Collective Density-Wave Excitations in Two-Leg $Sr_{14-x}Ca_xCu_{24}O_{41}$ Ladders

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Raman measurements in the 1.5–20 cm^{-1} energy range were performed on single crystals of $Sr_{14-x}Ca_xCu_{24}O_{41}$. A quasielastic scattering peak (QEP) which softens with cooling is observed only in the polarization parallel to the ladder direction for samples with $x = 0$, 8, and 12. The QEP is a Raman fingerprint of pinned collective density wave excitations screened by uncondensed carriers in the ladder structures. Our results suggest that transport in metallic samples, which is similar to transport in underdoped high-T_c cuprates, is driven by a collective electronic response.

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Competing ground states in low-dimensional doped Mott-Hubbard systems have been the subject of extensive research in recent years [1]. Two-leg Cu-O based ladder materials such as $Sr_{14-x}Ca_xCu_{24}O_{41}$ provide the opportunity to study not only magnetism in quasi-one-dimensional (1D) quantum systems but also carrier dynamics in an antiferromagnetic environment, with relevance to the phase diagram of high-T_c cuprates [2]. Magnetic correlations which give rise to a finite spin gap were predicted to generate an attractive interaction between doped carriers leading to superconductivity with a *d*-wave-like order parameter. Because of the quasi-1D nature of these systems, ground states with broken translational symmetry in which single holes or hole pairs can order in a crystalline pattern are also possible. The balance between superconducting and spin/charge density wave (DW) ground states is ultimately determined by the microscopic parameters of the theoretical models [3].

The single crystals of $Sr_{14-x}Ca_xCu_{24}O_{41}$ contain quasi-1D two-leg Cu_2O_3 ladder planes which are stacked alternately with planes of CuO_2 chains [4]. The ladder direction defines the *c* axis and the lattice constants of these two subsystems satisfy $10c_{\text{chain}} \approx 7c_{\text{ladder}}$. The nominal Cu valence in $Sr_{14-x}Ca_xCu_{24}O_{41}$ is +2.25, independent of Ca concentration. Transport and optical conductivity data suggest that Ca substitution induces a transfer of holes from the chains to the more conductive ladders [5,6]. The ladder carrier density was estimated from the optical spectral weight to increase from 0.07 for $x = 0$ to about 0.2 for $x = 11$ $Sr_{14-x}Ca_xCu_{24}O_{41}$ [6]. While $Sr_{14}Cu_{24}O_{41}$ is an insulator, a crossover to metallic conduction at high temperatures takes place around $x = 11$ and for $x = 12$ the *c*-axis *dc* resistivity has a minimum around $T = 70$ K separating quasilinear metallic and insulating behavior very similar to the case of high-T_c cuprates in the underdoped regime [7–10]. As opposed to $Sr_{14-x}Ca_xCu_{24}O_{41}$, the isostructural compound $La_6Ca_8Cu_{24}O_{41}$ contains no holes per formula unit. At high Ca concentrations superconductivity under pressure has been observed in $Sr_{14-x}Ca_xCu_{24}O_{41}$ crystals with $x \geq 11.5$ [11].

In the case of a DW instability, theory predicts the existence of phase and amplitude collective modes of the DW order parameter [12]. In an ideal system the current carrying phase mode can slide without friction [13], while impurities or lattice commensurability destroy the infinite conductivity and shift this mode to finite frequency as has been experimentally observed [14,15]. In addition, many well established DW compounds display a loss peak that has strongly temperature dependent energy and damping related to the *dc* conductivity of the material [16]. This screened longitudinal excitation has been usually observed in the transverse response by measurements of the complex finite frequency dielectric constant $\epsilon(\omega)$. Electronic Raman scattering directly probes the longitudinal electronic channel because the Raman response function, $\chi''(\omega)$, is proportional to $\text{Im}[1/\epsilon(\omega)]$ [17]. The existence of collective DW excitations is established for $Sr_{14}Cu_{24}O_{41}$ [18] by measurements of nonlinear conduction and relaxational dielectric response in the $10–10^6$ Hz region which displays a temperature dependent scattering rate that scales with the *dc* conductivity.

Important questions are whether DW correlations persist at higher carrier dopings in ladder structures and what are the Raman signatures of these collective excitations. Our low frequency Raman scattering results reveal longitudinal (screened) collective charge density oscillations between 250 and 650 K in $Sr_{14-x}Ca_xCu_{24}O_{41}$ crystals within a wide concentration range, $0 < x < 12$. The characteristic quasielastic scattering peak (QEP) we observed in the 1.5–8 cm^{-1} range above 300 K softens with cooling and is present only for polarization parallel to the leg direction. A two component hydrodynamic model [19] quantitatively accounts for the collective excitations seen in the Raman response for $Sr_{14}Cu_{24}O_{41}$. The observation

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of the QEP in $Sr_2Ca_{12}Cu_{24}O_{41}$ demonstrates that DW correlations are present at surprisingly high temperatures even in superconducting (under pressure) crystals.

We measured Raman scattering from freshly cleaved *ac* surfaces of $Sr_{14-x}Ca_xCu_{24}O_{41}$ and $La_6Ca_8Cu_{24}O_{41}$ single crystals grown as described in [6,9]. Excitation energies of 1.55 and 1.65 eV from a Kr^+ laser were used. The spectra were taken using a custom triple grating spectrometer and corrected for the spectral response of the spectrometer and detector. For measurements below 300 K the samples were mounted in a continuous flow optical cryostat and for above room temperature in a heat stage. Stokes and anti-Stokes spectra were taken to determine the temperature in the laser spot.

Figure 1 shows Raman spectra in *cc* polarization for $Sr_{14}Cu_{24}O_{41}$ and $Sr_2Ca_{12}Cu_{24}O_{41}$. The low frequency Raman spectra at high temperatures in both crystals look qualitatively similar. They are dominated by the presence of strong quasielastic scattering rising from the lowest measured energy of about 1.5 cm^{-1} and peaked about 7 cm^{-1} for temperatures around 620 K. With cooling the QEP shifts to lower frequencies and it gains spectral weight. Below $T \approx 450$ K the peak position moves below the instrumental cutoff energy and only the high frequency tail of the peak is observed.

The polarization dependence of the QEP is summarized in Fig. 2. For $Sr_{14}Cu_{24}O_{41}$ [Fig. 2(a)] the QEP is present in *cc* and absent in *aa* polarization. We do not observe the QEP in *cc* polarization for $La_6Ca_8Cu_{24}O_{41}$ [Fig. 2(b)] which contains no holes per formula unit. The presence of quasielastic scattering for $x > 0$ $Sr_{14-x}Ca_xCu_{24}O_{41}$ exhibiting the same polarization selection rules as shown in panels *c* and *d* of Fig. 2 proves that this feature is characteristic of these compounds at all Ca substitution levels. Applied magnetic fields up to 8 T influenced neither the energy of the QEP nor the modes seen in Figs. 2(a) and 2(b) at 12 cm^{-1} in $Sr_{14}Cu_{24}O_{41}$ and about 15 cm^{-1} in $La_6Ca_8Cu_{24}O_{41}$. We can conclude that the latter features are phonons. The unusually low energy of these modes which points towards a very high effective mass oscillator is interesting. These "folded" phonons appear as a result of chain-ladder incommensurability [4] that gives rise to a big unit cell.

The inset in Fig. 1 shows a typical deconvolution of the Raman data by a fit to a relaxational form:

$$\chi''(\omega) = A(T)\frac{\omega\Gamma}{\omega^2 + \Gamma^2}. \quad (1)$$

A second phenomenological term accounting for a small underlying electronic background was also used. The temperature dependent fitting parameters are shown in Fig. 3. An Arrhenius plot for the damping parameter Γ reveals an activated behavior of the form $\Gamma(T) \propto \exp(-\Delta/T)$ with $\Delta \approx 2100$ K and 2180 K for $Sr_{14}Cu_{24}O_{41}$ and $Sr_2Ca_{12}Cu_{24}O_{41}$, respectively. These energies are close to the activation energy of the *c*-axis *dc* conductivity for the $Sr_{14}Cu_{24}O_{41}$ crystal [9,20] shown in Fig. 3(a). The Raman QEP in $Sr_{14}Cu_{24}O_{41}$ traces to high temperatures the relaxational peak seen in transport [18], suggesting their common origin. Also, the frequency of the QEP, which is much lower than the thermal energy, the magnetic or *dc* activation gaps, points toward a *collective* rather than a single particle excitation.

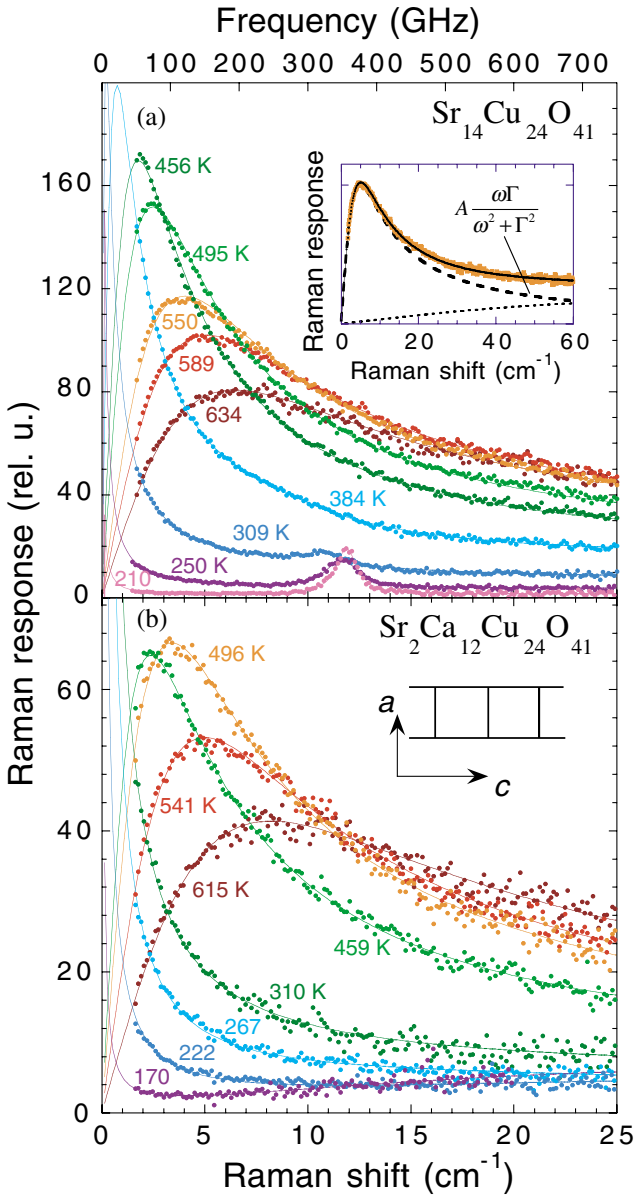

FIG. 1 (color online). Temperature dependent Raman response for *cc* polarization in $Sr_{14}Cu_{24}O_{41}$ and $Sr_2Ca_{12}Cu_{24}O_{41}$ taken with 1.55 eV excitation energy. Upper inset: typical fit of the Raman data with a relaxational form, Eq. (1), and a small contribution from an underlying background. For temperatures below 310 K the fits for $Sr_{14}Cu_{24}O_{41}$ also included the phonon around 12 cm^{-1}. Lower inset: Two-leg ladder structure.

For $Sr_2Ca_{12}Cu_{24}O_{41}$ the QEP is also present [Fig. 1(b)] and, surprisingly, in spite of a nonactivated *dc* conductivity which moreover turns metallic above 70 K, the relaxation is governed by the same activation energy. The *c*-axis conductivity data offer a clue for the

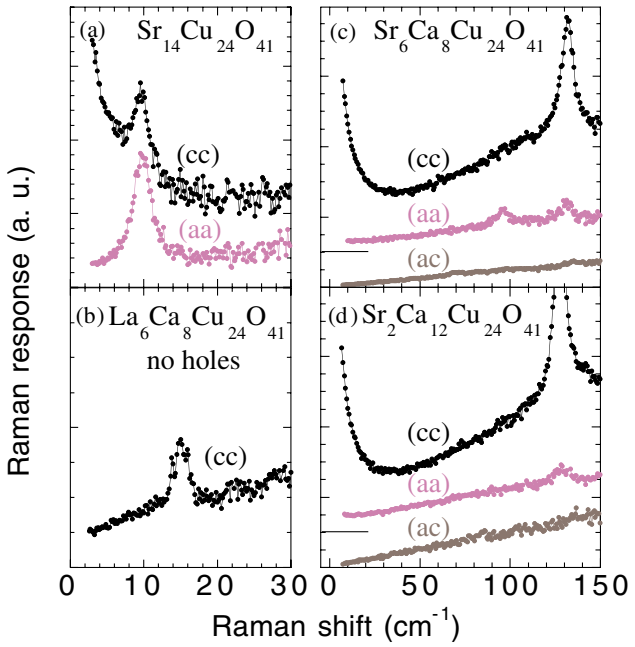

FIG. 2 (color online). Doping and polarization dependence at 295 K of the QEP in spectra taken with 1.65 eV laser excitation. (a) For $Sr_{14}Cu_{24}O_{41}$ the QEP is present in *cc* and absent in *aa* polarizations. (b) For $La_6Ca_8Cu_{24}O_{41}$ the QEP is not present. In panels (c) and (d) we observe the QEP for $x = 8$ and 12 $Sr_{14-x}Ca_xCu_{24}O_{41}$ only in *cc* polarization. The *aa* data is offset.

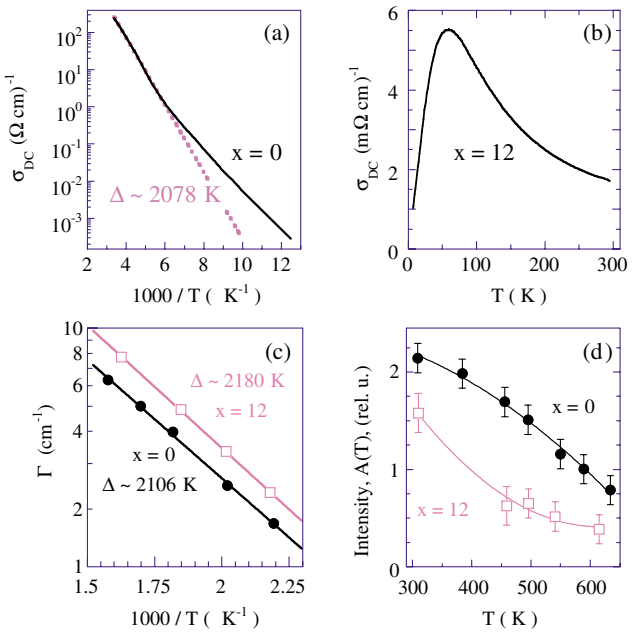

FIG. 3 (color online). Panels (a) and (b) show the temperature dependent *dc* conductivity for $x = 0$ and 12 $Sr_{14-x}Ca_xCu_{24}O_{41}$. Panel (c) shows Arrhenius temperature dependence of the relaxational rate Γ for $x = 0$ (filled circles) and $x = 12$ (empty squares). The variation of the quasielastic peak intensity, $A(T)$, with temperature (solid lines are guides for the eye) is shown in panel (d).

understanding of this behavior: in $Sr_{14}Cu_{24}O_{41}$ one can observe a relatively broad mid-IR peak [6,21] with an onset around 0.14 eV (1600 K). In $Sr_{14-x}Ca_xCu_{24}O_{41}$ this peak continues to be present [6] and remains a distinct feature concomitant with the redistribution of spectral weight below 1.2 eV as a result of carrier transfer from the chains to the ladder subsystems. We propose that the common mid-IR feature is responsible for the similarly activated behavior of the relaxation parameter $\Gamma(T)$ and observe that the energy scale of this peak (which is also observed in high-T_c cuprates [22]) is set by the ladder exchange energy $J \approx 1100$ K [23].

In the analysis of the Raman spectra shown in Fig. 1 we interpret the low frequency overdamped excitation as a DW relaxational mode in the longitudinal channel [18,19]. The interaction of longitudinal DW modes with normal (uncondensed) carriers resembles to some degree the problem of coupling of plasma oscillations to the longitudinal optical vibrations in doped semiconductors [24]. The longitudinal modes of one excitation interact with the electrostatic field produced by the other and as a result their bare energy gets renormalized due to screening effects. Essentially a feature which should be observed only in the longitudinal channel, the DW mode leaks into the transverse response due to the nonuniform pinning which introduces disorder, mixing the pure transverse and longitudinal character of the excitations [19]. This was seen in $Sr_{14}Cu_{24}O_{41}$ [18] as well as in other DW compounds [16].

The transverse response of the DW within a simple oscillator model is characterized by a pinning frequency Ω_0 and a DW spectral weight Ω_p^2. These parameters can be estimated from the microwave measurements and *c*-axis loss function as $\Omega_0 \approx 1$–4 cm^{-1} [25] and $\Omega_p \approx 3300$ cm^{-1} [21], respectively. A more realistic model would allow for a broad distribution of pinning frequencies Ω_0, extending over several decades, as inferred from the *ac* transport data [16,18]. Within a two-fluid model, we can evaluate the longitudinal response which accounts for screening effects and is relevant for Raman scattering [18]. The low frequency limit of this response reduces to the relaxational form of Eq. (1) with the intensity $A(T) \propto \Omega_p^2/\Omega_0^2$ and damping

$$\Gamma(T) \propto 4\pi\sigma_{dc}\Omega_0^2/\Omega_p^2. \quad (2)$$

The proportionality between Γ and the *dc* conductivity seen in Fig. 3 for $Sr_{14}Cu_{24}O_{41}$ is the result of normal carrier backflow which screens the collective polarization and dissipates energy, suffering lattice momentum relaxation [19]. The estimated Γ from Eq. (2) using a simple two-fluid model is affected by the broadening of the pinning frequency distribution and the fact that the contribution to the QEP comes only from the upper part of this distribution.

The strong similarities of the Raman results and the low energy scale of the quasielastic response for $x = 0$, 8, 12 in $Sr_{14-x}Ca_xCu_{24}O_{41}$ allow us to conclude that

collective DW correlations are also present at all Ca substitutional levels. While being able to quantify the results for $Sr_{14}Cu_{24}O_{41}$, we are still left with an intriguing picture: very similar finite frequency response along with qualitatively different *dc* conductivity data as the Ca concentration is increased. Clearly the observation of an activated relaxation rate in the metallic $x = 12$ compound is not consistent with Eq. (2), based on a simple two-fluid assumption. A speculative explanation for non-Fermi-liquid-like metallic *dc* conductivity in $Sr_2Ca_{12}Cu_{24}O_{41}$ could be based on a collective DW contribution. Ca substitution introduces disorder that shortens DW correlations and prevents effective pinning of the DW condensate. This may lead to a broadened Fröhlich-type component contributing to the *dc* conductivity, consistent with microwave data which are suggestive of the presence of an inhomogeneous collective response [26]. Another explanation for the metallic behavior in $Sr_2Ca_{12}Cu_{24}O_{41}$ could be based on an anisotropic and partially gapped Fermi surface in the context of increased dimensionality at higher Ca concentrations as suggested by *a*-axis conductivity [7] and x-ray absorbtion spectra [27]. Support for this conjecture comes from an angle resolved photoemission study [28] which shows that while for $Sr_{14}Cu_{24}O_{41}$ the gap is finite, for $Sr_5Ca_9Cu_{24}O_{41}$ the density of states rises almost to the chemical potential. This spectral weight transfer is enhanced with further increase in the ladder hole concentration [6]. Similar relaxation rates for $Sr_{14}Cu_{24}O_{41}$ and $Sr_2Ca_{12}Cu_{24}O_{41}$ might be reconciled with different transport properties assuming a strongly momentum dependent scattering rate and coupling of the DW to normal carriers. In this picture, carrier condensation in the DW state leads to a completely gapped Fermi surface resulting in an insulating behavior below $T = 70$ K. Irrespective of the exact microscopic model, strong similarities between local structural units and transport properties in Cu-O based ladders and underdoped high-T_c materials suggest that carrier dynamics in 2D Cu-O sheets at low hole concentration could be also governed by a collective DW response.

In conclusion, we have demonstrated the existence of DW correlations in doped two-leg $Sr_{14-x}Ca_xCu_{24}O_{41}$ ladders. We found Raman fingerprints of screened longitudinal collective modes in crystals with Ca concentrations from $x = 0$ to 12. A hydrodynamic model was used to quantitatively account for the existence of the charge collective mode in the insulating $Sr_{14}Cu_{24}O_{41}$ compound whose damping scales with the activated conductivity. This mode is also present in the superconducting (under pressure) $Sr_2Ca_{12}Cu_{24}O_{41}$ ladder. Our results demonstrate that the paired superconducting state competes in these materials with a crystalline charge ordered ground state.

Note added.—Vuletić *et al.* [29] recently studied the ladder compounds by far-IR optical spectroscopy. The authors have identified a long-range DW order for $x = 0$ only below 210 K which diminishes with doping and vanishes for x above 9. In contrast to their results, we detect local DW fluctuation from dynamical Raman response and find that the quasiparticle gap (at about 185 meV) is almost insensitive to hole concentration and persists to remarkably high temperatures.

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