Strain Amplification of the $4k_F$ Chain Instability in $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$

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We used resonant soft x-ray scattering to study the chain ordering in $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ (SCO). We observed, for the first time, both the chain and ladder orders in SCO with the same probe. We found that the chain modulation in SCO is incommensurate with wave vector $L_c = 0.318$, is strongly temperature (T) dependent, and is accompanied by a substantial hole modulation. By contrast, the chain modulation in a hole-depleted control sample $\text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41}$ was commensurate ($L_c = 0.3$), T independent, and purely structural. We conclude that the chain charge order in SCO is a $4k_F$ charge density wave stabilized by the misfit strain between the ladder and chain substructures.

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The “spin” ladder is a simplified version of the two-dimensional t - J model still believed by many to contain the physics of high temperature superconductivity. A doped spin ladder can exhibit either exchange-driven superconductivity [1,2] or an insulating “hole crystal” (HC) ground state in which the carriers crystallize into a Wigner lattice [1,3,4]. The competition between these two phases resembles that between ordered stripes and superconductivity in two dimensions [5]. An understanding of spin ladders is therefore critical for our understanding of superconductivity in two dimensions.

This has led to a great deal of work on $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ (SCCO), which contains both doped ladders and chains. The two substructures have incommensurate periods so SCCO is an “adaptive misfit” material in which the chains, which are flexible, buckle to accommodate the rigid ladders [6–10], creating a supermodulation along the c axis that has been observed with scattering probes [6–10].

The remarkable thing about SCCO is that it exhibits both of the ground states predicted for a doped spin ladder [1–4]. At $x > 10$ it exhibits superconductivity at pressures above 3 GPa [11]. At $x = 0$ it exhibits both the transport properties and elementary excitations of a charge density wave (CDW) [12,13]. Recently resonant soft x-ray scattering (RSXS) studies have shown that the CDW in this system is a commensurate Wigner crystal of holes or “hole crystal” (HC) in the ladder substructure [14,15].

Several earlier neutron [16] and hard x-ray scattering [17,18] studies reported a structural modulation in SCCO that they interpreted as a CDW in the chain substructure. It was pointed out by van Smaalen [7], however, that the reflections observed index to the supermodulation so may just arise from chain buckling. It was later shown that some

of these reflections have anomalous temperature dependence [8–10], though whether this is due to charge order [8,9] or just thermal contraction [10] is unresolved. Further, the relationship between this chain order and the HC in the ladder, which has been seen only with RSXS, is still a mystery. To reconcile these observations we present a study of the chain charge order with RSXS.

Single crystals of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ (SCO) and control samples of $\text{La}_6\text{Ca}_8\text{Cu}_{24}\text{O}_{41+\delta}$ (LCCO), which nominally have no doped holes, were grown by floating zone techniques described in Ref. [19]. The oxygen stoichiometry was controlled by measuring the magnetic susceptibility and comparing to Ref. [6]. The surfaces were prepared by

FIG. 1 (color online). Polarization-dependent XAS of SCO and LCCO at (a) the OK edge and (b) the CuL edges, taken at $T = 300$ K.

polishing with diamond film down to a grit of $0.05\ \mu\text{m}$. The samples were characterized with hard x-ray diffraction (XRD) and *in situ* x-ray absorption spectroscopy (XAS) at the OK, $\text{Cu}L_{3/2}$, and $\text{Cu}L_{1/2}$ edges. XRD gave mosaic spreads of 0.14° for SCO and 0.126° for LCCO, and refined lattice parameters consistent with previous studies [8,9]. Soft x-ray measurements were carried out on beam line X1B at the National Synchrotron Light Source with an in-vacuum diffractometer. The incident bandwidth was set to 0.2 eV. We will denote momenta with Miller indices of the chain; i.e., (H, K, L_c) implies $Q = (\frac{2\pi}{a}H, \frac{2\pi}{b}K, \frac{2\pi}{c_c}L_c)$, where c_c is the chain lattice parameter.

XAS spectra are displayed in Fig. 1. Data for both SCO and LCCO [Fig. 1(a)] are consistent with previous studies [20] indicating good surface quality (the same SCO data were reported in Ref. [21]). Using a fitting procedure described previously [21] we estimate the hole count per Cu atom in the chain to be $\delta_c = 0.32$ in SCO and $\delta_c = 0.056$ in LCCO. LCCO has a few residual holes but is sufficiently depleted to act as a control sample. XAS spectra at the $\text{Cu}L$ edges are displayed in Fig. 1(b). They reveal the presence of high energy sidebands at each Cu edge, denoted $L'_{3/2}$ (933 eV) and $L'_{1/2}$ (953 eV), as seen in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system [22]. The spectral weight in these sidebands, which are polarization-independent in the (a, c) plane, are a measure of the local hole density.

RSXS measurements were first carried out on SCO at $T = 20\ \text{K}$ at the OK edge. The x-ray energy was tuned to 528.4 eV at which scattering from the holes is enhanced by a factor of 10^3 [14,15,23–25]. We first performed a scan of L_c at $H = K = 0$ to search for a chain reflection, perhaps at $L_c = 0.2$ as had been reported previously [18] [Fig. 2(a)]. A reflection at $L_c = 0.142$ ($L_L = 0.20$ in ladder units) is visible, which is the previously reported hole

crystal in the ladder [14]. No chain buckling reflection was observed at this edge.

To increase our momentum range we tuned to the higher energy $\text{Cu}L'_{3/2}$ edge ($\omega = 933\ \text{eV}$) where a scan out to $L_c = 0.41$ was performed [Fig. 2(a)]. The ladder hole crystal was again observed. In addition, we observed an incommensurate reflection at $L_c = 0.318 \pm 0.005$ ($L_L = 0.454$ in ladder units), which in the superspacegroup formalism [7–10] indexes to $(0, 0, 1, \bar{1})$. This reflection therefore arises from buckling of the chains to accommodate the ladder. The peak was mapped in the $(H, 0, L_c)$ plane, shown in Fig. 2(b), giving coherence lengths $\xi_c = 1100 \pm 100\ \text{\AA}$ (~ 400 chain units) along the chain direction and $\xi_a = 983 \pm 100\ \text{\AA}$, i.e., ~ 87 neighboring chains. These quantities were observed to be independent of the photon energy, indicating that they are not influenced by penetration depth effects.

As a control measurement, we performed the same scan on the hole-reduced sample LCCO [Fig. 2(a), blue line]. No ladder HC was observed in this sample. However, the $(0, 0, 1, \bar{1})$ chain reflection was again seen, shifted now to the commensurate position $L_c = 0.300 \pm 0.005$ and 80 times weaker in intensity. That this modulation is present in a hole-depleted material is additional evidence that it is related to the chain buckling and is not a spontaneous CDW as suggested previously [16–18]. However the difference in intensity and wave vector in this sample requires explanation.

Our main experimental result is the “resonance profile” (RP) of the chain buckling reflections in SCO and LCCO, i.e., their energy dependence through the $\text{Cu}L_{3/2}$ edge, shown in Fig. 3(a). These data were taken at $T = 20\ \text{K}$. In SCO the RP has a strong resonance at the $\text{Cu}L'_{3/2}$ shoulder at 933 eV which indicates, like the HC studied earlier [14,15], the presence of a significant hole modulation. Unlike the HC, however, a second weaker resonance is also observed at 930 eV. Because the chain buckling is structural, unlike the HC which is mainly electronic, this resonance likely arises from structural displacement of the Cu atoms. Evidently the chain modulation in SCO, while clearly related to the misfit structure, has some of the character of a CDW. In contrast, the RP for LCCO (also shown in Fig. 3) exhibits only one resonance at 931 eV. Because this sample contains few holes it seems likely that this signifies a pure structural distortion, without a hole modulation. However, to be sure of this conclusion quantitative analysis is required.

The line shapes in Fig. 3 and the physical origin of the chain reflections in SCO and LCCO can be understood quantitatively with a method proposed by Abbamonte [26]. In this method one divides the atomic scattering factor into two parts, $f(\omega, v) = f_R(\omega) + v f_D(\omega)$, where f_R is the “raw” atomic scattering factor and f_D is the scattering factor of the doped holes. These two quantities can be determined from doping-dependent XAS measurements,

FIG. 2 (color online). (a) Broad L_c scans of SCO and LCCO at different photon energies, showing both the ladder hole crystal and the chain modulation. (b) Map of the chain reflection in the $(H, 0, L_c)$ plane, taken at $T = 20\ \text{K}$.

FIG. 3 (color online). (a) Resonance profiles of the chain superlattice peaks in SCO and LCCO near the $\text{Cu}L_{3/2}$ edge, compared to XAS data for SCO. RPs were measured at $T = 20$ K. Black circles, red circles, green circles, correspond, respectively, to XAS, the RP for SCO, and the RP for LCCO. Blue and magenta lines are fits using the form factors in (b) (see text). (b) Real and imaginary parts of the raw, $f_R(\omega)$, and hole, $f_D(\omega)$, form factors determined from the XAS data in Fig. 1(b). Form factors were placed on an absolute scale by fitting to the Henke tables [29] far from the edge.

such as that in Fig. 1, by applying the relation

$$\text{Im}[n(\omega, v)] = -\frac{r_e \lambda^2}{2\pi V_{\text{cell}}} \text{Im}[\sum_i f_i(\omega, v)], \quad (1)$$

solving a system of equations at each energy point, and performing a Kramers-Kronig transform. Here $\text{Im}[n]$ is the absorptive part of the refractive index (linearly related to XAS spectra), r_e is the classical electron radius, λ is the x-ray wavelength, and f_i is the complex atomic scattering factor. The integrated intensity of the charge reflection is then given by the quantity $\rho_Q(\omega) = |v_0 f_D(\omega) \exp(i\phi/2 + iQu_0 f(\omega, \langle v \rangle))|^2$, where $\langle v \rangle$ is the average atomic valence, v_0 is the charge modulation amplitude, u_0 is the (longitudinal) strain amplitude, Q is the wave vector of the CDW, and ϕ is their relative phase. By fitting the RP line shape with the form factors obtained from XAS, then, ϕ and the ratio $W = v_0/u_0$ can be determined. The latter is a measure of the degree to which the modulation is driven by interactions rather than structural effects [26].

To apply this method we used the data in Fig. 1(b) to determine $f_R(\omega)$ and $f_D(\omega)$ for Cu in this system [27]. The Cu atoms in the chains and ladders cannot be distinguished at this edge so we use the average values $\langle v \rangle = 0.25$ for SCO and $\langle v \rangle = 0.023$ for LCCO [28]. The resulting form factors, which are valid for both chain and ladder Cu atoms, are shown in Fig. 3(b). We find that $|f_D| = 75$ electrons per hole on the resonance maximum; i.e., at this resonance a doped hole scatters as strongly as a Rhenium atom.

Best fits to the RPs for SCO and LCCO are shown in Fig. 3(a). The RP line shapes are reproduced well, yielding the values $W = 1.13 \text{ \AA}^{-1}$ and $\phi = -23.1^\circ$ for SCO and $W = 0.065 \text{ \AA}^{-1}$ and $\phi = -90.1^\circ$ for LCCO. The physical meaning of the phase shift ϕ is illustrated for SCO in a sketch in Fig. 4(d). An important lesson from this fit is that the structural resonance in SCO at 930 eV is the same as the resonance at 931 eV in LCCO. It simply *appears* shifted to lower energy because of interference with the valence scattering. In Ref. [26] it was pointed out that $W \sim 0$ for a pure strain wave, $W \sim 1$ for a conventional Peierls CDW, and $W \sim 10$ for an “exotic” CDW like a Wigner crystal. Our measured values of W lead to the conclusion that the chain buckling in LCCO is a simple misfit strain wave, whereas in SCO, in which the reflection is 80 times stronger, it is a strain wave magnified by an

FIG. 4 (color online). (a) Temperature dependence of the chain modulation in SCO and LCCO. (b) L_c -scans for SCO at $T = 20$ K and 300 K. (c) L_c -scans for LCCO at $T = 20$ K and 300 K. (d) Real space sketch of the hole amplitude and Cu displacements in a chain in SCO. The size of the circles represents the hole density at a given site and the arrows represent the size and direction of the lattice displacement.

incipient CDW with a similar wave vector. We emphasize that this conclusion, which is based on the order of magnitude of W , is resilient to small errors in stoichiometry or in the hole count measured with XAS.

This picture is further supported by the temperature dependence. L_c scans in both SCO and LCCO were carried out at different temperatures, shown in Figs. 4(a)–4(c). In SCO a pronounced decrease is observed upon warming, again suggestive of CDW character. However, the peak intensity never goes completely to zero; as the temperature rises the intensity levels tend to a constant value. In LCCO, however, the peak intensity is virtually temperature-independent. This behavior is consistent with the picture that the chain modulation in LCCO is a simple strain wave, but in SCO it is a strain-stabilized CDW.

A final, important observation is that the wave vector of the chain modulation in SCO, $L_c = 0.318$, is very close to its hole count, $\delta_c = 0.32$. The Fermi momentum of a chain is given by $k_F = \pi\delta_c/2a$, so the observed wave vector $Q = 2\pi L_c/a$ is very close $4k_F$, which is a natural instability for a 1D system. We propose that the CDW is a $4k_F$ instability of the chain (though we cannot rule out more exotic orders [16]) stabilized by misfit strain. The CDW also acts back on the strain wave, amplifying its intensity ($80\times$, as observed) and shifting its wave vector to an incommensurate value. In LCCO, which has no incipient CDW, the strain wave is weak and just sits at the commensurate value $L_c = 0.30$.

Our results may help explain a discrepancy between results of low-frequency dielectric spectroscopy [12] and Raman scattering [13] studies of this compound. Vuletić *et al.* [12] found that the onset temperature of the CDW is about 210 K which is similar to the onset temperature of the HC in ladders found with RSXS [14]. Blumberg *et al.* [13], however, found evidence for a CDW even up to the highest measured temperature, 630 K. The Raman results of Blumberg may arise from fluctuations in this chain CDW, which can persist to very high temperature because of the stabilizing effect of the strain.

In conclusion, RSXS has been used to study the chain ordering in SCO, finally allowing observation of both chain and ladder orders in SCO with the same probe. We conclude that the chain modulation observed in several previous studies [6,8–10,16,17] is neither a pure CDW nor a simple misfit strain wave, but a modulation driven by the interaction between the two. Our results highlight the value of RSXS for separating electronic and structural effects in condensed matter.

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