Anisotropic Charge Modulation in Ladder Planes of Sr\(_{14-x}\)Ca\(_x\)Cu\(_{24}O_{41}\)

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The charge response of the ladders in Sr\(_{14-x}\)Ca\(_x\)Cu\(_{24}O_{41}\) 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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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\(_x\)Cu\(_{24}O_{41}\) has attracted much attention since it is the first superconducting copper oxide with a non-square 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\(_x\)Cu\(_{24}O_{41}\) \(^4,5,6\), 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\(^8\).

Of particular interest is to learn more about the nature of CDW order in the spin ladders, which present a nice experimental system of strongly interacting electrons. Although the ground state for \(0 \leq x \leq 9\) 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\(^5,6,7\), its origin certainly is 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 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 (1D)\(^2,11\) and that only the application of pressure induces the dimensional crossover from one to two\(^2\).

In this Communication, we address these important questions concerning the charge-ordered ground state in the ladders of Sr\(_{14-x}\)Ca\(_x\)Cu\(_{24}O_{41}\). 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\(_x\)Cu\(_{24}O_{41}\) \((x=0, 3, 6, 8, 9\) and \(11.5\)) was investigated in the temperature range \(2\text{K} < T < 700\text{K}\). The complex conductivity was measured in the frequency range \(0.01\text{Hz} < \nu < 10\text{MHz}\), using several set-ups. At frequencies \(\nu=6 - 10000\text{cm}^{-1}\) 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 \(6 - 20\text{cm}^{-1}\). 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).

Fig. 1 shows the conductivity spectra in a broad frequency range parallel to the rungs, \(E//a\). For \(x=0, 3,\) and \(6\) a strong \(T\)-dependent relaxation of the dielectric function \(\varepsilon(\omega)=\varepsilon' + i\varepsilon''\) is found (see insets). Fits by the generalized Debye expression \(\varepsilon(\omega)_\nu=\varepsilon_0+\varepsilon_H F\Delta\omega/\left[1+(i\omega\tau_0)^{\gamma}\right]\) yield the main parameters of this relaxation: the dielectric strength \(\Delta\varepsilon=\varepsilon_0\varepsilon_H F\approx10^3\) (\(\varepsilon_0\) is static and \(\varepsilon_H F\) is high-frequency dielectric constant), the symmetric broadening of the relaxation-time distribution given by \(1-\gamma\approx0.8\), and the mean relaxation time \(\tau_0\), which closely follows a thermally activated behavior similar to that of the dc conductivity. The dielectric response sets in below the phase transition temperatures \(T_c=210\text{K} (x=0),\) \(140\text{K} (x=3),\) and \(55\text{K} (x=6)\) 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 \( E||c \) (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 \( \text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41} \), parallel to the legs and to the rungs of the ladders. For higher Ca content \( x=8 \) (not 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 of mentioning that Ruzicka et al. have already suggested 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 \( \nu^2 \) contribution (Fig. 1, dash-dot line) of the low-energy phonon wing is observed.

\[
\begin{array}{c|c|c|c|c|c|c}
\hline
x & 0 & 3 & 8 & 9 \\
\hline
\Delta_{CDW} [\text{meV}] & 130 \pm 5 & 110 \pm 5 & 30 \pm 4 & 8 \pm 1 & 3 \pm 0.5 \\
\Delta_{HT-T} [\text{meV}] & 90 \pm 25 & 80 \pm 20 & 30 \pm 6 & 16 \pm 2 & 10 \pm 2 \\
\hline
\end{array}
\]

TABLE I: CDW gaps, \( \Delta_{CDW} \), are from dc and ac measurements of \( \text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41} \). Activation energies, \( \Delta_{HT-T} \), in the high-\( T \) insulating phase, are from dc measurements. \( \Delta_{CDW} \) and \( \Delta_{HT-T} \) are obtained with both the \( E||c \) and \( E||a \).

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 \( c \)-axis and \( a \)-axis, 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 both are 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
non-metallic. We explain this by electron-electron interactions within the ladder plane, leading towards a Mott insulator. We remind that the band filling in the ladder is close to 1/2 and the on-site Coulomb repulsion is $U=3-4$ eV, so that $U/t>1$. 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 $d(ln \rho)/dT^{-1}$ (Fig. 3). The broadening might be attributed to disorder introduced by Ca-substitution; a well known effect in quasi-1D compounds. Finally, for the pure compound ($x=0$) the dc resistivity along the third axis $E||b$ (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 $x \geq 3$ (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 $d(ln \rho)/dT^{-1}$ is found in $b$-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 Ruzička et al., which indicate $T$-independent insulating behavior along $b$-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. However, in a 2D system of coupled chains, CDW develops according to the ordering temperature $T_c$. 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$_x$Cu$_{24}$O$_{41}$. Ca-substitution quickly suppresses the length scale at which the 2D CDW in the ladder planes is developed, as 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 gap of 185 meV persist for all $x$ (including metallic $x=12$) at $T>300$ K, Ref.8, is difficult to reconcile with

![Graph showing temperature dependence of resistivity](image)

**FIG. 3:** (Color online) Upper and middle panels: dc resistivity logarithmic derivatives of Sr$_{14-x}$Ca$_x$Cu$_{24}$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 $d(\ln \rho)/dT^{-1}$ is observed in the $(c,a)$ ladder plane, but not perpendicular to them (along $b$-axis).
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. More importantly, we find that the conductivity anisotropy almost does not vary with Ca content at high-$T$; it is $T$-independent for $0 \leq x \leq 8$, and becomes enhanced at low $T$ for $x=9$ and 11.5, respectively. 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 inter-site Coulomb repulsion, due to an increased coupling between ladders and chains, 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 suppressed, is striking.

Same arguments can be applied to explain gradual suppression of the CDW in the ladders of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$, belonging 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. However, there is no theoretical prediction about collective excitations in these phases (except for CDW) and how they should respond to applied dc and ac fields. Wu et al. 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$_x$Cu$_{24}$O$_{41}$ is ten times broader (even in the Ca-free compound, $x=0$) than expected, indicating that probably a true long-range order is never reached.

In conclusion, we demonstrated that within the ladder planes of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$, the charge undergoes a 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 phason-like 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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