Magnetic structure and orbital state of Ca$_3$Ru$_2$O$_7$ investigated by resonant x-ray diffraction

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Received 14 March 2008; published 5 June 2008

Resonant x-ray diffraction at the L$_2$- and L$_3$-absorption edges of Ru has been used to investigate the magnetic structure of Ca$_3$Ru$_2$O$_7$, a material with a bilayer perovskite structure that undergoes a transition from a high-temperature metallic to a low-temperature insulating phase at 48 K. In the insulating phase, magnetic Bragg reflections characteristic of A-type antiferromagnetic order (that is, ferromagnetic RuO$_2$ bilayers coupled antiferromagnetically along the c-axis) were identified. The azimuthal-angle dependence of the diffracted intensity implies that the magnetic moments are aligned along the b-axis in the RuO$_2$ planes. In the metallic phase, the A-type magnetic order persists up to the Néel temperature of 56 K, but the sublattice magnetization decreases by a factor of ~1.7 and rotates by 90° within the planes. Resonant signals characteristic of uniform or staggered orbital order were not found within the experimental sensitivity, probably reflecting a weak orbital polarization in the insulating state.

DOI: 10.1103/PhysRevB.77.224412 PACS number(s): 78.70.Ck, 75.50.Ee

I. INTRODUCTION

Layered perovskite ruthenates exhibit a wide variety of interesting physical phenomena due to the interplay of spin, charge, lattice, and orbital degrees of freedom. Prominent examples include the $p$-wave superconducting state$^1$ in Sr$_2$RuO$_4$, whose unit cell encompasses one RuO$_2$ layer, and the electronic liquid-crystal state$^2$ recently discovered at high magnetic fields in Sr$_3$Ru$_2$O$_7$, which exhibits a bilayer perovskite structure. The Ca analogs of these two materials, Ca$_2$RuO$_4$ and Ca$_3$Ru$_2$O$_7$, have lower electrical conductivities and undergo first-order transitions between high-temperature metallic and low-temperature insulating phases at 357 and 48 K, respectively. The phase diagram of Ca$_3$Ru$_2$O$_7$ is metallic and low-temperature insulating phases at 357 and 48 K, respectively. The phase diagram of Ca$_3$Ru$_2$O$_7$ is

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The crystals are platelet shaped with the growth technique and the sample characterization have been given elsewhere.\textsuperscript{16} The crystals are almost untwinned, that is, the population ratio of the orthorhombic twin domains is smaller than 0.1. The rocking curves have full widths at half maximum of less than 0.15°. The intensities of both reflections show a strong resonant enhancement at the L\textsubscript{2}- and L\textsubscript{3}-absorption edges of Ru due to the electric dipole-allowed 2p→4d transitions which directly probe the partially occupied 4d orbitals responsible for magnetism. The observation of a resonant signal at these positions agrees with A-type AFM order, as suggested by magnetization,\textsuperscript{3} as well as Raman\textsuperscript{8} and neutron scattering\textsuperscript{13} data. Based on the absence of the (003) reflection in the neutron diffraction pattern, Yoshida \textit{et al.}\textsuperscript{13} proposed that the magnetic moments are aligned ferromagnetically within the bilayers and antiferromagnetically between adjacent bilayers. Our data are consistent with this suggestion since the (110) reflection would not be observed if another A-type AFM structure was realized.

In order to determine the direction of the magnetic moment, we studied the polarization and azimuthal-angle dependence of the intensity at the magnetic reflections (001) and (110). The experimental configuration is shown in Fig. 1. Here, σ and \( \pi \) denote the polarization components perpendicular and parallel to the diffraction plane, respectively. In the case of a horizontal scattering geometry, the incident beam has \( \psi \)-polarization and the total scattered intensity contains two polarization components, namely \( \sigma' \) and \( \pi' \). \( \alpha \) denotes the angle between the magnetic moment \( \mathbf{m} \) and the scattering vector \( \mathbf{Q} \), and the azimuthal angle \( \phi \) describes the rotation of the sample about the scattering vector.

The azimuthal-angle dependence of the resonant signal at reflection (001) measured below and above \( T_{MI} \) is shown in Fig. 3(a). In the low temperature phase, the maximum intensity is observed when the b-axis lies in the scattering plane (\( \psi=0^\circ \)), whereas the intensity almost vanishes when the a-axis is parallel to the diffraction plane (\( \psi=90^\circ \)).
A maximum intensity is found when the polarization channel at \( g_{001} \) is given by
\[
m^z = m \sin \alpha \cos \psi,
\]
where \( m \) and \( \alpha \) are the projections of the magnetic moment on the axes of the reference system. The calculated dependences, which are shown as solid curves in Fig. 3, are in good agreement with the experimental results, and hence, confirm magnetic moment orientations along the \( b \)-axis below and along the \( a \)-axis above \( T_{MI} \).

The azimuthal dependences at both reflections suggest a magnetic moment direction along the \( b \)-axis in the low-temperature phase and a reorientation to the \( a \)-axis at \( T_{MI} \). We therefore calculated the azimuthal dependence of the scattered intensity for both reflections based on \( A \)-type AFM structures with these moment directions. Following the analysis described in Ref. 21, the intensity \( I^{\mu \nu} \) in a particular polarization channel at \( 001 \) and \( 110 \) is given by
\[
I^{\mu \nu} = \sum_j e^{iQg_{\mu \nu}^{\mu \nu}} | g_{1 \mu}^{\mu \nu} - g_{1 \nu}^{\mu \nu} |^2 \approx | g_{1 \mu}^{\mu \nu} - g_{1 \nu}^{\mu \nu} |^2,
\]
where \( \mu \) and \( \nu \) denote the polarizations of the incident and diffracted beams, respectively, and \( g_{1 \mu} \) and \( g_{1 \nu} \) are the scattering lengths of the two spin directions, which are calculated as
\[
g_{1 \mu} = \begin{pmatrix} g_{1 \sigma}^{\pi \sigma} & g_{1 \pi}^{\pi \sigma} \\ g_{1 \sigma}^{\pi \pi} & g_{1 \pi}^{\pi \pi} \end{pmatrix},
\]
where
\[
g_{1 \sigma} = \begin{pmatrix} 0 & m_z \cos \theta + m_x \sin \theta \\ -m_x \cos \theta + m_z \sin \theta & -m_z \sin 2\theta \end{pmatrix}.
\]

![FIG. 3. (Color online) Azimuthal-angle dependence of the scattered intensity at the \( 001 \) and \( 110 \) reflection measured below and above \( T_{MI} \). The solid lines are calculations based on the electric-dipole approximation and a magnetic moment direction along the \( b \)-axis below and along the \( a \)-axis above \( T_{MI} \).](image3)

![FIG. 4. (Color online) Temperature dependence of the integrated intensity at the magnetic reflections \( 001 \) and \( 110 \) taken at the azimuthal position \( \psi=0^\circ \). The inset shows the temperature dependence of the scattered intensity at wave vector \( 110 \) for \( \psi=0^\circ \) and \( \psi=180^\circ \).](image4)

Here, \( \theta \) is the scattering angle and \( m_z=m \sin \alpha \cos \psi \), \( m_x=m \sin \alpha \sin \psi \), and \( m_y=-m \cos \alpha \) are the projections of the magnetic moment on the axes of the reference system. The calculated dependences, which are shown as solid curves in Fig. 3, are in good agreement with the experimental results, and hence, confirm magnetic moment orientations along the \( b \)-axis below and along the \( a \)-axis above \( T_{MI} \).

The temperature dependence of the intensities of the two reflections is displayed in Fig. 4. Both reflections exhibit almost the same temperature dependence at \( \psi=0^\circ \), which corresponds to the maximum intensity position in the low-temperature phase. Below \( T_{MI} \), the intensity remains approximately constant with increasing temperature, followed by an intensity loss of approximately two orders of magnitude at \( T_{MI} \). This drastic intensity change is mostly due to the reorientation of the magnetic moment and consistent with the azimuthal dependence in Fig. 3. In the metallic AFM phase, the intensity further decreases upon heating and continuously vanishes at \( T_N \), as expected for a second-order phase transition. The inset of Fig. 4 shows the temperature dependence at the wave vector \( 110 \) for \( \psi=180^\circ \), where the moment reorientation results in an intensity enhancement by almost one order of magnitude above \( T_{MI} \). From a comparison of the maximum intensities in the two phases, we conclude that the amplitude ratio of sublattice magnetizations in the metallic and insulating states is \( \sim 1/\sqrt{3} \).

Antiferromagnetic metallic states such as the one observed in \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) between \( T_N \) and \( T_{MI} \) are uncommon in oxides, but a related phenomenon has been observed in bilayer manganates which also exhibit \( A \)-type antiferromagnetism. The small amplitude of the ordered magnetic moment in this phase is presumably a consequence of charge and/or orbital fluctuations. Below \( T_{MI} \), a variety of experiments have provided indirect evidence of orbital order. Because of the strong spin-orbit interaction and the relatively weak Jahn–Teller coupling of the \( 4d \) \( t_{2g} \) valence electrons, one generally expects an unquenched orbital magnetization in a state with ordered Ru orbitals. Additional terms in the spin Hamiltonian induced by the orbital moment...
may then be responsible for the observed reorientation below \( T_{MI} \).

### B. Orbital order

In order to obtain direct evidence of orbital order, we searched for resonant superstructure reflections characteristic of a staggered ordering pattern ["antiferro-orbital order" (AFO)] at various high-symmetry positions in reciprocal space including \((1/2\ 1/2\ 0)\), \((0\ 0\ 1)\), \((1/2\ 0\ 0)\), and \((0\ 1/2\ 0)\), with the photon energy tuned to one of the Ru \( L \)-absorption edges, but we did not find any signal above background. In \( \text{Ca}_3\text{Ru}_2\text{O}_7 \), orbital order with the same propagation vector as the antiferromagnetically ordered state was inferred from the persistence of a weak resonant reflection above the magnetic ordering temperature.\(^\text{12}\) An analogous phenomenon (namely, weak \( A \)-type AFO) would not be detectable in \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) because the magnetic ordering temperature exceeds the onset of orbital order so that the magnetic intensity would dominate at all temperatures.

We also used a resonant diffraction method to check for the presence of a uniform polarization of the Ru orbitals ["ferro-orbital order" (FO)] in the insulating state. As FO manifests itself as resonant intensity at the main crystallographic Bragg reflections, it is difficult to separate this contribution from the regular Thomson scattering. To solve this problem, the authors of Refs. 24 and 25 developed an interference technique where the resonant FO signal is amplified by charge scattering. To this end, the analyzer is rotated out of the \( \sigma\pi' \)-position (\( \phi_A = 90^\circ \)), where the FO signal is expected to occur, to \( \phi_A = 90^\circ \pm \Delta \) (see Fig. 1 for the definition of the angles). The scattered intensity at a rotational analyzer angle \( \phi_A \) is given by

\[
I(\phi_A) = |F_{\sigma\pi'} \cos \phi_A - F_{\sigma\pi''} \sin \phi_A|^2 + |F_{\sigma\pi'} \sin \phi_A + F_{\sigma\pi''} \cos \phi_A|^2 \cos 2\theta_A, \tag{3}
\]

where \( F_{\sigma\pi'} \) and \( F_{\sigma\pi''} \) denote the form factors in the different polarization channels and \( \theta_A \) is the scattering angle of the analyzer. This leads to the following interference term:

\[
I(\phi_A = 90^\circ - \Delta) - I(\phi_A = 90^\circ + \Delta) = 2 \text{Re}(F_{\sigma\pi'} F_{\sigma\pi''}^\ast) \sin^2 2\theta_A \sin^2 2\Delta. \tag{4}
\]

In principle, this experiment can also be performed at the Ru \( L \)-edge where the FO signal is expected to be most pronounced. However, this option is unfavorable based on two considerations. First, all Bragg reflections that can be reached at this photon energy have a magnetic contribution that is expected to dominate the orbital one. Second, the polarization analyzer currently available for this energy, Si (111), has an extremely small mosaicity, which causes additional experimental problems. Following the protocol established in Refs. 24 and 25, we therefore performed the experiment at the \( K \)-absorption edge of Ru, using pyrolytic graphite as analyzer.

Figure 5 shows energy scans near the Ru \( K \)-absorption edge at the reflection \((0\ 6\ 0)\) taken at two azimuthal positions. The difference of the two signals measured at \( \phi_A = 85^\circ \) and \( \phi_A = 95^\circ \) does not indicate any FO contribution. In addition to the search for a FO signal within a wide azimuthal range of \( 180^\circ \), we also varied the angular difference \( \Delta \) between the two analyzer positions, but no FO intensity was detected.

Since an experiment with a very similar design revealed a substantial FO signal for \( \text{Ca}_3\text{Ru}_2\text{O}_7 \), we conclude that the amplitude of the FO order parameter, if present, is considerably weaker in \( \text{Ca}_2\text{Ru}_2\text{O}_4 \). This is not unexpected in view of the much lower metal-insulator transition temperature in \( \text{Ca}_2\text{Ru}_2\text{O}_4 \) and the apparent ability of a modest external magnetic field to rearrange or even obliterate the orbital order in this material.\(^\text{15}\) Corresponding magnetic field-induced transitions have not been reported for \( \text{Ca}_3\text{Ru}_2\text{O}_7 \). A reduction of the FO order parameter, yielding a resonant signal below our detection limit, could result from orbital quantum fluctuations and/or residual charge fluctuations in the insulating state.

### IV. CONCLUSION

Resonant x-ray diffraction on a small single crystal has provided a comprehensive picture of the magnetic structure of \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) in its insulating and metallic phases, illustrating the power of this method for magnetic structure determination in situations where large crystals for neutron diffraction are not available. As evidence for orbital order could not be found in \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) within the experimental sensitivity, it is likely that the orbital-order parameter is substantially weaker than in its single-layer counterpart, \( \text{Ca}_2\text{Ru}_2\text{O}_4 \). Weak orbital order, combined with strong spin-orbit coupling, are presumably at least partially responsible for the rich phase behavior of \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) observed in response to external magnetic fields.

### ACKNOWLEDGMENTS

We would like to thank F. Schaefer, M. Mertin, E. Dudzik, and R. Feyerherm for their assistance during beam
time at BESSY. Work at Cologne was supported by the DFG through SFB 608 and by the BMBF Project No. 05 ES3XBA/5. Work at Brookhaven was supported by the U.S. Department of Energy, Division of Materials Science, under Contract No. DE-AC02-98CH10886. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.