Charge-density wave formation in \( \text{Sr}_{14} \text{Cu}_{24} \text{O}_{41} \)

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The electrodynamic response of the spin-ladder compound \( \text{Sr}_{14-x} \text{Ca}_x \text{Cu}_{24} \text{O}_{41} \) (\( x = 0.3, 9 \)) has been studied from radiofrequencies up to the infrared. At temperatures below 250 K a pronounced absorption peak appears around 12 cm\(^{-1}\) in \( \text{Sr}_{14} \text{Cu}_{24} \text{O}_{41} \) for the radiation polarized along the chains/ladders (\( E \parallel c \)). In addition a strongly temperature dependent dielectric relaxation is observed in the kHz - MHz range. We explain this behavior by a charge density wave which develops in the ladders sub-system and produces a mode pinned at 12 cm\(^{-1}\). With increasing Ca doping the mode shifts up in frequency and eventually disappears for \( x = 9 \) because the dimensionality of the system crosses over from one to two dimensions, giving way to the superconducting ground state under pressure.

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Low-dimensional quantum spin systems with spins and charges arranged in chains and/or ladders are under intensive study theoretically as well as experimentally \([1]\). A number of intriguing magnetic and electronic properties are inherent to those systems because of their specific arrangement of spins and charges; also the interplay between spin and charge degrees of freedom produces a variety of unusual phenomena \([2,3]\). Most important, it was predicted \([4,5]\) that due to the presence of a spin gap and paired charge carriers, doped even-leg ladder compounds can produce superconductivity reminiscent to that in the underdoped high-\( T_c \) cuprates; alternatively, they can undergo a charge-density-wave (CDW) transition.

The spin-ladder system \( \text{Sr}_{14-x} \text{Ca}_x \text{Cu}_{24} \text{O}_{41} \), where the superconductivity was discovered under pressure \([5]\), has attracted much attention in the last years. Its structure contains mutually interpenetrating subsystems of \( \text{Cu}_2\text{O}_2 \) chains and \( \text{Cu}_2\text{O}_4 \) two-leg ladders \([6,7]\). The parent compound \( \text{Sr}_{14} \text{Cu}_{24} \text{O}_{41} \) is inherently doped with holes and has a rather high dc conductivity along the \( c \) axis (ladder/chain direction) of about 300 (\( \Omega \text{cm})^{-1} \) at 300 K, with an anisotropy \( \sigma_c : \sigma_a : \sigma_b \approx 1000:100:1 \) \([10]\) (\( a \) denotes the rung direction and \( b \) is the direction perpendicular to the ladders’ plane). When Sr is substituted by the isovalent Ca the conductivity along all three axes increases. It is under debate whether the electronic properties of \( \text{Sr}_{14-x} \text{Ca}_x \text{Cu}_{24} \text{O}_{41} \) are determined by a single-particle response or can be influenced by collective effects, like CDWs \([1,2,3]\). Even in the `simple’ \( \text{Sr}_{14} \text{Cu}_{24} \text{O}_{41} \) it is not clear what the mechanism of dc conductivity is, how the holes redistribute between chains and ladders when temperature and doping are changed; what is the nature and the interrelation of spin gaps and optical pseudogaps, the role of collective excitations, and the effect of the dimensionality on charge transport and superconductivity.

In order to address these questions we have investigated the charge dynamics of \( \text{Sr}_{14-x} \text{Ca}_x \text{Cu}_{24} \text{O}_{41} \) by means of optical spectroscopy. In this Letter we present clear evidence that a CDW forms in this quasi-one dimensional compound. Increasing the dimensionality by Ca doping and pressure suppresses the CDW ground state and makes the system superconducting.

The high-quality single crystals (cylinders of about 5 mm in diameter and 7 mm long) were grown by a traveling-solvant floating-zone method. For the dc resistivity measurements four electrical contacts to the sample were obtained with silver paste applied directly on the surface and heated to 600 K in oxygen. In the radiofrequency range (1 Hz to 1 MHz) the spectra of the real and imaginary parts of the dielectric constant \( \epsilon' \) and \( \epsilon'' \) were obtained from the complex admittance measured at 60 K \(< T < 110 \) K by a technique described in \([4]\). For frequencies 5 to 25 cm\(^{-1}\) a coherent source quasi-optical spectrometer was utilized for direct measurements of \( \epsilon' \) and \( \epsilon'' \) \([5]\). From the far infrared (FIR) up to 10,000 cm\(^{-1}\) we determined the polarized reflection by a Fourier transform spectrometer. The combined data sets were analyzed by the Kramers-Kronig relations in order to obtain the spectra of \( \epsilon' + i\epsilon'' \) were obtained from the complex admittance measured at 60 K \(< T < 110 \) K by a technique described in \([4]\). For frequencies 5 to 25 cm\(^{-1}\) a coherent source quasi-optical spectrometer was utilized for direct measurements of \( \epsilon' \) and \( \epsilon'' \) \([5]\). From the far infrared (FIR) up to 10,000 cm\(^{-1}\) we determined the polarized reflection by a Fourier transform spectrometer. The combined data sets were analyzed by the Kramers-Kronig relations in order to obtain the spectra of \( \epsilon' + i\epsilon'' \). In addition, the non-linear transport of \( \text{Sr}_{14} \text{Cu}_{24} \text{O}_{41} \) was investigated at various temperatures.

The frequency dependences of the \( c \)-axis conductivity and the real and imaginary parts of the dielectric constant of \( \text{Sr}_{14} \text{Cu}_{24} \text{O}_{41} \) are displayed in Fig. 1. Our findings agree with previous infrared experiments \([1,2,3,7]\). At 300 K the conductivity is Drude-like and coincides with the dc values. Weak phonon features are seen below 1000 cm\(^{-1}\), together with a bump around 2000 cm\(^{-1}\).
which is caused by the holes in the ladders \[\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}\]. Lowering the temperature, the overall conductivity from dc up to the FIR decreases making the phonons more pronounced; the bump loses its intensity. The new features we have observed are the intensive mode in the FIR range at 10–15 cm\(^{-1}\), and a strongly temperature dependent relaxation in the radiofrequency spectra of \(\epsilon'(\omega)\) and \(\epsilon''(\omega)\). No signs of the FIR mode are found in the a and b directions \[13\]. Predictions of a mode existing below 50 cm\(^{-1}\) were made earlier on the basis of infrared measurements in pure \[\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}\] (Fig. 1) and Ca-doped \[\text{Sr}_{14-x}\text{Cu}_{24}\text{O}_{41}\] (Fig. 1), and is pinned by imperfections (plus a Drude term for free carriers), it becomes more complicated at low temperatures \[15\].

The radiofrequency relaxation is clearly observed as a peak in the \(\epsilon''\) spectrum accompanied by a strong dispersion of \(\epsilon'\). These spectra can be described phenomenologically in terms of a generalized Debye expressions

\[\epsilon'(\omega) + i\epsilon''(\omega) = \Delta\epsilon/[1 + (i\omega\tau_1)^{1-\alpha}]\]  \(\text{Eq. (1)}\)

Here \(\Delta\epsilon\) is the strength of the relaxation, \(\tau_1\) is a mean relaxation time and \(1 - \alpha\) describes the relaxation time distribution. The solid lines in Fig. 1 result from fits of the spectra by Eq. (1). The so-obtained temperature dependences of the relaxation parameters are shown in Fig. 2 together with the dc conductivity of \(\text{Sr}_{14-x}\text{Cu}_{24}\text{O}_{41}\) (Fig. 2). We ascribe the 12 cm\(^{-1}\) mode to the CDW which develops on the ladders, where the majority of delocalized charges sit \[12\], and is pinned by imperfections; correspondingly, we assign the low frequency mode to the CDW relaxation broadened due to normal carriers, which flow around the pinned CDW and produce screening currents. Before we come to a detailed analysis, let us summarize the arguments for our interpretation: (a) It is unlikely that the discovered FIR mode is of simple phonon origin. While practically no change is seen in the phonon spectrum of \(\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}\) (above 100 cm\(^{-1}\)) when going from \(x = 0\) to \(x = 3\) \[13\], this mode shows a strong shift from 12 to 23 cm\(^{-1}\) (Fig. 1) and disappears with further doping (\(x = 9\)). We also rule out that the resonance is produced by pairs which form a correlated Luttinger liquid – a possibility proposed recently \[10\] – because the mode appears at elevated temperatures and cannot be fitted by the corresponding expressions. (b) The CDW is one of the possible ground states in a spin-ladder system like \(\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}\) \[11\] where the electronic bands are essentially of one-dimensional character \[20\]. (c) We observe the CDW-related absorptions only along the highly conducting c axis. (d) As expected for the formation of a CDW \[21\], experimental indications for the charge order \[10\] and lattice superstructure \[22\] are seen in the ladders of \(\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}\). The phonon spectrum shows signatures of a Brillouin zone folding below 200 K \[13\] which gives evidence for a lattice superstructure. (e) The resonance at 12 cm\(^{-1}\) is characterized by an enhanced effective mass, typical for collective excitations like the CDW. (f) We do not observe any resonance for \(x = 9\) when the system loses its one-dimensionality \[23\].

We assign the low-temperature decrease of the spectral weight in the FIR (below 1000 cm\(^{-1}\), see Fig. 1 and \[14\]) to the opening of a CDW pseudogap \(E_g/hc \approx 2000\) cm\(^{-1}\) (i.e., \(E_g \approx 0.27\) eV) and determine the CDW
mean-field temperature $T_{\text{CDW}}^{MF} = E_g/3.5k_B \approx 900$ K; this implies that CDW fluctuations should be observed well above the room temperature. Similar rather high mean-field temperatures were estimated in other quasi one-dimensional conductors like TTF-TCNQ ($T_{\text{CDW}}^{MF} \approx 450$ K) or $K_{0.3}$MoO$_3$ (330 K) [22]. The pseudogap should govern the activated behavior of the dc conductivity (Fig. 2. $170 \, K < T < 250 \, K$). The fact that $\sigma_{dc}(T)$ is not simply activated for $250 \, K < T < 300 \, K$ can be explained with CDW fluctuations which produce a collective contribution to the dc transport. This sort of paraconductivity was also detected in other one-dimensional CDW conductors, like $K_{0.3}$MoO$_3$ or TTF-TCNQ [27].

Below approximately $170 \, K$ the activation energy of $\sigma_{dc}(T)$ changes from $E_g = 0.27 \, eV$ to 0.12 eV. A number of magnetic, electronic and structural properties display an anomaly around $170 \, K$ [19,23], which may indicate some type of phase transition. We suggest that this transition is due to a second CDW which develops in the chain sub-system of Sr$_{14}$Cu$_{24}$O$_{41}$. Mobile holes in the chains, essential for the CDW formation, have been suggested on the basis of ESR measurements [3]. The additional peak observed in the microwave range at 1.7 cm$^{-1}$ for $T < 170 \, K$ [33], shown in Fig. 1, thus corresponds to the second pinned CDW mode; its spectral weight is much smaller compared to the FIR mode, due to the lower charge concentration in the chains. Similar to the FIR mode reported here, this microwave resonance is seen in pure Sr$_{14}$Cu$_{24}$O$_{41}$ and for small Ca doping of $x = 3$ while is disappears for larger $x$. We note that signs of this resonance lying below 8 cm$^{-1}$ are also clearly seen in our low temperature reflectivity spectra [3] for $x = 3$.

Although the presented results clearly point towards the collective CDW ground state in the spin-ladder system Sr$_{14}$Cu$_{24}$O$_{41}$ and can even be well described by Littlewood’s model, a few open questions remain. A signature of an absorption line at 14 cm$^{-1}$ was already observed in the Raman spectra at room temperature [18]. While the CDW phase fluctuations should be infrared active and the CDW amplitude fluctuations only Raman active [21], it is likely that both excitations mix due to symmetry breaking; hence the resultant excitation is observable by both techniques (but still only along the conducting $c$ direction). Interestingly, the Raman mode seems to be pinned even at 300 K, while we do not see any sign of the optical resonance at this temperature probably due to the large screening by free carriers. The CDW can be depinned by an external electric field leading to non-linear transport [21]. We do observe a field-dependent conductivity in our system, however, the non-linearity is very small and the threshold current cannot be clearly determined. An estimate of the threshold field $E_T \approx 0.1 \, V/cm$ (Fig. 2) cannot be related to the pinning frequency $\Omega_0$ by the standard expression $m^*\Omega_0^2 = 2eE_T/\lambda$, with the wavelength $\lambda$ of the CDW taken of the order of the distance between Cu atoms on the ladder ($\approx 4 \, Å$); a similar discrepancy was noticed for the microwave mode [3]. The effective mass $m^* \approx 200m_0$ is small compared to standard CDW materials where up to the order of ten thousand has been reported [21]. The mentioned points can be ascribed to an unusual CDW state formed in Sr$_{14}$Cu$_{24}$O$_{41}$, as compared to typical one-dimensional conductors. This is most likely due to the two interacting sublattices on the chains and on the ladders. Since each is characterized by magnetic, structural, and charge ordering, the ground state of the system is determined by a mixture of correspondent order parameters leading to excitations which may be rather unconventional. Detailed low-energy studies of the interplay between the spin and charge subsystems in (Sr,Ca,La)$_{14}$Cu$_{24}$O$_{41}$ for different doping and in magnetic fields are required. In addition, the internal deformations of the CDW and the pinning mechanism may be more complicated in this system of interacting chains and ladders compared to strictly one-dimensional compounds. It is not surprising that the observed CDW phenomenon is strongly modified compared to the conventional CDW compounds.

In summary, we presented evidence of a charge-density wave formation in the ladder subsystem in Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$. For $x = 0$ we observed a pinned CDW mode at 12 cm$^{-1}$ below 250 K and a strongly temperature dependent relaxation in the radiofrequency range due to single-particle screening currents. The pinned mode shifts up to 23 cm$^{-1}$ for $x = 3$ and disappears when the Ca doping reaches $x = 9$. From the two competing ground states (density wave and superconductivity) expected for spin-ladder compounds, the CDW instability dominates when Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ is highly one-dimensional ($0 \leq x < 3$) but shows a tendency to disappear when stronger Ca doping ($x = 9$) makes it more two-dimensional. When external pressure increases the coupling (and thus the dimensionality) even further, the system finally becomes superconducting.

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Fig. 1. (a) Frequency dependent conductivity of Sr$_{14}$Cu$_{24}$O$_{41}$ measured at different temperatures along the highly conducting $c$ direction. The arrows indicate the dc conductivity; the solid lines represent fits by the generalized Debye relaxation, the dashed lines are guides to the eye. The peak around 1 cm$^{-1}$ corresponds to the data from [5]. The inset shows how the shape of the pinned CDW resonance varies with temperature.

(b) Real and imaginary parts of the dielectric constant as a function of frequency; the solid lines are fits by the generalized Debye expression. The inset exhibits the evolution of the spectral weight in the FIR range with decreasing temperature: the dotted line shows the pinned CDW mode of Sr$_{14}$Cu$_{24}$O$_{41}$. Fig. 2. Temperature dependences of the dc conductivity of Sr$_{14}$Cu$_{24}$O$_{41}$ along the $c$ axis and of the parameters which characterize the dielectric relaxation at radiofrequencies [Eq. (1)]: the inverse time $1/(2\pi\tau_i)$ and the strength $\Delta\varepsilon$ of the dielectric relaxation, and the parameter $1-\alpha$ which describes the symmetrical broadening of the relaxation time distribution. The dc conductivity is thermally activated $\sigma_{dc} \propto \exp\{-\Delta/k_BT\}$ between 250 K and 170 K with an energy gap $\Delta \approx 0.27$ eV ($\Delta/hc \approx 2200$ cm$^{-1}$) in agreement with the onset of the low-temperature conductivity spectrum in Fig. 1 (inset of the lower panel) and is identified as a pseudogap due to CDW in the ladders. Below 170 K a change of the activation energy to $\Delta \approx 0.12$ eV is observed due to the onset of a CDW in the chains. The solid lines correspond to an activated behaviors of $\sigma_{dc}(T)$ and $1/\tau_i(T)$.

The inset shows an electric field dependent resistance of Sr$_{14}$Cu$_{24}$O$_{41}$ measured along the $c$ direction at 87 K.
Conductivity ($\Omega^{-1}\text{cm}^{-1}$)

Frequency (cm$^{-1}$)

$\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41} E||c$

Conductivity ($\Omega^{-1}\text{cm}^{-1}$)

Frequency (Hz)

$\varepsilon''/1000$

Frequency (Hz)
