Eur. Phys. J. B **6**, 301–305 (1998)

THE EUROPEAN PHYSICAL JOURNAL B

Temperature dependence of the anisotropic electrodynamics in the ladder compounds $Sr_{14-x}Ca_xCu_{24}O_{41}$

B. Ruzicka[1], L. Degiorgi[1,a], U. Ammerahl[2,3], G. Dhalenne[2], and A. Revcolevschi[2]

[1] Laboratorium für Festkörperphysik ETH-Zürich, 8093 Zürich, Switzerland
[2] Laboratoire de Chimie des Solides, Bâtiment 414, Université de Paris-Sud, 91405 Orsay Cedex, France
[3] II. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany

Received: 18 June 1998 / Accepted: 17 July 1998

Abstract. The optical reflectivity as a function of temperature of the title compound for $x = 0$, 5 and 12 has been measured over a broad spectral range from 4 meV up to 12 eV. Our findings suggest a very anisotropic dynamics of the charge excitation spectrum when measuring along or perpendicular to the ladders. Moreover, a metal-insulator transition develops at low temperatures, leading to a suppression of Drude spectral weight in the far and mid-infrared spectral range. We identify this behaviour as a consequence of the localization effects for small Ca substitution, and of the possible formation of a charge density wave condensate for large Ca substitution.

PACS. 78.20.-e Optical properties of bulk materials and thin films – 74.72.Jt Other cuprates

Renewed interest in low-dimensional quantum magnets has been raised by the discovery of high-temperature superconductivity. In this respect, the antiferromagnetic $S = 1/2$ two-leg ladder systems have recently attracted much attention, because their properties are reminiscent of some encountered in the high-temperature superconducting cuprates [1]. Particularly, the layered cuprate $Sr_{14-x}Ca_xCu_{24}O_{41}$, consisting of two-dimensional Cu_2O_3 ladder planes and one-dimensional CuO_2 chains [2], has been studied vigorously. Dagotto *et al.* first proposed that even-leg ladders have a spin liquid ground state with a spin gap and that doping (*e.g.*, by Ca substitution) into the spin ladders results in pairing of the doped holes [3]. Through hole-doping, the ground state should be either a charge density wave (CDW) or superconducting [1,3]. Such predictions have been extensively tested and a spin gap has been observed in the parent $SrCu_2O_3$ compound [4], and furthermore, the recent report of a superconductivity signal in $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41}$ by Uehara *et al.* [5] under a pressure of 3 GPa is expected to be a manifestation of the latter prediction.

As the Ca substitution in $Sr_{14-x}Ca_xCu_{24}O_{41}$ does not change the average valence of Cu, it is speculated that the holes become more mobile, *e.g.*, because of increased overlap of the Cu $3d$ and O $2p$ wave functions or through the redistribution of the hole density from immobile sites. In fact, the high temperature electrical resistivity along the ladder direction becomes small upon Ca substitution [6]. Nevertheless, recent transport data on polycrystalline samples pointed out that the insulating-like state in $\rho(T)$ at low temperatures implies that the holes in the ladder are localized below a characteristic temperature T_ρ [7]. The first optical investigations (mainly along the ladder direction) carried out at 300 K between 0.01 and 4 eV give indications that the low-energy excitations are ascribed to the ladders on which holes are much more itinerant than on the chains. Moreover, from sum rules spectral weight arguments it has been shown that holes are transferred from the chains to the ladders upon Ca substitution [8].

In this communication, we present our optical results on the temperature and polarization of light dependence of the electrodynamic response of single crystalline $Sr_{14-x}Ca_xCu_{24}O_{41}$ (with $x = 0$, 5 and 12). Our motivation was to monitor not only the Ca substitution dependence [8] but also the effects of the reduced dimensionality (*i.e.*, the crystallographic anisotropy) on the excitation spectrum of the ladder systems. Our data display a remarkable optical anisotropy between the spectra collected along the three crystallographic axes, indicative of the quasi one-dimensional electronic band structure. Moreover, for polarization directions parallel and perpendicular to the ladders we found a strong temperature dependence of the optical properties, suggesting the onset of a metal-insulator transition, due to localization effects.

[a] e-mail: degiorgi@solid.phys.ethz.ch

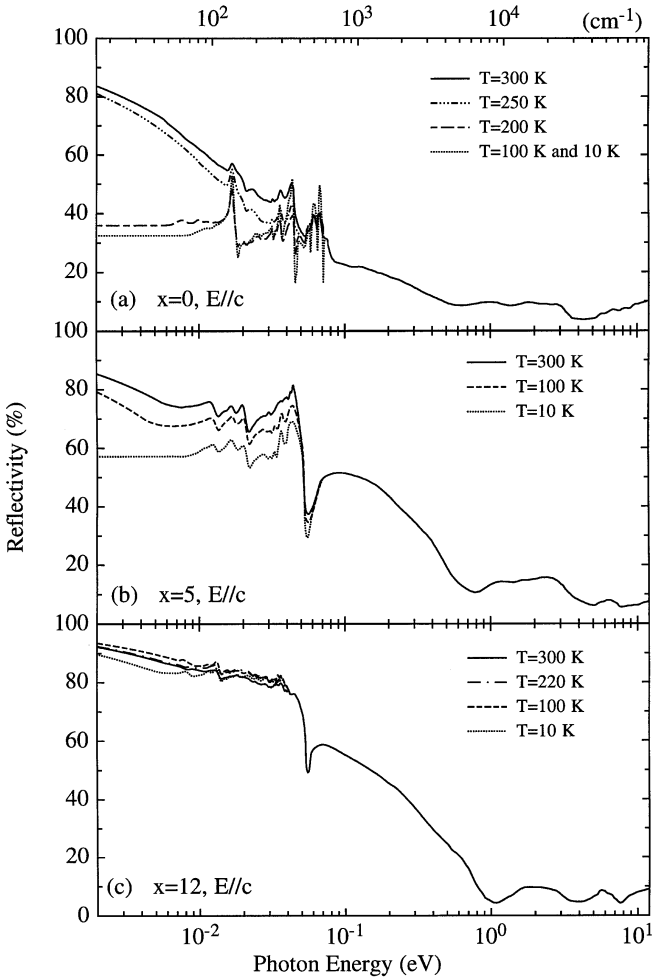

Fig. 1. Temperature dependence of the optical reflectivity along the c-axis for $x = 0$ (a), $x = 5$ (b) and $x = 12$ (c). Note the logarithmic energy scale.

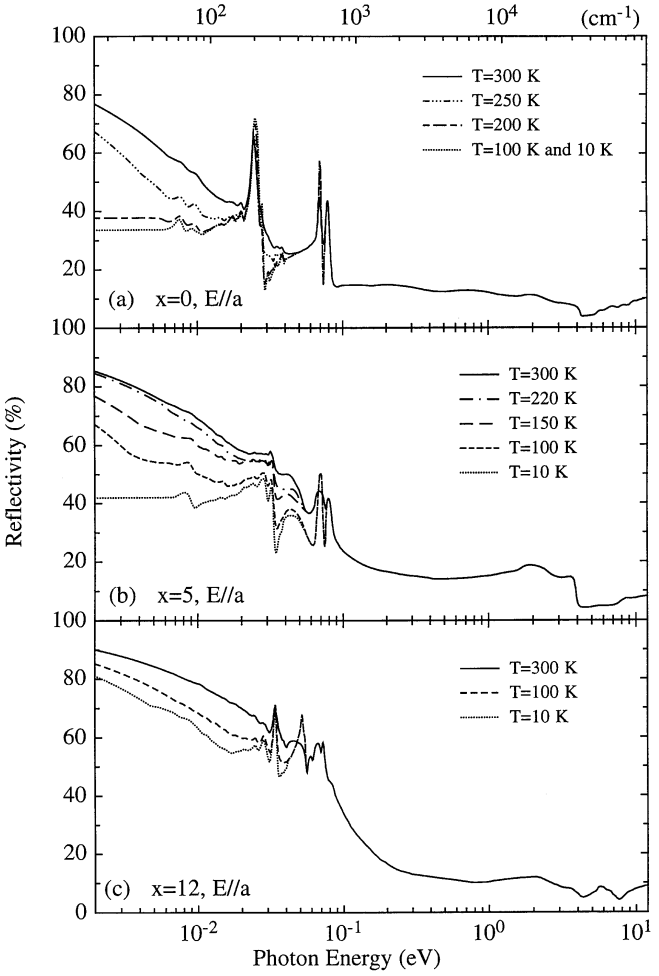

Fig. 2. Temperature dependence of the optical reflectivity along the a-axis for $x = 0$ (a), $x = 5$ (b) and $x = 12$ (c). Note the logarithmic energy scale.

Single crystals of $Sr_{14-x}Ca_xCu_{24}O_{41}$ were grown in an image furnace, under oxygen pressures varying from 1 to 13 atm, by the traveling solvent zone method [9], and are of high crystalline quality, as determined by neutron diffraction [10]. The optical reflectivity $R(\omega)$ was measured as a function of temperature over a broad spectral range from 4 meV up to 12 eV, using four different spectrometers, and for light polarization parallel (c-axis) and perpendicular (a-axis) to the ladder direction in the ladder planes, and orthogonal to the ladder planes (b-axis). The real part $\sigma_1(\omega)$ of the optical conductivity was obtained from Kramers Kronig transformations of the measured reflectivity (see Ref. [11] for more technical details).

Figure 1 shows the complete $R(\omega)$ spectra along the ladders ($E \parallel c$) for the three different Ca substitution values at several temperatures. At $T = 300$ K, $R(\omega)$ increases with decreasing photon energy for all three compounds and approaches total reflection as ω tends to zero, as expected for a metallic behaviour. An insulating behaviour (*i.e.*, $R(\omega)$ saturating to a constant value) is observed with decreasing temperature. We can also identify a plasma edge feature in the reflectivity, defined by the minimum in $R(\omega)$ where the increase towards total reflection takes place. The onset of the metallic contribution in $R(\omega)$ is centered at about 0.5 eV for the less conducting composition ($x = 0$) and shifts towards higher energies with increasing Ca substitution. At higher frequencies there are several broad absorptions, ascribed to electronic interband transitions, like the one, peaked at about 2 eV, due to a charge transfer excitation between Cu $3d$ and O $2p$ states [8]. Figure 2 displays $R(\omega)$ along the a-axis, while Figure 3 shows $R(\omega)$ for $x = 12$ along the three crystallographic axes. In analogy to the c-axis, $R(\omega)$ along the a-axis is metallic-like at high temperatures and decreases in the far-infrared (FIR) at low temperatures. Along the b direction, $R(\omega)$ (Fig. 3) is always insulating-like and temperature independent. $R(\omega)$ along the b-axis for $x = 0$ and 5 (not shown here) is similar to the spectra for $x = 12$ (Fig. 3). Moreover, all spectra are dominated by rather sharp absorptions in the far up to mid-infrared range. It is immediately evident that the optical properties are very anisotropic, with distinct temperature (Figs. 1 and 2)

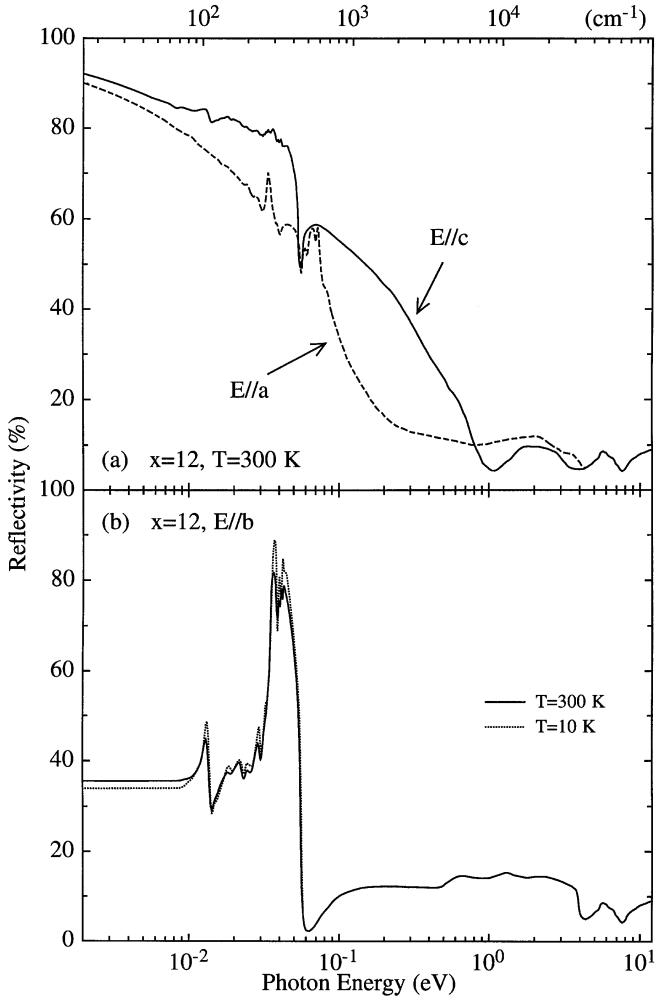

Fig. 3. Optical reflectivity at 300 K for $x = 12$ along the a- and c-axes (a), compared with the optical reflectivity for $x = 12$ along the b-axis at 300 and 10 K (b). Note the logarithmic energy scale.

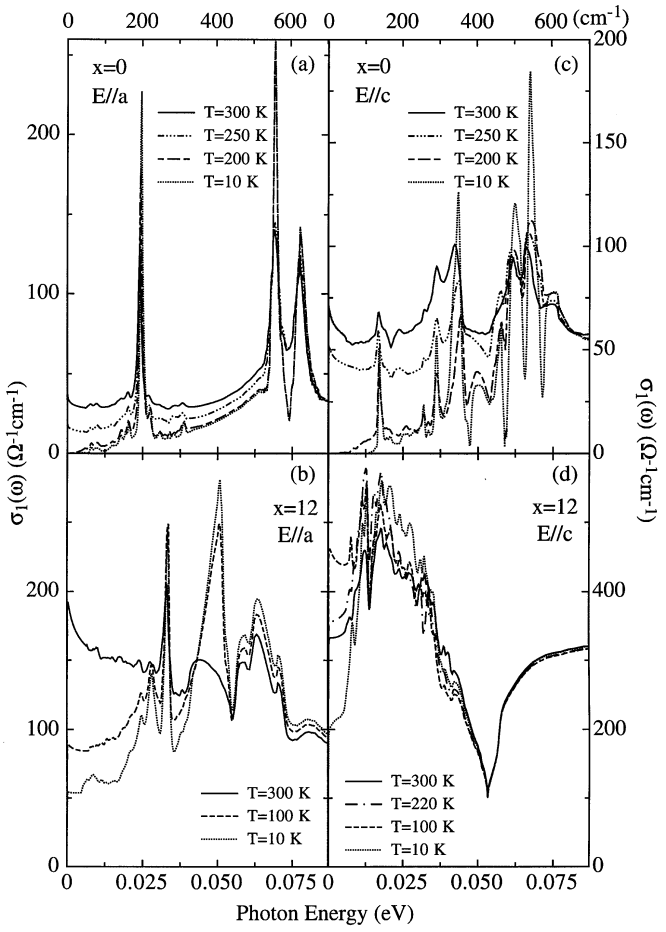

Fig. 4. Temperature dependence of the real part of the optical conductivity from 0 up to 90 meV along the a- and c-axes for $x = 0$ (a and c), and $x = 12$ (b and d), respectively.

and polarization (Fig. 3) dependence along the three crystallographic axes.

The real part $\sigma_1(\omega)$ of the optical conductivity for $x = 0$ and 12 with light polarized along the a- and c-axis is shown in Figure 4 in the FIR spectral range. Besides the already mentioned sharp modes, the low frequency part of $\sigma_1(\omega)$ is dominated at high temperatures by an effective (Drude) metallic contribution. Such a Drude component in $\sigma_1(\omega)$ is present even for $x = 0$, indicating that $Sr_{14}Cu_{24}O_{41}$ is not a genuine insulator and has a small amount of free charges. We note that there is a fair agreement between $\sigma_1(\omega \to 0)$ and the overall trend from the transport measurements [6,12]. Even though our data for $x = 12$ suggest a ratio $\sigma^c_{dc}/\sigma^a_{dc}$ smaller than in reference [6], there is a good agreement and consistency between $\sigma^c_1(\omega \to 0)$ and σ^c_{dc} from reference [12], where the same sample has been investigated. What is striking, besides the optical anisotropy (Fig. 3), is the metal-insulator transition both along the a- and c-axis, manifested by the suppression of the (Drude) spectral weight at low temperatures. On the one hand, for $x = 0$ along the a- and c-axis the spectral weight is suppressed below 0.1 eV, but it is fully recovered up to 0.2 eV. On the other hand, for $x = 12$ the Drude weight decreases with decreasing temperature at much lower energies (*i.e.*, below 0.02 and 0.035 eV) and piles up at energies up to 0.04 and 0.1 eV for the c- and a-axis, respectively.

Our spectra present some important differences with respect to previous data [8]. While the substitution dependence leads in both investigations to an effective blue shift of the plasma edge for light parallel to c-axis, the sharp excitations characterizing our data (Figs. 1–3) are barely observable in the spectra of reference [8]. The overall magnitude of $R(\omega)$ in FIR is slightly lower than in the spectra of reference [8], suggesting a smaller free charge carrier concentration and consequently a less effective screening of the modes. Another point of contrast concerns the a-axis spectra for large Ca substitution. For $x = 12$, we find a metallic behaviour at any temperature, even though the Drude weight decreases with decreasing temperature.

Osafune *et al.* find already at 300 K for $x = 11$ an insulating behaviour, without any sign of a Drude peak [8].

The sharp absorptions in FIR (Fig. 4) can be ascribed most probably to the optically active phonon modes of the ladder systems. Even though a full analysis of the lattice dynamics has not been performed so far, it seems that the Ca substitution affects the corresponding phonon spectrum. Indeed, upon increasing the free charge carrier concentration, a few modes for both $E \| a$ and $E \| c$ are progressively screened by the blue shift of the plasma edge or by the increased metallicity going from $x = 0$ to 12. Moreover, one can recognize small shifts in the resonance frequencies and/or a redistribution of spectral weight among the sharp absorptions upon doping, as consequence of changes in the modes' strength. This could indicate some important coupling between the charge carriers and the phonon modes, as well as a change in the lattice symmetry upon Ca substitution (*i.e.*, chemical pressure). Another interesting absorption develops at 50 meV for $x = 12$ and $E \| a$ with decreasing temperature. This feature is absent in the spectra for $x = 0$, while for $x = 5$, not shown here, we only see a very broad absorption in the same frequency range at any temperature. Interestingly enough, a similar puzzling feature was found in the low temperature c-axis (equivalent to the a-axis in the ladders) spectra of the underdoped $YBa_2Cu_3O_{7-x}$ superconductor [13]. It still remains to be seen what is the origin of this feature, which incidentally appears at an energy scale comparable to the spin gap [1,14]. Obviously and similarly to the cuprates [13], it could also be ascribed to a change in the lattice dynamics (*e.g.*, activation of silent or Raman active phonons) as consequence of the symmetry breaking due to the Ca-substitution.

The strong optical anisotropy also implies a one-dimensional electronic structure. In this respect, it is particularly compelling a comparison with one-dimensional (1D) linear chain Bechgaard salts $(TMTTF)_2X$ and $(TMTSF)_2X$ with X = Br, PF_6, and ClO_4 [11,15]. The degree of anisotropy in the Bechgaard salts is quantified by the magnitude of the interchain single-electron transfer integral (t_b). Electron-electron interactions together with Umklapp scattering lead to a correlation gap and to an insulating state for small t_b. Going from the (TMTTF)-salts to the (TMTSF)-ones, an insulator to metal transition takes indeed place, since t_b exceeds a critical value of the order of the correlation gap in the $(TMTSF)_2X$ compounds. This is manifested by the development at low temperatures of a sharp plasma edge feature for the (TMTSF)-salts along the direction perpendicular to the one-dimensional chain, while for the (TMTTF)-salts an overdamped (*i.e.*, the Drude scattering rate is much larger than the plasma frequency) plasma edge feature dominates at any temperature [15]. This contrasting behaviour is considered as an indication of a transition between a confinement (by the TMTTF-salts) and deconfinement (by the TMTSF-salts) regime, which also implies a 1D to 2D crossover [15]. Such a crossover can also be obtained in the (TMTTF)-salts upon application of pressure [16].

We want to argue that a similar behaviour happens in the ladder systems, as well. The analogy between the ladder systems and the Bechgaard salts has been recently pointed out by Mayaffre *et al.* in the course of transport and NMR investigation under pressure for the compound with $x = 12$ [12]. The degree of confinement of the carriers along the ladders could correlate with the size of the spin gap [3]: hole pairs are responsible for the conduction within the ladders as long as the magnetic forces can provide the binding of two holes on the same rung [3]. The vanishing of the spin gap upon application of pressure [12] or its reduction upon Ca substitution could thus be responsible for the dissociation of the pairs making in turn the hopping (deconfinement) of the transverse (a-axis) single particle easier. Therefore, pressure is believed to have an effect similar to that of the Ca substitution and, similarly to the Bechgaard salts, might induce a change in the intrinsic dimensionality of the system. In fact, from our data (Fig. 1) we observe that the increasing Ca substitution induces the formation of a well developed plasma edge feature in $R(\omega)$ along the c-axis. This is actually to be expected when the material undergoes small to large doping. From the spectral weight arguments (*i.e.*, the so-called f-sum rule) similar to reference [8], the development of the plasma edge upon doping along the c-axis is the consequence of the transfer of holes from the CuO_2 chains' reservoir to the ladder conduction paths. The total spectral weight (*i.e.*, the ratio n/m, where n is the concentration of carriers involved in the absorption spectrum and m their effective mass) for $x = 12$, encountered in $\sigma_1(\omega)$ for $E \| c$ up to approximately 1 eV but before the onset of interband transitions, corresponds to a plasma frequency of about 1 eV. By assuming m equal to the free electron mass m_e as in reference [8], we also obtain a hole density per ladder-Cu of about $n \sim 0.2$ [8]. However, the Drude weight ascribed to the effective metallic contribution in $\sigma_1(\omega)$ at low frequencies ($\omega < 60$ meV) corresponds to a plasma frequency of about 0.2 eV (for $x = 12$ and $E \| c$). This would suggest that either the free charge carriers have an effective mass of about $25m_e$ or alternatively that only a small fraction of holes $n_{eff} < n$ is effectively involved in the metallic contribution. Moreover, along the transverse direction (a-axis, Fig. 2) one can observe an increased metallicity upon doping, manifested by an incipient plasma edge development. This bears a remarkable analogy with the behaviour in Bechgaard salts and indicates a similar confinement-deconfinement crossover upon Ca-substitution.

The temperature dependence of $\sigma_1(\omega)$ for $x = 0$ and for both $E \| a$ and $E \| c$ (Figs. 4a and 4c), reveals the localization of the excess free charge carriers or of the preformed hole pairs. The temperature dependence of $\sigma_1(\omega)$ for $x = 12$ is qualitatively different between the two polarization directions (Figs. 4b and 4d). Along the a-axis, $\sigma_1(\omega)$ is continuously suppressed in FIR with decreasing temperature (as for $x = 0$), while along the c-axis $\sigma_1(\omega)$ first increases in FIR for decreasing temperature from 300 K down to $T_\rho \sim 100$ K and then is suppressed below 100 K. Anyway, a residual metallic component persists

down to 10 K for both directions. We can generally argue that the pre-formed hole pairs give a metallic behaviour ($d\rho/dT > 0$) along the c-axis above T_ρ, while localization takes place below T_ρ [7,17]. The energy range over which the Drude spectral weight is suppressed along the a-axis, gives an indirect estimate of the energy necessary for breaking the hole pairs (Figs. 4a and 4b). Furthermore and specifically for $x = 12$ along the c-axis, a (pseudo) gap-like feature seems to develop at about 20 meV, which could reveal the relevant energy scale associated with the low temperature CDW state. In fact, the theoretical investigation of the isolated $t-J$ ladder shows that, at $T = 0$, superconducting correlations are competing with strong CDW correlations of the pre-formed pairs; the dominant one depending very sensitively on the J/t ratio [17], and ultimately on the Ca substitution or on pressure.

In summary, the electrodynamics of

$$Sr_{14-x}Ca_xCu_{24}O_{41}$$

provides strong evidence for the quasi one-dimensionality of these ladder systems, manifested by the anisotropic optical response. Upon Ca substitution, there is a progressive deconfinement of the pre-formed hole pairs, establishing a similarity with the class of linear chain Bechgaard salts. Localization effects then develop at low temperatures, leading to a suppression of Drude weight. It is speculated that the low temperature insulating state could be associated with the formation of a CDW condensate (associated with the localized hole pairs for $x = 12$). Nonetheless, signatures of such a collective ground state, like, *e.g.*, the pinned phason mode, remain to be clearly discovered and are a matter of further investigations.

We thank E. Dagotto, D. Jerome, T. Müller, D. Poilblanc, T.M. Rice and P. Wachter for stimulating discussions, and J. Müller for technical help. The work at ETH benefited from the financial support of the Swiss National Foundation for the Scientific Research.

References

1. E. Dagotto, T.M. Rice, Science **271**, 618 (1996).
2. E.M. McCarron *et al.*, Mat. Res. Bull. **23**, 1355 (1988).
3. E. Dagotto *et al.*, Phys. Rev. B **45**, 5744 (1992).
4. M. Azuma *et al.*, Phys. Rev. Lett. **73**, 3463 (1994).
5. M. Uehara *et al.*, J. Phys. Soc. Jap. **65**, 2764 (1996).
6. N. Motoyama *et al.*, Phys. Rev. B **55**, R3386 (1997).
7. T. Adachi *et al.*, Solid State Commun. **105**, 639 (1998).
8. T. Osafune *et al.*, Phys. Rev. Lett. **78**, 1980 (1997).
9. A. Revcolevschi, J. Jegoudez in *Coherence in high temperature superconductors* edited by G. Deutscher, A. Revcolevschi (World Scientific, 1996), p. 19; U. Ammerahl *et al.*, Crys. Growth (in press).
10. A. Revcolevschi *et al.*, Physica C **282-287**, 493 (1997).
11. A. Schwartz *et al.*, Phys. Rev. B **58**, 1261 (1998).
12. H. Mayaffre *et al.*, Science **279**, 345 (1998).
13. C.C. Homes *et al.*, Phys. Rev. Lett. **71**, 1645 (1993).
14. T.M. Rice (private communication).
15. V. Vescoli *et al.*, Science **281**, 1181 (1998).
16. J. Moser *et al.*, Eur. Phys. J. B **1**, 39 (1998).
17. C.A. Hayward *et al.*, Phys. Rev. B **53**, R8863 (1996).