Charge density waves in Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$: electron correlations vs. structural effects

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We report inelastic light scattering experiments in the spin-chain and ladder system Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$. A depletion of an electronic background is observed for 0 ≤ x ≤ 5 at low temperatures and with light polarization both parallel to the leg and rung directions. This points to the formation of 2D charge density wave in the ladders. Furthermore, the Ca-substitution dependence of the 305- and 249-cm$^{-1}$ modes, sensitive to the lattice modulations of the respective chain and ladder system, suggests that the charge dynamics in the ladders is strongly influenced by the structural incommensurability.

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The spin-chain and ladder compound Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ (SCCO) has attracted intense theoretical and experimental attention over the last years [1]. This interest is triggered by the observation of a superconducting phase for x = 13.6 under pressure [2] and an unconventional charge density wave (CDW) state for x < 9 [3, 4, 5, 6, 7, 8, 9]. SCCO is built up by alternating layers of edge-sharing CuO$_2$ chains and two-leg Cu$_2$O$_2$ ladders in the ac plane [10]. These two sublayers are separated by (Sr,Ca) atoms, and stacked along the b axis. The chains and ladders run along the c axis and their unit cell parameters differ by a factor of $\sqrt{2}$ along this direction. This misfit leads to an incommensurate modulation of the two sublattices. In addition, SCCO is intrinsically (x = 0) hole-doped with a formal Cu valence of 2.25.

For x = 0 the chain system shows a dimerization and charge ordering for temperatures below 200 K [11, 12]. Specific modulations of the chain lattice are responsible for the formation of the dimers between two copper spins separated by one Zhang–Rice singlet [11, 12, 13]. The substitution of Sr by isovalent Ca leads to the instability of the dimerization and charge ordering [14]. Concerning the electronic state of the ladder, several spectroscopy studies [3, 4, 5, 6, 7, 8, 9] provide evidence for a CDW. In detail, however, there is a profound disagreement in the interpretation of the experimental data. Far-infrared (IR) results [5, 6, 7] show that the insulating CDW is two dimensional with an anisotropic dispersion and vanishes for x > 9. In contrast, a dynamic Raman response assigned to CDW fluctuations is shown to persist in the metallic phase of x = 12 [4]. Very recently, resonant X-ray scattering measurements [8, 9] reported the observation of a hole crystal at x = 0, 10, 11, and 12 with a commensurate wave vector, which is attributed to electronic correlations [15, 16]. Noticeably, the hole crystal is absent with intermediate dopings 1 ≤ x ≤ 5. The conflicting spectroscopy results highlight the unusual electronic and structural properties of the ladder and point to an intimate interplay between holes and lattice modulations as recent experimental and theoretical works suggest [17, 18, 19, 20].

Up to now, several Raman measurements have been reported on magnetic and charge excitations while focusing mainly on either the high-frequency or the low-frequency regime [3, 4, 21, 22, 23]. The intermediate frequency regime has not been carefully investigated in spite of its potential relevance to the charge ordered state in the ladders.

In this study, we report Raman scattering measurements of Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$. We highlight a pseudogap behavior of an electronic background for 0 ≤ x ≤ 5 with incident and scattered light scattering polarizations both parallel and perpendicular to the ladder direction and its disappearance for x = 12. This is attributed to the formation of a 2D CDW. In addition, we found that the substitution dependence of the CDW is closely associated with that of charge ordering in the chain system by accompanying lattice modulations of both subsystems. This suggests that the CDW relies on the mutual interaction of charge correlations and lattice incommensurability.

Single crystals were grown by a floating zone method [24]. The experiments were performed using the λ = 514.5 nm excitation line of an Ar$^+$ ion laser (laser fluency less than 20 W/cm$^2$). Thus, the incident radia-
tion did not increase the temperature of the samples by more than 1 K. The scattered spectra were collected by a DILOR-XY triple spectrometer and a back-illuminated CCD detector in a quasibackscattering geometry.

![Graph](image-url)

**FIG. 1:** (online color) Raman spectra of Sr$_{14}$Cu$_{24}$O$_{41}$ in (cc) and (aa) polarizations at 10 K and 350 K, respectively. A strong renormalization is observed in the electronic background for frequencies below 400 cm$^{-1}$ at low temperatures.

Raman spectra are displayed in Fig. 1 in (cc) and (aa) polarizations at 10 K and 350 K each. At 350 K we can resolve 31 peaks as one-phonon scattering in the frequency range up to 700 cm$^{-1}$. The broad peaks observed between 700-1300 cm$^{-1}$ are due to two-phonon scattering. A factor group analysis based on the independent chain (Ccmm) and the ladder (Fmmm) subsystem yields $\Gamma = 6A_{g}(aa, bb, cc) + 6B_{1g}(ab) + 4B_{2g}(ac) + 2B_{3g}(bc)$ [21]. The extra 13 modes should be attributed to the composite unit cell with the crystal symmetry of Pcc2. With decreasing temperature all peaks become sharp and grow considerably in intensity, suggesting an enhanced localization of charges, i.e., holes. Remarkably, the intense 376- and 391-cm$^{-1}$ modes appear below the charge ordering temperature at 200 K. This implies that they do not rely on the chain and ladder incommensurability. Furthermore, they are not zone-folded modes because they have no counterpart modes at high temperatures and have strong intensity in contrast to an usual zone-folded mode. Therefore, we propose that they are related to a structural symmetry change around 200 K as a neutron diffraction study indicates [19]. Our result suggests that charge ordering leads to an enhanced, additional deformation of the lattice. In the literature [21, 22, 23] the origin of several peaks at 269, 496, and 569 cm$^{-1}$ (indicated by arrows) is controversially discussed in terms of magnetic excitations. However, we assign them to phonons. This is because (i) in an external field they exhibit neither a shift of the peak energy nor a splitting, and (ii) the observed narrow peaks are not compatible with the pronounced dispersion of the triplet excitations [25].

The spectra show an important feature at low temperatures and for frequencies below about 400 cm$^{-1}$. There is a depletion of a continuous scattering background attributed to electronic scattering. Such a pseudogap behavior is typical for a charge ordered state in strongly correlated electron systems. To further substantiate this effect we will use specific phonon modes to probe the charge dynamics. The high sensitivity of phonons to charge disproportionation is due to the related modulation of lattice force constants [26, 27]. In SCCO, the 249- and 305-cm$^{-1}$ modes correspond to vibrations of the Cu ladder and chain atoms, respectively [21]. This enables us to address charge ordering within the two sublattices separately.

![Graph](image-url)

**FIG. 2:** (online color) (left panel) Temperature dependence of the 305- and 249-cm$^{-1}$ modes which correspond to vibrations of the Cu chain and ladder atoms, respectively. (right panel) Substitution dependence of the 305- and 249-cm$^{-1}$ modes at 10 K. All spectra were measured in (aa) polarization.

Figure 2 displays a zoom of the temperature (350 to 10 K) and substitution dependence ($0 < x < 12$) at 10 K of specific phonon modes in (aa) light scattering polarization. With decreasing temperature from 350 K to 10 K the 305-cm$^{-1}$ chain mode hardens by 7 cm$^{-1}$ while additional split-off modes show up at 294 cm$^{-1}$.
and 303 cm$^{-1}$ [see the left upper panel]. The latter correspond to zone-folding effects due to the formation of a superstructure. This confirms the presence of charge ordering in the chain. With increasing Ca-content the split-off modes are suppressed while the 312-cm$^{-1}$ mode broadens [see the right upper panel]. A distinct feature is that at the same time a new mode at the right shoulder of the main peak appears. This mode is more pronounced and observed as a separate peak 335 cm$^{-1}$ for $x = 12$. Thus, the gradual switching of the spectra from $x = 0$ and $x = 12$ can be ascribed to a continuous change of the lattice modulations leading to a suppression of the charge ordering. Note that only one broadened peak around 313 cm$^{-1}$ is expected in the case of a homogeneous charge distribution. In this light, an extra peak at the right shoulder implies an inhomogeneous charge distribution at high $x$. This is confirmed by ESR measurements [14].

Compared to the chain mode, the 249-cm$^{-1}$ phonon of the ladder system shows a less pronounced hardening by 4 cm$^{-1}$ [see the left lower panel]. Furthermore, we find no evidence for zone-folded modes. Instead, upon cooling all modes gain a strong intensity while the 237-cm$^{-1}$ mode appears below 150 K. This suggests that the charge ordering in the ladder is weakly coupled to lattice modulations. With increasing Ca-content the 253-cm$^{-1}$ at 10 K becomes broader and weaker [see the right lower panel]. This is related to the weakening of the CDW in the ladder [see Fig. 4 and below]. Noticeably, the doping dependence of the ladder mode resembles that of the chain mode because of an incommensurate lattice modulation of the two sublattices.

Shown in Fig. 3(a) is the temperature dependence of the peak position of the 305-cm$^{-1}$ chain mode as a function of Ca-content. To identify the charge ordering contribution to the frequency shift, we have estimated the anharmonic phonon contribution using a model based on phonon-phonon decay processes [28, 29],

$$\omega_{ph}(T) = \omega_0 + C[1 + 2/(e^{x} - 1)],$$

(1)

where $x = \hbar \omega_0/2k_BT$ with the value of $\omega_0 = 312$ cm$^{-1}$ and $C = -1.4$ cm$^{-1}$ for $x = 12$. The $x = 12$ sample shows good agreement between the fitted and experimental data in the overall temperature range. This means that the temperature dependence of the phonon frequency is solely due to lattice anharmonicity. With decreasing $x$ the deviations show up and develop in a systematic way. This gives evidence for the presence of other contributions in addition to anharmonic lattice effects. Here we mention that for small $x$ the fitting interval is restricted to the high temperature range where a linear temperature dependence is observed. Remarkably, for $x = 0$ the temperature dependence of the frequency shift below $T^* = 200$ K is similar to that of the X-ray scattering intensity of the superlattice reflections at (0,0,l) positions [11, 20]. Thus, we identify the characteristic temperature, $T^*$, where the discrepancy starts to appear as the onset of charge ordering. With increasing Ca-content $T^*$ shifts to lower temperature [see Fig. 3(a) and (b)].

These observations can be explained as follows: At high temperature the frequency of the O-vibration within the CuO$_4$ plaquette is given by $\nu_0 = \sqrt{\kappa/M}$ with $\kappa$ the lattice force constant and $M$ the O-mass. At low temperatures charge ordering leads to an additional modulation of the lattice. Thus, the lattice force constant changes due to Coulomb repulsion between the Cu sites $\delta_{\text{Cu}}$. Therefore, the renormalized frequency shift is given by $\nu = \sqrt{(\kappa + \delta_{\text{Cu}})/M}$. In this regard, the decrease of the deviation below $T^*$ with increasing $x$ implies that the charge ordering induced lattice distortion weakens. However, this does not mean that the chain and the ladder become homogeneous. As discussed above, the structural modulations are still substantial at $x = 12$ [see the right panel of Fig. 2].

![FIG. 3: (online color)(a) Temperature and substitution dependence of the peak position of the 312-cm$^{-1}$ mode. The solid lines represent a fitting by eq. (1). The characteristic temperature, $T^*$, is indicated by an arrow. (b) $T^*$ as a function of Ca-content. (c) The onset frequency of the pseudogap as a function of Ca-content.](image)

We will now turn again to the low-temperature depletion of the electronic background observed for frequencies below 400 cm$^{-1}$ in both (cc) and (aa) polarizations [see Fig. 1]. Figure 4 displays its substitution dependence at 10 K in (cc) polarization. Since the background level is constant in the frequency range 400 -1400 cm$^{-1}$, we use the intensity between 400-450 cm$^{-1}$ as a reference point for $x > 0$. The (aa) polarization displays a similar behavior (not shown here). With increasing $x$ the onset energy of the depletion shifts to lower energy (indicated by the vertical arrow) and the pseudogap closes and finally disappears for $x = 12$. The suppression of spectral weight can be taken as a definite signature of a CDW in the ladder system. Such a pseudogap behavior is charac-
teristic for a charge ordered state in strongly correlated electronic systems. This points to the significant role of electronic correlations in forming the CDW state.

Actually, Raman, IR, and x-ray scattering studies [3, 4, 5, 6, 7] provide evidence for the presence of such a modulated state. There are, however, differences in details derived from these experimental techniques. In Raman scattering measurements [3, 4] low energy quasielastic scattering (QES) is attributed to collective CDW excitations. An analysis of this dynamic Raman response seems to indicate that a 1D local CDW exists for all hole concentrations. In contrast, recent optical absorption spectra [7] show (i) a CDW response along both the leg and rung, (ii) the vanishing of the CDW signal along the rung at $x = 8$, and (iii) the disappearance of the CDW state for $x > 9$. This would imply a 2D nature of the observed CDW state. In 1D electron systems electronic Raman response which is proportional to a curvature of dispersion is possible only in one polarization direction. Therefore, the observation of the electronic response in both (aa) and (cc) polarization evidences the 2D nature of the CDW state for Sr concentrations at least up to $x = 5$. Thus, our Raman results with respect to the polarization and doping dependence are fully consistent with these IR results. The 2D CDW is further supported by x-ray scattering measurements which shows a coherent modulation across $\sim 50$ neighboring ladders [8].

The conflict in the derived pictures is in part related to the complexity of the present system with chains, ladders and coupled spin/charge degrees of freedom. The main problem, however, is based on the ambiguity of interpreting QES in terms of CDW excitations. Usually, an unspecific hydrodynamic model is adopted to analyze the QES with respect to electronic scattering from spins, impurities, and phonons. ESR measurements [14] evidence the significance of mobile holes in the chain for all $x$ above the charge ordering temperature. In this case, a scattering of mobile holes by spins in the chain contributes to a QES. Actually, QES is observed (i) in a wide concentration range, $0 < x < 12$, (ii) only for polarization parallel to the leg, and (iii) in the high temperature regime. Therefore, we come to the conclusion that the observed QES in earlier Raman studies [3, 4], might be governed by the charge dynamics of the chain rather than the CDW of the ladder.

In the following we will discuss the origin of the CDW order. Although there is some evidence for a conventional CDW [6], the presented Raman spectra show no characteristic features which are expected for a conventional Peierls mechanism. That is, there is no clear hint for the presence of a Raman-active amplitude mode. Furthermore, no significant lattice modulations are accompanied by the formation of the CDW [see the left lower panel of Fig. 2]. However, a Peierls mechanism cannot entirely be ruled out because the CDW-related superstructure might be negligibly weak and difficult to observe by Raman spectroscopy. Further high resolution x-ray or electron diffraction studies might be more decisive. Here, we want to recall that a recent resonating X-ray scattering experiment [8] uncover the important role of electronic correlations as the driving force to the CDW. If considering very weak electron-phonon interactions, the CDW-related pseudogap feature can be ascribed to electronic correlation effects. Noticeably, the substitution dependence of the CDW resembles that of the charge ordering in the chain [compare Figs. 3 (b) and (c)]. Thus, the full aspect of the CDW is described by the mutual interaction between the hole localization and a lattice modulation.

In a qualitative picture, the hole-lattice interactions can be explained as follows: The chain-lattice distortions lead to a pinning potential for the holes in the chain. In turn, the localized holes deform the lattice. The ladder-lattice is modulated according to the chain-lattice distortions. This influences the localization pattern of the holes in the ladder. In the same way, charge ordering in the ladder affects the chain-lattice modulation. We emphasize that recently increasing evidence exists for such an intrinsic interplay between the charge ordering and the lattice modulations from both experimental and theoretical sides [17, 18, 19, 20]. The controllability of the charge ordering by hole-lattice interactions has an analogy in the stripe scenario of high-$T_c$ single layer cuprates where the cooperative octahedral tilts induce a pinning potential for charge stripes [30].

![FIG. 4: (online color) Low temperature Raman spectra of Ca substituted Sr$_{1-x}$Ca$_x$Cu$_2$O$_{4+\delta}$ with $0 \leq x \leq 12$ for intraladder (cc) polarization. The dashed lines correspond to a reference point with respect to the unrenormalized electronic continuum of each spectrum and the arrows mark the onset of spectral weight depletion, i.e. opening of the pseudo gap.](image)
In summary, an intimate connection between the charge dynamics and the incommensurate lattice modulation in $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$ has been discussed. Evidence has been presented that the 2D CDW in the ladder system and the charge ordering in the chain system are based on an intriguing interplay between specific lattice modulations and electronic correlations. Our study highlights the significance of inhomogeneous lattice effects in understanding the electronic properties of $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$.

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