

RuO₂: a puzzle to be solved

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Altermagnetism is a topic that has lately been gaining attention and the RuO₂ compound is among one of the most studied altermagnetic candidates. However, the survey of available literature on RuO₂ properties suggests that there is no consensus about the magnetism of this material. By performing density functional theory calculations, we show that the electronic properties of stoichiometric RuO₂ are described in terms of a smaller Hubbard U within DFT+ U than the value required to have magnetism. We further argue that Ru vacancies can actually aid the formation of a magnetic state in RuO₂. This in turn suggests that a characterization of the amount of Ru vacancies in experimental samples might help the resolution of the controversy between the different experimental results.

I. INTRODUCTION

In recent years the topic of altermagnetism has been gaining attention, with significant efforts directed towards finding new altermagnetic materials [1, 2]. Altermagnetism is defined as a magnetic phase with symmetry-driven compensated net magnetization, where the symmetry operation responsible for this magnetic phase is neither inversion nor translation. A material exhibiting these properties combines characteristics of both ferromagnetism and antiferromagnetism. Furthermore, in regards to the electronic band structure, the bands in this phase are non-spin-degenerate, leading to intriguing applications.

Among the various proposed materials as altermagnetic candidates, RuO₂ is attracting much attention. However, the magnetism in this system is still in itself a controversial topic. On the one hand, the absence of a discernible phase transition in the heat capacity [3, 4] and the resistivity data suggests that RuO₂ is a Pauli paramagnet [5–9]. On the other hand, the existence of an antiferromagnetic configuration has been reported by resonant X-ray scattering [10] and neutron diffraction [11]. However, the latter measurements reported a rather small local magnetization value ($0.05 \mu_B$). Additionally, there have been observations of a sizeable anomalous Hall effect, consistent with a considerably larger magnetization [12, 13].

Unfortunately, the available neutron diffraction data on RuO₂ [11] are not sufficient to confidently resolve the controversy on the magnetization, for the reasons

described below. The main issue is that the quality of the magnetic component of the fit in these experiments depends on the quality of the structural refinement. In reference [11], the authors mention the possibility of a structural distortion in the rutile phase accompanied by antiferromagnetic order. However, Ref. [11] was unable to find a distorted structure that would fit both unpolarized and polarized neutron diffraction data, while the powder X-ray diffraction patterns are consistent with the undistorted rutile structure (see the crystal structure depicted in Fig. 1). To address this problem, Ref. [11] employed density functional theory (DFT) calculations in an attempt to find such a structure. A distorted $2 \times 2 \times 2$ rutile supercell was optimized in both the non-magnetic and antiferromagnetic states, and the rutile structure was obtained as the ground state. The available computational data on the lattice dynamics in RuO₂ [14, 15] confirm that the rutile structure is dynamically stable.

The absence of a structural phase transition is indirectly confirmed by other measurements. Two independent electron transport measurements, one conducted up to 300 K [8] and one up to 1000 K [9], show no changes in resistivity that could be caused by a structural phase transition. Both data sets are well described by a model that has three contributions to the resistivity: the electron-phonon interaction with acoustic (Bloch-Grüneisen) and optical modes, along with a term arising from electron-electron scattering. Moreover, there is no indication of a structural phase transition in the heat capacity measurements, which was measured up to ~ 340 K [3] and ~ 1050 K [4]. This same conclusion is supported by the available measurements of thermal expansion [16].

Based on the refinement using the rutile structure, the extracted magnetic moment per Ru atom is $0.23 \mu_B$ for unpolarized neutron diffraction and $0.05 \mu_B$ for po-

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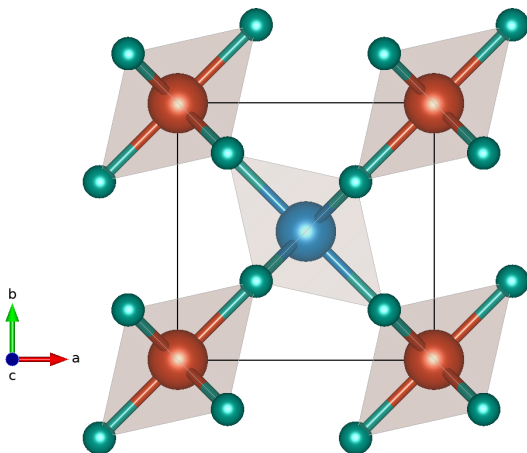


FIG. 1. Crystal structure of RuO_2 : Ru atoms are shown in red and blue (different colors denote different spin orientations), O atoms are shown in teal.

larized neutron diffraction measurements [11]. Furthermore, there is no evidence of a phase transition to an antiferromagnetic phase, neither in the susceptibility data of Ref. 11 nor in earlier measurements [5–7]. Additionally, nuclear magnetic resonance measurements strongly suggest the absence of long-range magnetic order. This conclusion is supported by the absence of any contribution from Ru d electrons in both the Knight shift and relaxation rate, as well as the absence of any hyperfine splitting [17]. The authors of this paper point out that, overall, the resonant magnetic properties closely resemble those of nonmagnetic Ru metal.

The controversy among the different experiments suggests that the existence of antiferromagnetic (and hence altermagnetic) order in RuO_2 is rather fragile, likely sample-dependent, and possibly present in only a fraction of the sample volume. In order to gain a better microscopic understanding of the magnetism (or lack thereof) in this material, we have systematically investigated the magnetic states of RuO_2 employing density functional theory (DFT), both with and without a Hubbard U correction applied to the Ru d -orbitals. Our tentative conclusion is that the perfectly ordered, stoichiometric RuO_2 is likely nonmagnetic, consistent with numerous experiments above. On top of that, a modest hole doping, for instance, by creating Ru vacancies (a common defect in this class of materials, cf. Ref. [18] that found 5% vacancies in their RuO_2 samples) promotes the RuO_2 to a magnetic state of exactly the same symmetry as suggested in Ref. 11 and utilized in Refs. [19, 20].

The amount of Ru vacancies is liable to vary from sample to sample, and even from one batch to another, depending on the growth procedure, and may even be nonuniform over a sample. This could explain the discrepancy between different experiments and leads us to conclude that a characterization of the Ru vacancies in the samples may be key to know about the magnetic character of RuO_2 .

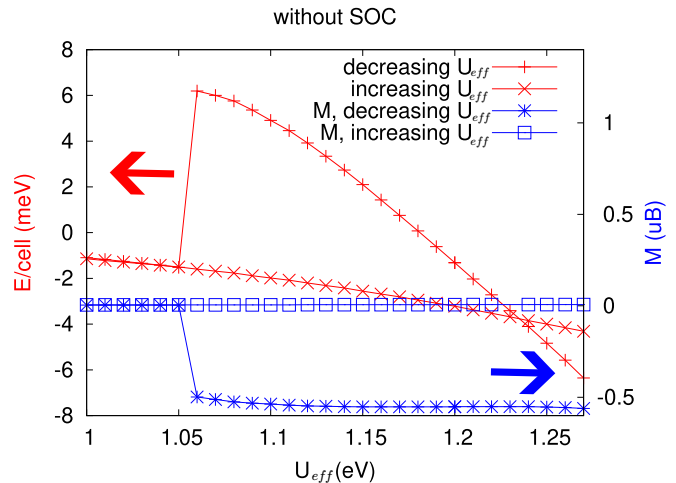


FIG. 2. Total energy (left) and local magnetization at the Ru site (right) as a function of $U_{eff} = U - J$ are explored in two sets of calculations. In one set (“increasing U_{eff} ”), denoted with \times (energy results) and \square symbols (magnetization results) the calculations were done starting from $U = 0$ eV and progressively increasing U in each subsequent calculation. In the other set (“decreasing U_{eff} ”), denoted with $+$ and $*$ symbols, the direction of the calculation was reversed. The calculations are without SOC contributions.

II. DISCUSSION

The first concern to cover is whether stoichiometric RuO_2 is magnetic or not. To account for the possible effects of electronic correlations in this system, we perform DFT+ U computations. In Fig. 2, we plot the dependency of the local magnetic moment at the Ru site for an anti-parallel spin orientation (a parallel orientation, as well as various magnetic arrangements with $q \neq 0$, are invariably higher in energy) over a range of U values. As seen from the overlap of the magnetic moment for small values of U in the plot, RuO_2 is non-magnetic up to a critical value, $U_{eff} = U - J \sim 1.06$ eV. After this, there is a discontinuous jump (see below the explanation) of the value of the magnetic moment to $\sim 0.5 \mu_B$. This jump is an order of magnitude larger than the $0.05 \mu_B$ obtained from polarized neutron scattering measurements [11], and more than twice larger than the $0.23 \mu_B$ value fitted to unpolarized data (claimed to be less reliable and contaminated by unknown structural factors).

Moreover, $U_{eff} > 1$ eV is rather large for this good-metallic, strongly-hybridized, $4d$ system. For comparison, first principles calculations of U_{eff} for the ruthenium-based spin-orbit Mott insulators $\alpha\text{-RuCl}_3$, RuBr_3 , and RuI_3 gave estimates of 2 to 1 eV [21]. Considering the metallic screening occurring in RuO_2 , it is expected that its U_{eff} will be noticeably smaller than the values given above. This leads us to conclude that for stoichiometric RuO_2 a smaller U_{eff} is likely more realistic to describe its properties than the required one

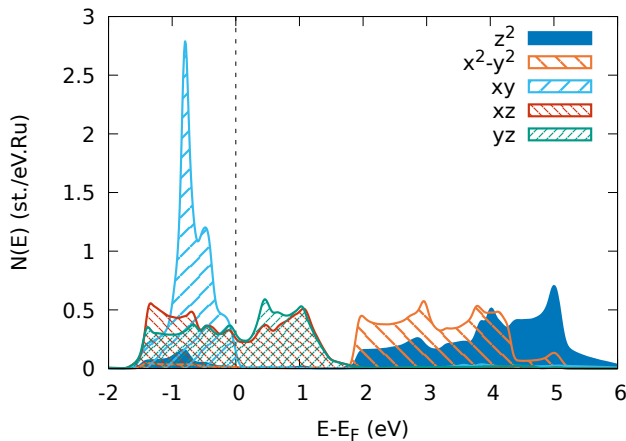


FIG. 3. Projected non-magnetic density of states onto Ru d -orbitals: blue, orange, cyan, red, and teal are used to depict z^2 , x^2-y^2 , xy , xz and yz orbitals respectively. The coordinate system is aligned with Ru-O bonds.

to have magnetism, and therefore stoichiometric RuO₂ is most probably non-magnetic.

Moving on to analyzing the projected density of states (DOS) (see Fig. 3), we observe that the main contribution to the DOS around the Fermi level comes from the xz/yz Ru d -orbitals. The value of the DOS at the Fermi level is relatively low and flat in its vicinity. This causes the Stoner criterion for ferromagnetism to be very hard to fulfill.

Zone-center antiferromagnetism, as in RuO₂, obeys a modified Stoner criterion, where instead of the uniform susceptibility, $\chi(\mathbf{q} = 0) = N(0)$ at some finite reciprocal lattice vectors appears, $\chi(\mathbf{G} \neq 0)$, but, it is quite obvious that highly dispersive bands at the Fermi level and low DOS are rather unfavorable in this case as well.

Another interesting aspect in the DOS is the narrow peak below the Fermi level coming from the xy Ru orbitals. If the Fermi level were shifted closer to this peak, it could potentially trigger a magnetic transition from the current non-magnetic state to a state with a significant magnetic moment.

The shift of the Fermi level can be accomplished through hole doping, changing the electron occupation. The only other alternative for generating a magnetic order *without doping* is to increase U , and thus the effective Stoner parameter $I_{eff} = I + (U - J)/5$ (see Ref. [22]) until the Stoner criterion ($I_{eff} > J$) is satisfied. To check this hypothesis we did a series of DFT+ U calculations varying both the value of U_{eff} and the number of electrons. Figure 4 shows the value of the local magnetic moment at the Ru site as a function of U_{eff} and the number of electrons per unit cell (two formula units). The isoline with $m = 0.05 \mu_B$, corresponding to the measured value from Ref. 11, is highlighted. One can see that there is a rather stable ground state for ~ 0.1 hole/Ru doping, within a reasonable range of $U_{eff} \lesssim 1$ eV. For the same U_{eff} , a larger doping of 0.4 hole/Ru, corresponding to

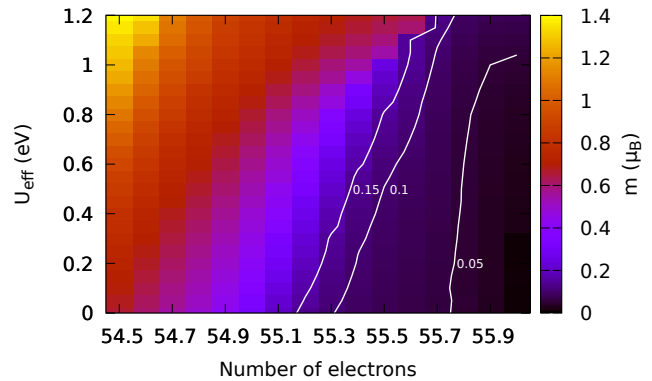


FIG. 4. Dependence of the local atomic magnetization m on hole doping (an undoped case corresponds to 56 electrons per cell, i.e., per two formula units) and the effective Hubbard parameter $U_{eff} = U - J$. Isolines for $m = 0.05$, 0.10 , and $0.15 \mu_B$ are depicted by white lines (with no attempts to smooth the plotted lines).

10% of Ru vacancies, generated a local magnetic moment of $m = 0.2 \mu_B$. It is worth pointing out that the discontinuous jump in the calculated magnetic moment for the undoped compound as a function of U_{eff} is immediately understood from the DOS on Fig. 3. That is because, in order to get a stable magnetic solution, the exchange splitting (proportional to U_{eff}) must reach the threshold (around 1 eV, from Fig. 3) corresponding to the separation between the xy band and the Fermi level.

Note that the data in Fig. 4 merely show a trend of the system to attain a magnetic moment with hole doping, but the preferred magnetic orientation may depend on the doping as well. In particular, when spin-orbit coupling (SOC) is accounted for, our DFT+ U calculations with $U_{eff} = 1.4$ eV show that the magnetic anisotropy energy $E_{100} - E_{001}$ changes linearly with doping and there is a transition from the easy axis along the c direction towards an easy plane at around 0.2 hole/Ru. However, the full sampling of magnetic ground states as a function of U_{eff} and hole doping is out of the scope of this work.

The next issue is to focus on the magnetic ground state when the system is in the regime where magnetization is permitted. To address this question, we initially calculated, using VASP [23–26], the energy difference between the ferromagnetic (FM) and antiferromagnetic (AM) stoichiometric RuO₂ configurations. The calculations were done without considering SOC effects while setting the value of U_{eff} to 1.3 and 1.4 eV and we analyzed the magnetization of both configurations. Interestingly, the AM configuration converged to $M_{Ru} = 0.66$ and $0.78 \mu_B$ for each Ru atom in the cell, respectively. In contrast, the FM ones essentially collapsed, yielding a total magnetization of $M_{tot} = 0.015$ (0.038) μ_B per Ru atom. Correspondingly, the AM energy was lower than the FM one by 3.3 (9.3) meV/Ru. Altogether, these results indicate that the antiferromagnetic configuration has the lowest energy. Besides that, the spin-spirals with $\vec{q} = (0, 0, q)$ and

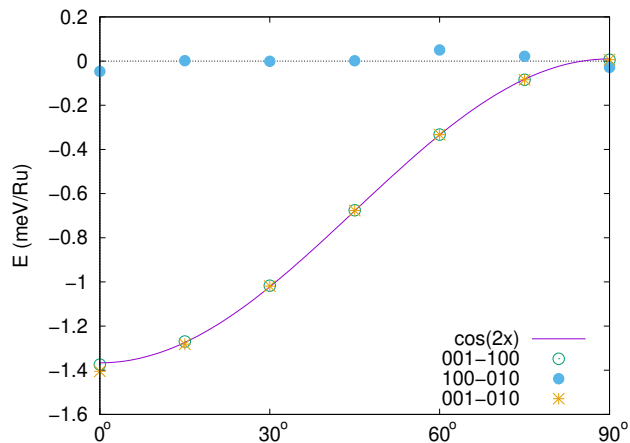


FIG. 5. Magnetic anisotropy as function of the angle in degrees, when rotating the Neel vector in the indicated planes.

$\vec{q} = (q, 0, 0)$ were checked leading to $q = 0$ as the lowest energy state in both cases.

We also checked the calculated magnetic anisotropy and compared it with the experiment. Including spin-orbit coupling, we found that the c axis is the easy axis along the direction, in agreement with experiment [11], as seen in Fig. 5.

Thus, the magnetic ground state is characterized by an antiparallel alignment along the c axis of the magnetic moments of two Ru atoms. This description can be described by the magnetic space group $P4'_2/mmm'$ (BNS 136.499).

III. CONCLUSIONS

Our DFT calculations show that, for a realistic value of U_{eff} (using Ru based insulators as reference), the stoichiometric RuO_2 compound is non-magnetic. However, hole doping due to Ru vacancies can induce a phase transition to the antiferromagnetic phase even for small val-

ues of U_{eff} . This observation may be a key to reconcile different, strongly mutually contradicting experiments. If our conjecture is correct, every experimental work on RuO_2 must begin with a careful characterization of the O and Ru content. Moreover, a systematic experimental investigation of magnetic properties as a function of the O and Ru content is absolutely necessary. One verifiable corollary is that with controllable Ru vacancies one should be able to observe the antiferromagnetic transition in thermodynamics, transport and magnetometry.

IV. COMPUTATIONAL DETAILS

Computations were done using density functional theory (DFT) in the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof [27, 28] functional as implemented in the VASP [23–26] package employing the projector augmented wave method (PAW) [29, 30], Ru_sv and O (or O_h, for structural optimization) pseudopotentials were used. The energy cutoff was set to 400 eV (for the test purpose, selected calculations were performed with a 900 eV cutoff) and the $8 \times 8 \times 12$ ($12 \times 12 \times 18$ for testing) k-points Monkhorst-Pack grid [31, 32] was used. For selected calculations, a cross-check using Wien2k was used.

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