Strain amplification of the $4k_F$ chain charge instability in Sr$_{14}$Cu$_{24}$O$_{41}$

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We have used resonant soft x-ray scattering (RSXS) to study the misfit strain in Sr$_{14}$Cu$_{24}$O$_{41}$ (SCO), a cuprate that contains both doped spin ladders and spin chains. The ladder and chain substructures in this material have incommensurate periods and are mated together under internal strain. At $x > 10$ this system was shown to exhibit superconductivity at pressures above $3$ GPa. Further, it exhibits both the transport properties and elementary excitations characteristic of a charge density wave (CDW). Recent studies were shown, with resonant soft x-ray scattering (RSXS) studies, to contain a commensurate Wigner crystal of holes or “hole crystal” (HC) in the ladder substructure.

Prior to these studies several authors, applying neutron and hard x-ray scattering methods, reported a distinct modulation of the crystal structure at low temperature which they interpreted as a CDW in the chain substructure. It was later pointed out by van Smaalen that the observed superstructures index to the large unit cell of the total structure, arise naturally from the misfit strain, and are not necessarily an indication charge order. It was later shown, however, that some of these reflections show anomalous temperature dependence and, regardless of their relation to the structure, may be a sign of charge order after all.

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feature at 530 eV is assigned to transitions into the upper Hubbard band (UHB) i.e. the Cu$3d$ orbitals, through $p-d$ hybridization. In contrast to SCO, in LCCO the doped hole features are absent which is consistent with the expectation that it is a zero hole system. Note that the UHB feature in LCCO is, correspondingly, stronger, indicating that spectral weight is transferred with doping in this system as in other cuprates[22].

Figure 1(b) shows the corresponding XAS at the Cu$L$ edge, also taken at room temperature. The Cu$L$ edge consists of two peaks at 931 eV and 951 eV which are transitions into the $3d$ band from a core $2p$ level with $j=3/2$ or $1/2$, respectively. The main difference between the two samples is the presence of a ligand hole side band at 933 eV and 953 in SCO which is absent in the undoped LCCO. The spectral weight in this side band can be considered a measure of the doped hole density. The XAS at both the Cu$L_{3/2}$ and the Cu$L_{1/2}$ edges was found to be polarization-independent in the $ac$-plane for both samples.

The first RSXS measurements were carried out on SCO at the OK edge. In this measurement the x-ray energy was tuned to 528.6 eV at which scattering from the holes is enhanced by a factor of $10^3$ [8, 10, 23, 24, 25]. We first looked for a Bragg reflection at $L_c = 0.20$ as was reported previously[12]. Figure 2 shows a reciprocal space scan from $(H, K, L_c) = (0, 0, 0.1)$ to $(0, 0, 0.23)$. A reflection at $L_c = 0.142$ is visible ($L_L = 0.2$), which is the previously reported hole crystal in the ladder[9]. No reflection was observed near $(0, 0, 0.2)$. It would also be desirable to search for a Bragg reflection at $L_c = 0.25$ as had been reported in ref. [12]. However this point in reciprocal space cannot be reached at the OK edge. We therefore turned to the Cu$L'_{3/2}$ edge ($\omega = 933$ eV). At this edge the chain and ladder holes cannot be distinguished because of its larger radiative broadening. However its higher energy allows larger Q values to be reached.

Figure 2 (left) shows an $L_c$ scan from $(H, K, L_c) = (0, 0, 0.075)$ to $(0, 0, 0.4)$ at $\omega = 933$ eV. The ladder hole crystal is again observed. No reflection was observed at either $L_c = 0.25$ or 0.20. Interestingly, however, we observed an incommensurate reflection at $L_c = 0.318 \pm 0.005$ (or $L_L = 0.454$ in ladder units). This reflection was mapped in the $(H, L)$ plane, shown in Fig. 2 (right), giving its coherence lengths $\xi_c = 1100 \pm 100$ Å ($\sim$ 400 chain units) along the chain direction and $\xi_a = 983 \pm 100$ Å, i.e. $\sim$ 87 neighbouring chains. It was also observed in the zero-hole sample LCCO at $L_c = 0.300 \pm 0.005$. This reflection was observed previously by Hiroi et al. [20] and identified, on the assumption that the chain structures are more flexible than the ladders, as a misfit strain reflection from the chain layer. We will accept this assignment and assume the modulation occurs in the chain.

Our central result is the “resonance profile” (RP) of these chain modulation peaks, i.e. their energy dependence through the Cu$L_{3/2}$ edge, shown in Fig. 3. These data were taken at $T = 20K$. In SCO the RP consists of a strong resonance peak at 933 eV preceded by a weak resonance at 930 eV. The former coincides with the doping-dependent sideband and indicates the presence of a significant hole modulation [3, 10]. The latter, occurring at lower energy, is likely due to the misfit strain modulation (see below). Evidently this chain Bragg reflection is not a simple misfit strain wave; it has a large charge modulation so has the character of a CDW. By contrast, the same weaker reflection in LCCO, also shown in Fig. 3, is much weaker and exhibits no hole resonance. In this sample the chain modulation appears to be a simple strain wave.

To characterize the chain modulation we wish to quantify the relative sizes of the charge and strain modulations. Because the two coexist they coherently interfere, which strongly influences the line shapes in Fig. 2.
FIG. 3: (a) A comparison of integrated Bragg intensity with XAS of SCO and LCCO. Black circles, red circles, and green circles and blue line are XAS, resonance profile (RP) of (0, 0, 0.318) of SCO, RP of (0.0, 0.300) of LCCO, and scattering simulation. The XAS are taken at room temperature (298 K) with E∥a while the RP at 20 K. (b) fD(ω) for hole and (c) fR(ω) for structural (see text for detail). Spectra were placed on an absolute scale by fitting to tabulated values [29] far from the edge.

recently Abbamonte [27] demonstrated a method for using this interference to determine the relative size, W, and phase φ of the two modulations. In this method one divides the atomic scattering factor into two parts, f(ω, ν) = fR(ω) + νfD(ω), where fR is the “raw” atomic scattering factor and fD is the scattering factor of the doped holes. These two quantities can be determined from doping-dependent XAS measurements, such as that in Fig. 1 (a, b), by applying the relation

\[ Im[n(ω, ν)] = -\frac{r_e \lambda^2}{2\pi V_{cell}} Im[\Sigma_i f_i(ω, ν)], \]

solving a system of equations at each energy point, and applying a Kramers-Kronig transform. Here Im[n(ω)] 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 atomic scattering factor. The integrated intensity of the charge reflection is proportional to the quantity |v_0 fD(ω) \exp iφ/2 + Q_0 f(ω, < ν>)|^2, where < ν > 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. A fit to the resonance profile yields values for φ and the ratio W = v_0/u_0. The latter is a measure of the degree to which the CDW is driven by interactions rather than structural effects [27].

To apply this method we used the data in Fig. 1 (b) to determine fR(ω) and fD(ω) for Cu[30] in this system. Because the Cu atoms in the chains and ladders cannot be distinguished in XAS we simply take < ν > = 0.25 for SCO and < ν > = 0 for LCCO and assume the resulting form factors are valid for all Cu atoms in the sample. The results are summarized in Figure 3. We find that the doped-hole form factor |fD| = 67 electrons per hole on the resonance maximum. That is, at this resonance a doped hole scatters as strongly as a Ho atom.

The best fit to the RP in SCO is shown in Fig 3 (a). Carrying out this fit, we find that the apparent two-peak structure of the RP is actually due to destructive interference between the charge and strain waves due to the phase offset between them. The fit yields the values W = 1.13Å⁻¹ and φ = -22.5°. By contrast, the RP for LCCO simply tracks its XAS spectrum. In this case a hole amplitude is not definable and the fit yields W ∼ 0 and φ undefined. In ref. [27] it was suggested that for a conventional Peierls CDW W ∼ 1Å⁻¹ whereas for a more “exotic” CDW, such as the static stripe in La1.875Ba0.125CuO4, W > 10Å⁻¹. We conclude that in LCCO the chain modulation is a pure misfit strain wave. In SCO, however, the modulation is a cooperative amplification of the misfit strain and an incipient CDW with the same wave vector.

This picture is further justified by the temperature dependence. Lc scans in both SCO and LCCO were carried out at different temperatures (see Fig. 4 (a) to (a-iii)). In SCO a pronounced decreased is observed upon warming, indicating that the modulation has some character of a CDW transition. Unlike a conventional CDW, however, the intensity never goes completely to zero; as the temperature rises it levels off to a constant value. In LCCO, by contrast, the peak intensity is virtually temperature-independent. This phenomenology is additional evidence that the chain modulation in LCCO is a simple misfit strain wave, but in SCO it is a cooperative effect between strain and a CDW.

In the case of SCO it was possible to determine φ, therefore we can sketch the relationship between the charge and strain modulations (Fig. 4 (b)). We find that the charges tend to accumulate on the “crest” of the strain wave. In a simple sinusoidal picture one might expect, by symmetry, that the charges would cluster in regions where the strain is either maximum or minimum, i.e. φ = ±90°. Evidently in the current case the symmetry is broken, most likely by strong anharmonicity of the modulation as evidenced by the large number of harmonics visible in electron diffraction [26].

The presence of a strain-stabilized chain CDW at higher temperature may explain the discrepancy between results of low-frequency dielectric spectroscopy [14] and
Raman scattering studies of this compound. Vuletić et al. [7] 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 [9]. Blumberg et. al [8], however, found evidence for the presence of a CDW even up to the highest measured temperature, 630 K. We propose here that the Raman results of Blumberg arise from fluctuations in this chain modulation, in which the CDW can persist to very high temperature because of the stabilizing effect of the misfit structure.

Finally, we point out an important connection between the wave vector of this reflection, the wave vector of the ladder hole crystal reported previously [9, 10], and the hole count in the chains and ladders of SCO [21]. We recently reported a reexamination of the hole density in this system with polarization-dependent XAS. We concluded that, in SCO, 2.8 out of 6 holes reside in the ladders [21], giving \( \delta_L = 0.2 \). This number is much higher than previous estimates [10, 28] and is more sensible given the ladder hole crystal wave vector of \( L_L = 0.2 \). Here we point out that this study also implies the chain hole density is \( \delta_c = 3.2/10 = 0.32 \), which is very close to the current observed wave vector of \( L_c = 0.318 \). In other words the wave vector of the chain modulation we report here is very close to its \( 4k_F \) instability. We therefore conclude that the chain modulation in SCO is an interplay between the misfit strain and the \( 4k_F \) instability of the chain holes.

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FIG. 4: (a-i) Temperature dependence of SCO and LCCO. (a-ii) L-scans for selected temperature, 20 K and 300 K, of (a-ii) SCO and (a-iii) LCCO. (b) Interplay between strain and charge modulation in SCO. Black and blue circles are the charge and strain modulation, respectively. The size of the circles represents the amplitude and the arrows represent the direction of the lattice distortion.

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