

Weak electronic correlations in SrRuO₃: Evidence from first-principles calculations

C. Etz,^{1,2} I. V. Maznichenko,³ D. Böttcher,¹ J. Henk,³
A. N. Yaresko,⁴ W. Hergert,³ I. I. Mazin,⁵ I. Mertig,^{1,3} and A. Ernst¹

¹*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

²*Department of Physics and Astronomy, Uppsala University, Box 516, S-75120 Uppsala, Sweden*

³*Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany*

⁴*Max-Planck-Institut für Festkörperforschung, Heisenberg Strasse 1, D-70569 Stuttgart, Germany*

⁵*Code 6393, Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 22031*

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We provide, by a detailed first-principles investigation, evidence for weak electronic correlations in SrRuO₃. The magnetism in SrRuO₃, in terms of the equilibrium magnetization and critical temperature, is well described by the generalized gradient approximation (GGA). Including Hubbard-type correlations results in worse agreement with experiment.

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In the past decades, much attention has been paid to *3d* transition-metal compounds, but nowadays also *4d* and *5d* electron systems are intensively explored. Among *4d* or *5d* 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 crystalline structure. One of the members of the perovskite-oxide-based family, SrRuO₃ (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 μ_B /Ru and 1.7 μ_B /Ru [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 eV to 7.0 eV 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 regards to theoretical prediction for the magnetic moments, crystal structure, and critical temperatures. Besides addressing the correlation strength, we investigate also the strength of inter-atomic 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.

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 [15], LDA+*U* [16, 17], GGA [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 non-spherical charge distributions and provides an accurate electronic-structure description. In the following, we present selected results obtained for SrRuO₃ in the experimentally obtained distorted perovskite structure, that is the low temperature bulk phase (space group *Pbnm*) [20, 21]. We have also performed full structural optimization using the Vienna Ab-initio Simulation Package (VASP) (see Table...) and found that the GGA method provides the best description of the experiment (basically, within the discrepancy between different experimental papers).

Knowing that GGA provides a good description of the structural properties of the system, we would like to address magnetic properties, which are more 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 calculat-

ing 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 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), the random phase approximation (RPA) [27] and using Monte Carlo simulations [28, 29].

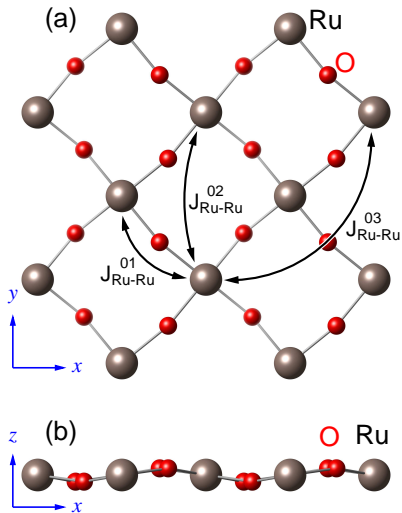


FIG. 1: (color online) Schematic representation of a RuO_2 layer in top (the XY -plane) and side view (along the Y -axis). For clarity, Sr atoms are not represented. Arrows indicate the type of exchange interactions and the atoms involved.

First, we determined the exchange constants in SRO in the experimentally observed crystal structure (orthorhombic $Pbnm$) [20, 21]. For convenience, we distinguish between the intra-layer and inter-layer interactions among the local magnetic moments of Ru. We choose layers as shown in Fig. 1a: in 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 less than 180° not only in plane, but also out of plane (Fig. 1b).

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 LDA+U, from $1.2 \mu_B$ ($U^* = U - J_H = 0$) to $1.8 \mu_B$ ($U^* = U - J_H = 15$ eV) with increase of U^* , while the GGA yields Ru moments of $1.4 \mu_B$. The total magnetization varies between $1.4 \mu_B/\text{Ru}$ ($U^* = 0$) and $2 \mu_B/\text{Ru}$ ($U^* \gtrsim 0.6$ eV); in GGA, it is $1.9 \mu_B/\text{Ru}$, slightly larger than the experimentally measured $1.4\text{--}1.7 \mu_B/\text{Ru}$.

One of the fingerprints of strong on-site Coulomb correlations is severe underestimation of magnetic moments in LDA and GGA (*cf.* high- T_c cuprate or 3d oxides). On the other hand, 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 LDA reproduces the experimental magnetization in SRO very accurately, and GGA slightly overestimates it, suggests that Hubbard correlations are not operative in this compound, while itinerant spin fluctuations play only a small, albeit non-negligible 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 estimated within the mean-field, the random phase approximation, and the Monte Carlo method (lower panel). Although the intra- (J^{\parallel}) and inter-layer (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 slope becomes less steep when J approaches 20 meV. For $U^* \geq 7$ eV the exchange parameters are almost constant with increase of U^* and approach the result obtained with the self-interaction correction method (not shown here). The exchange constants between the second nearest neighbors increase as well with U^* , although their contribution to the critical temperature is rather small.

This dependence is very natural. Indeed, the main sources of ferromagnetic interactions in the calculation are double exchange, proportional to the d -band width, and the Hund’s coupling on oxygen [5]. Both terms do not depend directly 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

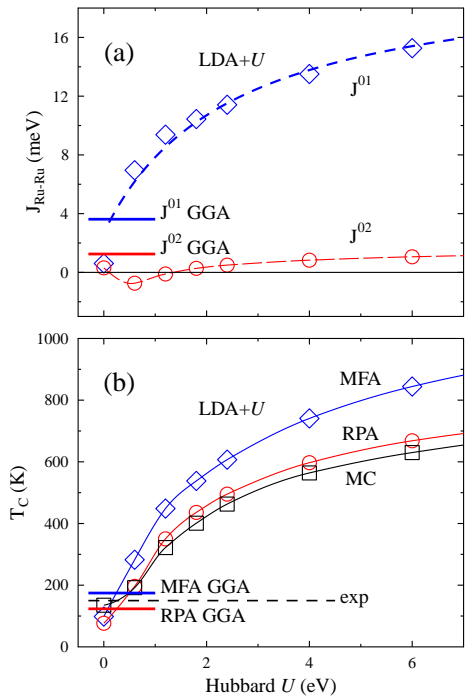


FIG. 2: J (color) Calculated exchange interaction constants between Ru atoms (a) and critical temperatures (b) within different approximations for the exchange-correlation functional. Results within GGA are represented by lines, while the open symbols are results obtained within LDA+U. SRO is in the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

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 of flipping a local spin; in straight LDA the energy scale of Δ is set by the Stoner I , in LDA+U with large U by U^* .

The Curie temperature raises 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, for calculated $U^* = 1.2$ eV is about 320 K. The experimental value of $T_C = 160$ K is achieved at $U^*=0.3$ 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 usually underestimate the critical temperature and the MFA overestimates it, the fact that $T_{C(\text{exp})} = 160$ K suggests that the GGA is the most appropriate approximation for this system. Both LSDA-SIC and LDA+U fail to describe quantitatively the exchange interactions in SRO.

In order to understand better the obtained results we have analyzed the density of states calculated within the LDA, the GGA and the LDA+U with U^* of 6 eV. [WE NEED NONMAGNETIC DOSs AS WELL] One can see that the nonmagnetic DOS is hardly affected by the approximations used, and for the magnetic DOS the main difference is on the resulting exchange splitting. As discussed in Ref. 5, the exchange splitting is determined mainly by the effective Stoner factor I . In GGA I is usually larger than in LDA by about 20%. In LDA+U, the effective Stoner atomic factor [17] $I_{eff} = I + U^*/5$, which for $U^*=6$ eV results in nearly threefold increase of I_{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 $U^* > 0.3$ 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 $2 \mu_B/\text{Ru}$. 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 turn affects the superexchange interaction. It has been known[5] that in the ideal structure the equilibrium moment is much reduced. 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 is higher at the Fermi level, than in the actual $Pbnm$ structure, and the Stoner product $IN(E_F)$ is even larger. The 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 magnetic energy there is to gain.

On the other hand, the fact that the straight Ru-O-Ru bonds provide 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 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_{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 very slightly antiferromagnetic. On the other hand, the double exchange, being a long range interaction, survives in the farther exchange constants, so the ground state remains ferromagnetic, albeit barely so (according to our calcula-

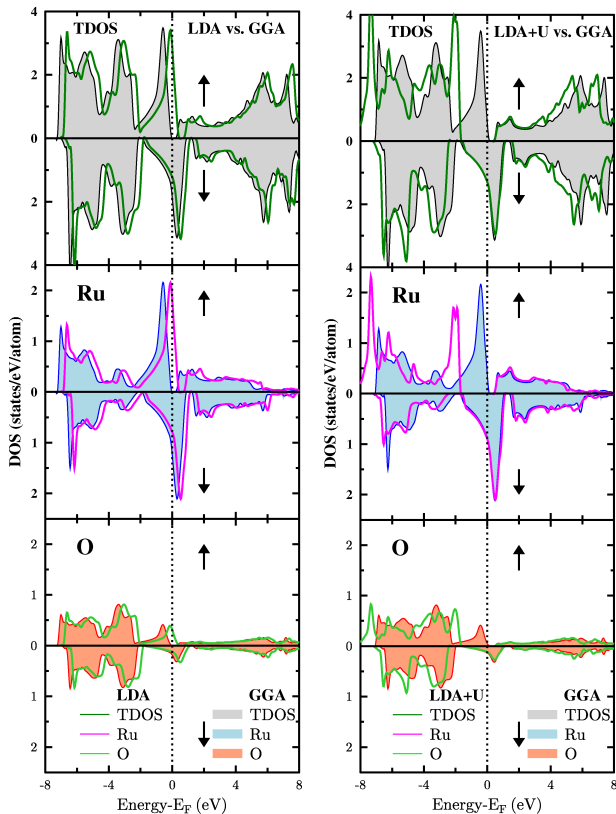


FIG. 3: (color online) Comparison between the density of states for bulk SRO in the orthorhombic structure, calculated within LDA, LDA+U and GGA. Left panel, LDA vs. GGA. Right panel, LDA+U for $U=6$ eV vs. GGA.

tions, the Curie temperature is reduced to 30 K).

In summary, we have calculated magnetic properties of SrRuO₃, including the Curie temperature, using various approximation within and beyond the density functional theory (DFT). By far the best overall agreement is achieved when using the generalized gradient approximation (GGA) within the DFT, without additional attempts to account for on-site correlations by adding Hubbard U or self-interaction corrections. The latter result in substantial strong underestimation of the antiferromagnetic superexchange, and thus to a strong overestimation of the net ferromagnetic exchange. We conclude that SrRuO₃ should be considered to be a weakly correlated itinerant magnet.

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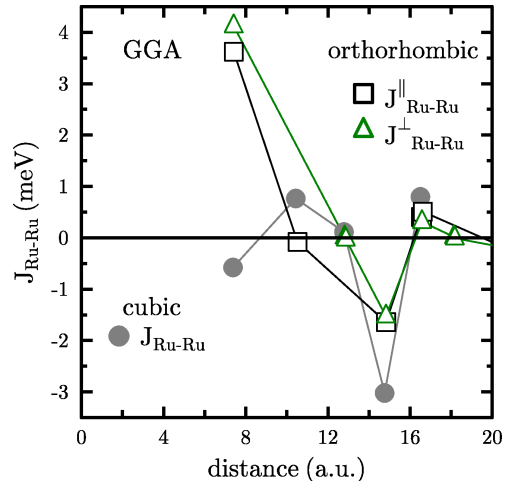


FIG. 4: (color online) Calculated Ru-Ru intra- (J^{\parallel}) and inter-layer (J^{\perp}) exchange constants (within GGA) for SRO in the orthorhombic and the ideal perovskite structure, respectively, versus Ru-Ru distances in atomic units.

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