Phonon softening and anomalous mode near the $x_c=0.5$ quantum critical point in Ca$_{2-x}$Sr$_x$RuO$_4$

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Inelastic neutron scattering is used to measure the temperature-dependent phonon dispersion in Ca$_{2-x}$Sr$_x$RuO$_4$ ($x=0.4, 0.6$). The in-plane $\Sigma_4$ octahedral tilt mode softens significantly at the zone boundary of the high-temperature tetragonal (HTT) $I4_1/acd$ structure as the temperature approaches the transition to a low-temperature orthorhombic (LTO) $Pbca$ phase. This behavior is similar to that in La$_2$CuO$_4$, but an inelastic feature that is not found in the cuprate is present. An anomalous phonon mode is observed at energy transfers greater than the $\Sigma_4$, albeit with similar dispersion. This anomalous phonon mode never softens below $\sim 5$ meV, even for temperatures below the HTT-LTO transition. This mode is attributed to the presence of intrinsic structural disorder within the $I4_1/acd$ tetragonal structure of the doped ruthenate.

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The discovery of exotic superconductivity in Sr$_2$RuO$_4$ and its structural similarity to La$_2$CuO$_4$ has generated much interest in the Ca$_{2-x}$Sr$_x$RuO$_4$ (CSRO) family of compounds. Their physical properties as a function of doping have revealed remarkable similarities with those of the high-temperature superconductor La$_2$−$x$Sr$_x$CuO$_4$ (LSCO). Nevertheless, it is important to realize that Sr and Ca are isoelectronic, such that Ca substitution does not change the valence electron number, i.e., does not change the band filling, in contrast with Sr doping of the cuprate. In addition to providing a new system where the evolution from antiferromagnetism to superconductivity can be explored, the phase diagram of the single-layered Ruddlesden-Popper CSRO compounds contains rich and exotic behavior attributed to numerous nearly degenerate structural and magnetic instabilities. For instance, for $x<0.2$, an antiferromagnetic (AFM) insulating ground state and metal-insulator phase transitions are observed, while a metamagnetic transition is observed for $x \sim 0.2$ accompanied by anisotropic thermal-expansion anomalies that can be reversed in a magnetic field. For $0.2 \leq x < 0.5$, short-range AFM correlations exist but vanish at $x_c=0.5$, where the spin susceptibility is critically enhanced, indicating a ferromagnetic instability point. This critical concentration, $x_c=0.5$, is also the $T=0$ K terminus quantum critical point (QCP) for the line of structural phase transitions between the high-temperature tetragonal (HTT) and low-temperature orthorhombic (LTO) phases.

Inelastic-neutron-scattering (INS) measurements of the temperature dependence of the $\Sigma_4$ phonon mode in Ca$_{2-x}$Sr$_x$RuO$_4$ ($x=0.4, 0.6$) were performed. These concentrations are in immediate proximity to the QCP while allowing investigation of mode softening both with and without traversing the HTT-LTO phase boundary. This choice of concentrations is also motivated by interest in surface phases and phase transitions in CSRO, and the possibility of resolving questions concerning surface mechanisms by understanding the bulk phonon behavior.

Figure 1 summarizes the three structural phases of the CSRO compounds for $x \leq 0.5$. Generically, the structure consists of Ru sites in an octahedral coordination with neighboring O sites. The octahedra form a layered structure in the $ab$ plane with neighboring planes along the $c$ axis separated by Ca/Sr layers. The structural phase transitions are associated with changes in the octahedral tilt and rotation as well as the octahedral stacking sequence along the $c$ axis. While both $x=0.4$ and $x=0.6$ start in the HTT $I4_1/acd$ symmetry at room temperature, $x=0.4$ enters into a LTO $Pbca$ symmetry upon cooling.

FIG. 1. (Color online) Structural phases of the CSRO family for $x \leq 1.5$. RuO$_6$ octahedra are illustrated with yellow (blue) octahedra representing clockwise (counterclockwise) rotation relative to the $c$ axis. Oxygen (Ca/Sr) sites are represented by green (red) spheres and unit cells are shown as black lines. Only octahedra along the [100] and [010] faces are shown for clarity. CSRO $x=0.2$ presents the (a) $Acam$ symmetry at high temperatures and (b) $Pbca$ symmetry at low temperatures. Both $x=0.4$ and $x=0.6$ present the (c) $I4_1/acd$ symmetry at high temperatures but the LTO phase of $x=0.4$ involves a structural frustration between the preferred RuO$_6$ rotation stacking periodicity of the $I4_1/acd$ phase and the induced tilt periodicity of the $Pbca$ phase (Refs. 4 and 10).
cooling. While the LTO phase is created by a static tilt of the RuO₆ octahedral layers, structural frustration is introduced due to the preferred stacking periodicities along the c axis observed for x away from the QCP. The Σ₄ transverse-acoustic phonon mode is related to the tilt of the layered Ru octahedra and, as such, is particularly sensitive to their distortions in different portions of the CSRO phase diagram.

Single-crystal samples were grown using the floating-zone technique, m₀=3 g and m₀=4 g. INS measurements for x=0.4 were performed using the HB1 triple-axis spectrometer (TAS) at the High Flux Isotope Reactor (HFIR) at ORNL and the BT-7 TAS at the NIST Center for Neutron Research. INS measurements for x=0.6 were performed using the HB3 TAS at HFIR. The HB1 and HB3 instrument configurations consisted of a fixed-focus PG(002) monochromator and a flat PG(002) analyzer with collimations of open-50'-40'-240'. The BT-7 configuration consisted of a variable-focus PG(002) monochromator and a focusing PG(002) analyzer with collimations of open-50'-40'-open. All measurements employed a fixed final neutron energy of 14.7 meV with a pyrolitic graphite (PG) filter in the scattered beam. Samples were mounted in the (hkl) scattering plane and indexed in the I4/mmm symmetry of pure Sr₂RuO₄. Unless noted, all (hkl) coordinates refer to this notation. The (1 1 1/2) wave vector is a zone boundary for both the I4/mmm and I4₁/acd symmetries. However, due to the static RuO₆ rotation, a glide plane symmetry is established and the (1 1 1/2) Bragg peak is extinguished for T>Tₐ. As one cools through the HTT-LTO transition, the ensuing static distortion results in the appearance of this Bragg peak as this wave vector becomes a zone center for the orthorhombic Pbca phase. Using the Bragg peak intensity as an order parameter, we find Tₐ~155 K for the x=0.4 sample, consistent with prior studies. No hysteresis for the order parameter is observed, consistent with the expected second-order phase transition.

Constant wave-vector scans were performed to determine the temperature-dependent dispersion of the Σ₄ phonon mode. This phonon propagates in the [1 1 0] direction, but the motion of the oxygen atoms due to the static rotation results in mixed longitudinal and transverse components. Regions near the (1 1 1/2) and (0 5/2 0) wave vectors provided clean Σ₄ phonon measurements because of structure factor considerations similar to those of La₂CuO₄ and Sr₂RuO₄. Phonon-dispersion curves were found by comparing individual constant wave-vector scans to multiple Gaussian fits. Anomalous mode is clearly visible in Fig. 3 with a dispersion contrast to La₂CuO₄, where only the single Σ₄ mode is present and possesses an intensity and wave-vector modulation which mimics the Σ₄ mode. This anomalous mode is not expected from normal-mode analysis and, as such, it is anomalous in nature. The fundamental reasons for the existence of this anomalous mode must be explored to fully understand the physics of the system. In addition to these two modes, a higher-energy lattice excitation is also seen in Fig. 2 that is not examined here.

Constant- Q scans near (1 1 1/2) and (0 0 6) are combined to form the dispersion curves shown in Fig. 3. This dispersion is plotted in the I4/mmm notation to allow comparison with similar soft-mode behavior in La₂CuO₄. The anomalous mode is clearly visible in Fig. 3 with a dispersion that mimics the Σ₄ mode displaced in energy. This is in contrast to La₂CuO₄, where only the single Σ₄ mode is observed. The Σ₄ phonon mode is doubly degenerate with two possible tilt modes around [010] and [100]. The simplest explanation for the presence of two modes would be a lifting of this degeneracy. However, since the space group is tetragonal, the [010] and [100] directions are identical and we do not expect the degeneracy to be lifted. Cooling results in increased softening of the Σ₄ mode in both samples. For x=0.6, the phonon energy never reaches zero at the zone boundary as the crystal remains in the tetragonal phase. A summary of the temperature-dependent softening of the two modes at (1 1 1/2) is shown in Fig. 4. Similar linear softening with tem-
temperature is observed in both samples for both modes with the exception of a deviation from linearity for $x=0.4$ below 200 K as the lower branch softens to zero energy at $T \approx 150$ K. Note that while this mode softens completely, its corresponding anomalous mode never softens below 5 meV.

SrTiO$_3$ and La$_2$CuO$_4$ are classic examples where soft-phonon behavior drives structural instabilities.\cite{4,15} Displacive phase transitions are typically associated with a soft-phonon mode that freezes into a static lattice distortion at a critical temperature.\cite{15} For example, the energy of the $\Sigma_4$ tilt mode reduces to zero at the Brillouin-zone boundary in La$_2$CuO$_4$ at the HTT-LTO phase transition.\cite{11} The $\Sigma_4$ transverse-acoustic phonon mode represents a rotation (in-plane tilt) of the CuO$_6$ octahedron about an axis in the $ab$ plane.\cite{17} Because Ca$_{2-x}$Sr$_x$RuO$_4$ has the same oxygen octahedron structure and also undergoes a HTT-LTO phase transition ($0.2 < x < 0.5$), one expects similar softening behavior in the CSRO family. However, there are significant differences in symmetry for the LSCO and CSRO systems. At higher values of $x=1.5$, CSRO has already undergone a structural transition resulting from the freezing of a $\Sigma_3$ phonon mode with corresponding static rotation of the octahedra about the $c$ axis.\cite{4} Thus, the HTT-LTO transition in CSRO (LSCO) is from space group $I4_1/acd$ to $Pbcn$ ($I4_1/mmm$ to $Cmca$). One obvious consequence of the different space groups is that there is no change in the shape of the Brillouin zone during the HTT-LTO phase transition in CSRO. Despite this difference, the point-group symmetry for Ru is identical in both $I4_1/mmm$ and $I4_1/acd$ and, therefore, one does not expect any degeneracy lifting as a result of this difference.

Little is known about the tetragonal-to-tetragonal phase transition in CSRO that occurs at $x=1.5$. The transition is from the space group $I4_1/mmm$ to $I4_1/acd$, caused by the rotation of the RuO$_6$ octahedra about the $c$ axis. It is believed that the $x=1.5$ structural transition in Sr$_2$RuO$_4$ results from the softening of the $\Sigma_4$ mode.\cite{4} For $0.5 \leq x < 1.5$, a second-order structural phase transition into the $I4_1/acd$ phase is observed.\cite{4,10} Although the symmetry is $I4_1/acd$, disorder in the $c$-axis periodicity of the RuO$_6$ rotation is observed. Such disorder introduces stacking faults, resulting in a mixture of $I4_1/acd$ and $Acam$ symmetries as shown in Fig. 1. As $x$ is decreased, the disorder in the $c$-axis periodicity is reduced and a more perfect $I4_1/acd$ phase is formed.\cite{4,10}

This anomalous mode was reported previously in the thesis of Friedt\cite{10} and tentatively attributed to interactions resulting from the different stacking periods of the tilt and rotational distortions combined with disorder in Cu/Sr mixing.\cite{10} The lack of anomalous phonon mode observations in other doped transition-metal oxides, such as the cuprates, and the static energy of the anomalous mode as the $\Sigma_4$ mode softens through the phase boundary suggest an alternate mechanism. We propose a simple model of intrinsic disorder within the $I4_1/acd$ symmetry to explain the anomalous mode. While the symmetry for $0.5 < x < 1.5$ is $I4_1/acd$, disorder along the $c$ axis exists with a coherence length of approximately two unit cells observed for $x \sim 1.0$.\cite{10} It has also been observed that as more Ca is added to the system, a more perfect $I4_1/acd$ symmetry forms, resulting in fewer faults and an increased coherence length. It should be noted that long-range order exists within individual $ab$ planes and it is only the $c$-axis disorder in the stacked layers of rotated RuO$_6$ that varies with $x$. Disorder in the $c$-axis octahedral rotation periodicity has also been observed in similar materials such as Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$.\cite{18} While interlayer coupling along the $c$ axis is assumed weak as previous experiments suggest, it must occur for the well-coordinated RuO$_6$ rotations and tilts to exist along the $c$ axis.\cite{4,12} The $I4_1/acd$ symmetry encodes four RuO$_6$ layers with a $c$-axis lattice parameter of $\sim 25$ Å. The structural frustration created from the rotational periodicity mismatch combined with the intrinsic stacking faults could lead to the formation of impurity domains of different symmetry ($Acam$) along the $c$ axis and lift the phonon degeneracy. While locally the domains would appear to be

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**FIG. 3.** (Color online) Dispersion of the $\Sigma_4$ (filled symbols) and anomalous (open symbols) phonon modes for both $x=0.4$ and $x=0.6$. The dispersion curves are plotted with the $I4_1/mmm$ Brillouin zone of the parent compound Sr$_2$RuO$_4$. The $\Sigma_4$ mode shows typical soft-mode behavior and the anomalous mode mimics the $\Sigma_4$ dispersion. Lines are added as guides for the eyes.

**FIG. 4.** (Color online) Zone-boundary softening for the $\Sigma_4$ and anomalous modes. The $\Sigma_4$ mode reaches zero energy as the phase boundary is crossed.
In summary, inelastic-neutron-scattering experiments have been performed to measure the dispersion of the $\Sigma_4$ tilt mode phonon in Ca$_{1.4}$Sr$_{0.6}$RuO$_4$. The $\Sigma_4$ mode demonstrates typical soft-phonon behavior similar to La$_2$CuO$_4$, but an anomalous phonon mode also appears. The anomalous mode mimics the $\Sigma_4$ dispersion except at the phase boundary where the anomalous mode remains at finite energy, while the $\Sigma_4$ mode softens to zero energy, creating the orthorhombic phase. The anomalous mode is most likely due to disorder in the layered stacking sequence lifting the $\Sigma_4$ degeneracy. Further investigation is required to fully understand the role of defects and stacking faults in the CSRO family.

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†Present address: Stanford Synchrotron Radiation Lightsource, Nature (London) 372, 532 (1994).

‡Y. Maeno, T. M. Rice, and M. Sigrist, Phys. Today 54(1), 42 (2001).

§S. Nakatsuji and Y. Maeno, Phys. Rev. Lett. 84, 2666 (2000); Phys. Rev. B 62, 6458 (2000).

¶O. Friedt, M. Braden, G. Andre, P. Adelmann, S. Nakatsuji, and Y. Maeno, Phys. Rev. B 63, 174432 (2001).

†S. Nakatsuji, D. Hall, L. Balicas, Z. Fisk, K. Sugahara, M. Yoshioka, and Y. Maeno, Phys. Rev. Lett. 90, 137202 (2003).

|B. Keimer, N. Belk, R. J. Birgeneau, A. Cassanho, C. Y. Chen, M. Greven, M. A. Kastner, A. Aharony, Y. Endoh, R. W. Erwin, and G. Shirane, Phys. Rev. B 46, 14034 (1992).|

Z. Fang, K. Terakura, and N. Nagaosa, New J. Phys. 7, 66 (2005).

J. Baier et al., Physica B 378-380, 497 (2006).

R. G. Moore et al., Science 318, 615 (2007); R. G. Moore, V. B. Nascimento, J. Zhang, J. Rundgren, R. Jin, D. Mandrus, and E. W. Plummer, Phys. Rev. Lett. 100, 066102 (2008).

O. Friedt, Ph.D. thesis, University of Paris, 2003.

11R. J. Birgeneau, C. Y. Chen, D. R. Gabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, T. Thio, T. R. Thurston, H. L. Tuller, J. D. Axe, P. Boni, and G. Shirane, Phys. Rev. Lett. 59, 1329 (1987).

12M. Braden, W. Reichardt, S. Nishizaki, Y. Mori, and Y. Maeno, Phys. Rev. B 57, 1236 (1998).

13E. D. Kolaczyk, Astrophys. J. 483, 340 (1997).

14C. Charles et al., Surf. Interface Anal. 36, 49 (2004).

15G. Shirane, Rev. Mod. Phys. 46, 437 (1974); J. F. Scott, ibid. 46, 83 (1974).

16R. A. Cowley, Adv. Phys. 29, 1 (1980).

17V. B. Grande, Hk. Müller-Buschbaum, and M. Schweizer, Z. Anorg. Allg. Chem. 428, 120 (1977).

18M. K. Crawford, M. A. Subramanian, R. L. Harlow, J. A. Fernandez-Baca, Z. R. Wang, and D. C. Johnston, Phys. Rev. B 49, 9198 (1994); M. A. Subramanian, Physica C 235-240, 743 (1994).

19L. Petersen, Ismail, and E. W. Plummer, Prog. Surf. Sci. 71, 1 (2002); R. Pérez, J. Ortega, and F. Flores, Phys. Rev. Lett. 86, 4891 (2001); A. V. Melechko, M. V. Simkin, N. F. Samatova, J. Braun, and E. W. Plummer, Phys. Rev. B 64, 235424 (2001).