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Comment on "Evidence for strong electronic correlations in the spectra of Sr_2RuO_4"

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It is pointed out that O 2p states dominate the electronic structure of Sr_2RuO_4 in the ~−3 eV region and can explain the observation of a peak in the density of states in photoemission experiments. This contradicts claims that a lower Hubbard band is needed at 3 eV binding energy.

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Sr_2RuO_4 is the subject of much interest both because of its superconductivity[1,2] and because of its proximity to complex ground states. These include ferromagnetism ($SrRuO_3$),[3] metamagnetic quantum criticallity ($Sr_3Ru_2O_7$),[4] orbital ordering ($Ca_{2-x}Sr_xRuO_4$), Fermi surface instability ($Ca_3Ru_2O_7$),[5] and an antiferromagnetic insulator (Ca_2RuO_4).[6] The superconductivity of Sr_2RuO_4 was shown to be unconventional by a wide variety of experiments, and may be triplet in nature, though the symmetry has not been proven.[2,7,8] Understanding the electronic structure and interactions in Sr_2RuO_4 is a key ingredient to sort out its superconductivity. This is facilitated by the facts that the crystal structure is relatively simple (Fig. 1) and that highly perfect crystalline material can be made thereby enabling detailed investigation by a wide variety of experiments. Standard local density approximation (LDA) band structure calculations show three Fermi surfaces derived from the three Ru t_{2g} orbitals, strongly hybridized with O p_π orbitals, specifically the degenerate d_{xz},d_{yz} pair and the d_{xy} orbital.[9–11] This complex multiorbital predicted Fermi surface has been confirmed in detail by quantum oscillation, photoemission, and other experiments,[2] and consequences including predicted magnetic fluctuations[12] at the Fermi surface nesting vector are seen experimentally.[13]

The situation is, however, not so simple. While the Fermi surface topology and partial orbital occupations are given precisely within the LDA, quantum oscillation measurements show strong mass renormalizations of approximately a factor of 4 relative to the LDA. Furthermore, there is evidence, both directly from experiment and also from the comparison of LDA calculations with experiment, for proximity to a magnetic quantum critical point.[14] From this point of view, it is interesting to note that the other perovskite ruthenates ($CaRuO_3$, $SrRuO_3$, $Ca_{2-x}Sr_xRuO_4$, $Ca_3Ru_2O_7$, and $Sr_3Ru_2O_7$) are apparently more magnetic and/or more renormalized than Sr_2RuO_4, which is, however, the only superconductor found to date in the family. Nonetheless, the mass renormalization of approximately four in Sr_2RuO_4 is large, and it indicates substantial correlation effects. It is tempting therefore to make an analogy between Sr_2RuO_4 and more common correlated materials, particularly the Mott (charge transfer) insulators in the 3d oxides, where the correlation effects are driven by on-site Coulomb repulsion, i.e., the Hubbard U.

Pchelkina *et al.* recently reported dynamical mean field theory calculations in relation to photoemission and based on the results that claimed evidence for strong correlations of the Hubbard type in the spectra of Sr_2RuO_4.[15] Their argument is, in essence, that an observed peak at ~3 eV, binding energy cannot be explained by conventional band theory and since it does appear in their calculations with a Hubbard interaction, it must be taken as evidence for strong effects of Coulomb correlations. The purpose of this paper is to present arguments refuting this claim and specifically to point out that the feature that they claim as the lower Hubbard band is present in standard LDA calculations and is derived from O p states.

One approach for incorporating effects of Coulomb correlations in the 3d oxide insulators is the LDA+U method,[16–18] where an effective interaction U_{eff} is introduced. This interaction favors integer occupations of the orbitals, and splits bands derived from occupied d orbitals from those derived from unoccupied d orbitals by an amount related to U_{eff}, leading to a much improved description of 3d oxides at the expense of a single parameter that can be adjusted to reproduce the experimental position of the occupied lower Hubbard band.[17,18] Calculations can also be done taking U_{eff} from constrained LDA calculations. However, the values of U_{eff} obtained in this way depend on the band structure method, basis set, choice of orbitals, and other parameters used, and these problems may be expected to be more severe in cases with more extended orbitals and more hybrid-

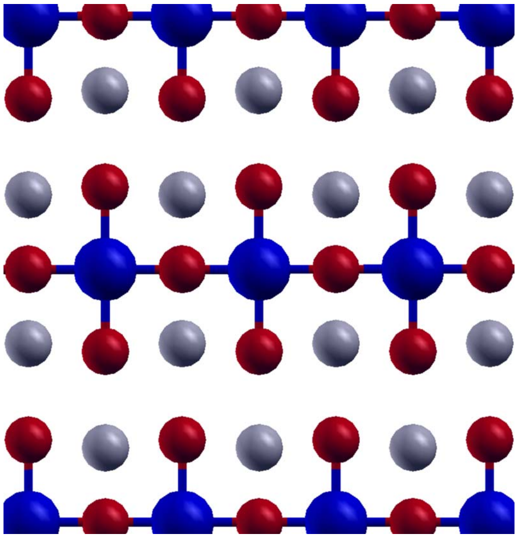

FIG. 1. (Color online) Structure of $I4/mmm$ Sr_2RuO_4 shown in a (100) plane with the c axis in the vertical direction. Sr is denoted by light gray spheres, O by small red spheres, and Ru by large blue spheres.

ization with ligands.[19] In metals, fluctuations are important. This work against the tendency toward integer orbital occupations presents in the static LDA+U method. However, Hubbard-type correlations may still be important, for example, in producing the satellites seen in photoemission in metals such as Ni. These satellites, along with metallic conduction, can be reproduced using dynamical mean field theory (DMFT) calculations.[20] While this is a much more sophisticated approach than the static LDA+U method, in most implementations, it shares in common with the LDA +U method the use of an effective interaction U_{eff}, which determines the position of the lower Hubbard band, i.e., the position of the photoemission satellite.[21] Key assumptions made in DMFT calculations are that the relevant correlations that need to be added are on on-site Coulomb repulsion, and that the value to apply is known, e.g., from a constrained LDA calculation with some band structure method and choice of orbitals or from the position of a photoemission satellite. In the case of Sr_2RuO_4, the fact that the topology of the Fermi surface is accurately reproduced by LDA calculations is a challenge for methods incorporating a U_{eff}, as shifts in orbital occupation will change the topology due to the nearby van Hove singularity.[22]

However, there are other correlation effects that can lead to mass renormalization, including interaction with itinerant electron spin fluctuations,[23,24] which as mentioned, may be important in Sr_2RuO_4, and which have been shown to be able to yield renormalizations of the observed magnitude using realistic parameters.[11,12] Besides, the physics of 4d oxides may be essentially different from 3d oxides. The 4d orbitals are much more spatially extended than 3d orbitals. This leads to weaker on-site Coulomb interactions, stronger hybridization with ligands, and larger hopping matrix elements. Consequences include a greater role for band structure effects and stronger sensitivity of the properties to lattice structure. Evidence for this is seen in the **k**-dependent spin fluctuations connected with Fermi surface nesting and in the wide variety of ground states seen in perovskite derived ruthenates, which all have the same electron count, but differ in structural details.

There are several photoemission studies reported for Sr_2RuO_4.[25–33] Concerning the Fermi surface, these show close correspondence with quantum oscillation measurements and LDA calculations, particularly after accounting for the surface reconstruction.[29,30,34] The measurements and also quantum oscillation measurements show a renormalization of the bands near the Fermi energy. This renormalization is smaller in angle resolved photoemission spectroscopy (ARPES) than in quantum oscillations except perhaps that very close to E_F, where a kink structure is reported.[32,33] Measurements at higher energy reveal a peak at ~3 eV below E_F. This is the peak that Pchelkina *et al.* associate with the lower Hubbard band. In particular, they used DMFT calculations within the linearized muffin-tin orbital (LMTO) framework to show that with a U_{eff} of ~3 eV, they obtain a lower Hubbard band at this energy.[15] The essence of their argument is that since this peak is not present in LDA calculations, it must be that it is evidence for the type of correlations that they include. However, accurate LDA calculations done with the full potential linearized augmented plane wave (LAPW) method[35] and no Hubbard U, and therefore no lower Hubbard band, show structure in the density of states in this energy range.[9,10] On the other hand, early calculations at the LDA level with the less accurate LMTO method [this is a fast method that uses a restricted basis set and makes atomic sphere approximations (ASAs)] do not show a strong peak but rather only a weak structure at ~3 eV binding energy derived mainly from the nonbonding p_z states of the O1 but apparently not the O2 atoms,[26] while the peak appears in other LMTO-ASA calculations.[36] There is also no such structure found in Hartree-Fock calculations, and arguments were made that the observation of this peak experimentally but not in those Hartree-Fock calculations is evidence for correlation effects.[31]

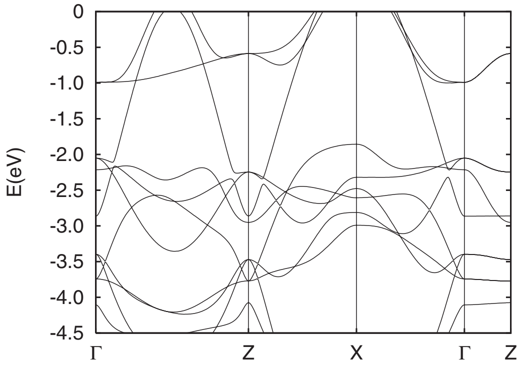

FIG. 2. LDA band structure of Sr_2RuO_4. The Fermi energy is at 0 eV. The lines plotted are as in Ref. 10.

Figure 2 shows the LDA band structure, as obtained in calculations similar to Ref. 10, but with more **k** points. The LAPW method with local orbitals[37] was used with LAPW sphere radii of 2.10a_0, 1.95a_0, and 1.65a_0, for Sr, Ru, and O, respectively. The bands crossing E_F are the d_{xy}, gamma band, which extends down to ~2.5 eV in the LDA and the less dispersive d_{xz}, d_{yz} bands, which extend down to ~1 eV. It may be noted that the band structure also shows several weakly dispersive bands in the range of 2–4 eV binding energy. These weakly dispersive bands in the LDA electronic structure at ~3 eV binding yield a prominent peak in the density of states (DOS) in the same energy region as the peak in photoemission that Pchelkina *et al.* associated with the lower Hubbard band. This is shown in Fig. 3, which shows the DOS for the ideal bulk structure of Sr_2RuO_4, and for a cell with a 5.94° rotation of the octahedra which simulates the effect of the surface reconstruction.[30] This peak has very little Ru character and is quite insensitive to the rotation.

The structure of Sr_2RuO_4 (Fig. 1) contains two O sites: an in-plane O (O1) and an apical O (O2). The in-plane O1 atoms have two, nominally tetravalent Ru neighbors, while the apical O2 has only one Ru neighbor. As such, the Ewald potential at the O1 sites is deeper. This is seen in the 1s positions, which are at 1.4 eV higher binding energy for the O2 atoms relative to the O2 atoms in our LDA calculations. This lower Ru coordination of the O2 sites also means that the p states on them will be less strongly affected by hybridization with Ru than those of the O1 sites. This is seen in the

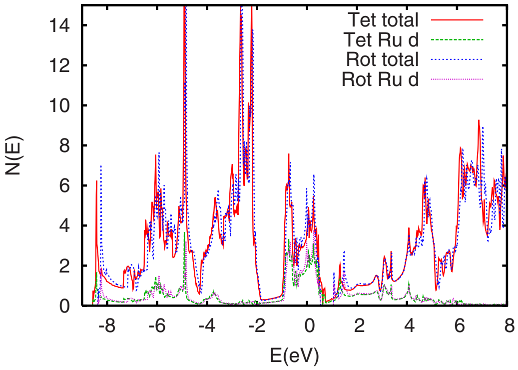

FIG. 3. (Color online) LDA DOS of Sr_2RuO_4, per f.u., for the bulk structure (Tet) and for a doubled cell with rotated octahedra (Rot). The Fermi energy is at 0 eV. The Ru d component is the projection onto the Ru LAPW sphere.

O components of the DOS, shown in Fig. 4. The bottom of the O bands is dominated by O1 $p\sigma$–Ru $d_{x^2-y^2}$ bonding combinations. Similarly, the bands comprising the lowest part of the O2 DOS come from O2 $p\sigma$–Ru d_{z^2} combinations. For both O atoms, these are followed in order of increasing energy by $p\pi$–Ru t_{2g} bonding combinations, weakly bonding p orbitals, and $p\pi$–Ru t_{2g} antibonding combinations. The O1–Ru t_{2g} antibonding combinations are the dominant contributors to the states at E_F. The O character in the region from 4 to 2 eV binding energy is mainly from the apical O2 site weakly bonding states. These are the p_x and p_y states on the apical O atoms. With a surface (destroying c-axis reflection symmetry), these have the same symmetry as the Ru d_{xz}, d_{yz} states. Thus, it may be expected that these states cannot be easily distinguished from hybridized Ru t_{2g} states by polarization analysis. Furthermore, because the t_{2g} bands near E_F are actually hybridized bands with ~1/3 O 2p character, distinguishing the weakly bonding O peak that we find at 2–4 eV binding energy from a lower Hubbard band of mixed Ru-O character is not simple. Yokoya *et al.*[26] argued that the structure is the lower Hubbard band based on the observations of an enhancement in the range of photon energies with onset at 36 eV and extending up to 50 eV. They associate this onset with with the Ru 4p to 4d threshold and, based on the observed enhancement, claim that the peak is Ru d derived. However, in their experiments, the peaks at the bottom of the O p bands (associated with the O1 $p\sigma$–Ru e_g bonding states, which have high Ru d character) and the t_{2g} derived states near E_F show no such large enhancement in this photon energy range. According to our LDA calculations, the binding energy of the Ru 4p level with respect to the Fermi energy, which is roughly the 4p–4d energy, is 44 eV; the calculated Sr 4s binding energy is 34 eV, which is closer to the observed onset. Also, the LDA invariably underbinds core states due to self-interactions. This would mean that the Ru 4p states are at even higher binding energy even further away from the observed onset. Finally, other photoemission studies of chemically similar $SrRuO_3$ and $CaRuO_3$ place the Ru 4p resonance at 52 eV.[38,39] It would be surprising if chemically similar stable oxides with the same nominal valence would have such different core level positions. The enhancement of the weakly bonding O 2p derived DOS (i.e., from orbitals not directed at Ru) over other O and Ru derived states is natural if the level excited in the resonance is the Sr 4s. Moreover, there is an issue of surface sensitivity, since with the surfaces that were available at that time, the electronic structure as determined by ARPES did not agree with either quantum oscillation or LDA calculations, for example, finding extended van Hove singularities,[25,27] which detailed subsequent investigations did not find[28] (note also the complication of the surface reconstruction[29]).

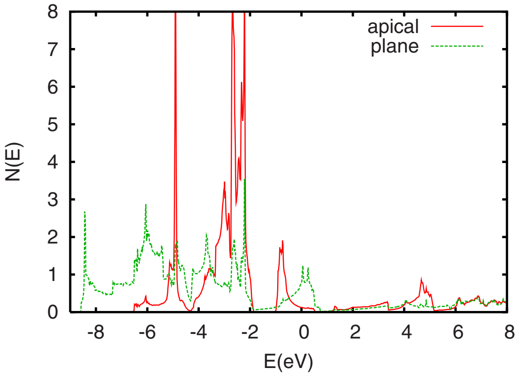

FIG. 4. (Color online) O p component of the LDA DOS per f.u. basis for the bulk structure. The Fermi energy is at 0 eV. This is from the projection onto the O LAPW spheres.

In any case, from a chemical point of view, the weakly bonding O 2p states should be present in the electronic structure and should lie above the bonding Ru d–O p combinations and below the antibonding Ru t_{2g}–O p combinations, consistent with a position around ~3 eV binding. Large shifts of on-site energies that could move the states away from this energy region would be expected to change the Ru-O hybridization and the balance between the Ru orbitals changing the Fermi surface, which without such changes agrees with experiment.

To summarize, accurate LDA calculations show a prominent DOS peak in the around 3 eV binding energy. This corresponds well with a peak observed in photoemission experiments. Therefore, it may be concluded that the lower Hubbard band arising from Coulomb correlations, which was claimed to be essential to explain the observed spectra, may not be needed after all. While the possibility of important Coulomb correlations is not excluded, it seems that the evidence for strong electronic correlations in the spectra of Sr_2RuO_4, due to Hubbard interactions claimed in Ref. 15, is not yet established.

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