Experimental report

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Proposal: **5-51-558**

Council: 10/2019

Title: Spin-density distribution and crystal structure in CaRuO3

Research area: Physics

This proposal is a new proposal

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Samples: CaRuO3

Instrument	Requested days	Allocated days	From	To
D9	4	4	10/09/2020	15/09/2020
D3 High field >1T	8	0		

Abstract:

The ruthenates exhibit a variety of exotic quantum phenomena like superconductivity, metamagnetism, quantum criticality and Mott-insulating phases which stimulates the active research in this field. In particular, the perovskite member CaRuO3 sparks an ongoing debate where its non-Fermi-liquid behavior and its proximity to a magnetic quantum critical point is discussed. Like in Ca2RuO4, the orbital arrangement plays an important role in the interpretation of various experimental results concerning the magnetic and electronic properties of the ruthenates. Therefore an exact knowledge of the crystal structure and of the local distribution of magnetization is crucial for fully understanding the physics in CaRuO3. Using our experience with its counterpart SrRuO3 we like to study the spin-density distribution combined with the crystal structure of CaRuO3.

Experimental Report

Instrument	D9
Proposal Number	5-51-558
Proposal	Spin-density distribution in $CaRuO_3$
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The Ruddlesden-Popper series of ruthenates hosts a number of exotic quantum phenomena: metamagnetism, superconductivity, switchable Mott states, quantum criticality and spin-density waves [1-3]. All are connected to the corner-sharing RuO_6 octahedra with a central Ru^{4+} ion and driven by the electronic correlations and spin-orbit coupling (SOC). The perovskite members are of particular interest because of their use as conducting layers in thin-film heterostructures. Additionally, the appearance of ferromagnetism combined with metallic behavior in $SrRuO_3$, rarely observed in the broad field of transition-metal oxides, is quite important for the unconventional superconductivity in Sr_2RuO_4. The perovskite material draws further attention because of non-Fermi-liquid behavior [4]. Finally we could recently establish that Weyl points, arising from the interplay of SOC and exchange splitting in $SrRuO_3$, not only cause a peculiar anomalous Hall effect but also impact the spin dynamics, both the magnon gap and the stiffness [5]. The sister compound $CaRuO_3$ features quite different properties and promotes a controversial and ongoing discussion about its ground state. While optical conductivity and resistivity measurements have suggested a non-Fermi-liquid ground state [6-9], a recent ARPES study finds heavy quasi particle bands close to the Fermi energy which are consistent with a heavy Fermi liquid and explain previous experimental results [10]. The magnetic ground state is widely proposed as paramagnetic [11]. It has been suggested that $CaRuO_3$ is close to a magnetic quantum critical point [7,9,12], supported by strong ferromagnetic fluctuations in NMR and by doping induced ferromagnetism [13-17]. Similar to $Ca_{2-x}Sr_xRuO_4$ [18] it can be expected that the differences in the system $Ca_{1-x}Sr_xRuO_3$ are connected to the structural differences. The two materials on the edge of this system crystallize in *Pnma* structure where the deviation to the ideal cubic perovskite structure originates from the rotation and tilting of the RuO_6 octahedra. Compared to $SrRuO_3$, $CaRuO_3$ exhibits a stronger orthorhombic splitting and higher structural transition temperatures [19,22]. In the 4d-oxides one always expects a strong hybridization of Ru-4d and O-2p states resulting in a sizeable amount of magnetic moment residing on the O position. In metamagnetic layered $Ca_{1.5}Sr_{0.5}RuO_4$ a spin density experiment by Gukasov et al. indeed found that about 30% of the magnetization reside on only one of the two oxygen positions [20]. Also our recent study of the spin-density distribution in $SrRuO_3$ revealed a strong polarization of all oxygen sites carrying 30 % of the total magnetization; in addition we obtained perfect agreement between the experimental aspheric spin density and a DFT calculation [21]. It was the aim of this project to determine the precise spin-density distribution in $CaRuO_3$ through a fliiping ratio experiment on D3, but only the first step a single-crystal structure determination on the hot four-circle diffractometer D9 was realized in this experiment.

A crystal of cubic shape with ~3mm edge length was mounted in the cryostat and cooled to 9K. All measurements were performed with a neutron wavelength of 0.837Å. It turned out that there are several domains in the crystal following the symmetry reduction from cubic to tetragonal and to orthorhombic. Such multidomain crystals can be well studied nowadays, but in the case of $CaRuO_3$ the orthorhombic splitting is rather large. While normalized values for *b* and *c* (using the space group setting Pnma) are rather similar, *a* is significantly larger. Since one domain was largely dominating, see below, we recorded data using an ub matrix for this individual domain.

The data analysis was performed by J. Siems in her bachelor thesis at University of Cologne. It turned out that the standard treatment of all data yielded poor results, so that the integration of all reflections was verified. 105 reflections with a splitting of the domain contributions that could not be properly integrated were excluded from the refinements, which were performed with the Jana2006 package. The resulting R values for the 471 reflections (merged according to Laue class mmm) amount to R_w=8.9% and R=7.0%, they are clearly higher than expected for a normal problem but still reasonably low. The contributions of the 6 twin domains correspond to 58(2), 28(1), 11(1), 5(1), 1(1) and -3(1)%. The dominance of the first largest domain used in the orientation matrix clearly helps stabilizing the refinement.

The structural parameters can be determined with good precision, see table. The tilting angle of the octahedron (nearly) around orthorhombic *a* amounts to 16 degrees and the rotation around orthorhombic *b* amounts to 11 degrees (note that there are slightly different definitions in the literature). Both values are thus significantly enhanced compared to $SrRuO_3$ in accordance with the much higher transition temperatures and with the smaller ionic radius of Ca. In contrast the distortion of the octahedron that seems to be essential for the magnetic anisotropy in $SrRuO_3$ is even reduced. In summary the structure analysis and the refinement of the crystal structure could be performed yielding reliable results in spite of the severe twinning problems of this material. However, in view of a future spin-density study it seems preferable to obtain a sample with a more dominating domain.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	0.9441(7)	0.25	0.0139(6)	614	697	736	0	-37	0
Ru	0.5	0.0	0.0	1273	92	1154	56	-12	-44
O1	0.0260(6)	0.25	0.5927(6)	865	621	1178	0	53	0
O2	0.2018(4)	0.4518(2)	0.1985(3)	891	779	839	-213	27	-27

Table: Results of the structural analysis of $CaRuO_3$ on D9 at 9K. The positions are given in spacegroup Pnma; anisotropic atomic displacement parameters U_{ij} are given in 10^{-5} Å^2.

[1] Mackenzie et al., Rev. Mod. Phys. 75, 657 (2003). **[2]** Grigera et al., Science 294, 329 (2001). **[3]** Koster et al., Rev. Mod. Phys. 84, 253 (2012). **[4]** P. Kostic et al., PRL **81**, 2498 (1998), M. S. Laad PRL **87**, 246402 (2001). **[5]** K. Jenni et al., PRL **123**, 017202 (2019). **[6]** Lee et al., PRB 66, 041104 (2002). **[7]** Klein et al., PRB 60, 1448 (1999). **[8]** L. Capogna et al., PRL 88, 076602 (2002). **[9]** Cao et al., Solid State Commun. 148, 305 (2008). **[10]** Liu et al., PRB **98**, 041110(R) (2018). **[11]** Kikugawa et al., J. Phys. Soc. Jpn. **78** 014701 (2009). **[12]** Mazin et al., PRB 56, 2556 (1997). **[13]** Yoshimura et al., PRL 83, 4397 (1999). **[14]** T. He et al., PRB 63, 172403 (2001). **[15]** Maignan et al., PRB 74, 024410 (2006). **[16]** Durairaj et al., PRB 73, 214414 (2006). **[17]** Felner et al., PRB **62** 11332-11335 (2000). **[18]** Friedt et al., PRB **63** 174432 (2001). **[19]** Bensch et al., Solid State Ion. **43** 171-177 (1990). **[20]** Gukasov et al., PRL **89**, 087202 (2002). **[21]** Kunkemoeller et al., PRB **100** 054413 (2019). **[22]** Catchen et al., PRB **49** 318-326 (1994).