Suppression of the Charge-Density-Wave State in $Sr_{14}Cu_{24}O_{41}$ by Calcium Doping

T. Vuletić,* B. Korin-Hamzić, and S. Tomić†
Institut za fiziku, P.O. Box 304, HR-10001 Zagreb, Croatia

B. Gorshunov,‡ P. Haas, T. Rõõm,§ and M. Dressel
1. Physikalisches Institut, Universität Stuttgart, D-70550 Stuttgart, Germany

J. Akimitsu, T. Sasaki, and T. Nagata
Department of Physics, Aoyama-Gakuin University, Tokyo, Japan
(Received 15 November 2002; published 26 June 2003)

The charge response in the spin chain and/or ladder compound $Sr_{14-x}Ca_xCu_{24}O_{41}$ is characterized by dc resistivity, low-frequency dielectric spectroscopy and optical spectroscopy. We identify a phase transition below which a charge-density wave (CDW) develops in the ladder arrays. Calcium doping suppresses this phase with the transition temperature decreasing from 210 K for $x = 0$ to 10 K for $x = 9$, and the CDW gap from 130 meV down to 3 meV, respectively. This suppression is due to the worsened nesting originating from the increase of the interladder tight-binding hopping integrals, as well as from disorder introduced at the Sr sites. These results altogether speak in favor of two-dimensional superconductivity under pressure.

DOI: 10.1103/PhysRevLett.90.257002 PACS numbers: 74.72.Jt, 71.45.Lr, 74.25.Nf, 77.22.Gm

The discovery of superconductivity under pressure in the two-leg ladder compound $Sr_{14-x}Ca_xCu_{24}O_{41}$ has provoked much attention since it is the first superconducting (SC) copper oxide material with a non-square-lattice layered pattern [1,2]. Theoretically, in an undoped spin ladder system, spin singlets in rungs produce the ground state, usually referred to as a gapped spin liquid [3]. Upon Ca doping, the added charge carriers (holes) tend to share the same rung on the ladder in order to minimize the energy paid to break the spin singlets. The formation of hole pairs is expected to lead to superconductivity with d-wave symmetry, whereas the spin gap remains the same or decreases equally in size. Because of the quasi-one-dimensional nature of ladders, a competing charge-ordered state (charge-density wave), with hole pairs as building entities, may prevent the occurrence of superconductivity. The ladder systems provide, therefore, a nice possibility to study spin and charge dynamics, and their interplay in a spin-gapped environment with significance to the phase diagram of high-temperature (HT) superconducting cuprates.

$Sr_{14-x}Ca_xCu_{24}O_{41}$ is such a quasi-one-dimensional system but it shows additional complexity since it contains a plane of Cu_2O_3 ladders, a plane of one-dimensional CuO_2 chains, and a (Sr, Ca) layer. These three distinct layers are placed in the crystallographic a-c plane and stack alternatingly along the b axis. The spin gaps are found to induce the activated temperature dependence of the spin-lattice NMR relaxation rate and the Knight shift in both the CuO_2 chains and the Cu_2O_3 ladders below about 50 and 200 K, respectively [4,5]. While the spin gap for the chain $\Delta_{spin}^{chains} \approx 14$ meV remains constant on doping, the spin gap for the ladder $\Delta_{spin}^{ladders} \approx 50$ meV decreases linearly with the Ca content. As far as the charge order is concerned, its existence is well established in the CuO_2 chain subunit below 200 K as a result of the antiferromagnetic dimers pattern. The charge gap induced by this order leads to a sharp peak observed in magnetic Raman-scattering measurements [6,7].

No definite understanding has been reached yet on the nature of the charge-ordered state in the ladders (the subsystem responsible for the conductivity and superconductivity of the compound) and its evolution on calcium doping, which leads to superconductivity. Along the most conducting direction (c axis), a semiconductorlike temperature dependence of the dc resistivity is observed, which does not change appreciably upon doping, while a metallic behavior is found only for $x \geq 11$ and $T > 50$ K [8]. The low-frequency dielectric and the optical response of the parent compound $Sr_{14}Cu_{24}O_{41}$ reveals a broad relaxation centered in the radio-frequency range with an Arrhenius-like decay determined by the resistive dissipation [9]. We have shown that this relaxation is due to screened phason excitations of the charge-density wave (CDW), which develops in the ladders and produces a CDW pinned mode at microwave frequencies, thus determining the low-temperature insulating ground state in pure $Sr_{14}Cu_{24}O_{41}$. Our findings were confirmed by Blumberg *et al.* [10].

In order to address the relationship between CDW, gapped spin liquid, and superconducting states, and thus to get an insight on the mechanism of superconductivity in spin ladders, we have performed systematic investigation of how the CDW instability in $Sr_{14}Cu_{24}O_{41}$ evolves upon Ca doping, which is essential to achieve superconductivity. We find that (i) the phase transition to the CDW state is strongly suppressed by calcium doping, revealing a competition between the charge-density wave and superconductivity; and (ii) a complex relation exists between CDW and gapped spin liquid ground states.

The dc resistivity was measured between 2 and 700 K. In the frequency range 0.01 Hz–1 MHz the spectra of the dielectric function were obtained from the complex conductance measured at $2 < T < 200$ K [11]. These spectra were complemented by reflectivity measurements at 8–10 000 cm^{-1} using quasioptical [12] and infrared spectrometers, from which the spectra of the complex dielectric function were obtained by a Kramers-Kronig analysis. All measurements were done along the crystallographic c axis of high-quality single crystals.

Figure 1 shows the frequency dependent complex dielectric response at three selected temperatures for $x = 0$, 3, and 9. A pronounced dielectric relaxation is observed for all three compositions providing evidence for the CDW formation [9]. The screened loss peak (ε'') centered at τ_0^{-1} moves toward lower frequencies and smaller amplitudes with decreasing temperature. The main features of this relaxation do not qualitatively change on doping: the dielectric strength $\Delta\varepsilon = \varepsilon_0 - \varepsilon_{\mathrm{HF}} \approx 5 \times 10^4$ (ε_0 and $\varepsilon_{\mathrm{HF}}$ are static and high-frequency dielectric constants), 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 in a manner similar to the dc resistivity [$\tau_0(T) \propto \rho(T)$]. Our results clearly demonstrate a distinct phase transition to the CDW ground state, which is strongly suppressed by Ca doping (Fig. 2): on decreasing temperature, a sharp growth of $\Delta\varepsilon$ starts in the close vicinity of T_c and reaches the huge value of the order of 10^4–10^5 at $T_c = 140$ K and $T_c = 10$ K for $x = 3$ and 9, respectively. These T_c values perfectly correspond to the temperature of the phase transition as determined in the dc resistivity measurements, indicated by pronounced peaks at T_c in the derivative of the resistivity [13]. The overall decrease of $\Delta\varepsilon$ below T_c for $x = 0$ is substantial, while it becomes much less pronounced for $x = 3$ and $x = 9$. While for $x = 3$ and 9 we were able to track the dielectric mode into the respective phase transition region; for $x = 0$ the mode leaves the upper bound (1 MHz) of our frequency window already at $T > 110$ K.

Figure 3 shows the low-temperature spectra of the optical conductivity for three different Ca compositions, $x = 0$, 3, and 9. The optical conductivity decreases below approximately 2500 cm^{-1} for $x = 0$ and 3, and around 25 cm^{-1} for $x = 9$, which we associate with the opening of the CDW gap. This decrease is observed only for $x = 0$,

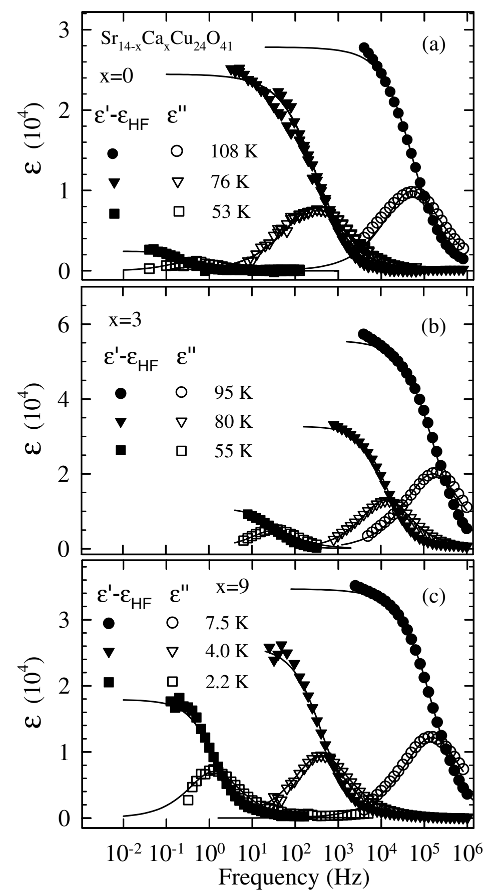

FIG. 1. Real and imaginary parts of the dielectric function of $Sr_{14-x}Ca_xCu_{24}O_{41}$ for (a) $x = 0$, (b) $x = 3$, and (c) $x = 9$ measured at three representative temperatures as a function of frequency with the ac electric field applied along the c axis. The solid lines are from fits by the generalized Debye expression: $\varepsilon(\omega) - \varepsilon_{\mathrm{HF}} = \Delta\varepsilon/[1 + (\imath\omega\tau_0)^{1-\alpha}]$.

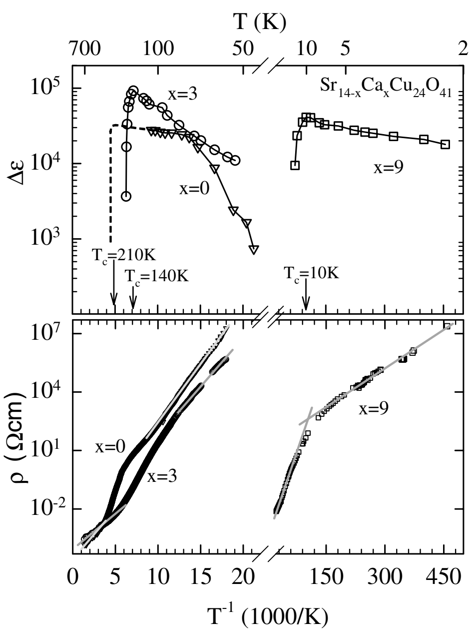

FIG. 2. Temperature dependence of the dielectric strength $\Delta\varepsilon$ of the radio-frequency CDW-related mode (upper panel) and dc resistivity ρ (lower panel) in $Sr_{14-x}Ca_xCu_{24}O_{41}$ for three different Ca concentrations x. The arrows indicate the CDW phase transition temperature T_c. In the upper panel the solid lines guide the eye, while in the lower panel the lines represent fits by Arrhenius functions. An assumed behavior of $\Delta\varepsilon$ for $x = 0$, based on that observed for $x = 3$ and 9, is represented by a dashed line.

$x = 3$, and $x = 9$ at temperatures lower than 240, 150, and 20 K, respectively [9,13]. These temperatures agree nicely with the CDW phase transition temperature T_c as determined from our dc and low-frequency dielectric measurements (Fig. 2), [13]. Moreover, the CDW gap values extracted from these measurements (130 meV $\approx$ 900 cm^{-1}, 110 meV $\approx$ 750 cm^{-1}, and 3 meV $\approx$ 20 cm^{-1}, for $x = 0$, 3, and 9, respectively) correspond well to the edges seen in the optical conductivity spectra. We thus conclude that the broad peaklike feature around 100 cm^{-1} for $x = 9$, which appears only for $T \leq 20$ K, cannot be assigned to the pinned CDW mode as suggested by Osafune *et al.* [14], rather it can simply be attributed to the opening of the CDW gap. High ac conductivity, as compared with the dc value, which remains at frequencies lower than the CDW gap, is due to a power law dispersion.

Figure 4 demonstrates the doping dependence of the CDW-related parameters: the CDW gap Δ, the critical temperature T_c, and Δ/T_c, which is a measure of the interaction strength leading to the CDW formation. A strong decrease of the CDW phase transition temperature and the CDW single-particle gap induced by Ca doping is striking. The broadening of the phase transition (as seen from the logarithmic derivative of resistivity versus inverse temperature [13]) and the decrease of T_c might be attributed to a disorder introduced by Ca doping at Sr sites. In order to explain such a pronounced effect, we suggest that in addition to the above, the CDW ground state is suppressed because the warping of the quasi-one-dimensional band, which is associated with the ladder subunits, increases with Ca doping. Indeed, a more two-dimensional hole distribution in the ladders has been revealed recently by x-ray absorption spectroscopy as the major effect of the Ca substitution [16]. The "strength" of the phase transition Δ/T_c is much larger than the mean field $\Delta/T_c = 3.5$ for $x = 0$ and 3, and drops to about 3.5 for $x = 9$. In the quasi-1D CDW systems, Δ/T_c is usually found to be enhanced above the mean-field value and ascribed to strong 1D correlations. The observed drop for $x = 9$ may be due to the increased dimensionality induced at high Ca-doping levels.

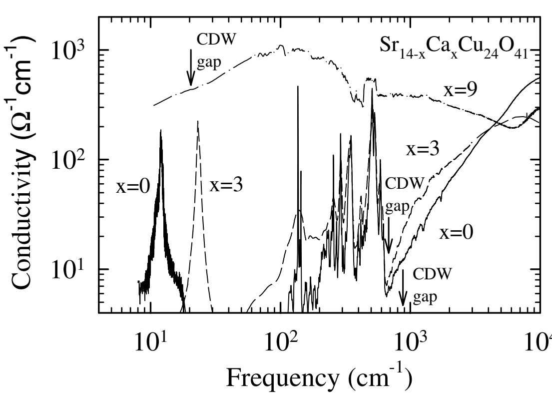

FIG. 3. Low-temperature ($T = 5$ K) optical conductivity of $Sr_{14-x}Ca_xCu_{24}O_{41}$ for $x = 0$, 3, and 9. The spectra are obtained for the electric field vector of radiation $E \parallel c$. The arrows show the CDW gaps obtained from activated dc resistivity.

Now we address the question of the nature and the origin of the observed CDW ground state. The peak we previously assigned to the pinned phason mode [9] centered at 12 cm^{-1} for $x = 0$ shifts to 23 cm^{-1} for $x = 3$ and eventually disappears for $x = 9$ (see Fig. 3). In our recent optical measurements on $La_3Sr_3Ca_8Cu_{24}O_{41}$ we see the same peak centered at about 12 cm^{-1} [17] although there is no hole transfer into the conducting ladders [16,18]. Hence we conclude that the 12 cm^{-1} peak is not a signature of the CDW phason mode [19].

Therefore, we follow the assignment of the peak at 1.8 cm^{-1} to the CDW phason pinned mode, proposed by Kitano *et al.* [20]. The mode was detected for $x = 0$ and 3 doping, but not for $x = 9$ [21], which may be due to the screening by the large number of free carriers at this high doping level. Since we observe the screened temperature-dependent response in the radio-frequency range centered at τ_0^{-1} (see Fig. 1), which represents a fingerprint of the CDW phason response [22], for $x = 0$ all the way up to $x = 9$, we can safely assume that the pinned mode always exists around $\Omega_0 \approx 1.8$ cm^{-1}. Littlewood [22] developed an expression, which connects the microwave unscreened phason mode at Ω_0 with the screened loss peak in the radio-frequency range at τ_0^{-1}:

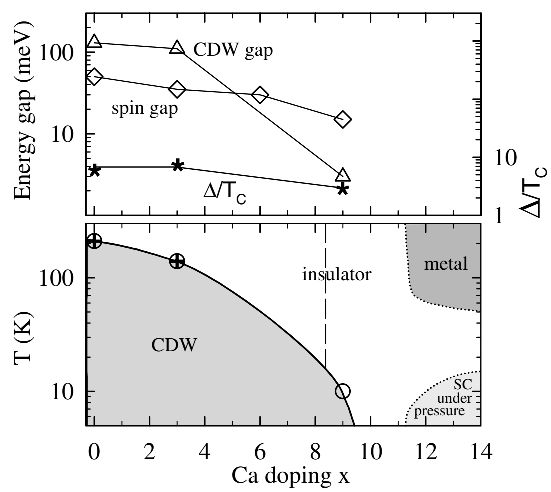

FIG. 4. Upper panel: Dependences of the CDW related parameters in $Sr_{14-x}Ca_xCu_{24}O_{41}$ on the calcium concentration: CDW gap Δ (triangles) and the "strength" of the CDW interaction Δ/T_c (stars). The dependence of the spin gap (diamonds) in the ladders is also shown [5]. Lower panel: Qualitative phase diagram for $Sr_{14-x}Ca_xCu_{24}O_{41}$ as a function of Ca doping. The CDW phase is determined by the CDW critical temperature T_c (open circles), which coincides with the paramagnetic–spin-gapped phase crossover temperature T^* (crosses) [15]. Also sketched are the insulating and the metallic phases [8], as well as the superconducting phase that appears under pressure. The activation energy in the insulating phase equals the CDW gap on the left of the dashed line, while it is close to the spin gap of the ladders on the right side.

$$m^* = \frac{e^2 n}{\sigma_{dc} \tau_0 m_0 \Omega_0^2}.$$

With $\sigma_{dc} = 1/\rho$ and n the carrier concentration condensed into the CDW, we can estimate the effective mass m^* of the condensate. We have suggested that the CDW forms in the ladder subunit because the ladders rather than the chains represent the conducting channel in $Sr_{14-x}Ca_xCu_{24}O_{41}$ [9]. In $La_3Sr_3Ca_8Cu_{24}O_{41}$, which contains no holes in the ladders, we did not find any signature of the CDW-related dielectric response: a strong confirmation of our assumption [17]. If only one out of six holes condenses into the CDW on the ladders, we estimate the CDW effective mass to be in the range $20 < m^* < 50$, with basically no dependence on temperature or Ca content for x between 0 and 9. Note that the values for the CDW effective mass are usually in the range $10^2 < m^* < 10^4$ [23]. The small values clearly indicate that electron-phonon interactions are weak. Therefore, a superstructure, which accompanies the CDW, is expected to be weak and difficult to observe by x-ray diffuse scattering. Besides the small value of m^*, the CDW state differs from those commonly observed in one-dimensional conductors [23] by the small nonlinearity of resistivity with no finite threshold field [9,20,24], and a strongly temperature-dependent $\Delta\varepsilon$, which may be connected to a redistribution of the holes between chains and ladders and an interplay between spins and charges [13].

Finally, we comment on the complex relation of charge-density wave and gapped spin liquid ground states. The CDW phase transition temperature T_c, from the HT phase into the CDW ground state, coincides with the crossover temperature T^*, which separates the high-temperature paramagnetic regime from the spin-gapped ground state in the ladders [15] (see Fig. 4). A similar gradual x dependence is also seen by both the CDW gap and the spin gap. However, this seemingly direct interdependence turns over completely at high Ca-doping levels, where the CDW gap drops to 3 meV, which is 5 times smaller than the spin gap [5].

This result supports the scenario according to which superconductivity is established in the presence of a finite spin gap at doping levels where the competing CDW order fully vanishes. Pressure suppresses an insulating HT phase, which still persists at these doping levels. Namely, the activation energy for low Ca contents ($x = 0, 3$) in the HT phase is very close to the CDW gap in the CDW ground state, while for high $x = 9$ it drops substantially, but clearly less than the CDW gap, down to a size of 12 meV, close to the value of spin gap in ladders. This means that the ambient pressure HT insulating state at high doping levels is different in nature as compared to the one at low doping, as indicated by the dashed line in Fig. 4. The origin of the HT insulating phase is not clear yet and might indicate strong electron correlation effects. The role of applied pressure is then to diminish these correlations, to drive the system away from the CDW instability by increasing further its dimensionality from 1 to 2, and setting finally the SC state, which is thus of a two-dimensional nature.

We demonstrated the phase transition from a high-temperature insulating phase to the charge-density wave ground state of $Sr_{14-x}Ca_xCu_{24}O_{41}$ and the gradual suppression of the CDW by Ca substitution of Sr. We propose that at high doping levels the CDW order fully vanishes due to increased two dimensionality and disorder, while a finite spin gap is still present. External pressure then suppresses an insulating high-temperature phase and establishes superconductivity.

We thank G. Untereiner for the preparation of the samples. This work was supported by the Croatian Ministry of Science and Technology and the Deutsche Forschungsgemeinschaft (DFG).

*Electronic address: tvuletic@ifs.hr
†URL: http://www.ifs.hr/real_science
‡Permanent address: General Physics Institute, Russian Academy of Sciences, Moscow, Russia.
§Permanent address: National Institute of Chemical Physics and Biophysics, Tallinn, Estonia.

[1] M. Uehara *et al.*, J. Phys. Soc. Jpn. **65**, 2764 (1996).
[2] T. Nagata *et al.*, Physica (Amsterdam) **282C–287C**, 153 (1997).
[3] M. Takigawa *et al.*, Phys. Rev. B **57**, 1124 (1998).
[4] T. Takahashi *et al.*, Phys. Rev. B **56**, 7870 (1997).
[5] K. Kumagai *et al.*, Phys. Rev. Lett. **78**, 1992 (1997).
[6] A. Gozar *et al.*, Phys. Rev. Lett. **87**, 197202 (2001).
[7] K. P. Schmidt *et al.*, Phys. Rev. Lett. **90**, 167201 (2003).
[8] N. Motoyama *et al.*, Phys. Rev. B **55**, R3386 (1997).
[9] B. Gorshunov *et al.*, Phys. Rev. B **66**, 060508(R) (2002).
[10] G. Blumberg *et al.*, Science **297**, 584 (2002).
[11] M. Pinterić *et al.*, Eur. Phys. J. B **22**, 335 (2001).
[12] G. Kozlov and A. Volkov, in *Millimeter and Submillimeter Wave Spectroscopy of Solids*, edited by G. Grüner (Springer-Verlag, Berlin, 1998).
[13] B. Gorshunov *et al.* (to be published).
[14] T. Osafune *et al.*, Phys. Rev. Lett. **82**, 1313 (1999).
[15] T. Imai *et al.*, Phys. Rev. Lett. **81**, 220 (1998).
[16] N. Nücker *et al.*, Phys. Rev. B **62**, 14 384 (2000).
[17] T. Vuletić *et al.*, Phys. Rev. B **67**, 184521 (2003).
[18] T. Osafune *et al.*, Phys. Rev. Lett. **78**, 1980 (1997).
[19] The 12 cm^{-1} peak should rather be attributed to a phonon. This is supported by the fact that our low-frequency dielectric spectroscopy measurements on $La_3Sr_3Ca_8Cu_{24}O_{41}$ show no sign of the dielectric relaxation associated with the CDW screened response.
[20] H. Kitano *et al.*, Europhys. Lett. **56**, 434 (2001).
[21] H. Kitano *et al.*, Physica (Amsterdam) **341C–348C**, 463 (2000).
[22] P. B. Littlewood, Phys. Rev. B **36**, 3108 (1987).
[23] G. Grüner, Rev. Mod. Phys. **60**, 1129 (1988).
[24] We have only, in contrast to Blumberg *et al.* [10], observed a negligibly small nonlinear conductivity for $x = 0, 3$, and 9, which emerges from the noise background.