Electronic structure and the origin of the high ordering temperature in SrRu_{2}O_{6}

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Phys. Rev. B **91**, 214420 — Published 16 June 2015

DOI: 10.1103/PhysRevB.91.214420

Electronic structure and the origin of the high ordering temperature in $SrRu_2O_6$

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$SrRu_2O_6$ is a layered honeycomb lattice material with an extraordinarily high magnetic ordering temperature. We investigated this material using density functional calculations. We find that the energy scales for moment formation and ordering are similar and high. Additionally, we find that the magnetic anisotropy is high and favors moments oriented along the *c*-axis. This provides an explanation for the exceptionally high ordering temperature. Finally, the compound is found to be semiconducting at the bare density functional level, even without magnetic order. Experimental consequences of this scenario for the high ordering temperature are discussed.

I. INTRODUCTION

Hiley and co-workers recently reported synthesis of the layered honeycomb lattice oxide $SrRu_2O_6$, which contains pentavalent Ru^{5+} ions in octahedral coordination.[1] The compound has antiferromagnetic ordering with an ordering temperature above 500 K, which is an extremely high value, particularly considering the layered crystal structure. In fact, while a number of remarkably high magnetic ordering temperature 4d and 5d oxides have been discovered, most notably $SrTcO_3$, $CaTcO_3$ and $NaOsO_3$,[2–5] $SrRu_2O_6$ is the first example of an apparently 2D material in this category, and in fact its ordering temperature exceeds that of $NaOsO_3$.

The crystal structure of $SrRu_2O_6$ consists of honeycomb lattice planes of Ru^{5+} ions, stacked directly on top of each other with intervening Sr^{2+} to form a hexagonal lattice, as shown in Fig. 1. There is one formula unit (two Ru atoms) per unit cell.

II. APPROACH

We did density functional calculations using the experimental crystal structure, which was determined by synchrotron xray and neutron diffraction.[1] The accuracy of this structure is supported by the fact that our calculated forces in the antiferromagnetic ground state with this structure are below 4 mRy/bohr. This is essentially zero at the precision of density functional calculations. The calculations were done using the general potential linearized augmented planewave (LAPW) method[6] as implemented in the WIEN2k code.[7] This is an all electron method, which includes full self-consistent treatments of core and valence electrons and uses charge densities including both of these. We used LAPW sphere radii of 2.05 bohr for Sr and Ru and 1.55 bohr for O. We used well converged LAPW basis sets and included local orbitals[8] for the semi-core states of Sr and Ru.

Interestingly, the calculated force is also small in non-spin-polarized calculations with the experimental structure. The force in this case is 8 mRy/bohr. This indicates non-zero but still relatively modest magnetoelastic coupling. Relaxation of the O position without spin polarization leads to a shortening of the Ru-O bond length by only 0.005 Å. This is in contrast to for example Fe-based superconductors, which show much larger effects.[9]

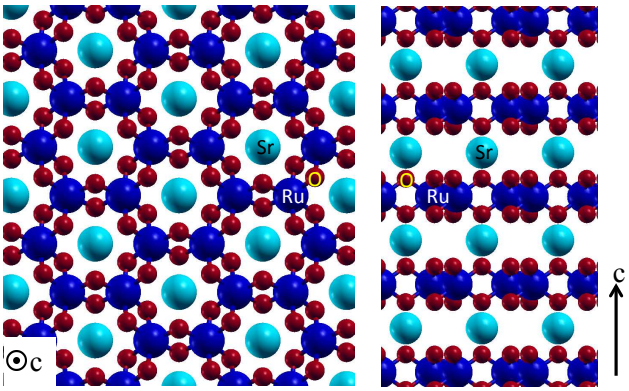

FIG. 1. Crystal structure of $SrRu_2O_6$ showing the honeycomb lattice planes separated by Sr ions.

We did calculations both in a scalar relativistic approximation and with inclusion of spin-orbit, and find similar results. The calculations were done using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE).[10]

III. RESULTS AND DISCUSSION

We start with the electronic structure. The calculated density of states without spin polarization as obtained with the PBE GGA is shown in Fig. 2, along with the band structure near the Fermi level. As expected, the electronic structure shows Ru^{5+}, with a half-filled Ru t_{2g} derived manifold. Since there are two Ru ions per unit cell, there are six t_{2g} bands and a band gap is possible without magnetism even though there are an odd number of t_{2g} electrons per atom. This is the case. The calculated non-spin-polarized band gap is 0.06 eV, including spin-orbit and 0.05 eV in a scalar relativistic approximation. Importantly, substantial hybridization between Ru $4d$ and O $2p$ is evident in the Ru d projected density of states. For example, there is substantial Ru d character in the O $2p$ bands, especially at the bottom, but extending almost to the top of this manifold.

The honeycomb lattice is not frustrated against near

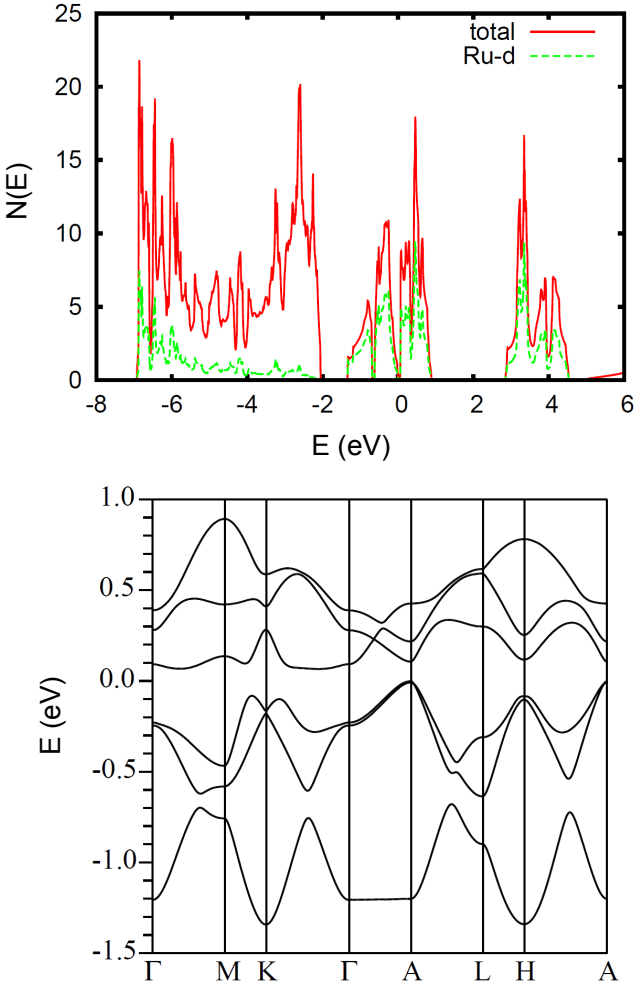

FIG. 2. Electronic density of states and Ru d projection (top) and band structure in the range around the Fermi level (bottom) as obtained in non-spin-polarized PBE GGA calculations, including spin orbit. The valence band maximum is set to 0 eV.

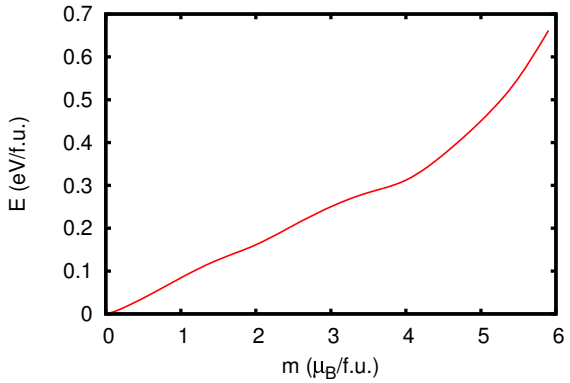

FIG. 3. Fixed spin moment energy as a function of spin magnetization on a per formula unit basis as obtained with the PBE GGA.

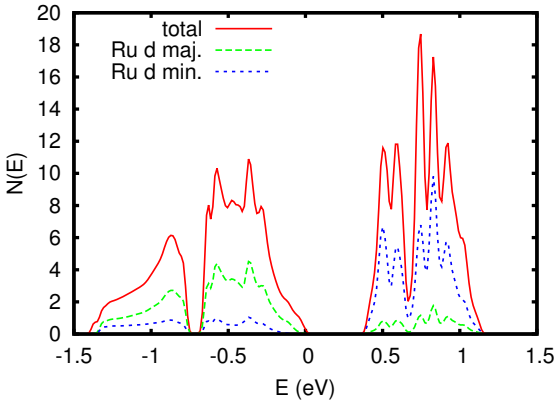

FIG. 4. Density of states for the AF1 ground state including spin orbit.

neighbor antiferromagnetism. We did spin-polarized calculations for various ordering patterns. These were the near neighbor antiferromagnetic state, in which neighboring Ru in plane are antiferromagnetically aligned, and the c-axis stacking is also antiferromagnetic (denoted AF1), the same in-plane order, but stacked ferromagnetically along the c-axis (denoted AF2), a ferromagnetic order (denoted F), and ferromagnetic planes stacked antiferromagnetically (denoted AF3).

Neither of the orders with ferromagnetic planes (F or AF3) yielded a spin-polarized solution with the PBE GGA. This was confirmed by fixed spin moment calculations (Fig. 3). These show a monotonically increasing energy with constrained spin magnetization. The fixed spin moment curve shows a roughly linear increase in energy with magnetization at low magnetizations, reflecting the presence of a band gap. We note that the strong hybridization with O is evident in the fixed spin moment results. In particular, with an imposed ferromagnetic spin magnetization of 3 μ_B/Ru only $\sim$ 1.8 μ_B is in the Ru LAPW sphere (radius 2.05 bohr). Considering the extent of the Ru 4d atomic orbitals, the implication is that roughly 1 μ_B/Ru, i.e. 1/3 of the total imposed magnetization lies on the O atoms. This is qualitatively similar to the Ru^{5+} double perovskite oxide, Sr_2YRuO_6,[11] and the Ru^{4+} ferromagnet, $SrRuO_3$.[12]

On the other hand, we find very stable AF1 and AF2 orderings. The lowest energy AF1 order, is 0.20 eV lower in energy per formula unit than the non-spin-polarized case, while the AF2 order is only 0.003 eV per formula unit higher than the ground state. The small energy difference between the AF1 and AF2 states means that the out-of-plane interactions are very weak compared to

the in-plane ordering energy. Low dimensional magnets, as defined in terms of low interlayer couplings relative to in-plane couplings, can have suppressed ordering temperatures, usually logarithmically in the ratio of the out-of-plane to in-plane magnetic interactions.[13] This is expected to be the case for Heisenberg or XY moments, but not for Ising like moments. We find that $SrRu_2O_6$ has a strong magnetic anisotropy that favors moment directions along the c-axis. For the AF1 ground state, we find that the energy with moments along the c-axis is 2.8 meV per formula unit lower than with moments oriented along the a-axis in PBE-GGA calculations with spin orbit. Therefore, a suppression of the ordering due to the layered structure is not expected even though the interlayer magnetic interactions are weak.

The calculated spin moment in the Ru sphere for the AF1 ground state is 1.3 μ_B/Ru, even lower than the induced moment in the fixed spin moment calculations. Nonetheless the ordering opens a sizable gap in the t_{2g} bands. The band gap for the AF1 ordering with the PBE GGA is 0.43 eV without spin orbit. With spin orbit, there is an orbital moment, opposite to the spin moment following Hund's rule, of size 0.09 μ_B and the PBE-GGA band gap is 0.39 eV. The t_{2g} density of states is shown in Fig. 4. The moment on the Ru of 1.3 μ_B is strongly reduced relative to the nominally expected spin moment of 3 μ_B for a half-filled t_{2g} band. Based on the fixed spin moment results and the strong covalency we infer that most of this reduction is a consequence of covalency between the Ru 4d and O 2p states. This is similar to recent results for the 5d double perovskite Sr_2ScOsO_6.[14] We note that this is a mechanism that has been discussed previously,[15,16] but appears to be particularly large for these more covalent 4d and 5d materials.

This covalency between Ru and O is important for understanding the high energy scale associated with magnetic ordering, which in turn provides an explanation for the high ordering temperature. Magnetism is much more common in 3d oxides than in 4d and 5d oxides. Because of this it is often presumed that the magnetism of 4d and 5d oxides is inherently weak. However, this is clearly not the case, as is evident when one considers the ferromagnetism of metallic $SrRuO_3$[17,18] and the very high ordering temperature in $SrTcO_3$.[2] Middey and co-workers have discussed the magnetism of $SrTcO_3$ in terms of the half filled t_{2g} shell, which favors spin polarization.[19]

Actually, as is well known, magnetism arises from intersite coupling of moments on ions. In oxides, as in other materials, strong intersite coupling of moments is favored by strong covalency.[20,21] Most magnetic materials are described within a local moment picture, in which moments that exist due to on-site atomic interactions independent of ordering are subject to inter-site couplings that determine the ordering temperature. The reason why most 4d and 5d oxides are not magnetic is not that these interactions, which would determine the ordering temperature are weak. Rather it is because that these elements have more extended d orbitals than 3d transition metals.

Moment formation is a consequence of the Coulomb interaction, mainly the exchange interaction in solids. The 4d shell of elements such as Ru, is much more extended than the 3d shell of Fe. Thus the Coulomb integrals that give the onsite exchange interaction in 4d elements are smaller than in 3d elements. Furthermore, the more extended 4d orbitals overlap more with neighboring atoms, leading to generally more covalent electronic structures. These two differences from the 3d elements both work against formation of local moments.

Importantly, as covalency is increased, one expects the intersite interactions, and the ordering temperature to increase so long as moments can form. However, they will then to vanish with the disappearance of the moments. In the region of highest ordering temperature the energy scales for moment formation and for ordering the moments will be comparable and therefore the existence of moments will depend on the ordering. For metallic magnets this is the itinerant limit.[22]

The elemental ferromagnets, Fe, Co and Ni have Curie temperatures of 1043 K, 1400 K and 627 K, respectively. Taking into account the different moments of 2.1 μ_B, 1.6 μ_B, and 0.6 μ_B, respectively, one observes that the relative ordering strength increases strongly as the system becomes more itinerant, i.e. going from Fe to Co to Ni.[23] Cr metal, which has a spin density wave, is an example of an antiferromagnet with substantial itinerant character.[24] Thus it can be seen that increasing itinerancy favors increasing Curie temperature. The same principle is operative here. In fact this has been discussed previously in the context of $SrRuO_3$, $CaTcO_3$ and $SrTcO_3$ based on density functional calculations,[2,3,11] and subsequently for $SrTcO_3$, in terms of dynamical mean field calculations with similar conclusions.[25]

The origin of magnetism and the high ordering temeprature of Ni in particular is the itinerant Stoner instability. This comes from both from theoretical calculations,[23] and direct neutron scattering experiments.[26] A key difference between the local moment and itinerant limits is the presence in the itinerant case of longintudinal spin fluctuations. These are Stoner excitations in ferromagnets. In the local moment limit transverse spin wave excitations lead to disordering of the moments as temperature is increased but the moments persist on short time scales well above the ordering temeprature. This means that the Hund's exchange energy leading to moment formation is available both to the ordered phase and the phase above the ordering temperature, with the well known consequence that it does not contribute to the ordering temperature, which is instead controled by the inter-site exchange couplings. In contrast, for the itinerant limit longitudinal fluctuations are excited by temperature. These lead to a collapse of the moment size near the ordering temperature, so that the Hund's energy is not available to stabilize the high temperature phase. The present results for $SrRu_2O_6$ show that the Ru moments are not stable against disordering and in particular, do not exist at all for some spin con-

figurations including the ferromagnetic case. This places antiferromagnetic $SrRu_2O_6$ close to the itinerant limit, similar to Ni.

Within the picture discussed above, the moment reduction and high ordering temperature are connecting by a common origin, specifically covalency between the metal d states and the O p states. Thus it may be anticipated that magnetic $4d$ and $5d$ oxides with high ordering temperatures also have moments that are substantially reduced from their nominal values. It will be interesting to test this systematically using neutron scattering.

IV. SUMMARY AND CONCLUSIONS

The extremely high ordering temperature of $SrRu_2O_6$ in a layered oxide provides a new model system for exploring the interplay of covalency and moment formation in a $4d$ oxide. The results suggest some experimental expectations that may be tested. First of all, the comparable energy scales for moment formation and ordering imply that the moments should strongly decrease as the ordering temperature is approached from below. Secondly, the band gap should show a rather strong temperature dependence near the ordering temperature, falling to a reduced value above the ordering. These two expectations are similar to what is seen in $NaOsO_3$,[5] except that in the present case, the non-magnetic case is a small band gap semiconductor instead of a metal. In this sense $SrRu_2O_6$ may provide an interesting exception to one of the standard experimental characterizations of a Mott insulating oxide, specifically an oxide with an odd number of electrons per transition metal atom that has an antiferromagnetic insulating ground state and stays insulating above the magnetic ordering temperature. Third, even though the magnetoelastic coupling is not nearly as large as in the Fe-based superconductors for example, the reduction in the moments near the ordering temperature may lead to interesting lattice behavior, such as an invar effect or even a slight contraction as the ordering temperature is approached from below.

ACKNOWLEDGMENTS

This work was supported by the Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division.

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