Orbital Ordering in Calcium Ruthenates

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Introduction

Layered ruthenates exhibit a variety of phases with properties that include superconductivity, itinerant ferromagnetism, and colossal magnetoresistance. While the metal-insulator transitions, structural distortions and transitions, and magnetic correlations in these materials clearly indicate the relevance of the charge, lattice, and spin degrees of freedom, attention has recently focused on the role played by the orbital degree of freedom. For example, in the two ruthenates that are described below, ordering of the ruthenium 4d t_{2g} orbitals has been reported to cause the metal-insulator transition (in Ca_2RuO_4),[1] while its field-induced destruction has been reported to give rise to colossal magnetoresistance (in $Ca_3Ru_2O_7$).[2] Yet the orbital degree of freedom is difficult to measure directly, so such reports remain a subject of debate, and questions about the role of the orbital degree of freedom— and more fundamentally, its state (i.e., the orbital occupation)— in layered ruthenates remain.

In both Ca_2RuO_4 and $Ca_3Ru_2O_7$, the ruthenium ion is in a 4+ oxidation state, with a $4d^4$ electronic configuration. The large crystal-field splitting results in a low-spin state, with only the t_{2g} orbitals occupied in the ground state. All three of these orbitals are expected to be occupied by a majority spin electron, and the orbital degree of freedom pertains to the orbital occupation of the fourth, minority spin, electron. The x-ray scattering studies described here, which include both direct and indirect measurements, attempt to shed light on this orbital degree of freedom. In the direct measurement, ordering of the 4d t_{2g} orbitals in Ca_2RuO_4 was probed using resonant x-ray scattering techniques at the ruthenium L_2 and L_3 edges ($2p \rightarrow 4d$ transitions).[3] The orbital ordering was observed to have the same propagation vector as the antiferromagnetic order, and disappeared at a temperature well below the metal-insulator transition. In the indirect measurement, the c-axis lattice parameter collapse of $Ca_3Ru_2O_7$ was studied as a function of temperature and magnetic field. This collapse has been argued to be associated with a Jahn-Teller-like distortion of the RuO_6 octahedra, in which the degeneracy of the 4d t_{2g} orbitals is lifted and the in-plane, d_{xy}, orbital is preferentially occupied.[4] Therefore high-field studies directly probed the interplay between the lattice and spin degrees of freedom, and provided indirect information about the proposed orbital order.

Methods and Materials

The single-crystal samples of Ca_2RuO_4 and $Ca_3Ru_2O_7$ were grown using the floating-zone method.[5,6,7] The platelet-shaped samples have mosaic widths of a few hundredths of a degree.

The resonant x-ray scattering studies of Ca_2RuO_4 were carried out on APS beamline 4ID-D, which has a modified storage ring chamber to reach photon energies as low as 2.6 keV, and has been optimized to minimize absorption by air and windows at such low energies. The samples were mounted in a closed-cycle cryostat, on an 8-circle diffractometer, and a Si(111) crystal was used for polarization analysis.

The high-field studies of $Ca_3Ru_2O_7$ were carried out on NSLS beamline X21, using the 13 T, High-Field Facility (HFF), which is shown below in Fig. 1. The HFF consists of a superconducting, split-coil magnet that applies field vertically, and a diffractometer table with **x**, **y**, and **z** translations stages, orthogonal ±4° tilt stages, and a 2-circle goniometer. An avalanche photodiode, which can accommodate high count rates and is not affected by stray magnetic field, was used as the detector. The sample was mounted with the c-axis in the horizontal scattering plane, and was rotated azimuthally to apply magnetic field along each of the in-plane directions. Data were collected in both fixed field and fixed temperature modes.

Fig. 1: The High-Field Facility at NSLS beamline X21.

Results

Ca_2RuO_4, which exhibits a metal-insulator transition at $T_{m\text{-}i}$ = 357 K and orders antiferromagnetically at T_N = 110 K,[8,9] was first studied at the (100) magnetic wavevector. A large resonant enhancement, which is displayed in Fig. 2, was observed upon tuning the incident photon energy through the ruthenium L_2 and L_3 edges. Polarization and azimuthal dependences of this scattering are consistent with the known antiferromagnetic ordering; however in addition, finite scattering intensity at the (100) wavevector— but well above T_N— was observed, and exhibited a transition at a temperature of ~260 K. Based on the temperature and polarization dependences of this additional scattering, as well as muon spin resonance results that showed no measurable magnetic moment above T_N, it is indicative of 4d t_{2g} orbital ordering.[3]

$Ca_3Ru_2O_7$ also exhibits a metal-insulator transition and antiferromagnetic ordering, but the magnetic ordering sets in at the higher temperature (T_N = 56 K, $T_{m\text{-}i}$ = 48 K).[10] In zero

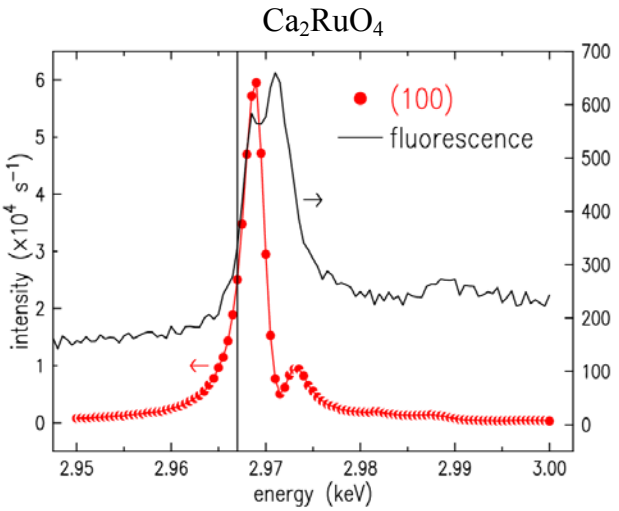

Fig. 2: The fluorescence and the scattering intensity at the (100) wavevector of Ca_2RuO_4 as the incident photon energy is tuned through the Ru L_2 edge.

field, a ~0.1% decrease in the c-axis lattice parameter is observed at the metal-insulator transition.[11] Following published work— reporting resistivity, magnetization, and Raman scattering measurements— that indicate anisotropic behavior as a function of applied magnetic field,[12,13,14] the structural change was measured using x-ray scattering with the field applied along each of the in-plane directions. An example of the fitted results from a fixed field data set is shown below in Fig. 3. As can be seen in this figure, the structural change has shifted to a lower temperature upon application of a 5 T field. Such shifts were observed for field applied along both of the in-plane directions, but the magnitude of the shift for a given H was clearly anistropic.

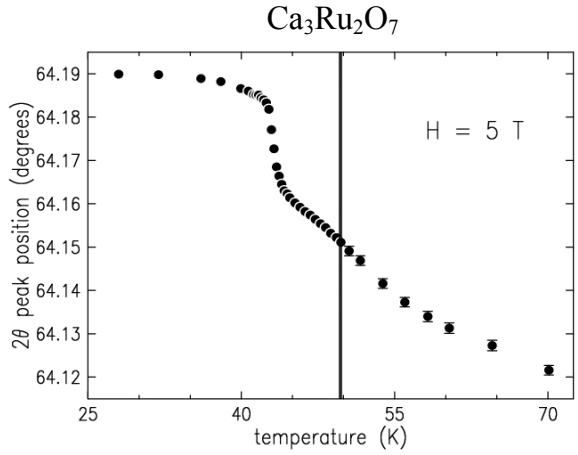

Fig. 3: Fitted peak position of the (0 0 20) Bragg peak of $Ca_3Ru_2O_7$, as a function of temperature, with the sample in a 5 T field applied along its b-axis. The vertical line indicates the temperature at which the structural change is observed for the sample in zero field.

Discussion

The x-ray scattering studies of the orbital degree of freedom in single-layer and bilayer calcium ruthenate have produced some surprising results. In Ca_2RuO_4, the orbital ordering observed directly using resonant x-ray scattering techniques is surprising with respect to both its ordering temperature and its wavevector. That is, the T = 260 K onset is far from the metal-insulator transition, and is also well below the crossover from elongated to compressed octahedra reported to occur at T = 300 K.[15] With regard to its wavevector, the only theoretical prediction of an antiferro-type orbital order structure would result in (½ ½ L) peaks,[16] which were not observed.[3] In $Ca_3Ru_2O_7$, the anisotropy of the structural change with field applied along the two in-plane directions was found to be broadly consistent with published results,[12,13,14] but no evidence of reentrant, orbital order-to-orbital disorder-to-orbital order, behavior was observed. Taken together, these studies underscore the subtlety of the orbital degree of freedom, and the power that x-ray scattering techniques provide toward its study.

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References

[1] J.H. Jung, Z. Fang, J.P. He, Y. Kaneko, Y. Okimoto, and Y. Tokura, *Phys. Rev. Lett.* **91**, 056403 (2003).
[2] G. Cao, L. Balicas, X.N. Lin, S. Chikara, E. Elhami, V. Duairaj, J.W. Brill, R.C. Rai, and J.E. Crow, *Phys. Rev. B* **69**, 014404 (2004).
[3] I. Zegkinoglou, J. Strempfer, C.S. Nelson, J.P. Hill, J. Chakhalian, C. Bernhard, J.C. Lang, G. Srajer, H. Fukazawa, S. Nakatsuji, Y. Maeno, and B. Keimer, *Phys. Rev. Lett.* **95**, 136401 (2005).
[4] G. Cao, L. Balicas, Y. Xin, J.E. Crow, and C.S. Nelson, *Phys. Rev. B* **67**, 184405 (2003).
[5] H. Fukazawa and Y. Maeno, *J. Phys. Soc. Jpn.* **70**, 460 (2001).
[6] Y. Yoshida, I. Nagai, S.I. Ikeda, N. Shirakawa, M. Kosaka, and N. Mori, *Phys. Rev. B* **69**, 220411(R) (2004).
[7] N. Kikugawa *et al.*, (unpublished).
[8] M. Braden, G. Andre, S. Nakatsuji, and Y. Maeno, *Phys. Rev. B* **58**, 847 (1998).
[9] C.S. Alexander, G. Cao, V. Dobrosavljevic, S. McCall, J.E. Crow, E. Lochner, and R.P. Guertin, *Phys. Rev. B* **60**, R8422 (1999).
[10] G. Cao, S. McCall, J.E. Crow, and R.P. Guertin, *Phys. Rev. Lett.* **78**, 1751 (1997).
[11] G. Cao, L. Balicas, Y. Xin, E. Dagotto, J.E. Crow, C.S. Nelson, and D.F. Agterberg, *Phys. Rev. B* **67**, 060406(R) (2003).
[12] S. McCall, G. Cao, and J.E. Crow, *Phys. Rev. B* **67**, 094427 (2003).
[13] J.F. Karpus, R. Gupta, H. Barath, S.L. Cooper, and G. Cao, *Phys. Rev. Lett.* **93**, 167205 (2004).
[14] X.N. Lin, Z.X. Zhou, V. Durairaj, P. Schlottmann, and G. Cao, *Phys. Rev. Lett.* **95**, 017203 (2005).
[15] O. Friedt, M. Braden, G. Andre, P. Adelmann, S. Nakatsuji, and Y. Maeno, *Phys. Rev. B* **63**, 174432 (2001).
[16] T. Hotta and E. Dagotto, *Phys. Rev. Lett.* **88**, 017201 (2002).