Indications of weak electronic correlations in $SrRuO_3$ from first-principles calculations

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We provide, by a detailed first-principles investigation, evidence for weak electronic correlations in $SrRuO_3$. The magnetism in $SrRuO_3$, in terms of the equilibrium magnetization and critical temperature, is well described by the generalized gradient approximation. Including Hubbard-type correlations results in worse agreement with experiment.

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I. INTRODUCTION

In the past decades, much attention has been paid to 3*d* transition-metal compounds, but nowadays also 4*d* and 5*d* electron systems are intensively explored. Among 4*d* or 5*d* compounds, transition metal oxides and in particular perovskites have attracted enormous interest. The perovskites present multifunctional properties: different types of magnetic ordering, charge and orbital ordering, as well as ferroelectricity, all of these being the result of a strong interplay between spin, charge, and orbital degrees of freedom. Even more, the properties of these compounds are very susceptible to transformations of the crystal structure. One of the members of the perovskite-oxide-based family, $SrRuO_3$ (SRO), has a great potential for future oxide electronic devices. This compound has been extensively studied; it is reported that below 160 K, SRO shows long-range ferromagnetic order, with an experimentally measured saturation magnetization moment between 1.4 and 1.7 μ_B/Ru (Refs. 1–3).

These experimental findings have triggered many theoretical works. In particular, the electronic correlations were modeled in many ways. The question of whether such correlations play an important role in SRO has already been addressed by both experimental and theoretical studies, but no general consensus has been reached yet.[1,4–13] Often SRO is assumed to be a strongly correlated system. Thus, a widely used approximation adopted by many groups for the treatment of exchange and correlations in this material is LDA + U (the local density approximation with a Hubbard U).[7,9,10,13] The value of U in SRO has never been calculated from first principles, to our knowledge, and *ad hoc* values from 0.6 to 7.0eV have been used. It has also been suggested that the generalized gradient approximation (GGA) method is more appropriate for this system than the local density approximation (LDA).[4,5,12]

This discordance of various approaches for SRO motivated us to study the degree of electron correlations and to determine which approximation for the exchange-correlation functional is best suited to describe the electronic structure of this system. In order to do this, we compare our first-principles results, obtained with various approximations, to experimental data, in particular, with regard to the theoretical prediction for the magnetic moments and critical temperatures. Besides addressing the correlation strength, we investigate also the strength of interatomic exchange interactions between Ru atoms as well as between Ru and polarized O sites. Knowing the range and magnitude of these interactions, we obtain a deeper insight into the fundamental physics governing the intriguing properties of this compound.

II. DETAILS OF CALCULATIONS

For our study we used a multiple-scattering Korringa-Kohn-Rostoker Green's function method,[14] except when explicitly stated otherwise, and employed various approaches in order to account for the electron correlations, i.e. LDA (Ref. 15), LDA + U (Refs. 16 and 17), GGA (Ref. 18), and LSDA-SIC (self-interaction corrected local spin-density approximation).[19] The calculations were performed using a full-charge density approximation, which accounts for nonspherical charge distributions and provides an accurate electronic-structure description. In the following, we present selected results obtained for $SrRuO_3$ in the experimentally obtained distorted perovskite structure, that is, in the low temperature bulk phase (space group *Pbnm*).[20,21]

In order to access the correlation effects in SRO, we have looked at the magnetic properties, which are usually rather sensitive to electronic correlations. In particular, the critical temperature of the ferromagnetic transition is a good choice because it is a sensitive parameter that can be accurately calculated from first principles. Our method of calculating exchange interaction parameters has been rigorously tested for a wide range of compounds.[22–25] In each case, the experimental critical temperatures were well reproduced. Here, we apply this approach to SRO. Having calculated the exchange constants by means of the magnetic force theorem,[26] we compute the critical temperatures within the mean field approach (MFA) and the random phase approximation (RPA),[27] and using Monte Carlo simulations.[28,29]

III. RESULTS AND DISCUSSION

First, we determined the exchange constants in SRO in the experimentally observed crystal structure (orthorhombic *Pbnm*).[20,21] For convenience, we distinguish between the intralayer and interlayer interactions among the local magnetic

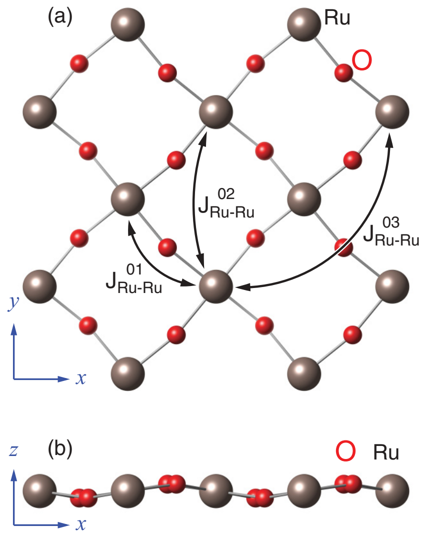

FIG. 1. (Color online) Schematic representation of a RuO_2 layer in the (a) top (the xy plane) and (b) side view (along the Ru-O bonds). For clarity, Sr atoms are not represented. Arrows indicate the type of exchange interactions and the atoms involved.

moments of Ru. We choose layers as shown in Fig. 1(a): in the xy plane for *Pbnm* symmetry. Ru^{4+} being a non-Jahn-Teller ion, all Ru-O bonds have almost the same length. The RuO_6 octahedra are not significantly distorted, while they are tilted so that Ru-O-Ru angles become smaller than 180° not only in plane, but also out of plane [Fig. 1(b)].

The calculations were performed within various approximations for the exchange and correlation: LDA, GGA, LSDA-SIC, and LDA + U, varying U from 0 eV (LDA) to 15 eV, and keeping the Hund's $J_H = 0.7$ eV. A simplified estimate of U and J_H using intra-atomic-sphere screening, as described in Ref. 17, gives $U = 1.9$ and $J_H = 0.7$ eV. For double counting we tried both the "around mean field"(AMF) scheme, and the fully localized limit (FLL).[17] The former functional is generally believed to be more suitable for delocalized electrons, while the latter is appropriate for systems with strongly localized electrons, and for valence states it approaches the LSDA-SIC method for large U. However, according to our calculations, for SRO both LDA + U functionals provide very similar results.

The Ru local magnetic moment is found to be monotonically changing, in the LDA + U, from 1.2 μ_B ($U^* = U - J_H = 0$) to 1.8 μ_B ($U^* = 15$ eV) with increase of U^*, while the GGA yields Ru moments of 1.4 μ_B. The total magnetization varies between 1.4 μ_B/Ru ($U^* = 0$) and 2 μ_B/Ru ($U^* \gtrsim 0.6$ eV); within the GGA, it is 1.9 μ_B/Ru, slightly larger than the experimentally measured 1.4–1.7 μ_B/Ru.

One of the fingerprints of strong on-site Coulomb correlations is severe underestimation of magnetic moments in the LDA and GGA (cf. high-T_c cuprate or 3d oxides). On the other hand, the LDA and GGA tend to overestimate the tendency to magnetism in weakly correlated itinerant magnets ($ZrZn_2$, Ni_3Al, Fe-based superconductors), since these methods neglect the destructive effect of zero-point spin fluctuations. The fact that the LDA reproduces the experimental magnetization in SRO very accurately, and the GGA slightly overestimates it, suggests that Hubbard correlations are not operative in this

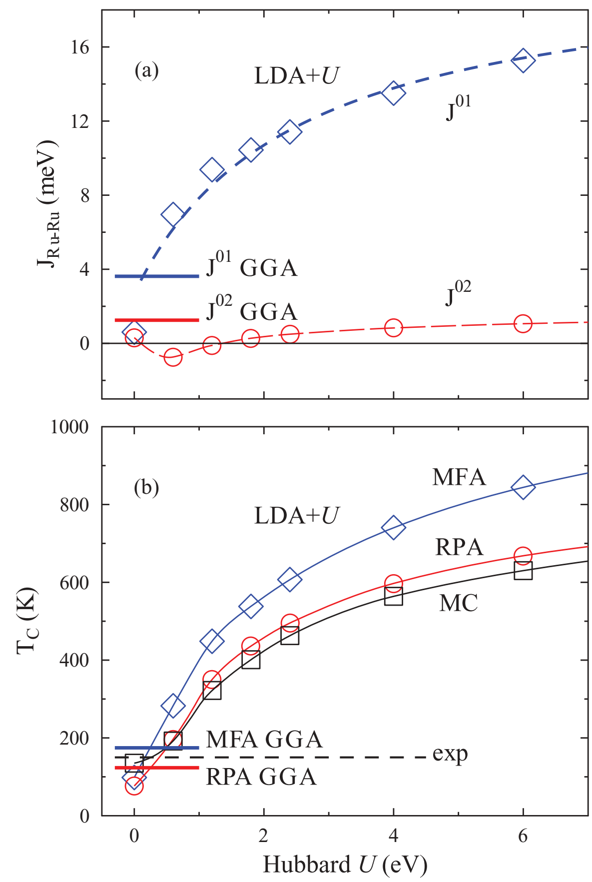

FIG. 2. (Color online) (a) Calculated exchange interaction constants between Ru atoms and (b) critical temperatures within different approximations for the exchange-correlation functional. Results within the GGA are represented by lines, while the open symbols are results obtained within the LDA + U. SRO is in the experimentally observed orthorhombic structure.

compound, while itinerant spin fluctuations play only a small, albeit nonnegligible, role.

The induced moments on the O atoms are parallel to the magnetic moments on the Ru sites. As discussed previously,[5] this is an important factor in the overall balance of magnetic interactions, favoring ferromagnetism over antiferromagnetism. In Fig. 2 we present the calculated exchange constants (upper panel) and the corresponding Curie temperatures (lower panel) estimated within the mean-field approach, the random phase approximation and the Monte Carlo method. Although the intra- ($J^{\parallel}$) and interlayer ($J^{\perp}$) exchange constants differ in the orthorhombic structure, their magnitudes vary by less than 0.6 meV. Therefore, only averaged exchange constants values are shown.

The main result of our simulations is a very strong dependence of the nearest-neighbors exchange constants on the value of $U^* = U - J_H$. They increase rapidly from 0.7 meV for $U^* = 0$ eV to 11 meV for $U^* = 1$ eV, following a $J(U^*) = b - a/U^*$ dependence (a and b are positive). The $J(U^*)$ fitting of J^{01} is represented by the dashed line in Fig. 2. The slope becomes less steep when J approaches 20 meV. For $U^* > 7$ eV the exchange parameters are almost constant with increasing U^* and approach the result obtained

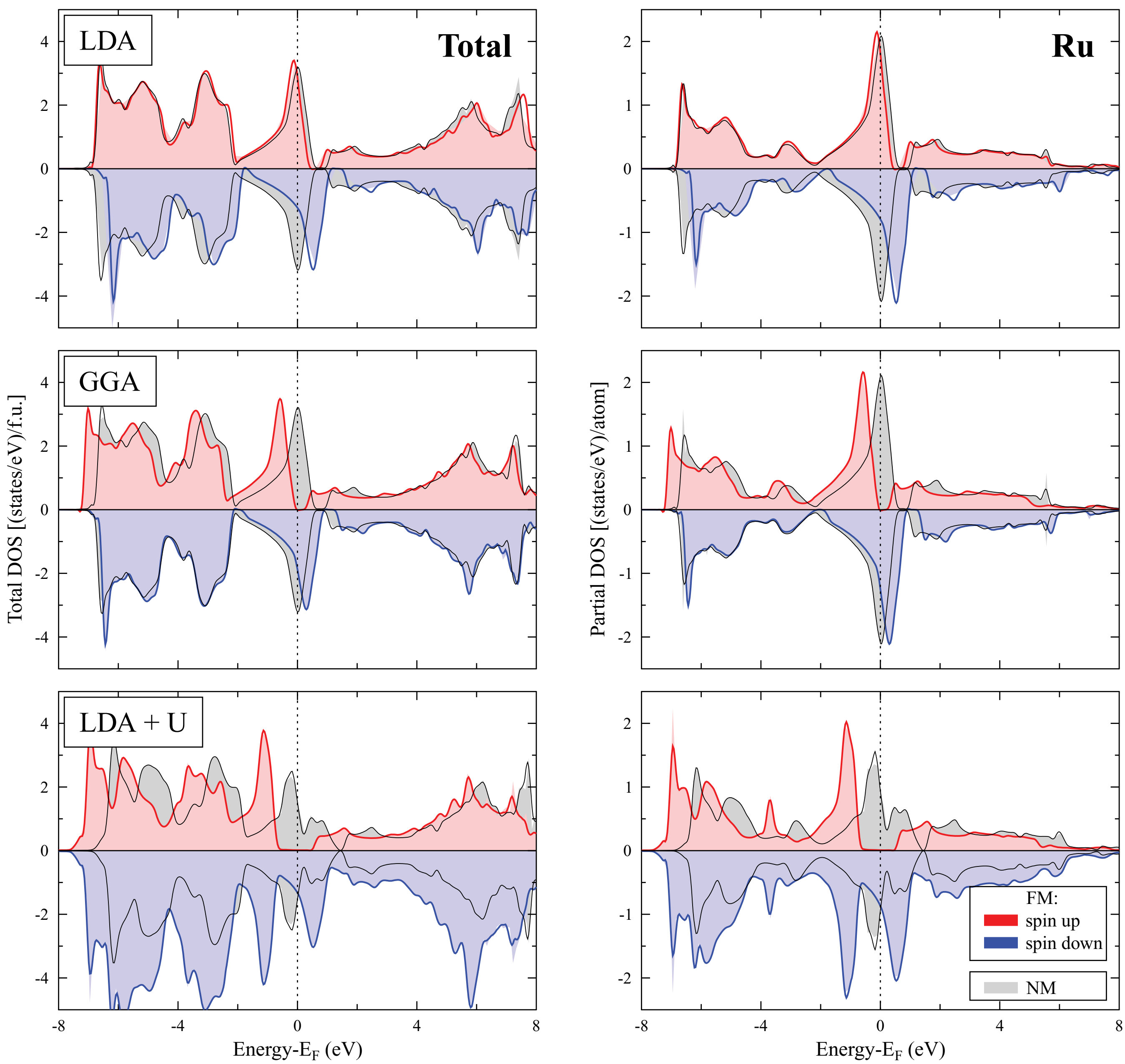

FIG. 3. (Color) Comparison between the density of states for bulk SRO in the orthorhombic structure, calculated within the LDA, GGA, and LDA + U for $U = 3$ eV . The total density of states is shown in the left panel; the DOS of Ru is shown in the right panel.

with the self-interaction correction method (not shown here). The exchange constants between the second nearest neighbors increase as well with U^*, but their contribution to the critical temperature is rather small.

This dependence is quite natural. Indeed, the main sources of ferromagnetic interactions in the calculation are the double exchange, proportional to the d-band width, and the Hund's coupling on oxygen,[5] Neither of the two terms directly depend on U^* (there is an indirect dependence due to the fact that U tends to localize d-electrons somewhat, but this is a relatively weak effect). On the other hand, the antiferromagnetic interaction is provided by the classical superexchange, and is proportional to $t_{pd}^4/(E_d - E_p)^2\Delta$, where $E_{d,p}$ are the energies of the Ru d and O p levels, and Δ is the energy cost for flipping a local spin; in the standard LDA the energy scale of Δ is set by the Stoner parameter, I, in the LDA + U with a large U, by U^*.

The Curie temperature rises almost monotonically with J, and thus with U^*. For the often used $U^* = 3$ eV the Curie temperature, computed by the Monte-Carlo method, is about 500 K, and for our calculated $U^* = 1.2$ eV it is about 320 K. The experimental value of $T_C = 160$ K is achieved at $U^* = 0.5$ eV, consistent with a recent estimate by Rondinelli *et al.*, who found that $U^* = 0.6$ eV provides the best description of experimental spectroscopic data.[9]

The best agreement with experiment is obtained within GGA. In this case, the MFA gives 175 K and both the RPA and the Monte Carlo simulations give 142 K. Since the RPA and MC approaches usually underestimate the critical temperature and the MFA overestimates it, the fact that $T_{c(\exp)} = 160$ K suggests that the GGA is the most appropriate approximation for this system. Both the LSDA-SIC and LDA + U fail to describe quantitatively the exchange interactions in SRO.

In order to better understand the obtained results we have analyzed the density of states calculated within the LDA, the GGA, and the LDA + U with a U^* of 3 eV. One can see that the nonmagnetic density of states (DOS) is hardly affected by the approximations used, while for the magnetic DOS the main difference is on the resulting exchange splitting (see Fig. 3). As discussed in Ref. 5, the exchange splitting is determined mainly by the effective Stoner factor I. In the GGA, I is usually larger than in the LDA by about 20%. In the LDA + U, the effective atomic Stoner factor[17] $I_{\rm eff} = I + U^*/5$, which for $U^* = 3$ eV results in a nearly threefold increase of $I_{\rm eff}$, with the corresponding increase of the exchange splitting.

As pointed out in Ref. 5, SRO is very close to a half metal. Indeed, applying $U^* > 0.6$ eV shifts the Ru $4d$ spin-up states to lower energies, opens a band gap in the majority spin channel, and creates a half metal with the total magnetization of 2 μ_B/Ru. The self-interaction correction method has the same effect. The LSDA-SIC, albeit lacking a firm theoretical justification, empirically works well for $4f$ states[23,30] and for strongly correlated oxides; in SRO, however, it leads to an unphysically strong localization of the Ru $4d$ states, and fails to describe its magnetic properties correctly.

Magnetism in Ru based perovskites is known to be very sensitive to tilting and rotating the oxygen octahedra. This happens because the Ru-Ru hopping via O is strongly affected by the Ru-O-Ru bond angle, which in turns affects the superexchange interaction. It has been shown[5] that in the ideal structure the equilibrium moment is much reduced but the reason is not that the overall bandwidth of the Ru d band is increased (although it is). As a result of the higher symmetry, the DOS at the Fermi level is higher than in the actual $Pbnm$ structure, and the Stoner product $IN(E_F)$ is even larger. The main reason is that the peak at the Fermi level is higher, but narrower, so that it takes a smaller magnetic splitting to fully split this peak and gain all the magnetic energy there is to gain.

On the other hand, the fact that the straight Ru-O-Ru bonds provide a better hopping has a profound effect on the exchange interaction. In Fig. 4 we compare the calculated exchange constants in the ideal perovskite (cubic) and the experimentally observed crystalline structure (orthorhombic *Pbnm*). The cubic structure was derived from the experimental one by changing the tilt angles and lattice constants but keeping the experimental volume. The ferromagnetic double exchange part of the interaction is less affected by the improved Ru-O-Ru hopping than the antiferromagnetic superexchange part (the former is proportional to the effective Ru-Ru hopping $t_{\rm eff}$, and the latter to its square). As a result, the antiferromagnetic part becomes relatively stronger and overcomes the ferromagnetic part, so that the net nearest neighbor interaction becomes slightly antiferromagnetic. On the other hand, the double exchange, being a long range interaction, survives in the farther exchange constants, so that the ground state remains ferromagnetic, albeit barely so (according to our calculations, the Curie temperature is reduced to 30 K).

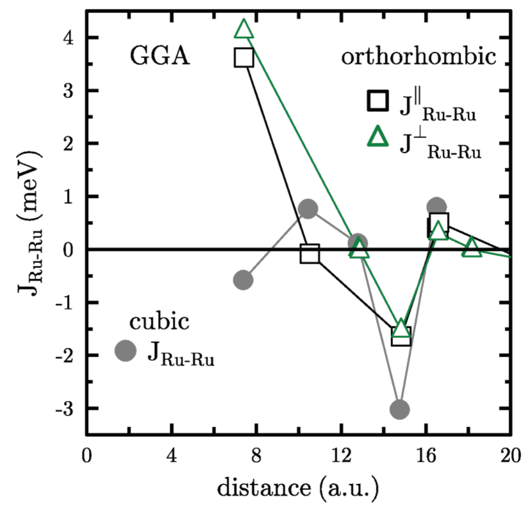

FIG. 4. (Color online) Calculated Ru-Ru intra-($J_\parallel$) and interlayer ($J_\perp$) exchange constants (within the GGA) for SRO in the orthorhombic and the ideal perovskite structure (squares, triangles, and filled circles, respectively) versus Ru-Ru distances in atomic units.

IV. SUMMARY

In summary, we have calculated the magnetic properties of $SrRuO_3$, including the Curie temperature, using various approximations within and beyond the density functional theory (DFT). By far the best overall agreement is achieved when using the generalized gradient approximation (GGA) within DFT, without additional attempts to account for on-site correlations by adding a Hubbard U or self-interaction corrections. The latter schemes result in a substantial underestimation of the antiferromagnetic superexchange, and thus to a strong overestimation of the net ferromagnetic exchange. We conclude that $SrRuO_3$ should be considered to be a weakly correlated itinerant magnet. We emphasize that this conclusion applies only to $SrRuO_3$ and should not be perceived as a fundamental claim regarding all Ru perovskites. The final conclusion of the role of electronic correlation, in each case, should be made with account of dimensionality, crystallographic distortions, etc.

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