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Localized itinerant electrons and unique magnetic properties of SrRu_2O_6

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SrRu_2O_6 has unique magnetic properties. It is characterized by a very high Néel temperature, despite its quasi-two-dimensional structure, and has a magnetic moment more than twice reduced compared to the formal ionic count. First principles calculations show that only an ideal Néel ordering in the Ru plane is possible, with no other metastable magnetic solutions, and, highly unusually, yield dielectric gaps for both antiferromagnetic and nonmagnetic states. We demonstrate that this strange behavior is the result of the formation of very specific electronic objects, recently suggested for a geometrically similar Na_2IrO_3 compound, whereby each electron is well localized on a particular Ru_6 hexagon, and completely delocalized over the corresponding six Ru sites, thus making the compound *both* strongly localized and highly itinerant.

The recently discovered[1] SrRu_2O_6 has attracted considerable attention because, despite being a very 2D material, it shows an exceptionally high Néel temperature of ~ 560 K [2, 3]. As we will argue in this paper, this is by far not the only, and maybe not even the most intriguing property of this material. Ru^{5+} has a half-filled t_{2g} electronic shell, and exhibits insulating behavior. Naturally, it was interpreted as a Slater insulator (maybe Mott-enhanced), with Ru in the high spin state, $S = 3/2$. However, the experimentally measured ordered magnetic moment is only $M = 1.3 - 1.4 \mu_B$ [2, 3], 2.3 times smaller than expected for $S = 3/2$ ($M = 3 \mu_B$). This was ascribed to hybridization with oxygen[2–4], but it should be noted that such strong suppression of magnetic moment in a good insulator is unheard of. Even in the metallic SrRuO_3 the hybridization suppresses the total magnetic moment of Ru^{4+} only from 2 to $1.7 \mu_B$, and in Sr_2YRuO_6 Ru^{5+} has essentially exactly $3 \mu_B$, with basically the same Ru-O distances as in SrRu_2O_6 [5]. Hiley *et al* [2] mention the case of Li_3RuO_4 [6], where a suppression down to $M = 2.0 \mu_B$ was reported for the same oxidation state, which is, however, still twice smaller a reduction compared to SrRu_2O_6 , and the material might actually be a metal (no transport data have been published).

Electronic structure calculations [3, 4] so far have not resolved the mystery, but have only added to the confusion. It was found that only the ideal Néel state can be stabilized in the calculations, even though ions with $S = 3/2$ are usually very stable and while they disorder with temperature, never lose their magnetic moment completely. At the same time the moment found in the calculations matches the experimentally measured one within 8%, suggesting that the role of Coulomb correlations beyond the standard density functional theory (DFT) is negligible[7]. The instability of the ferromagnetic (FM) state was traced down to the presence of a dielectric gap in nonmagnetic calculations[4], but that es-

entially translates one mystery into another: why does a highly symmetric Ru sublattice, with no dimerization or clusterization, with a half-filled t_{2g} band, show a sizeable nonmagnetic gap? Singh mentions[4] that the gap is allowed by symmetry, since the unit cell includes two Ru atoms that can, in principle, form a bonding and an antibonding band, but does not elaborate about how a structure with each Ru having three equivalent bonds manages to develop a bonding-antibonding splitting.

Similarly, it was pointed out that, even though SrRu_2O_6 is extremely 2D magnetically, there is still some residual interlayer coupling, $J_{\perp} M^2 \approx 1.5$ meV, as well as a single-ion magnetic anisotropy, estimated to be ≈ 1.4 meV/Ru [4]. It was suggested that the anisotropy [4] or interlayer coupling [3] are responsible for the large T_N , implying that the (unknown) mean field transition temperature is extremely high. Tian *et al*[3] attempted to describe this system by a three nearest neighbor Heisenberg model with parameters derived within the perturbation theory in the limit of a Hubbard U much larger than the hopping, $U \gg t$. However, the fact that ferromagnetic arrangement is completely unstable (in fact, as we show below, no parallel nearest neighbor moments are stable), indicates that the system is strongly non-Heisenberg, casting very strong doubt on the relevance of such models. Additionally, the fact that the system is very weakly correlated makes such a perturbation theory unphysical. Hiley *et al* [2] used a hybrid functional that overestimates the equilibrium magnetic moment and thus the exchange parameters,[8] as well as yields a very large band gap of 2.15 eV, totally inconsistent with the observed weak temperature dependence of the resistivity.

An explanation of all these oddities can be consistently found in the so-called molecular orbitals (MO) picture, which was first brought up in connection to Na_2IrO_3 [9] and later found also in RuCl_3 [10]. Basically, this picture is based on the idea that for ideal 90° Ru-O-Ru bond angles (the actual angles are 101°) the O-assisted Ru-Ru

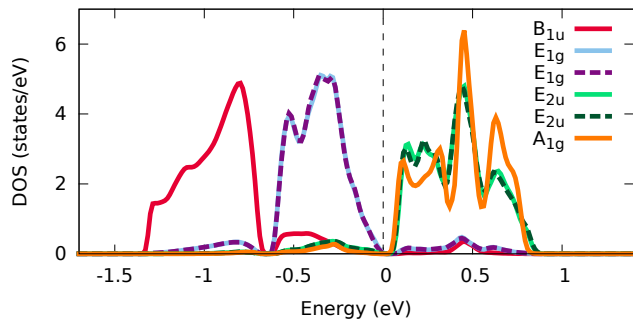


FIG. 1. Density of states (DOS) projected on molecular orbitals of different symmetries in nonmagnetic GGA calculations (WIEN2k results). The Fermi energy is set to zero.

hopping is only allowed for one particular pair of the t_{2g} orbitals for each hexagonal bond, denoted t'_1 in Ref. [9]. If all other hoppings are neglected, it leads to a curious situation where every electronic state is fully delocalized over a particular hexagon, but never leaves this hexagon. One can say that the electrons are fully localized (form nondispersive levels) and fully delocalized (each state is an equal weight combination of six orbitals belonging to six different sites). If a direct overlap of the t_{2g} orbitals (which always exists in the common edge geometry) is included, as well as deviations of the angle from 90° , two more hoppings emerge: one between the same orbitals on the neighboring sites, t_1 , and the other an O-assisted second neighbor hopping between unlike orbitals, t'_2 . As long as t'_1 is dominant, the MO model still applies, and can be readily solved. The solution entails six bands, A_{1g} , E_{2u} , E_{1g} and B_{1u} (the E bands being double degenerate in each spin channel), whose dispersion is controlled by t_1 , and whose centers are located at $2(t'_1 + t'_2)$, $(t'_1 - t'_2)$, $-(t'_1 + t'_2)$ and $-2(t'_1 - t'_2)$, respectively. In Na_2IrO_3 $t'_1 \approx -3t'_2$, so that the A_{1g} and E_{2u} practically merge. This accidental degeneracy also leads to much stronger spin-orbit effects than would have been possible had the MO bands remained well separated, and to considerable destruction of the MO picture in the relativistic case. On the other hand, the hopping parameters for SrRu_2O_6 , as calculated in Ref. [11], are similar to those in Na_2IrO_3 , in the sense that again $t'_1 = 300$ meV is by far the largest hopping, and the only other sizeable hoppings are $t_1 = 160$ meV and $-t'_2 \approx 100 - 110$ meV. Note that here $|t'_2|$ is again about $1/3$ of t'_1 . Thus, the A_{1g} and E_{2u} bands merge, while E_{1g} and B_{1u} remain separated, as one can see in Fig. 1. Projecting the density of states onto MOs, we observe that the predicted characters are very well reproduced. The distance between the centers of the E_{2u} and E_{1g} bands is about 0.8 eV, and their width is about 0.6-0.7 eV, thus providing for a small gap of ≈ 50 meV.

It is instructive to compare SrRu_2O_6 with Na_2IrO_3 and with Li_2RuO_3 . All these compounds share the same crystallographic motif, but feature a different number of

d electrons: 5, 4 or 3. In the iridate, a single hole in the upper A_{1g} singlet is prone to both strong correlations and, due to near degeneracy between A_{1g} and E_{2u} , to spin-orbit interaction. As a result, as one increases the spin-orbit coupling, the A_{1g} singlet is gradually transformed into the $j_{\text{eff}} = 1/2$ singlet [9]. Either way, a half-filled singlet triggers Mott physics even if the Hubbard U is small. This transformation controls most of the interesting physics in this compound. Li_2RuO_3 has two d holes, providing it with an opportunity to form strongly bound covalent dimers. This is exactly what happens, and the MO on the hexagons transforms to an MO on the Ru dimers resulting in the spin singlet ground state [12]. Neither Mott nor spin-orbit physics is relevant on the background of the strong covalent bonding in dimers. Finally, SrRu_2O_6 has the six MO bands half-filled, and the gap is formed between the lower and the upper MO triads. Similar to Li_2RuO_3 , both Mott and spin-orbit effects are of minor importance, and the gap structure inherent to the MO picture gives rise to unique magnetic properties.

Let us now turn to the energetics of the material. First, we have confirmed, using the WIEN2k package [13, 14], the numbers published by Singh[4] regarding the interplanar coupling, single-site anisotropy and Ru magnetic moment. We also confirmed that the ferromagnetic structure cannot be stabilized. Moreover, the so-called stripy and zigzag magnetic patterns[9], where one or two out of three bonds are ferromagnetic, and the net moment is zero, cannot be stabilized. This indicates that besides the obvious influence of the nonmagnetic gap there are other factors strongly disfavoring ferromagnetic bonds. In fact, given that the gap value is ten times smaller than Ru Stoner factor[5], and the calculated magnetic moment in the Néel state is $\sim 1.3 \mu_B$, it is surprising that the ferromagnetic bonds do not stabilize with a finite moment.

In order to gain more insight into the problem, we turned to the VASP code [14, 15], which is faster and has the capability to restrict magnetic moments to a certain direction, or to both a direction and a magnitude (we confirmed that the energies of collinear magnetic states agree with those found in WIEN2k). First, we computed the total energy for a canted antiferromagnet (AFM), restricting the angle with the z axis to be $\pm\phi$ for the two Ru's in the cell. The results are shown in Fig. 2. Note that for the largest canting angle we were able to converge, 35° , the energy of the magnetic state is already higher than that of the nonmagnetic one. Also note how soft the magnetic moments are: despite the sizeable equilibrium moment, the energy cost of total suppression of magnetism is less than 80 meV, only 50% larger than the transition temperature. This is, again, an indication of the great role of itinerancy, and specifically, delocalization over Ru_6 hexagons.

Interestingly, suppression of magnetism with canting

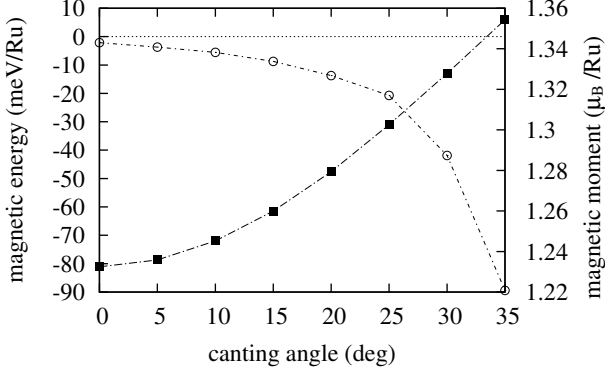


FIG. 2. Magnetic energy (squares) and magnetic moments (circles) as a function of the canting angle of spins, starting from the Néel antiferromagnetic structure. Results are from VASP calculations.

cannot be described by a naive combination of a local Hamiltonian for itinerant magnets[16], $E = \sum_{i \geq 0} a_i M^{2i}$,

where M is the magnetization, with a Heisenberg term. While the total energies at a fixed canting angle $\phi \lesssim 35^\circ$ can be very well described by this Hamiltonian with just three terms, $E(M) - E(0) = a_1 M^2 + a_2 M^4 + a_3 M^6$, not only does the first coefficient show appreciable angular dependence (as in the Heisenberg model), but also the second, and, to a lesser degree, the third. Instead, a good fit could be obtained with the following formula:

$$E = -81.3M^2 + 16.9M^4 + 2.0M^6 + 359.2M^2 \sin^2(\phi) - 165.8M^4 \sin^2(\phi) + 27.6M^6 \sin^2(\phi), \quad (1)$$

in meV/Ru. Note that the angle between the moments is $\theta = \pi - 2\phi$, and that there are 1.5 times more bonds than sites. Thus, the proposed Hamiltonian looks as follows:

$$H = \sum_{\text{sites}} \{98.3M^2 - 66.0M^4 + 15.8M^6\} + \sum_{\substack{n.n. \\ \text{bonds}}} \{179.6(\mathbf{M} \cdot \mathbf{M}') - 82.9|\mathbf{M}||\mathbf{M}'|(\mathbf{M} \cdot \mathbf{M}') + 13.8|\mathbf{M}|^2|\mathbf{M}'|^2(\mathbf{M} \cdot \mathbf{M}')\}. \quad (2)$$

The Heisenberg term is extremely strong ($JM^2 = \partial H / \partial \cos(\theta) \approx 1600$ K), and, without it, local magnetic moments fail to form.

To this Hamiltonian one needs to add a small interlayer term $\sum J_\perp \mathbf{M}_i \cdot \mathbf{M}_{i'}$, where i and i' belong to the neighboring planes, and the magnetic anisotropy $\sum DM_z^2$, where $J_\perp \approx 0.9$ meV, and $D \approx 0.8$ meV.

In principle, at this point one would need to perform a Monte Carlo simulation using this Hamiltonian and determine the transition temperature. However, it is

notoriously difficult to distinguish a Kosterlitz-Thouless phase in a quasi-2D system from the true long range order, so that one should be very skeptical of any Monte Carlo simulation that claims to establish a Néel temperature, T_N , without first showing that in the isotropic 2D limit T_N truly vanishes. The softness of the moment, expressed *via* Eq. 2, additionally complicates the simulation. We leave this daunting task to more experienced Monte Carlo simulators, but mention that the numbers that we have deduced are in the right ballpark. For instance, Costa and Pires showed[17] that for the square lattice $T_N/T_{MF} \approx 0.8(D/J)^{0.2}$. For three neighbors, the mean field transition temperature $T_{MF} \approx JM^2 \approx 1600$ K, which together with $DM^2 \approx 1.4$ meV results in $T_N \sim 500$ K. On the other hand, for the cubic quasi-2D model with $J_\perp \neq 0$, $D = 0$, Yasuda *et al*[18] found that $T_N \approx 4.27JM^2/[3.12 + \log(J/J_\perp)]$, which for our parameters translates into 900 K. Thus, we conclude that (a) the Mermin-Wagner theorem is mainly lifted *via* the interplanar coupling[3], and not *via* the single site anisotropy[4], and (b) the softness of the magnetic moment, *i.e.*, longitudinal fluctuations, plays an important role, suppressing T_N by up to a factor of two.

Let us now discuss how and why MOs support a Néel antiferromagnetism in SrRu_2O_6 . In the nonmagnetic state, the three lower MO bands, B_{1u} and E_{1g} , are fully occupied. Imposing uniform spin polarization does not change the occupancy of these states, unless the induced exchange splitting is larger than the gap, and this is why the ferromagnetic order is unstable. On the contrary, imposing the staggered magnetic field of $\pm\Delta$ does not break the MO band structure, but rather increases the gap between E_{1g} and E_{2u} (in the lowest order in Δ , by Δ^2/t'_1). In the same order, we can calculate the change of the occupancies and find that the spin-up sites acquire magnetization of $5\Delta/2t'_1 \mu_B$, and the spin-down sites $-5\Delta/2t'_1 \mu_B$. The signs are consistent with the assumed signs of Δ , which tells us that with sufficiently large Hund's rule coupling the system will become unstable against such a staggered magnetization (but will resist any ferromagnetic component); of course, quantitative analysis is impossible on this level of simplification. Obviously, the equilibrium moment can be anything between 0 and $3 \mu_B$. It is not "suppressed" from the putative $S = 3/2$ state, but is set by the interplay between the Hund's rule coupling on Ru and the details of the density of states of MOs. A corollary from the above arguments is that the dielectric gap depends quadratically on the Ru moment; Fig. 3 illustrates that this is indeed the case, to a reasonable accuracy.

Let us emphasize, that the molecular orbitals are not just another way to describe the electronic structure of SrRu_2O_6 , but have profound physical meaning. It is instructive to compare it with another recently investigated high- T_N material, SrTcO_3 , where the transition metal also has a $4d^3$ configuration and $S = 3/2$. It was argued

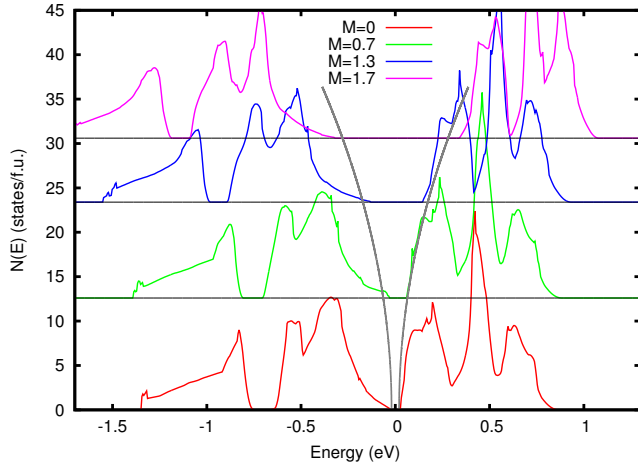


FIG. 3. Total density of states (DOS) calculated for several values of Ru moments, M , in the fixed-spin-moment procedure for the Néel AFM. The black lines illustrate the fact that the band gap is approximately quadratic in M . Results of the VASP calculations.

[19] that T_N is so high because SrTcO_3 is in an intermediate regime between itinerancy and localization, which is optimal for magnetic interactions. Indeed, LDA+DMFT calculations, well suited to this regime, have been performed by Mravlje *et al.* [19], who found $T_N \approx 2200$ K. The experimental number is about 1100 K. To compare this result with SrRu_2O_6 , we have also performed LDA+DMFT calculations with the AMULET code[20], using an effective Hamiltonian constructed for Ru t_{2g} orbitals and interaction parameters $U = 2.7$ and $J = 0.3$ eV as calculated in Ref. [3] (parameters for Tc are very similar). The corresponding temperature dependence of the magnetic moment is shown in Fig. 4. Not surprisingly, we found about the same Néel temperature (2000 K) as Mravlje *et al.* [19], and an even larger magnetic moment ($M \approx 2.7$ vs. $2.5 \mu_B$). The difference, however, is that experimentally in SrRu_2O_6 both T_N and M are about twice smaller than in SrTcO_3 . Mravlje *et al.* ascribed their overestimation of T_N to nonlocal fluctuations, missing in the DMFT, but observed no reduction in the ordered moment at all, while in our case the reduction in *both* T_N and M^2 is of the same order, about a factor of 4. This clearly indicates that there is a fundamental difference between the two compounds, going much beyond just the difference in dimensionality, which is related to the presence of MOs in one and their absence in the other compound. A proper account of the molecular orbitals within DMFT can only be done in the cluster extension of this method [21], which could shed more light on this compound.

Another interesting question that arises in connection with this material is what would happen if it were doped with, for instance, a rare earth element. To address this scenario, we simulated doping by adding electrons to the

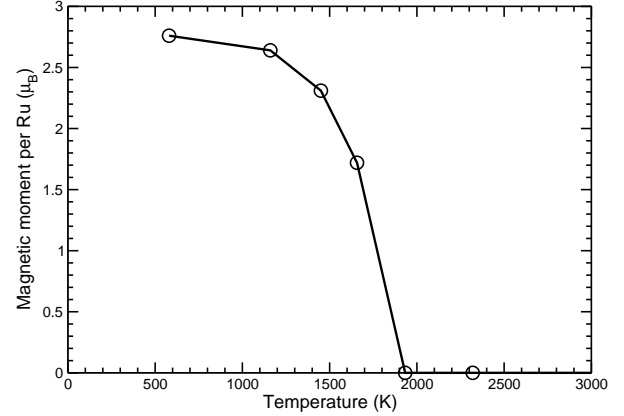


FIG. 4. Magnetic moment as calculated in the LDA+DMFT approach. The continues-time quantum Monte-Carlo (CT-QMC) solver [22] was used in these calculations.

system (with a compensating constant background). The energy difference between the FM and Néel AFM states decreases upon electron doping, as seen from Fig. 5. The FM configuration immediately becomes metastable, whereby all doped electrons go into one spin subband, rendering the material half-metallic. The ground state remains antiferromagnetic, but its energy advantage is gradually decreasing. Thus, one expects that the critical angle ϕ (which was $\sim 35^\circ$ in undoped case) will grow with doping, and the Hamiltonian (2) will be correspondingly modified; this may result in a rapid change of magnetic properties with doping, which deserves further theoretical and experimental investigation.

To summarize, we have found that:

- (i) The electronic structure of SrRu_2O_6 is dominated by molecular orbitals. Each electron is, to a good approximation, localized on a particular Ru_6 hexagon, and completely delocalized over the corresponding six Ru sites.
- (ii) This structure sports an excitation gap that prevents formation of ferromagnetic bonds, but is consistent with nearest neighbor antiferromagnetism. The corresponding magnetic interactions cannot be mapped onto a localized spin model, be it Heisenberg or biquadratic Hamiltonian with arbitrary long range. Neither can it be described as purely itinerant magnetism, but features interesting elements of both. This duality reflects the dual character of the electronic structure, where electrons are simultaneously completely delocalized and strongly localized on the Ru hexagons. A corollary is that any deviation from the collinear Néel order is severely punished by kinetic energy, which, in turn, provides for the anomalously large transition temperature.
- (iii) The gaps in the non-magnetic and antiferromagnetic states have the same nature, and one is continu-

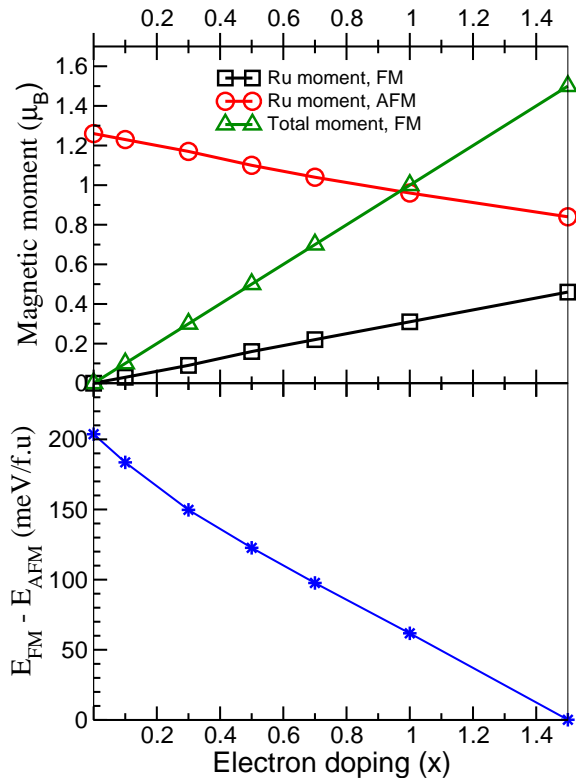


FIG. 5. Electron doping dependence of magnetic moments (per Ru and total) and total energy difference between FM and Néel AFM states on the electron doping.

ously transformed into the other as the magnetization increases. On the contrary, the ionic picture assigning the moment of $3 \mu_B$ to each Ru and associating the gap in magnetic states with spin-up/spin-down splitting is qualitatively incorrect. The observed and calculated magnetic moment of $1.3 \mu_B$ is a manifestation of the molecular orbital nature of electronic states, and should not be viewed as a spin $S = 3/2$ reduced by hybridization.

(iii) The magnetic properties of doped SrRu_2O_6 (e.g. by Na or La) are expected to be very different from the stoichiometric case. One may anticipate interesting and very different physics emerging, which can be a subject of forthcoming research.

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