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Resonant two-phonon Raman scattering as a probe of hole crystal formation in $Sr_{14-x}Ca_xCu_{24}O_{41}$

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The charge dynamics of the spin ladder compound $Sr_{14-x}Ca_xCu_{24}O_{41}$ with $x=0,6,13.6$ has been investigated using wavelength- and temperature-dependent phonon Raman scattering on single crystals. In the unsubstituted, $x=0$, compound, a set of sharp two-phonon lines shows a strong increase in intensity below $T\sim 200$ K for light polarized along the ladder layer and with excitation energy close to the charge transfer gap ~ 1.9 eV. The temperature dependence of the strongly enhanced two-phonon bands below 200 K closely follows the recently reported formation of a standing charge density wave in the ladders [P. Abbamonte *et al.*, Nature **431**, 1078 (2004)]. Upon calcium substitution the polarized resonant Raman response rapidly decreases, signaling an increase of hole mobility in the ladder units. Temperature-dependent measurements of the $x=13.6$ sample indicate mobility of holes down to <8 K.

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I. INTRODUCTION

More than 15 years after the discovery of high-temperature superconducting cuprates (HT_c) materials,[1] there are still large gaps in our understanding of their basic physical properties. Superconductivity arises within the two-dimensional (2D) CuO_2 planes into which charge carriers are redistributed upon doping. In contrast to conventional superconductors, the nonsuperconducting ground state of these planes is not a Fermi liquid, but a strongly correlated 2D antiferromagnet (AFM). Understanding the complex development of this parent state upon doping is one of the main difficulties of finding a working model for the HT_c cuprates. However, in theory, not all strongly correlated systems are equally complicated. A unique position is held by one-dimensional systems, for which there exists exactly solvable models. This has motivated a considerable research effort directed towards the quasi-1D compounds commonly referred to as spin ladder systems.

One particularly interesting material is $Sr_{14-x}Ca_xCu_{24}O_{41}$, which has many similarities with the original HT_c cuprates. $Sr_{14-x}Ca_xCu_{24}O_{41}$ consists of layers of copper and oxygen atoms arranged in ladder and chain motifs, with strontium and calcium stacked in between them along the *b* direction of the structure. The average formal Cu valence is close to +2.25 for all x with the majority of holes believed to reside in the chain substructure. Under pressure and upon Ca doping, the compound can be made to superconduct along the ladders at low temperatures if $x\geq 11.5$.[2] The electronic dynamics for this system as a function of calcium substitution, pressure, and temperature on the way to the SC state is of great importance for understanding of the SC mechanism. Osafune *et al.* have shown some indication of hole transfer from chain layers to ladder layers upon Ca doping from reflectivity measurements,[3] while other authors—for example, Nücker *et al.*[4]—suggest that the ladder and chain hole occupation is invariant upon Ca substitution. Recently Piskunov *et al.*[5] performed a pressure- and doping-dependent NMR study of the compound; their data show no redistribution of holes upon Ca doping. However, the introduction of Ca seems to increase the interladder coupling, while pressure causes a hole redistribution from chains to the ladders. It has also been suggested that Ca substitution causes a dimensional crossover from a quasi-one-dimensional to a quasi-two-dimensional system.[6] Pressure is also considered to cause a dimensional crossover,[7] in the sense that the interladder coupling increases with compression. The ladder layers have been found to exhibit a charge density wave (CDW) phase for $x=0$ (Ref. 8) from dynamical (low-frequency) Raman measurements. According to far IR studies of Vuletic *et al.*[9] the CDW phase is suppressed to lower temperatures for increasing Ca content and vanishes in the heavily doped region for x $\geq$9. However, this is contradicted by Blumberg and co-workers,[8,10] who claim a CDW phase that persists far above room temperature (RT) and that is almost unchanged for a wide Ca range—i.e., up to $x=12$. The chain layers also exhibit a charge-ordered state, which results in a dimerization of the chain into Cu^{2+} and Cu^{3+} ions.[11,12] Clearly the phase diagram, the effect of dimensionality, and the impact of temperature on the electronic structure of these compounds are not yet fully understood.

In this study, resonance Raman spectroscopy (RRS) was used to analyze the charge dynamics of the $Sr_{14-x}Ca_xCu_{24}O_{41}$ spin ladder compounds. Raman scattering is a powerful probe of strongly correlated systems as it can simultaneously provide information on charge, spin, and lattice degrees of freedom. A number of earlier Raman studies of $Sr_{14-x}Ca_xCu_{24}O_{41}$ have been performed; for example,[13,14] Popović *et al.*[15] noted the activation of longitudinal optical (LO) infrared (IR) modes and strong two-phonon overtones in Raman spectra collected with excitation energies close to the ladder charge transfer energy gap for $Sr_{14}Cu_{24}O_{41}$, while the effect of temperature and Ca substitution on the two-magnon excitation was studied by Sugai and Suzuki.[16]

Herein we present RRS data for a wide excitation energy range (1.83–2.41 eV) and show the emergence of a complex two-phonon spectrum when lowering the temperature for the $x=0$ sample. The temperature dependence of the resonantly enhanced two-phonon region is found to be closely linked to the growth of a standing CDW (hole crystal) phase in the ladders.[17] Our results demonstrate the extreme sensitivity of Raman scattering to the local electronic structure at energies close to the charge transfer (CT) gap due to the Fröhlich electron-phonon interaction. The impact of Ca substitution on this effect is also investigated, and a strong suppression of the resonance enhancement for $x=6$ and $x=13.6$ samples is found that is linked to the breakdown of the conditions required for Fröhlich interaction induced resonance.

II. EXPERIMENT

Single crystals of $Sr_{14-x}Ca_xCu_{24}O_{41}$ with $x=0$, 6 were grown by the NaCl flux method[18] and $Sr_{14-x}Ca_xCu_{24}O_{41}$ with $x=13.6$ was prepared by a high-pressure method.[2] The composition and structure of the crystals used for the Raman experiments were analyzed with energy-dispersive X-ray (EDX) and single-crystal X-ray diffraction. The EDX measurements confirmed the nominal sample composition within an experimental accuracy of ±10%. The Raman measurements were performed in back-scattering geometry using a DILOR-XY800 spectrometer and Raman microscope equipped with notch filters and operated in the single-grating mode. The spectral resolution was $\sim 2\ \mathrm{cm}^{-1}$, and the diameter of the probed area was $\sim 2\ \mu$m. An Ar^+/Kr^+ laser was used for excitation with a laser power at the sample kept at 1 mW to avoid laser heating. The wavelengths used were 514.5 nm (2.4 eV), 530.9 nm (2.3 eV), 568.2 nm (2.2 eV), 647.1 nm (1.92 eV), and 676.5 nm (1.83 eV). The crystals were probed in different scattering geometries. To denote the scattering geometries in our Raman experiments we use the Porto notation—i.e., $d_1(p_1p_2)d_2$. Here d_1 and d_2 are the directions of the incoming and detected light, respectively, and p_1 and p_2 are the polarization of the incoming and detected light respectively. The Porto labels are to be taken along the crystal axes—i.e., $x=a$ axis, $y=b$ axis and $z=c$ axis. Variable temperature measurements were performed using a cold-finger LHe cryostat, and Raman intensity calibration was done using a BaF crystal as a standard. The temperature dependence study is performed at an energy (2.2 eV) where the imaginary part of the dielectric function along the chains and ladders varies by less than 10% across the temperature range.[19] For the $x=0$ sample, the intensity of resonance measurements differs by more than one order of magnitude in the two-phonon region from a resonant to a nonresonant excitation energy. This by far exceeds any optical corrections depending on the variation of the dielectric function with excitation energy. Similarly, for the investigations of the $x=6$ and 13.6 samples, any effects due to resonance scattering would be expected to greatly exceed any small correction linked to changes in optical properties.

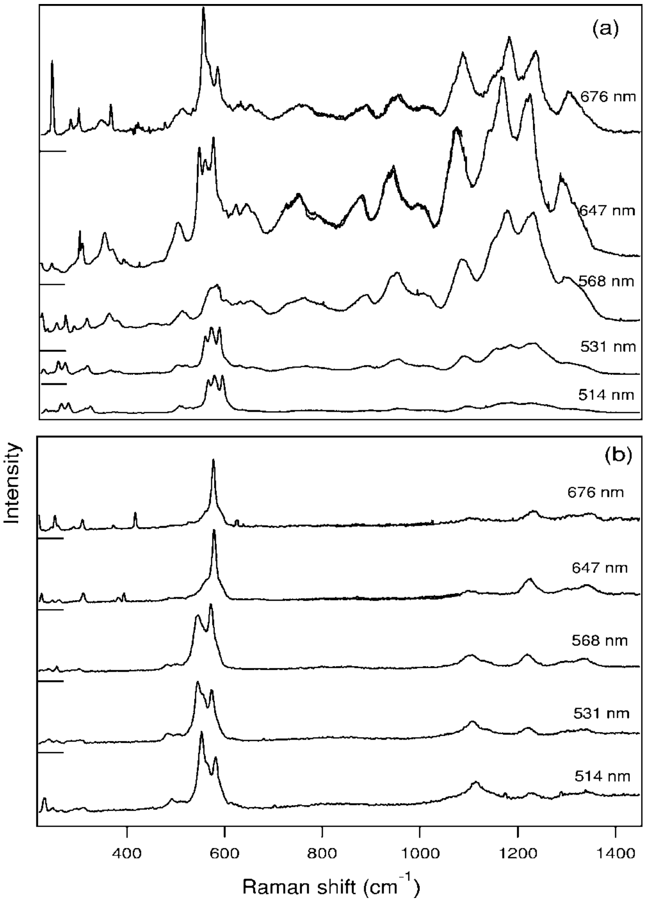

FIG. 1. Resonance Raman spectra of $Sr_{14}Cu_{24}O_{41}$ single crystals in (a) $y(zz)\bar{y}$ and in (b) $y(xx)\bar{y}$ scattering configurations at $T=20$ K. Base lines for each wavelength are marked in the spectra.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) shows the highly anisotropic RRS data for the $x=0$ sample with the scattering configurations $y(zz)\bar{y}$ and $y(xx)\bar{y}$, respectively—i.e., light polarized along and across the chain and ladder subunits, respectively, as a function of wavelength in the range from 676.5 nm (1.83 eV) to 514.5 nm (2.4 eV) at $T=20$ K. From the polarization dependence it is clear that the resonance responsible for the enhanced two-phonon scattering is associated with the quasi-1D character of the material's composite structure. The figure shows that the extreme enhancement of the two-phonon region ($700-1400\ \mathrm{cm}^{-1}$) for the undoped compound occurs close to 647 nm (~ 1.9 eV). As noted previously by Popović *et al.* the resonant energy lies close to the charge transfer gap between the Cu $3d$–O $2p$ states that reside in the ladder layers as determined by polarized dielectric (ϵ_{zz}) measurements.[15] This close association of the second-order Raman response to a CT gap points to a Fröhlich interaction process which has been observed for similar low-dimensional cuprates.[21,22] The presence of a Fröhlich interaction induced resonance process for $Sr_{14}Cu_{24}O_{41}$ is further supported by the appearance of new single phonon modes assigned as IR LO modes in low-temperature Raman spectra.[15] It is apparent from Fig. 1(a) that for energies close

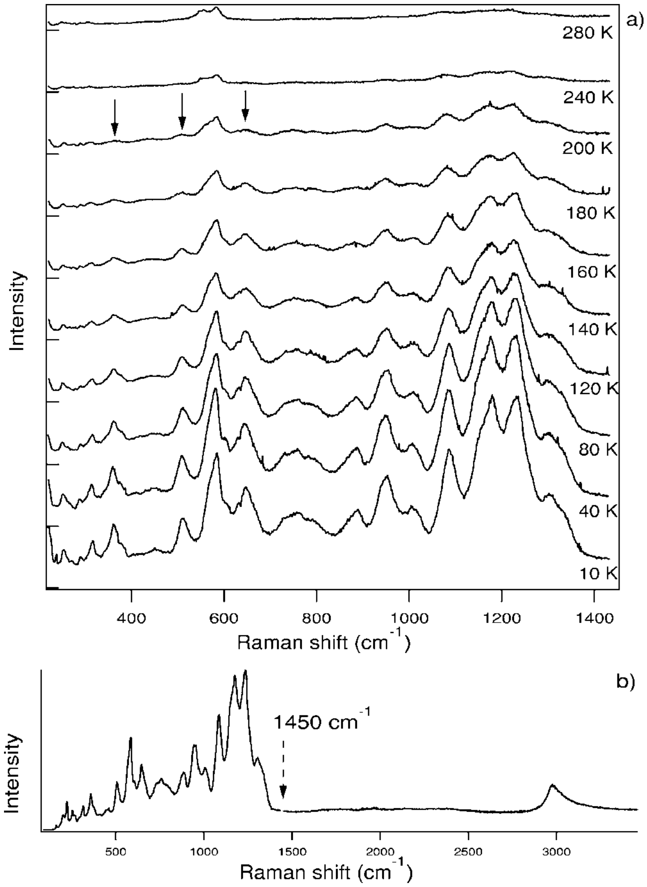

FIG. 2. Temperature dependence of $Sr_{14}Cu_{24}O_{41}$ in the $y(zz)\bar{y}$ configuration for an excitation wavelength of 568.2 nm. Base lines are indicated as horizontal bars at the left of the figures. Arrows mark the appearance of new single-phonon modes as discussed in the text. (b) Raman spectra 200–3400 cm^{-1} at 40 K.

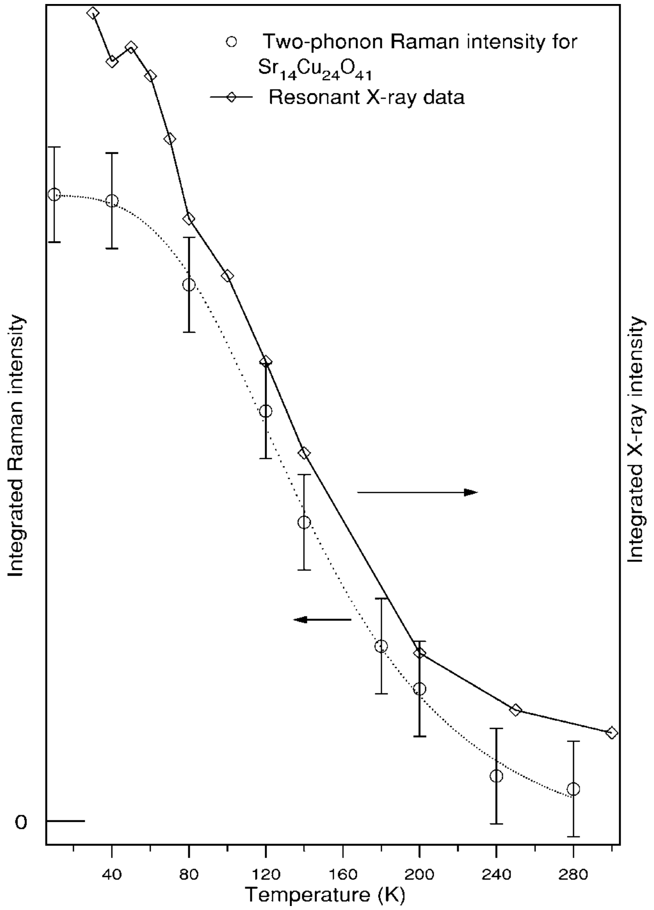

FIG. 3. Temperature-dependent integrated intensities of the two-phonon region (700–1400 cm^{-1}) for $Sr_{14}Cu_{24}O_{41}$(circles) (Ref. 20). The dotted line is a guide for the eye. The solid line shows the temperature dependence for the integrated intensity of the X-ray diffraction peak tuned to the oxygen mobile carrier prepeak in the ladders. The data are extracted from Ref. 17.

to the CT gap, more phonons are observed in the single-phonon region (0–700 cm^{-1}) than the predicted six Raman active Ag modes.[15,23] From Fig. 2(a), which shows the temperature dependence of the spectra obtained with $\lambda = 568.2$ nm, we observe the appearance of new modes at 360, 510, and 647 cm^{-1} which have been identified as having an IR origin in Ref. 15 as T approaches 200 K. The observation of new modes, in combination with strong second-order scattering, strongly indicates a Fröhlich interaction induced resonance.

The growth of the resonant two-phonon Raman response on cooling shown in Fig. 2(a) is our central observation. At RT the Fröhlich resonance appears to be effectively screened. Some weak two-phonon intensity is seen at around 1200 cm^{-1} typical of broad nonresonant overtone bands. As the energy of the measurements lies close to the CT gap of the Cu_2O_3 ladder sub-unit we conclude that the electronic structure of the ladder layers undergoes a significant modulation on cooling, which allows the Fröhlich interaction induced resonance to emerge. Further, we note that the temperature dependence of the higher-order scattering (700–1400 cm^{-1}) of the $x=0$ sample shown in Fig. 3 is remarkably similar to that of the growth of a superlattice reflection observed in recent resonant X-ray scattering measurements.[17] As for the ladder superlattice peak, a rise in the intensity of the two-phonon region is already apparent at temperatures above 200 K. The superlattice reflection was attributed to crystallization of holes in the ladder layers with a periodicity of 5× the ladder subcell. This hole ordering is argued to be too weak to induce any detectable structural perturbation but it will affect the local electronic structure probed by RRS through electron-phonon coupling. It is well established that charge carrier mobility has a detrimental effect on the Fröhlich interaction induced resonance condition, as the LO phonons are screened.[24,22,25] Consequently, this effect cannot be seen in metallic and superconducting materials such as $YBa_2Cu_3O_7$.[26] The fact that the charge-transport properties of $Sr_{14}Cu_{24}O_{41}$ reflect the mobility of holes in the ladders,[3,27] therefore, only serves to support the view that the emergent second-order phonon region is directly linked to hole localization within the ladder layer as the temperature is decreased.

A second observation, apparent from the resonantly enhanced Raman spectra of $Sr_{14}Cu_{24}O_{41}$, is the presence of a cutoff energy at around 1400 cm^{-1} (~170 meV) for the resonantly enhanced Raman spectra; see Fig. 2(b). The second-

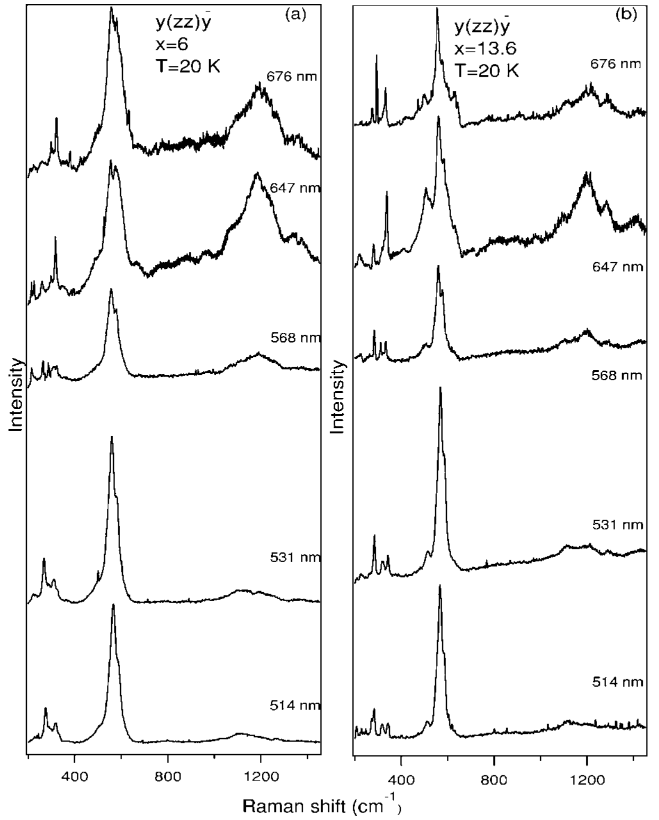

FIG. 4. Resonant Raman spectra in the $y(zz)\bar{y}$ scattering configuration at the doping (a) $x=6$ and (b) $x=13.6$. All spectra are taken at 20 K.

order phonon scattering exhibits an increasing intensity with vibration energy until it sharply drops to a more or less constant background level. Although only shown for $\lambda=568.2$ nm at 20 K, this observation is clearly repeated for other excitation energies close to the CT gap. From the Fröhlich interaction induced resonance Raman mechanism there is nothing to prevent higher-order overtone bands from being resonantly enhanced and such higher-order scattering is often observed.[24] Although significantly weaker than the second-order phonons, $l=3$ modes are discernible for Fröhlich-resonant Raman measurements performed on the chain containing compound $SrCuO_2$ at energies >1700 cm^{-1}.[21] We observe no such well-defined features in our data above 1500 cm^{-1} except for the two-magnon excitation at 3000 cm^{-1}. This behavior suggests that for energy transfers >170 meV the resonance conditions are disrupted. In this context it is relevant to note that activation energies of 185 and 180 meV [180 meV corresponds to a Raman shift of 1450 cm^{-1} marked with an arrow in Fig. 2(b)] for ladder hole mobility have been determined from low-frequency Raman,[10] and dc conductivity,[27] measurements, respectively. Therefore, one possibility is that for Raman shifts above the activation threshold, hole mobility is induced in the hole crystal phase which effectively screens the Fröhlich interaction induced resonance.

Further evidence to support this conjecture is found from the behavior of the background intensity that for Raman scattering is directly linked to the electronic continuum. A long-standing source of uncertainty for $Sr_{14}Cu_{24}O_{41}$ has been the intense high-energy spectral weight.[28] Gozar *et al.*[29] in a study focused primarily on the two-magnon response have observed the transfer of spectral weight from the low-energy (<700 cm^{-1}) region of their Raman spectra to higher energy as T is decreased. The disappearance of low-energy continuum states on cooling has also been observed Sugai and Suzuki.[16] Such a redistribution of energy to the higher-frequency electronic continuum supports the picture that as hole localization occurs, the excess excitation energy from the laser light may access the continuum at energies above the activation energy. Thus spectral weight is transferred to energies above the activation gap. In fact Gozar *et al.*[29] have proposed that the damping of the two-magnon response at higher T may be linked to the additional relaxation channels provided by the low-energy continuum states which they speculate may be associated with the charge carriers found in the ladder layers. Sugai and Suzuki[16] use a similar reasoning to argue that (a) the strongly localized nature of the magnetic excitation results in the extremely sharp two-magnon peak of $Sr_{14}Cu_{24}O_{41}$ and (b) the introduction of itinerant carriers on heating disrupts the short-range AF correlation, leading to a weakening and broadening of the two-magnon. Thus these results support the understanding that hole mobility is significantly reduced on cooling below $T\sim 200$ K.

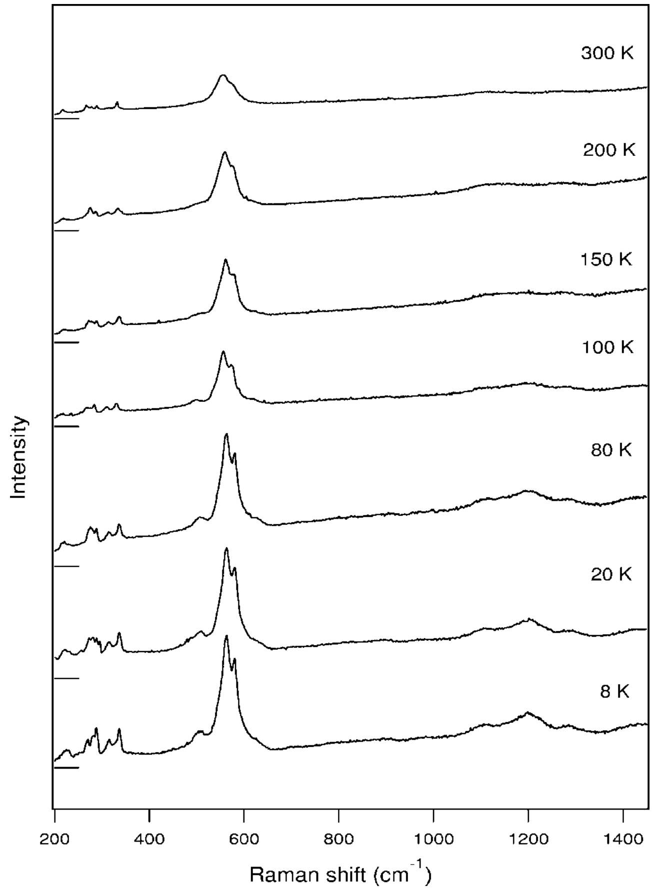

FIG. 5. Temperature dependence in the $y(zz)\bar{y}$ scattering configuration for an excitation wavelength of 568.2 nm and doping $x=13.6$.

We now turn our attention to the effect of Ca substitution on the RRS. In Figs. 4(a) and 4(b) we show RRS data recorded at the different excitation wavelengths for the $x=6$ and $x=13.6$ crystals, respectively. It is clear that the pronounced two-phonon resonance at excitation wavelengths around 647 nm (1.9 eV) is strongly suppressed by Ca doping. Furthermore, neither sample shows additional one-phonon modes activated via the Fröhlich mechanism. This behavior can be explained by the increased metallic character of the Ca-substituted phases suppressing the CT excitation and significantly reducing the efficiency of the Fröhlich interaction induced resonance. As for the undoped sample at temperatures ≥ 200 K, hole mobility will also play a role by screening the LO phonons and higher-order scattering. The enhanced carrier mobility is consistent with the decreased c-axis resistivity exhibited by Ca-doped samples.[30] Increased hole mobility upon Ca doping is also supported by X-ray absorption spectroscopy[4] and optical reflectivity measurements.[31] The resonant behavior, however, does not vanish completely. Both the $x=6$ and, to a lesser extent, the $x=13.6$ crystals exhibit a resonant two-phonon region at around 1200 cm^{-1}. The intensity enhancement is strongest for $\lambda=647$ nm, as for the $x=0$ phase, implying that the energy of the CT gap is not greatly affected by Ca substitution. In accordance, Osafune *et al.*[3] observe a decrease in the 2.0-eV CT spectral weight but no significant energy shift as Ca is introduced. The same authors also claim to see a transfer of holes from the chains to the ladders upon Ca substitution.[3] In the present case hole mobility more than their density impacts on the Fröhlich interaction induced resonance. We cannot therefore comment on whether or not there is an increase of the hole density in the ladders upon Ca substitution. In Fig. 5 we show the temperature dependence for the $x=13.6$ sample with light polarized along the c axis. No significant two-phonon resonance can be seen down to 8 K, indicating hole mobility in the highly Ca doped compounds down to very low temperatures. The weak two-phonon resonance seen indicates that the CO effects that persists in the ladders do so over length scales drastically reduced from the unsubstituted phase.

IV. SUMMARY

In summary, the charge dynamics of the spin ladder compounds $Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x=0$, 6, 13.6) has been investigated in oriented single crystals using RRS. We have observed a strong chain- and ladder-polarized electronic resonance at ~ 2 eV, which gives rise to a number of extra one-phonon modes as well as intense two-phonon Raman scattering below ~ 200 K in the undoped case. Our data thus support the picture of the development of a standing CDW phase in the ladder layers below ~ 200 K in the sense that the RRS is sensitive to the mobility of the charges. Calcium substitution results in a sharp loss of resonantly enhanced intensity, reflecting decreased CT and increased carrier delocalization. Further investigations are likely to be of importance to clarify the interplay between charge ordering effects in the chains and ladders substructures. Our results indicate that ladder hole localization produces strong changes in the resonant two-phonon Raman response. This raises the intriguing prospect of using RRS to probe the impact of, for example, an applied magnetic field on ladder charge dynamics.

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