fermi level has been completely removed for the highpressure dimerized phases. The bond lengths of the dimerized Ru-Ru bonds (X bonds) in Na₂RuO₃ (~2.62 Å) are shorter than those in Ru metal (~2.7 Å), therefore the overlap between the orbitals becomes larger when the pressure brings the two adjacent Ru ions close enough. the isolated d_{xy} orbitals located in the lowest and highest energy positions of the t_{2g} states, which are separated from the degenerated d_{vz} and d_{xz} orbitals, manifesting strong covalent interactions in the Ru-Ru dimers and the formation of bonding and antibonding states.



Real-space visualization of the bonding σ and antibonding σ^* .



Schematic diagram of the molecular orbitals and electronic configuration.

We further analyzed the electronic structure of the dimerized phase using the real-space wavefunction. As shown in the left figure, due to the enhanced direct hopping along the Ru-Ru dimer bonds, the d_{xy} orbitals of neighboring RuO₆ octahedra sharing an edge form strong bonding and antibonding molecular orbitals, labeled as σ and σ^* , respectively. Additionally, the remaining t_{2g} states, d_{xz} and d_{yz} , in the Ru-Ru dimers form π and δ -type molecular orbitals. According to this molecular orbital diagram, the σ molecular orbital originates solely from the d_{xy} orbitals, while the π and δ molecular orbitals are formed by linear combinations of $d_{xz}+d_{yz}$ and $d_{xz}-d_{yz}$ orbitals, respectively. Ideally, the eight electrons from the two dimerized Ru⁴⁺ ions can achieve a non-magnetic electronic configuration by fully occupying the bonding σ , π , and δ orbitals, as well as the antibonding δ^* orbital, as illustrated in the

Conclusions

right figure. Interestingly, when both U (Coulomb interaction) and SOC (spin-orbit coupling) are included, the degenerate d_{yz} and d_{xz} bands split into several isolated narrow bands, opening an insulating gap between the π^* and δ^* antibonding states. This transition allows dimerized Na₂RuO₃ to remain in a non-magnetic insulating state, completing the transformation from a $J_{eff}=0$ non-magnetic insulating state to a molecular orbital-driven non-magnetic insulating state.

Our calculated results indicate that the insulating nonmagnetic J =0 ground state of Na₂RuO₃ at ambient conditions is originated from the electron correlation enhanced SOC effect. Furthermore, we discover a pressure-induced structural dimerization of the Ru-Ru bonds featuring with a parallel pattern of the Ru-Ru dimers, which leads to an electronic structure reconstruction by emergence of molecular orbital. Interestingly, Coulomb interactions collaborating with SOC effect can promote the band-gap opening for the nonmagnetic high-pressure dimerized phase.

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