Inhomogeneous CuO_6 tilt distribution and charge-spin correlations in $La_{2-x-y}Nd_ySr_xCuO_4$ around the commensurate hole concentration

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Phononic and magnetic Raman scattering are studied in $La_{2-x-y}Nd_ySr_xCuO_4$ with three doping concentrations: $x\approx 1/8$, $y=0$; $x\approx 1/8$, $y=0.4$; and $x=0.01$, $y=0$. We observe strong disorder in the tilt pattern of the CuO_6 octahedra in both the orthorhombic and tetragonal phases that persist down to 10 K and are coupled to bond disorder in the cation layers around 1/8 doping independent of Nd concentration. The weak magnitude of existing charge-spin modulations in the Nd-doped structure does not allow us to detect the specific Raman signatures of lattice dynamics or two-magnon scattering around 2200 cm^{-1}.

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The evolution of ground state properties with carrier doping and the nature of electronic excitations in correlated systems continues to be a subject of intensive research.[1] After emerging as the mean field solution for the ground state at low hole concentrations in doped Mott-Hubbard antiferromagnets (AF),[2] stripes have become one paradigm for understanding the properties of high-T_c cuprates.[3] Extensive studies of incommensurate neutron scattering peaks have been performed on $La_{2-x}Sr_xCuO_4$(LSCO) crystals, and the development of magnetic fluctuations were related to the onset of superconducting order.[4] Transport measurements demonstrate that the charge degrees of freedom self-organize into quasi-one-dimensional (quasi-1D) structures in these materials.[5] It was shown that Nd substitution in LSCO and the proximity to the commensurate 1/8 doping level enhances the stripe correlations and static stripes were observed in $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ (LNSCO).[6] X-ray diffraction data also observed weak charge order superlattice peaks in this compound.[7]

Lanthanum cuprates are also characterized by disorder introduced by cation substitution and distortions of the CuO planes.[8] Above room temperature, LNSCO undergoes a transition from a high-temperature tetragonal (HTT) to a low-temperature orthorhombic (LTO) phase, and around 70 K a transition from the LTO to a low-temperature tetragonal (LTT) phase.[9,10] The LSCO system does not enter the LTT phase, but the orthorhombicity decreases with increase in Sr doping. The order parameter of these transitions is the tilt angle of the CuO_6 octahedra shown in Fig. 1. It was noticed in LNSCO that the LTO-LTT transition takes place over a range of temperatures, and that disorder in the striped phase leads to a glassy nature of the ground state.[11] The coexistence in L(N)SCO of several phases in a complex mixture was suggested by transmission electron microscopy.[12,13]

The importance of the local CuO_6 tilt dynamics for the superconducting properties characterized in cuprates by a short coherence length cannot be ignored. The stabilization of the LTT phase was observed to trace the suppression of superconductivity in Nd-doped LSCO (Ref. 10) and also in the related $La_{2-x}Ba_xCuO_4$ compounds.[14] A critical value of the tilt angle was associated with the stabilization of magnetic against superconducting order.[9] Rapid suppression of superconductivity, similar to that due to Cu substitution by nonmagnetic impurities, was observed with increasing the cation radius variance.[15] By providing information about the energy, scattering width, intensity, as well as symmetry of the excitations, Raman scattering has been powerful in studying the structural, electronic, and magnetic properties of cuprates.[16–19] Optical phonons can be used as local probes of fast changes in the charge distribution, and magnetic Raman scattering provides information about local AF correlations.[18,20] This was the case in related $La_{2-x}Sr_xNiO_{4+\delta}$ compounds[21,22] where the existence of fully developed striped phases is well established.[23]

Our study provides direct spectroscopic information about the LTO-LTT transition in LNSCO and local deviations from the average structure existent in Nd-doped and Nd-free LSCO structures. Strong local disorder in the octahedra tilts persists down to $T=10$ K and reveals strong disorder in the cation-oxygen layers. The distinct Raman signatures accompanying a transition to a state with deep spin/charge modulations are not observed in the temperature dependence of the two-magnon (2M) scattering around 2200 cm^{-1} and the *c*-axis-polarized phonons below 500 cm^{-1}.

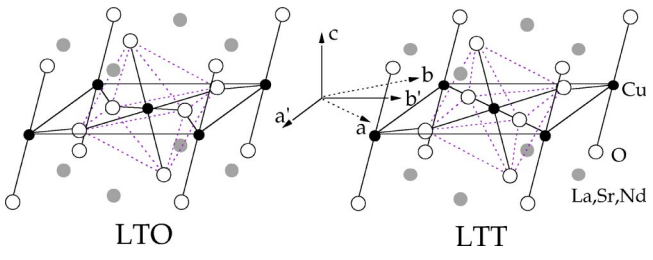

FIG. 1. Buckling of the Cu-O plane in the LTO and LTT phases and adjacent cation-oxygen layers. The a', b' axes are rotated by 45° with respect to the *a* and *b* coordinates. In a rigid approximation, the CuO_6 octahedra (shown by dotted lines) are tilted around the a' axis in the LTO and *a* axis in the LTT phase.

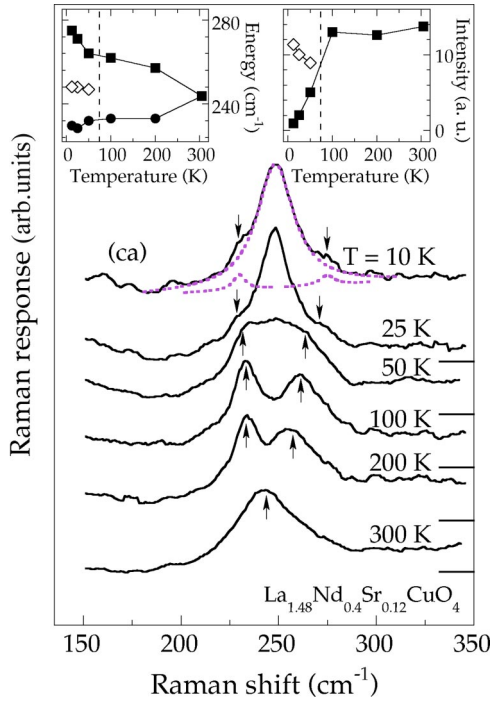

FIG. 2. Raman spectra of LNSCO with light polarization of the incoming and outgoing photons along the c and a axes show the temperature evolution of the apical oxygen vibrations. The arrows trace the peak positions of the orthorhombic components (a 3 Lorentzian fit is shown for the 10-K data). Insets: Temperature dependence of the energy and integrated intensity of the oxygen modes in the LTO (filled symbols) and LTT (empty diamonds) phases. The vertical dashed lines in the insets mark the LTO-LTT transition.

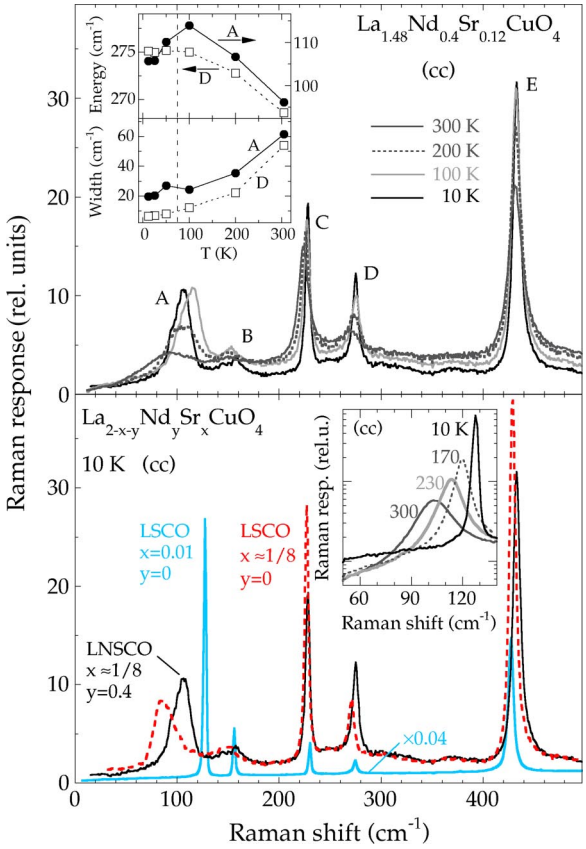

FIG. 3. Top: Temperature dependence in (cc) polarization of the five fully symmetric modes in LNSCO. Variation with temperature of the energy (upper inset) and the full width at half maximum (lower inset) of modes A (solid circles) and D (empty squares). Vertical lines in the insets correspond to the structural LTO-LTT transition. Bottom: 10 K Raman spectra in (cc) configuration for L(N)SCO. Inset: Temperature dependence of the intensity of mode A in $x=0.01$ LSCO. Note the semilog scale.

Single crystals of LNSCO, $x=0.01$ and $x\approx 1/8$ LSCO were grown by the traveling-solvent floating-zone technique. Raman spectra were taken from the (ac) and (ab) faces of $x\approx 1/8$ L(N)SCO and from the $(a'c)$ face of $x=0.01$ LSCO crystals as determined by x-ray diffraction. Unless otherwise stated the laser excitation energy was $\omega_{in}=1.92$ eV.

Raman spectra taken in the (ca) geometry provide direct information about tetragonal to orthorhombic distortions. In this polarization we probe phononic modes with B_{2g} and B_{3g} symmetries in the LTO phase, which become degenerate with E_g symmetry in the LTT phase. The temperature dependence of the modes around 250 cm^{-1} corresponding to the apical oxygen vibrations parallel to the Cu-O plane in LNSCO is shown in Fig. 2. We observe a broad peak around 245 cm^{-1} at room temperature which, with cooling, becomes resolved into two components. A new central peak can be seen at 50 K around 248 cm^{-1}, which gains spectral weight as the temperature is decreased to 10 K. While the total integrated intensity of the modes remains constant, we observe a redistribution of spectral weight among the three modes as a function of temperature. The split components become weaker but can still be seen as ''orthorhombic satellites'' of the central peak down to 10 K. The coalescence of the features into the 248 cm^{-1} mode signals the recurrence of a phase with tetragonal symmetry, which should be the expected LTT phase of LNSCO. However, the finite residual intensity of the satellites appearing on the tail of the broad central peak shows an incompletely developed LTT phase, and that even at 10 K there exists about 7% LTO phase (determined from the relative ratio of phonon intensities).

Raman data in (cc) polarization is well suited for the study of lattice dynamics due to weaker coupling to underlying electronic excitations. Group theory predicts five fully symmetric modes at $\mathbf{k}=0$ in each of the LTO and LTT phases, and this is what we observe in Fig. 3 for L(N)SCO crystals in (cc) geometry. These modes correspond to the tilt of the CuO_6 octahedra (mode A), the vibration of La/Sr/Nd atoms in the direction imposed by the CuO_6 tilt (mode B), and along the c-axis (mode C), the c axis vibrations of the in-plane O (mode D) and apical O atoms (mode E)[16,17] (modes C and E are the two fully symmetric modes predicted by group theory for the HTT phase). The above qualitative description indicates that we could expect a strong coupling between the lowest energy modes (A and B). These two modes can be distinguished because they remain much broader even at the lowest temperature in comparison with modes C–E, which harden and sharpen smoothly through the LTO-LTT transition. The temperature variation of modes

C and *E* inherited from the HTT phase is not as pronounced. The large variation in the energy and width of mode *A* above the transition, the softening below 70 K, as well as its energy around 110 cm^{-1} in agreement with neutron-scattering studies[24] show that this mode corresponding to the octahedra tilt is the soft mode of the structural changes. The apparently smooth decrease in energy in the LTT phase is peculiar because this space group is not a subgroup of the LTO group, and as a result, a true LTO-LTT transition is expected to be of first order. Although unresolved due to broadening effects, the large width of mode *A* around 70 K shows the coexistence of the LTO and LTT tilts, the latter appearing as a result of folding of the LTO *Z* point to the Γ point of the LTT phase as observed, for instance, in La_2NiO_4.[25]

To understand the surprising behavior of the tilt pattern as reflected in the LNSCO phononic data, a comparison with different materials from the same class is necessary. In the lower panel of Fig. 3 we show the 10 K (cc) polarized Raman spectrum of L(N)SCO. In particular, mode *A* at 128 cm^{-1} for $x=0.01$ LSCO has a full width at half maximum (FWHM) of 2.5 cm^{-1}. Note in the inset the strongly temperature-dependent intensity and width, which is a characteristic of a soft mode. For $x\approx 1/8$ LSCO the same phonon is around 85 cm^{-1} and its FWHM of about 23.5 cm^{-1} is larger than the width of mode *A* in the Nd-doped crystal where it is slightly below 20 cm^{-1}. Comparison of the relative phononic widths for both the soft mode and the *c*-axis vibrations shows that Nd doping of LSCO crystals and the closer proximity to the T' phase induced by Nd doping in the La_2CuO_4 structure cannot be responsible for the large observed broadening effects. Intrinsic phonon anharmonicity would lead to a broad mode A in $x=0.01$ LSCO, which is not the case. The tilt disorder across twin domains cannot be the cause of such dramatic effects because the volume fraction occupied by these boundaries is expected to be very small.[12,13] The 7% relative ratio of the orthorhombic satellites to the central peak in Fig. 2 may be consistent with such a small contribution. If the satellites are indeed due to twinning effects, the data show that at 10 K the larger LTT domains are separated by regions of pure LTO tilt. The absence of the broadening effects on the vibrations along the *c* axis points towards an ''anisotropic'' disorder relating primarily to bond randomness along directions parallel to the CuO planes.

Could the spin-lattice coupling or the interaction with the stripe-ordered carriers in CuO planes be the main cause of broadening? Stripe correlations are enhanced in LNSCO, which however displays a smaller width of mode *A*. Also, it is not clear how the *c*-axis polarizability would couple to quasi-2D magnetic properties of the CuO planes and why only modes *A* and *B* are affected by this interaction. In this sense one expects the in-plane atomic movements to be more sensitive to stripe ordering but we see no similar effects on mode *D*. Although less probable, spin-lattice-induced broadening cannot be completely ruled out, and the answer to this question lies in a Sr doping dependence of the (cc) polarized spectra. Our data can be reconciled, however, with recent studies of local structure in Nd-free and Nd-doped L(N)SCO systems.[26,27] Model analysis of the pair distribution function

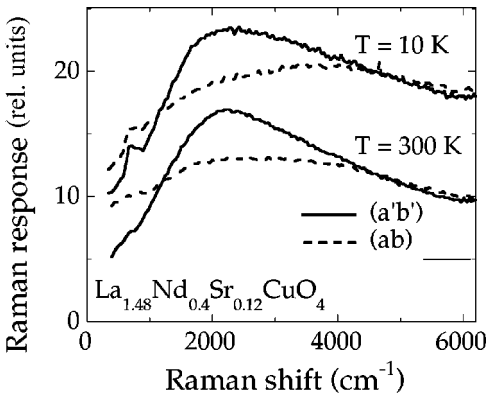

FIG. 4. High energy two-magnon Raman scattering spectra in (ab) and $(a'b')$ polarizations at 300 and 10 K taken with $\omega_{in}=3.05$ eV excitation energy. The 10 K spectra are offset.

from x-ray absorption fine structure suggest that in this material class the average structure determined by diffraction is different than the local pattern which is characterized by disorder in the CuO_6 tilt direction and magnitude.[26,27] The Raman data shown in Fig. 3 is a direct spectroscopic evidence that the L(N)SCO system is characterized by strong disorder in the cation layers. The locally fluctuating octahedra tilt is responsible for the observed effects.

Information about the relative magnitude of charge disproportionation in LNSCO can be gained by comparison with Raman spectra in compounds where charge modulations are well established. New Raman active modes have been observed in $x=0.33$ and 0.225 $La_{2-x}Sr_xNiO_4$ by Raman scattering.[21,22] Lowering of the crystal symmetry at the stripe ordering transition gives rise to folding of the Brillouin zone (BZ) and the appearance of extra $\mathbf{k}=0$ phononic modes. Charge localization creates nonequivalent Ni sites generating phonon ''splitting.'' The *c*-axis stretching modes corresponding to La and apical oxygens are split by 14 and 30 cm^{-1}, respectively.[21] Within the 3 cm^{-1} resolution imposed by the phononic widths, we do not observe such a split in our spectra. The ratio of the integrated intensities of the split oxygen modes in Ref. 21 is about the same as the ratio of doped versus undoped Ni sites. If we assume that the same relation holds for the case of cuprates, a factor of $\approx 1/8$ in split phononic intensity should have been seen in the spectra.[28] We conclude that any charge ordering taking place in our case is much weaker than in the related compounds referred to above. This does not contradict the x-ray-diffraction data[7] that estimated a factor of 10^2 relative difference between the magnitude of charge modulations in cuprates and nickelates.

For 2D magnetic square lattices a 2M peak in the $(a'b')$ geometry is expected.[18,20] Figure 4 shows 2M scattering around 2200 cm^{-1} at 300 and 10 K taken with the resonant $\omega_{in}=3.05$ eV incident frequency. As in other tetragonal 2D AF's we observe the spin-pair excitations in the expected geometry, which corresponds to B_{1g} symmetry in the HTT phase. Renormalization of the 2M excitation energy occurs across the spin ordering transition in the striped phase of $La_{2-x}Sr_xNiO_4$. The 2M Raman band around 1650 cm^{-1} characteristic of the undoped case[19] is not seen while the

spectra exhibit lower-energy peaks below the magnetic ordering temperature as a result of the new spin-exchange channels within and across the antiphase AF domains.[21,22] Our data in LNSCO shows only slight changes from 300 to 10 K emphasizing weak local spin modulations.

The differences observed between cuprates and nickelates can be related to the much stronger carrier self-confinement in the latter.[29] It has also been shown[30] that anomalies in phonon dispersions occur in $La_{2-x}Sr_xCuO_4$at points in the BZ commensurate with charge ordering wave vectors inferred from neutron-scattering studies. But as discussed, the charge modulation in Nd-doped structures, where the stripe correlations were shown to be stabilized, is too weak to produce observable changes (at $\mathbf{k}=0$) in the lattice unit cell on time scales longer than the phononic frequencies. The number of phononic modes observed can be explained solely in terms of LTO/LTT distortions. Our data, however, do not contradict the possible existence of charge modulations in the Cu-O plane. In fact, the dynamics in the cation-O layers and the magnitude of octahedra tilt disorder affects the carrier distribution, and our Raman results impose constraints on the magnitude of the charge modulations.

We studied lattice dynamics and magnetic scattering in stripe-ordered L(N)SCO crystals. The transition to the LTT phase in LNSCO is not complete as shown by the behavior of the split oxygen modes around 250 cm^{-1}. The large widths of the soft modes demonstrate a locally fluctuating pattern of the CuO_6 octahedra tilts. This disorder effect is even stronger in the Nd-free LSCO compound at $x\approx 1/8$, while it is not present for $x=0.01$ Sr concentration. Quantitative comparison with lanthanum-nickelate compounds shows that the magnitude of the existent spin/charge disproportionations in L(N)SCO are relatively weak, and that, as in other cuprates, the two-magnon excitation can be described within the usual high-temperature tetragonal structure.

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