Anisotropic charge modulation in ladder planes of $Sr_{14-x}Ca_xCu_{24}O_{41}$

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The charge response of the ladders in $Sr_{14-x}Ca_xCu_{24}O_{41}$ is characterized by dc resistivity, low frequency dielectric, and optical spectroscopy in all three crystallographic directions. The collective charge-density wave screened mode is observed in the direction of the rungs for $x=0$, 3, and 6, in addition to the mode along the legs. For $x=8$ and 9, the charge-density-wave response along the rungs fully vanishes, while the one along the legs persists. The transport perpendicular to the planes is always dominated by hopping.

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The physics of doped Mott-Hubbard insulators challenges conventional theories of metals and insulators.[1] The effect of strong Coulomb interactions produces a rich variety of exotic ordering phenomena, which have been the focus of intense scientific activity in recent years. The spin-chain and ladder self-doped compound $Sr_{14-x}Ca_xCu_{24}O_{41}$ has attracted much attention since it is the first superconducting copper oxide with a nonsquare lattice.[2] Theoretically, in doped two-leg Cu—O ladders, superconductivity (SC) is tightly associated with the spin gap and in competition with charge-density wave (CDW).[3] While both the spin gap and CDW were established in the ladders of $Sr_{14-x}Ca_xCu_{24}O_{41}$,[4–6] the relevance of these objects to electronic properties and superconductivity is still subject of intensive discussion. Recently, it was shown, on the basis of dielectric response data, that substitution of Sr^{2+} by Ca^{2+} gradually suppresses the insulating CDW phase, which eventually vanishes for $x>9$, Ref. 7. In contrast to these results, dynamical Raman response observed above RT for $x=0$ was assigned to CDW fluctuations and found to persist in the metallic phase of $x=12$, a system which becomes SC under pressure.[8]

It is of particular interest to learn more about the nature of CDW order in the spin ladders, which presents a nice experimental system of strongly interacting electrons. Although the ground state for $0 \leqslant x \leqslant 9$ reveals a number of well-known fingerprints of the conventional CDW, such as the pinned phason[9] and the broad dispersion at radio frequencies due to screening of the CDW by free carriers,[5–7] its origin is certainly more complicated, since the system does not undergo a *metal*-to-insulator but an *insulator*-to-insulator transition. The role of Ca substitution is another open issue. Suppression of the CDW phase was ascribed[7] to worsened nesting conditions[10] implying that the system becomes more 2D already at ambient pressure for large x. On the other hand, it was suggested that at ambient pressure (for all x) the charge dynamics is essentially one-dimensional[2,11] (1D) and that only the application of pressure induces the dimensional crossover from 1 to 2.[2]

In this Report, we address these important questions concerning the charge-ordered ground state in the ladders of $Sr_{14-x}Ca_xCu_{24}O_{41}$. Our results give evidence that the CDW is two dimensional with an anisotropic dispersion: the long-range charge order develops only in ladder planes, leading to a screened collective response along the both legs and rungs of the ladders.

The dc resistivity of $Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x=0$, 3, 6, 8, 9, and 11.5) was investigated in the temperature range 2 K $<T<$ 700 K. The complex conductivity was measured in the frequency range 0.01 Hz $<\nu<$ 10 MHz, using several setups. At frequencies $\nu=6$–10 000 cm^{-1} the complex dielectric function was obtained by a Kramers-Kronig analysis of the infrared reflectivity and by measurements of the complex transmission coefficient at the lowest frequencies 6–20 cm^{-1}. All experiments were conducted on high-quality single crystals along the three crystallographic axes: c (along the legs), a (along the rungs), and b (perpendicular to the ladder planes).

Figure 1 shows the conductivity spectra in a broad frequency range parallel to the rungs, $E \parallel a$. For $x=0$, 3, and 6 a strong T-dependent relaxation of the dielectric function $\varepsilon(\omega)=\varepsilon' + i\varepsilon''$ is found (see the insets). Fits by the generalized Debye expression $\varepsilon(\omega)-\varepsilon_{HF}=\Delta\varepsilon/[1+(i\omega\tau_0)^{1-\alpha}]$ yield the main parameters of this relaxation: the dielectric strength $\Delta\varepsilon=\varepsilon_0-\varepsilon_{HF}\approx 10^3$ (ε_0 is static and ε_{HF} is high-frequency dielectric constant), the symmetric broadening of the relaxation-time distribution given by $1-\alpha\approx 0.8$, and the mean relaxation time τ_0, which closely follows a thermally activated behavior similar to that of the dc conductivity. The dielectric response sets in below the phase transition temperatures $T_c=210$ K ($x=0$), 140 K ($x=3$), and 55 K ($x=6$) in the same manner as found parallel to the legs of the ladder (see Fig. 2 in Ref. 7), only the dielectric strength $\Delta\varepsilon$ along the a axis is much smaller than that for $E \parallel c$ (Fig. 2). This analogy suggests that the same mechanism, i.e., the screening of a CDW phason, is responsible for the ac properties in both directions of $Sr_{14-x}Ca_xCu_{24}O_{41}$, parallel to the legs and to the rungs of the ladders. For higher Ca content $x=8$ (not

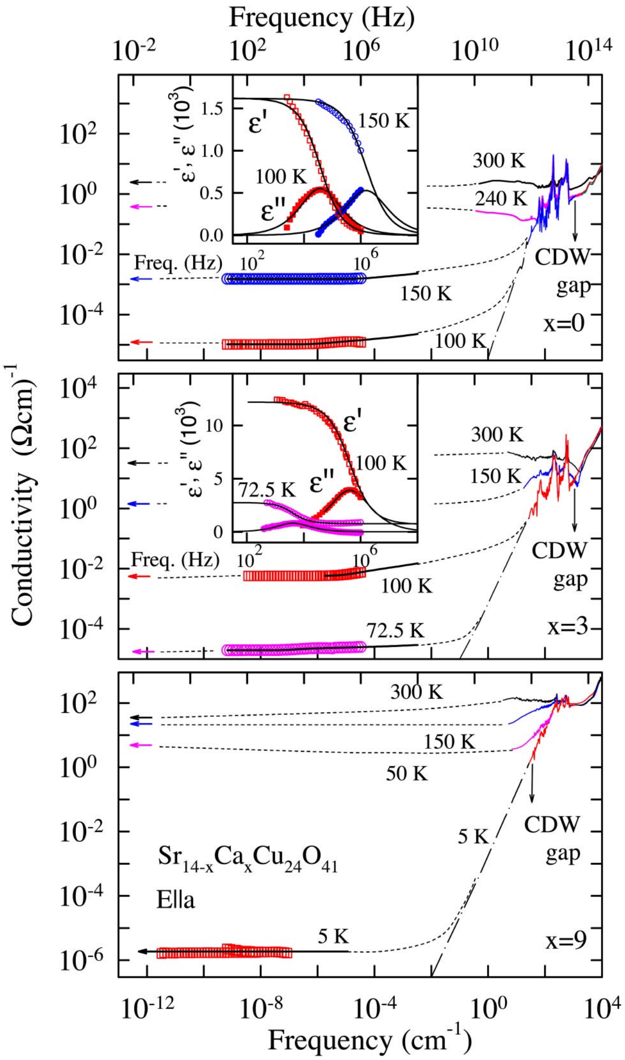

FIG. 1. (Color online) Broad-band spectra of conductivity and complex dielectric function (real ε' and imaginary ε'' parts) of $Sr_{14-x}Ca_xCu_{24}O_{41}$ along the a axis for Ca contents $x=0$, 3, and 9 at a few selected temperatures. Strong T-dependent relaxationlike dispersion of ε' and ε'' (insets, the full lines are from fits to the generalized Debye expression, see text), seen also as a smooth increase in the conductivity spectra, is a fingerprint of the screened CDW collective response. This response is observed at all $T<T_c$ for $x=0$ and 3, but not for $x=9$. Decrease of the infrared conductivity at low T corresponds to the opening of an energy gap. At the lowest T only the lowest-frequency phonon tail is seen and represented with the dash-dot ν^2 line. The arrows denote the dc conductivity. Dotted lines are guides to the eye.

shown) and 9 the analogy breaks down since no such dispersion is detected for $E\|a$ down to 4 K. In the third direction ($E\|b$), we find no signature of a CDW-related dielectric response at any Ca content.

The energy gap associated with the CDW formation is also seen in the infrared spectra for $E\|a$, where the conductivity at the lowest frequencies decreases upon cooling. The estimated gap values for different x correspond well to those determined from the activated dc resistivity (Fig. 3 and Table I); the values are also close to those found for $E\|c$. It is worth mentioning that Ruzicka *et al.*[12] have already sug-

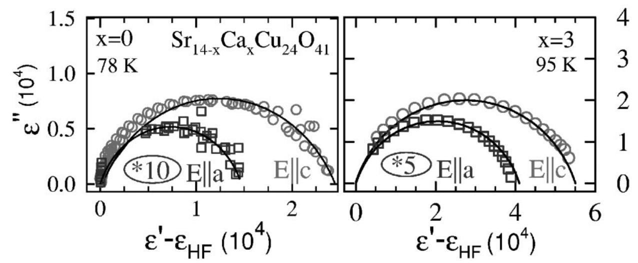

FIG. 2. Representative Cole-Cole plots of the dielectric dispersion, connected to the anisotropic collective CDW response of $Sr_{14-x}Ca_xCu_{24}O_{41}$ for $x=0$ (left panel) and $x=3$ (right panel) with the $E\|c$ (along legs) and $E\|a$ (along rungs). Note that plots for the response along the a axis are blown up 10 ($x=0$) and 5 ($x=3$) times. Full lines are from fits to the generalized Debye expression. The intersections of the arcs with $\varepsilon'-\varepsilon_{HF}$ axes indicate the values of $\Delta\varepsilon$.

gested from their optical spectra the existence of the metal-to-insulator phase transition both along the c and a axes. The phonon bands become less pronounced for higher Ca contents x due to screening by free carriers. At low T only a ν^2 contribution (Fig. 1, dash-dot line) of the low-energy phonon wing is observed.

We now compare the dc transport properties along all three directions. The upper two panels of Fig. 3 reveal that the phase transition temperatures T_c, when measured along the c and a axes, are equal in value and have the same dependence on Ca content x. The same holds for the energy gaps in the insulating phase above T_c and in the CDW ground state, which are both isotropic and show the same dependence on x. The energy gaps become larger when going from high temperatures into the CDW phase, indicating that an additional gap opens for $x \lesssim 6$ (Table I). While in a standard CDW, a transition from a metallic state to an insulating state is observed due to the opening of an energy gap,[10] in the present case the transport in the high-T phase is already nonmetallic. We explain this by electron-electron interactions within the ladder plane, leading towards a Mott insulator. We remind the reader that the band filling in the ladders is close to 1/2 and the on-site Coulomb repulsion is $U=3-4$ eV, so that $U/4t>1$. CDW order in such a system of strongly interacting charges might fall between the two well-defined limits: the CDW order of itinerant charges and the charge order of localized charges. The transition broadens substantially with increasing x, as reflected by an increase of the transition width and a decrease of the peak height of $d(\ln\rho)/d(T^{-1})$ (Fig. 3). The broadening might be attributed to disorder introduced by Ca substitution; a well-

TABLE I. CDW gaps Δ_{CDW} are from dc and ac measurements of $Sr_{14-x}Ca_xCu_{24}O_{41}$. Activation energies Δ_{HT} in the high-T insulating phase, are from dc measurements. Δ_{CDW} and Δ_{HT} are obtained with both the $E\|c$ and $E\|a$.

	$x=0$	$x=3$	$x=6$	$x=8$	$x=9$
Δ_{CDW} [meV]	130 ± 5	110 ± 5	30 ± 4	8 ± 1	3 ± 05
Δ_{HT} [meV]	90 ± 25	80 ± 20	30 ± 6	16 ± 2	10 ± 2

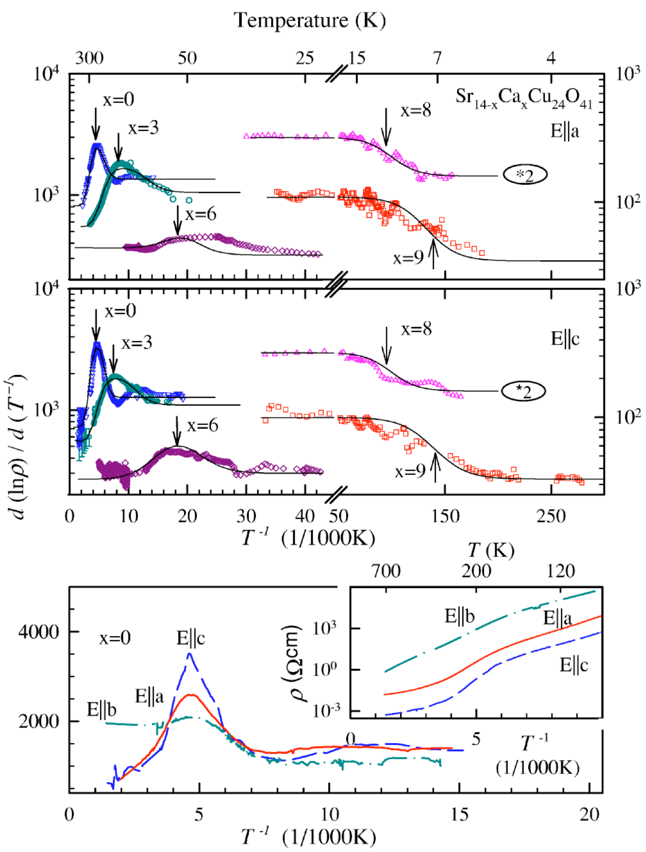

FIG. 3. (Color online) Upper and middle panels: dc resistivity logarithmic derivatives of $Sr_{14-x}Ca_xCu_{24}O_{41}$ for different Ca contents x along the c and a axes; $x=8$ is multiplied by 2, for clarity. Full lines are guides for the eye in the transition range, while above and below they are based on the fits to $\ln\rho$ vs T^{-1}. The arrows indicate the CDW phase transition temperature T_c. Lower panel: dc resistivity (inset) and corresponding logarithmic derivatives of $Sr_{14}Cu_{24}O_{41}$ along c (dashed), a (solid), and b (dash-dot line) axes. The peak in $d(\ln\rho)/d(T^{-1})$ as a signature of the phase transition is observed in the (c,a) ladder plane, but not perpendicular to them (along the b axis).

known effect in quasi-1D compounds.[13] Finally, for the pure compound ($x=0$) the dc resistivity along the third axis $E\parallel b$ (lower panel of Fig. 3) shows that the activation energy is much larger at high T (190 meV) and becomes smaller with decreasing temperature. For $x\geqslant 3$ (not shown) there is a single activation in the whole T range. This simple activation process indicates that the charge transport perpendicular to the ladder planes happens via nearest-neighbor hopping, as expected between disordered chains. Since no peak of $d(\ln\rho)/d(T^{-1})$ is found in the b direction, the CDW does not develop a long-range order in 3D. These findings are in accord with our optical data, as well as data by Ruzicka *et al.*,[12] which indicate T-independent insulating behavior along the b axis, distinct from the charge dynamics in the ladder planes.

Our observations have several implications. Generally, in a 1D metal one expects the development of a CDW only along the chain axis. Hence the existence of the loss peak as the signature of the screened phason relaxation in the perpendicular direction (along the rungs) is surprising.[14] However, in a 2D system of coupled chains, CDW develops according to the ordering vector Q. An ac electric field applied either parallel or perpendicular to the chains couples to the CDW developed along Q^{-1} resulting in an anisotropic dispersion.[15] Indeed, we find that the radio-frequency loss peak centered at τ_0^{-1} decays Arrhenius-like for both directions $E\parallel c$ and $E\parallel a$; these are well established features to characterize the CDW phason screened response. The dielectric strength of the loss peak found along the a axis is about 10 times smaller than the one observed along the c axis, which corresponds to the single-particle conductivity anisotropy. Based on this anisotropic dispersion in the radio-frequency range, we may extrapolate from the standard phason dispersion in 1D, which connects the screened loss peak centered at τ_0^{-1} to the unscreened pinned mode at Ω_0 (Refs. 7 and 14) to the 2D case. Assuming that CDW effective mass anisotropy is given by the band mass anisotropy,[10] we get an estimate of the pinning frequency of the CDW along the rungs: $\Omega_0^2(a)=\Omega_0^2(c)\times[\sigma_{dc}(c)/\sigma_{dc}(a)]\times[m_{band}(c)/m_{band}(a)]$. Taking $m_{band}(c)/m_{band}(a)\approx 0.1$, Ref. 16, $\Omega_0(c)=1.5-1.8$ cm^{-1}, Ref. 9 and $\sigma_{dc}(c)/\sigma_{dc}(a)\approx 10-30$, we find $\Omega_0(a)\approx 1.5-3.5$ cm^{-1}. Indeed, a thorough analysis of the relevant data in Ref. 9 identifies the pinned mode along rungs at $\Omega_0(a)=1.5$ cm^{-1}.

Our findings indicate that a CDW develops in the (c,a) ladders plane with a 2D long-range order. Further, we address the robustness of the CDW inside the phase diagram of $Sr_{14-x}Ca_xCu_{24}O_{41}$. Ca substitution quickly suppresses the length scale at which the 2D CDW in the ladder planes is developed, as the broadening of the CDW phase transition indicates. For $x=8$ the absence of the peak in dc resistivity logarithmic derivative suggests that the long-range order in planes is destroyed; subsequently the CDW is able to respond only along the legs of the ladders before disappearing completely from the phase diagram for $x>9$. The picture in which CDW fluctuations and a gap of 185 meV persist for all x (including metallic $x=12$) at $T>300$ K, Ref. 8, is difficult to reconcile with our data. This picture also meets difficulties because the changes of the unit cell parameters a and c (at RT), induced by Ca substitution, are small and comparable in size.[17] More importantly, we find that the conductivity anisotropy almost does not vary with Ca content at high T; it is T independent for $0\leqslant x\leqslant 8$, and becomes enhanced at low T for $x=9$ and 11.5.[2,11,18] No increase in dimensionality indicates that standard nesting arguments cannot explain the suppression of the CDW by Ca substitution. Therefore, we propose an alternative scenario based on the low-doped Mott insulator nature of the high-T phase from which CDW in the ladders originates. According to this scenario, CDW phase is suppressed by Ca substitution by the deviation from half filling (which might be induced by even slight increase of the hole transfer into the ladders), as well as by an increase in intraladder overlap integrals, when $U/4t$ decreases. Changes of the intersite Coulomb repulsion, due to an increased coupling between ladders and chains,[17] might also influence the stability of CDW phase. The similar rate by which charge order, associated with the 2D antiferromagnetic dimer pattern, in the chains is supressed, is striking.[19] The same arguments can be applied to explain gradual suppression of the high-T insulating phase. However, CDW phase is clearly less robust and the influence of disorder introduced by Ca substitution at Sr sites plays an important role. Tsuchiizu *et al.* have recently derived the model for two-leg extended Hubbard ladder with both on-site and intersite Coulomb repulsion.[20] They show that decreasing the latter, together with increasing the doping, destabilizes the CDW and p-density wave, which coexist in the phase diagram, in favor of the d-SC state.

The charge-ordered phase in the ladders of $Sr_{14-x}Ca_xCu_{24}O_{41}$ belongs to the class of broken symmetry patterns, predicted theoretically for strongly correlated electronic systems, including charge and spin density waves, both of the site and bond order, and of d symmetry.[20,21] However, there is no theoretical prediction about collective excitations in these phases (except for the CDW) and how they should respond to applied dc and ac fields. Wu *et al.*[21] showed that charge-ordered phases in two-leg ladders at low doping levels can develop only quasi-long-range order due to degeneracies appearing in the systems away from half filling. Indeed, the CDW transition in the ladders of $Sr_{14-x}Ca_xCu_{24}O_{41}$ is ten times broader (even in the Ca-free compound $x=0$) than expected,[13] indicating that true long-range order is probably never reached.

In conclusion, we demonstrated that within the ladder planes of $Sr_{14-x}Ca_xCu_{24}O_{41}$, the charge undergoes two-dimensional ordering, whose length scale is quickly reduced by Ca substitution due to an increased disorder. Similar to a CDW, the collective excitations of this charge order possess an anisotropic phasonlike dispersion, which we detect as broad screened relaxation modes along both the rungs and legs of the ladders. We propose that the charge-ordered phase vanishes at high Ca levels ($x>9$) due to an increased deviation from half filling and an increase in intraladder overlap integrals when $U/4t$ decreases. At this point, angle-resolved photoemission studies of momentum-resolved gaps and self-energies as a function of temperature and Ca substitution could help in understanding the mechanism responsible for producing this charge-ordered state. Also, further experiments have to clarify whether such a dispersion is a unique feature of the charge order in ladders or whether it is common to quasi-2D systems with charge order.

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1 M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998).
2 T. Nagata *et al.*, Phys. Rev. Lett. **81**, 1090 (1998).
3 E. Dagotto, Rep. Prog. Phys. **62**, 1525 (1999).
4 S. Katano, T. Nagata, J. Akimitsu, M. Nishi, and K. Kakurai, Phys. Rev. Lett. **82**, 636 (1999).
5 B. Gorshunov *et al.*, Phys. Rev. B **66**, 060508(R) (2002).
6 G. Blumberg *et al.*, Science **297**, 584 (2002).
7 T. Vuletić *et al.*, Phys. Rev. Lett. **90**, 257002 (2003).
8 A. Gozar *et al.*, Phys. Rev. Lett. **91**, 087401 (2003).
9 H. Kitano *et al.*, Europhys. Lett. **56**, 434 (2001).
10 G. Grüner, Rev. Mod. Phys. **60**, 1129 (1988).
11 N. Motoyama, T. Osafune, T. Kakeshita, H. Eisaki, and S. Uchida, Phys. Rev. B **55**, R3386 (1997).
12 B. Ruzicka, L. Degiorgi, U. Ammerahl, G. Dhalenne, and A. Revcolevschi, Physica B **259–261**, 1036 (1999).
13 S. Tomić, J. R. Cooper, W. Kang, D. Jérome, and K. Maki, J. Phys. I **1**, 1603 (1991).
14 P. B. Littlewood, Phys. Rev. B **36**, 3108 (1987).
15 The phason screened dielectric relaxation was only observed for ac electric field applied along the best conductivity axis of the quasi-1D compounds. In our best knowledge there was no attempt until now to measure it along the less conductivity axes.
16 M. Arai and H. Tsunetsugu, Phys. Rev. B **56**, R4305 (1997).
17 S. Pachot *et al.*, Phys. Rev. B **59**, 12 048 (1999).
18 T. Osafune, N. Motoyama, H. Eisaki, S. Uchida, and S. Tajima, Phys. Rev. Lett. **82**, 1313 (1999).
19 V. Kataev *et al.*, Phys. Rev. B **64**, 104422 (2001).
20 M. Tsuchiizu and Y. Suzumura, J. Phys. Soc. Jpn. **73**, 804 (2004).
21 C. Wu, W. V. Liu, and E. Fradkin, Phys. Rev. B **68**, 115104 (2003).