# Experimental report

08/12/2021

**Proposal:** 5-51-581 **Council:** 10/2020

**Title:** Spin-density distribution in Ca2RuO4: Searching for magnetic oxygen moments

**Research area:** Physics

**This proposal is a resubmission of 5-51-568**


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**Experimental team:** Kevin JENNI

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**Samples:** Ca2RuO4

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D3 | 7 | 7 | 17/02/2021 | 25/02/2021 |


## Abstract:

The Mott insulator Ca2RuO4 represents a challenging system to test theoretical models with strong spin-orbit coupling while the complete description of the Mott state has not yet been found. Measurements of the magnon dispersion indicate an extra low-energy branch that was attributed to magnetic moments on the O sites. This interpretation was supported by DFT calculations indeed finding sizeable O moments. Here we propose to directly study the spin-density distribution with the flipping ratio methods by applying the magnetic field along the direction of weak ferromagnetism. This study will unambiguously clarify the impact of magnetic moments on O in Ca2RuO4.

**Experimental Report**

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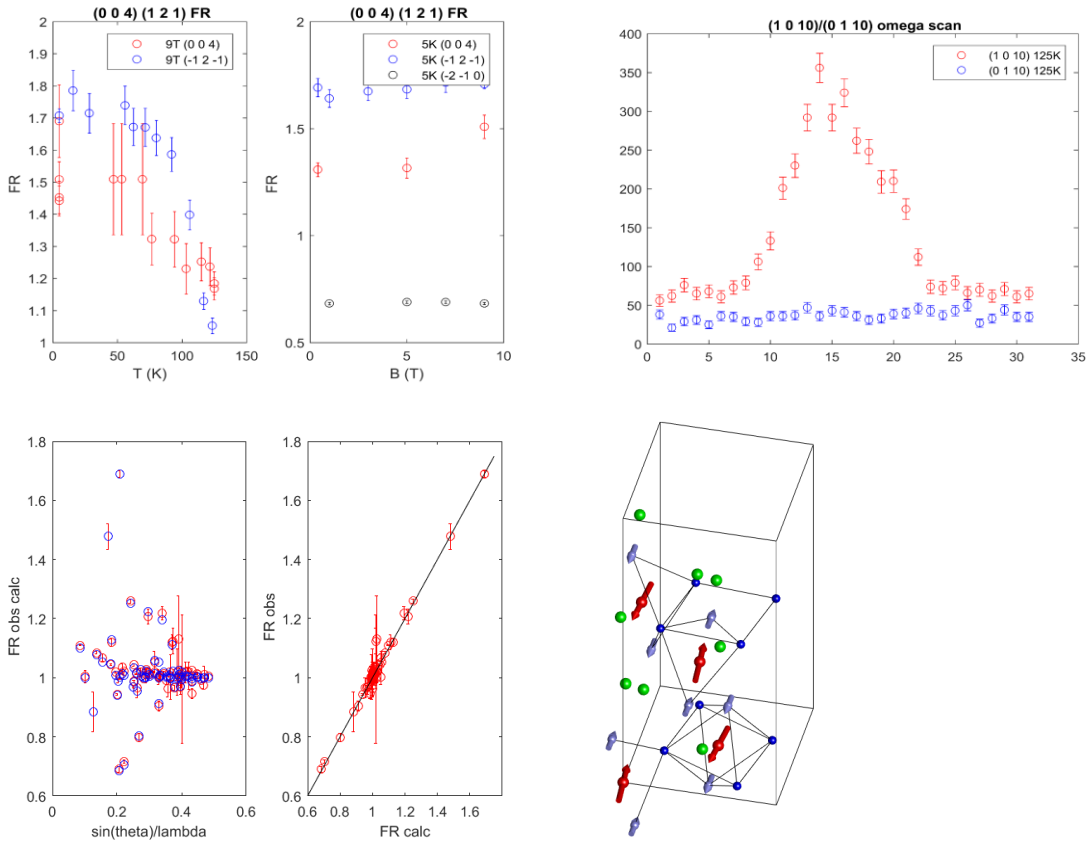
|---|---|
| **Instrument** | D3 |
| **Proposal Number** | 5-51-581 |
| **Proposal** | Spin-density distribution in $Ca_2RuO_4$: Searching for magnetic oxygen moments |
| **Experimentalist** | Kevin Jenni, Akshay Tewari, Markus Braden University of Cologne |
| **Local Contact** | Anne Stunnault, Alberto Velamazan |

Ruthenates exhibit various interesting phenomena reaching from unconventional superconductivity in $Sr_2RuO_4$ to a Mott-insulating state in $Ca_2RuO_4$ and a metamagnetic transition associated with quantum-critical behaviour [1-4]. The Mott antiferromagnetic insulating state in pure $Ca_2RuO_4$ [3] documents the strength of the correlations, but the theoretical understanding of the Mott transition in this multi-band system with four electrons per Ru site continues to generate controversy [4-16]. At 110 K antiferromagnetic order sets in [16-18] accompanied by structural anomalies. The magnetic structure corresponds to the simple G-type antiferromagnetic order observed in many 214 materials with magnetic moments along the b-direction (parallel to the planes). There seems to be consensus concerning orbital ordering ending in enhanced or full occupation of the $d_{xy}$ orbital and that the remaining two electrons occupy the other $d_{xz,yz}$ orbitals. Such interpretation roughly corresponds to the measured ordered moment of 1.3 $\mu_B$ although this is significantly below the expectation [16]. Strong spin-orbit coupling can couple the spin and orbital moments to a non-magnetic j=0 ground state in $Ca_2RuO_4$ so that magnetic moments only arise from the excited levels as in a van-Vleck material [13]. Such model, however, appears to underestimate the crystal fields arising from the strong structural distortions generating strong orbital polarization as well as the large hopping terms [3,19,10]. Our group analyzed the magnon dispersion of $Ca_2RuO_4$ mostly using crystals containing 1% of Ti [19]. With this small amount of Ti, large crystals can be cooled through the structural change at the MIT [17]. Most importantly, one large crystal was found to be essentially untwinned. The magnon dispersion is well described by the spin-wave theory with a conventional Heisenberg model suggesting a local moment model with nearest-neighbor interaction J = 5.6 meV [19]. However, anisotropic next-nearest neighbor interactions as well as small inter-layer coupling parameters are required to properly describe the entire dispersion. In addition to the magnon dispersion expected for a simple square-lattice antiferromagnet we find a low-energy mode at 5 meV with a flat dispersion. DFT calculations for $Ca_2RuO_4$ reveal a sizeable magnetic moment on the apical oxygens of 0.11 $\mu_B$ [19] while the magnetization of oxygen in other ferromagnetic ruthenates amounts to even 30 % of the entire magnetization [20]. Experimentally the magnetization of oxygen has been found in flipping-ratio experiments on $Ca_{1.5}Sr_{0.5}RuO_4$ [21] and on $SrRuO_3$ [22], and the additional mode in our magnon study can be well explained as the oxygen magnon mode [19].

The aim of the experiment on D3 was to study the spin-density distribution by the flipping ratio method at high fields, which has proven its efficiency in documenting O moments in ruthenates [21,22]. However, this is a more challenging task for an antiferromagnetic material, as the magnetization enforced by the external field remains small, in particular compared to the ordered moment. An untwined single crystal was mounted with the magnetic field applied parallel to the orthorhombic *a* axis, while the antiferromagnetically ordered moments (mainly) point along the *b* direction. Within a single layer there is a weak ferromagnetic canting along *a* that even adds to a macroscopic magnetization in our crystals [19]. In a first data collection a large set of 71 independent flipping ratios was measured at 5K and a field of 9T along *a*. A smaller data set was collected slightly above the AFM ordering (~125K) containing 57 independent flipping ratios.

Characteristic flipping ratios were followed upon cooling at a field of 9T (see Fig. (a)), and it was verified that the single crystal is untwinned (Fig. b comparing the (1 0 10) and (0 1 10) Bragg reflection intensities). The first analysis of the low-temperature data was performed with the standard maximum entropy procedures but gave strange results that seemed very improbable. Close inspection of the temperature dependence shown in Fig. (a) indicates that the two flipping ratios exhibit a different temperature dependence as the (2 1 0) value does not deviate from 1 above the antiferromagnetic ordering while the flipping ratio at (004) seems to follow the magnetization. Note that in strength there is no longer a well-defined phase transition due to the impact of the large field.




**Figures:** (a) temperature dependence at B=9T and magnetic field dependence at T=5K of characteristic flipping ratios; (b) rocking scans across two superstructure reflections that reveal the monodomain character of our sample; (c) comparison of the experimental and calculated flipping ratios of the 5K 9T data set; (d) illustration of the magnetic model that describes the experimental flipping ratios with canted moments at the Ru position and sizeable moment at the apical oxygen.

The strong (in the sense of difference to 1) flipping ratio observed at several (hkl) values directly stems from the antiferromagnetic order. The antiferromagnetically ordered moment essentially points along the *b* direction and thus is vertical to the field direction along *a*. However, the staggered moment can nevertheless generate a nuclear-magnetic interference if the scattering vector has a finite component parallel to the field. In this case $\mathbf{M}_{\perp}(\mathbf{Q})$ also has a finite component parallel to the field. The standard analysis routines cannot treat this problem which is quite generic. We, therefore, fitted the parameters of the magnetic model with a Matlab routine implementing the Blume-Maleev rules. Various models were tested which include magnetic moments of the Ru in *a,b* and *c* directions with a different arrangement (for example G-type *b* component and ferromagnetic *a* component) and moments on the in-plane and apical oxygen positions. At the in-plane oxygen positions there is no magnetic component visible, which is not astonishing as the antiferromagnetic moments (along *b*) cannot polarize a moment at this oxygen. The canted Ru components appear to be too small to yield a measurable polarization

at this oxygen. However, the fitting clearly confirms a sizeable magnetic moment at the apical oxygen, see Fig. (d). Both, the parallel alignment with respect to the Ru moment and the size, are in excellent agreement with DFT calculations.

Sizeable polarization of the oxygen carrying a large fraction of the total magnetic moment is thus not only important for ferromagnetic ruthenates [21,22] but also for the insulating ones exhibiting an antiferromagnetic order.

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