*J. Phys. IV France* **131** (2005) 299–304
© EDP Sciences, Les Ulis
DOI: 10.1051/jp4:2005131076

# Phase diagrams of (La,Y,Sr,Ca)$_{14}$Cu$_{24}$O$_{41}$: Switching between the ladders and the chains

T. Vuletić[1,*], T. Ivek[1], B. Korin-Hamzić[1], S. Tomić[1], B. Gorshunov[2,**], M. Dressel[2], C. Hess[3], B. Büchner[3] and J. Akimitsu[4]

[1] *Institut za fiziku, Zagreb, Croatia*
[2] *1. Physikalisches Institut, Universität Stuttgart, Germany*
[3] *Leibniz-Institut für Festkörper- und Werkstoffforschung, Dresden, Germany*
[4] *Department of Physics, Aoyama-Gakuin University, Kanagawa, Japan*

**Abstract.** The most comprehensive charge response study of the intrinsically hole doped, spin-chain and spin-ladder composites is overviewed. Results of dc and electric-field-dependent resistivity, low frequency dielectric, and optical spectroscopy in all crystallographic directions are used to build phase diagrams of the underdoped materials (hole count= $6 - y$ per formula unit, f.u.) and of the fully doped , 6 holes per f.u. The underdoped materials are insulators with hopping transport along the chains, which behave as a one-dimensional disordered system. For the fully doped materials the charge transport switches to the ladders due to transfer of holes from the chains. Two-dimensional (2D) charge-density wave (CDW) ground state is formed, i.e. besides CDW phason response along the ladders for $0 \leq x \leq 9$, we also found it along the ladder rungs for $x \leq 6$. However, CDW sliding conductivity, as observed in the standard CDW materials, is not observed in either of directions. Normal to the ladder planes no CDW response was found, and transport is presumably hopping-like. For the first time in any system, CDW response away from the principal direction was identified. For $x > 9$ both CDW in ladders and CO in chains are supressed.

## 1. INTRODUCTION

In the quasi-one-dimensional (quasi-1D) systems superconductivity is always in competition and/or coexistence with other collective electronic ground states, like charge and spin-density waves [1]. This competition appears also in the quasi-1D cuprates [2]. These materials are intrinsically hole doped composites consisting of cuprate spin-chains and spin-ladders [3, 4]. They have attracted much attention, mainly because they represent the first superconducting copper oxides with a non-square lattice. In the case of quasi-1D cuprates experiment was preceded by a theoretical idea that, in isolated hole-doped two-leg ladders, the spin-gap will occur and lead to the hole-pairing on the ladder rungs, and to superconductivity, although in competition with a charge-density wave [5]. Eventually, after superconductivity [6], both the gapped spin-liquid [7] and charge-density wave states [8–10] have been observed in the doped spin-ladders of $Sr_{14-x}Ca_xCu_{24}O_{41}$. The relevance of these states to the nature of superconductivity is still subject of intensive discussion. In order to catalyze this process we have used our charge response studies, as well as many results reported in the literature, to assemble comprehensive phase diagrams of materials as a function of La,Y content and of $Sr_{14-x}Ca_xCu_{24}O_{41}$ materials as a function of Ca content [11].

Stoichiometric reasons limit trivalent La, Y substitution for divalent Sr, Ca to a maximum of six per f.u., which equals to the total hole count $n_h = 6$ per f.u. An undoped Cu-site is characterized by a spin $S = 1/2$ of the $Cu^{2+}$ ion, while a hole doped may be regarded as a $Cu^{3+}$ ion. Here, the spin $S = 0$ is observed because a Zhang-Rice singlet forms [12]. In this manner the hole and spin arrangements become

* *Corresponding author*: e-mail: tvuletic@ifs.hr
** *Permanent address*: B. Gorshunov: A. M. Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia.

complementary within the chains or ladders. The distribution of holes between the ladders and chains depends on the La,Y substitution level. Even when La, Y= 0, it depends on Ca substitution [13, 14] and on temperature, *e.g.* all the holes back-transfer into the chains at low temperatures [15, 16]. Based on the above, quasi-1D cuprates are separated into underdoped and fully doped $Sr_{14-x}Ca_xCu_{24}O_{41}$.

## 2. UNDERDOPED $(La,Y)_y(Sr,Ca)_{14-y}Cu_{24}O_{41}$

The ladders contain no holes and the ground state is a non-magnetic, gapped spin-liquid. Therefore, the phase diagram reduces to the phase diagram of chains. In order to establish the nature of insulating phase of underdoped materials, we have performed electrical transport measurements on $La_3Sr_3Ca_8$-$Cu_{24}O_{41}$, $n_h = 3$ and $La_{5.2}Ca_{8.8}Cu_{24}O_{41}$, $n_h = 0.8$ materials. In the left panel of Fig.1 dc conductivity along the chains/ladders, *i.e.* along *c*-axis, is shown *vs.* inverse square root of temperature scale. It can be seen that the dc conductivity follows a simple activation behavior $\sigma_{dc}(T) \propto \exp(\Delta/T)$ only at high temperatures, while at the crossover temperature $T_{co}$ it enters into a variable-range hopping regime: $\sigma_{dc} \propto \exp[-(T_0/T)^{1/(1+d)}]$. Fits to the latter behavior appear as straight solid lines in Fig.1, *i.e.* the parameter $d$ was found to have the value of one. This confirms the 1D nature of the observed transport mechanism: hopping transport along the chains, which are randomly distorted by irregular coordination of La/Sr/Ca ions. From our results and result by [17] on $YSr_{13}Cu_{24}O_{41}$, $n_h = 5$, it is evident that the chain subsystem behaves as a 1D disorder-driven insulator for the whole range $0 \leq n_h \leq 5$. A further evidence comes from the conductivity measured in the broad frequency range, presented in [18].

Using the above, we present the phase diagram of chains in underdoped as a function of La,Y content, Fig.1, right panel. The high temperature phase is a paramagnetic 1D disordered insulator. Circles denote the observed $T_{co}$. The antiferromagnetic order of ferromagnetic chains (AF ferro) was established for $6 \geq y \geq 5$ below the phase transition studied by magnetic susceptibility, specific heat and inelastic neutron scattering (INS) measurements [19]. Short-range AF correlations persist up to $y \lesssim 2$ [20]. The AF dimers phase was indicated to exist at short scales for $2 \gtrsim y \geq 0.1$ by INS and dc susceptibility measurements [21, 22]. Therefore, for $1 \geq y \geq 0$, we concluded that the number of holes in the chains remains fixed at five, while ladders start to be doped gradually to accommodate one hole per f.u. for $y = 0$, $n_h = 6$ [22]. In this process respective room temperature conductivity increases for orders of magnitude, indicating that the charge transport switches from the chains to the ladders.

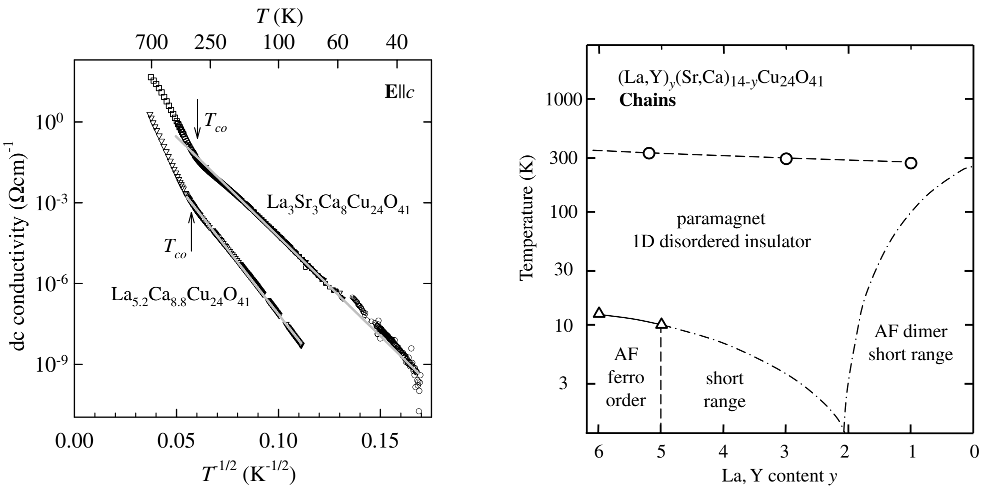


**Figure 1.** Left panel: The dc conductivity along the *c*-axis as a function of $T^{-1/2}$. Right panel: Qualitative phase diagram of the chains in , as a function of La,Y content.

### 3. FULLY DOPED $Sr_{14-x}Ca_xCu_{24}O_{41}$

In the following we briefly show the phase diagram for the chains in $Sr_{14-x}Ca_xCu_{24}O_{41}$, which merges with the one already shown for $(La,Y)_y(Sr,Ca)_{14-y}Cu_{24}O_{41}$. Compared to the ladders, the chains in $Sr_{14-x}Ca_xCu_{24}O_{41}$ are relatively inert in the charge sector, and charge response measurements do not probe them. However, due to the complementary spin and charge arrangements the magnetic measurements also provide knowledge of charge sector, Fig. 2, left panel. Presumably, the high temperature phase is also a paramagnetic 1D disordered insulator, as in $(La,Y)_y(Sr,Ca)_{14-y}Cu_{24}O_{41}$. ESR as well as NMR/NQR investigations show the crossover temperature, below which 2D AF dimer and complementary charge order set in for $0 \leq x \lesssim 6$ [23, 24]. While in the chains of $(La,Y)_y(Sr,Ca)_{14-y}Cu_{24}O_{41}$, $y \lesssim 2$ this order can develop only at short length scales, here the number of holes is close to six per f.u. at low temperatures (due to the back transfer of holes), and therefore permits the AF dimer order to develop fully. Short-range AF dimer correlations persist up to $x \approx 11.5$ [25]. For $x \geq 11$ the antiferromagnetic Néel order is established below the phase transition characterized by ESR, static susceptibility measurements, specific heat, NMR and neutron scattering [23, 25–27].

The phase diagram of doped ladders of $Sr_{14-x}Ca_xCu_{24}O_{41}$ is shown in Fig. 2, right panel. Already for $x = 0$ there is around one hole in the ladders, increasing upon Ca substitution. However, the amount of hole transfer is still under investigation. The high temperature (normal) phase of such hole doped ladders is a doped Mott insulator. Holes in the ladders appear as being mobile when compared with the holes in the chains. Gapped spin-liquid (which is a ground state of the undoped ladders) and two-dimensional (2D) charge-density wave (CDW) order set in concomitantly, at least for $x \leq 4$, as shown by NMR, and by our charge response studies [28–34]. This CDW, with periodicity of five ladder unit-cell parameters [35], develops in 2D in the *ac* ladder planes. Both dc resistivity and low frequency dielectric spectroscopy show that increasing the Ca content destroys the long-range order rapidly (for $6 < x \leq 9$) so that only CDW short-range order survives, before it vanishes completely for $x > 9$ [33, 34]. For $x > 4$ the crossover from gapped spin-liquid to paramagnetic regime remains independent of Ca content and corresponding hole transfer into the ladders [31, 32]. Sketched are also metallic and antiferromagnetic phases [17, 25] observed for large Ca substitution. In $Sr_{14-x}Ca_xCu_{24}O_{41}$ pressure is an additional important parameter besides Ca content $x$. Upon application of pressure, for $10 \leq x \leq 13.6$ materials, the spin gap decreases but remains finite when superconductivity sets in within the pressure range of 3–8 GPa. The role of the

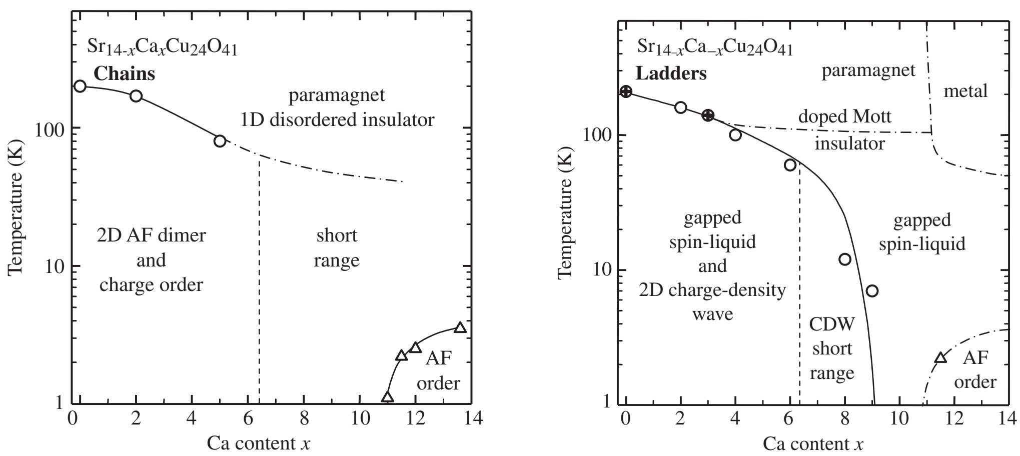


**Figure 2.** Qualitative phase diagrams of the subsystems in $Sr_{14-x}Ca_xCu_{24}O_{41}$, as a function of Ca content: in the left panel for the chains, in the right panel for the hole doped ladders.

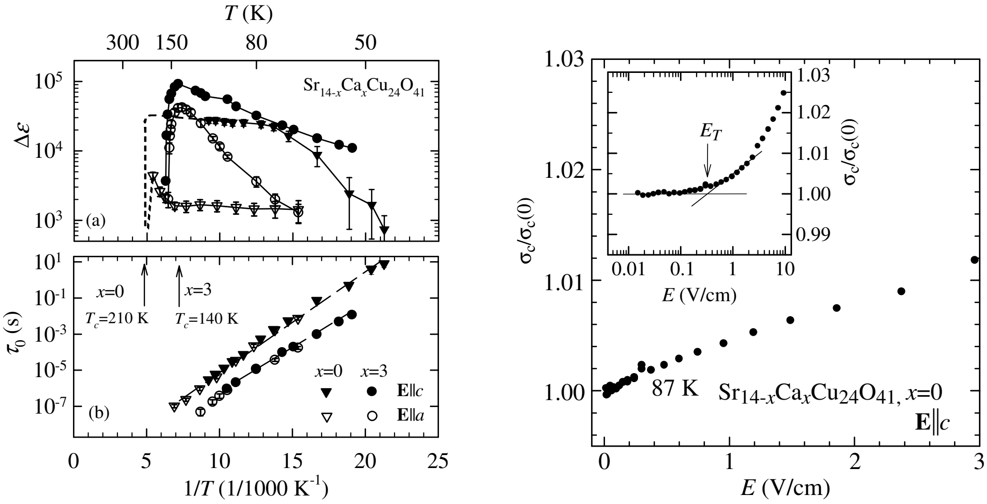


**Figure 3.** Left panel: Parameters of the anisotropic dielectric relaxation in the ladders of $Sr_{14-x}Ca_xCu_{24}O_{41}$ with $x = 0, 3$ as a function of the inverse temperature. Right panel: Electric-field-dependent conductivity ($\sigma_c$) of $Sr_{14-x}Ca_x$-$Cu_{24}O_{41}$, $x = 0$ along the $c$-axis, normalized to the low-field value $\sigma_c(0)$.

spin gap in superconducting pairing is not clear yet, since there is some NMR evidence for the presence of quasi-particles with a finite density of states at the Fermi level, which contribute to superconductivity [36].

Our charge response study has mostly concentrated on the properties of the CDW phase. The low-frequency dielectric dispersion characteristic of CDW phason response is, for the first time in any material, reported for both longitudinal and perpendicular direction. In Fig. 3, left panel, we show as a function of temperature the parameters describing the observed dispersions – the dielectric strength $\Delta\varepsilon$ and the mean relaxation time $\tau_0$. Charge-density wave phase transition temperatures $T_c$ are also indicated. Upon decreasing temperature a sharp growth of $\Delta\varepsilon$ occurs in the vicinity of $T_c$, reaching $\Delta\varepsilon = 10^4 - 10^5$ at $T_c$ for $\mathbf{E}||c$, along the ladders, and an order of magnitude lower for $\mathbf{E}||a$, along the ladder rungs. However, the central relaxation time $\tau_0^{-1}$ has the similar values for both directions $\mathbf{E}||c$ and $\mathbf{E}||a$ and decays Arrhenius-like ($\tau_0(T) \propto \exp(\Delta_{\mathrm{CDW}}/k_BT) \propto \rho(T)$). Finally, we note that Ca content quickly suppresses the length scale at which the 2D CDW develops in the ladder plane, and that response in perpendicular direction is not observed for $x = 8$ and 9. Besides the low-frequency mode, another feature of the phason response of CDW – pinned mode in microwave – is also observed for $x = 0$, for both $\mathbf{E}||c$ and $\mathbf{E}||a$ [8, 11, 34].

We note that $\Delta\varepsilon$ is lower than the magnitude typical for 1D CDW materials, $10^7 - 10^8$ [37], probably due to $Sr_{14-x}Ca_xCu_{24}O_{41}$ being intrinsically disordered due to Ca content. In standard CDW materials $\Delta\varepsilon$ is also simply related to the threshold electric field for nonlinear conductivity: $\Delta\varepsilon \times E_T =$ constant [37]. In this manner we estimate $E_T = 400$ V/cm for $Sr_{14}Cu_{24}O_{41}$, a value far above the applied fields of 10 V/cm. Indeed, apart from a weak nonlinear effect of the order of 1%, no sliding conductivity characterized by a threshold field is observed at linear scale, Fig. 3, right panel. Note that the same data, if plotted at logarithmic scale, indicate the existence of $E_T$ (inset of Fig. 3, right panel). Indeed, claims for the sliding CDW with finite $E_T$ were raised by other authors [9, 38]. This issue deserves more studies in future.

## 4. CONCLUSION

In conclusion, we note that both collective electronic ground states, theoretically predicted for doped ladders, deserve more attention. For superconductivity, the question is whether the spin-gap is important, or SC may be explained by the same mechanisms as for high-temperature superconducting cuprates. For CDW, the response in two dimensions raises the issue of nature of CDW in this strongly correlated electron system. For both phases, the pairing is probably of non-*s*-wave nature [39, 40]. With regard to the recent theoretical efforts, we note that detailed theoretical studies of the ladders phase diagram are still necessary.

**References**


[1] V. J. Emery, in *Highly Conducting One-Dimensional Solids*, eds J. Devreese, R. Evrard and V. van Doren, (Plenum, New York, 1979).

[2] E. Dagotto, Rep. Prog. Phys. **62**, 1525 (1999).

[3] T. Siegrist, L. F. Schneemeyer, S. A. Sunshine, J. V. Waszczak and R. S. Roth, Mat. Res. Bull. **23**, 1429 (1988).

[4] E. M. McCarron, M. A. Subramanian, J. C. Calabrese and R. L. Harlow, Mat. Res. Bull. **23**, 1355 (1988).

[5] E. Dagotto, J. Rieira and D. Scalapino, Phys. Rev. B **45**, 5744 (1992).

[6] M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Môri and K. Kinoshita, J. Phys. Soc. Jpn. **65**, 2764 (1996).

[7] K. Kumagai, S. Tsuji, M. Kato and Y. Koike, Phys. Rev. Lett. **78**, 1992 (1997).

[8] H. Kitano, R. Isobe, T. Hanaguri, A. Maeda, N. Motoyama, M. Takaba, K. Kojima, H. Eisaki and S. Uchida, Europhys. Lett. **56**, 434 (2001).

[9] G. Blumberg, P. Littlewood, A. Gozar, B. S. Dennis, N. Motoyama, H. Eisaki and S. Uchida, Science **297**, 584 (2002).

[10] B. Gorshunov, P. Haas, T. Rõõm, M. Dressel, T. Vuletić, B. Korin-Hamzić, S. Tomić, J. Akimitsu and T. Nagata, Phys. Rev. B **66**, 060508(R) (2002).

[11] T. Vuletić, B. Korin-Hamzić, T. Ivek, S. Tomić, B. Gorshunov, M. Dressel and J. Akimitsu, submitted to Phys. Rep. (2005).

[12] S.-C. Zhang and T. M. Rice, Phys. Rev. B **37**, R3759 (1988).

[13] T. Osafune, N. Motoyama, H. Eisaki and S. Uchida, Phys. Rev. Lett. **78**, 1980 (1997).

[14] N. Nücker, M. Merz, C. A. Kuntscher, S. Gerhold, S. Schuppler, R. Neudert, M. S. Golden, J. Fink, D. Schild, S. Stadler, V. Chakarian, J. Freeland, Y. U. Idzerda, K. Conder, M. Uehara, T. Nagata, J. Goto, J. Akimitsu, N. Motoyama, H. Eisaki, S. Uchida, U. Ammerahl and A. Revcolevschi, Phys. Rev. B **62**, 14384 (2000).

[15] M. Isobe, M. Onoda, T. Ohta, F. Izumi, K. Kimoto, E. Takayama-Muromachi, A. W. Hewat and K. Ohoyama, Phys. Rev. B **62**, 11667 (2000).

[16] Y. Piskunov, D. Jérome, P. Auban-Senzier, P. Wzietek and A. Yakubovsky, cond-mat/0505561 (2005).

[17] N. Motoyama, T. Osafune, T. Kakeshita, H. Eisaki and S. Uchida, Phys. Rev. B **55**, R3386 (1997).

[18] T. Vuletić, B. Korin-Hamzić, S. Tomić, B. Gorshunov, P. Haas, M. Dressel, J. Akimitsu, T. Sasaki and T. Nagata, Phys. Rev. B **67**, 184521 (2003).

[19] M. Matsuda, K. M. Kojima, Y. J. Uemura, J. L. Zaretsky, K. Nakajima, K. Kakurai, T. Yokoo, S. M. Shapiro and G. Shirane, Phys. Rev. B **57**, 11467 (1998); M. Matsuda, K. Katsumata, T. Yokoo, S. M. Shapiro and G. Shirane, Phys. Rev. B **54**, 15626 (1996).

[20] V. Kataev, K.-Y. Choi, M. Grüninger, U. Ammerahl, B. Büchner, A. Freimuth and A. Revcolevschi, Phys. Rev. Lett. **86**, 2882 (2001).

[21] M. Matsuda, K. Katsumata, H. Eisaki, N. Motoyama, S. Uchida, S. M. Shapiro and G. Shirane, Phys. Rev. B **54**, 12199 (1996); M. Matsuda, K. Katsumata, T. Osafune, N. Motoyama, H. Eisaki, S. Uchida, T. Yokoo, S. M. Shapiro, G. Shirane and J. L. Zarestky, Phys. Rev. B **56**, 14499 (1997).

[22] M. Kato, T. Adachi, Y. Koike, Physica C **265**, 107 (1996).

[23] V. Kataev, K.-Y. Choi, M. Grüninger, U. Ammerahl, B. Büchner, A. Freimuth and A. Revcolevschi, Phys. Rev. B **64**, 104422 (2001).
[24] M. Takigawa, N. Motoyama, H. Eisaki and S. Uchida, Phys. Rev. B **57**, 1124 (1998).
[25] S. Ohsugi, K. Magishi, S. Matsumoto, Y. Kitaoka, T. Nagata and J. Akimitsu, Phys. Rev. Lett. **82**, 4715 (1999).
[26] T. Nagata, H. Fujino, J. Akimitsu, M. Nishi, K. Kakurai, S. Katano, M. Hiroi, M. Sera and N. Kobayashi, J. Phys. Soc. Jpn. **68**, 2206 (1999).
[27] M. Isobe, Y. Uchida and E. Takayama-Muromachi, Phys. Rev. B **59**, 8703 (1999).
[28] T. Imai, K. R. Thurber, K. M. Shen, A. W. Hunt and F. C. Chou, Phys. Rev. Lett. **81**, 220 (1998).
[29] C. Hess, C. Baumann, U. Ammerahl, B. Büchner, F. Heidrich-Meisner, W. Brenig and A. Revcolevschi, Phys. Rev. B **64**, 184305 (2001).
[30] K. R. Thurber, K. M. Shen, A. W. Hunt, T. Imai and F. C. Chou, Phys. Rev. B **67**, 094512 (2003).
[31] K. Magishi, S. Matsumoto, Y. Kitaoka, K. Ishida, K. Asayama, M. Uehara, T. Nagata and J. Akimitsu, Phys. Rev. B **57**, 11533 (1998).
[32] Y. Piskunov, D. Jérome, P. Auban-Senzier, P. Wzietek and A. Yakubovsky, Phys. Rev. B **69**, 014510 (2004).
[33] T. Vuletić, B. Korin-Hamzić, S. Tomić, B. Gorshunov, P. Haas, T. Rõõm, M. Dressel, J. Akimitsu, T. Sasaki and T. Nagata, Phys. Rev. Lett. **90**, 257002 (2003).
[34] T. Vuletić, T. Ivek, B. Korin-Hamzić, S. Tomić, B. Gorshunov, P. Haas, M. Dressel, J. Akimitsu, T. Sasaki and T. Nagata, Phys. Rev. B **71**, 012508 (2005).
[35] P. Abbamonte, G. Blumberg, A. Rusydi, A. Gozar, P. G. Evans, T. Siegrist, L. Venema, H. Eisaki, E. D. Isaacs and G. A. Sawatzky, Nature **431**, 1078 (2004).
[36] N. Fujiwara, N. Mori, Y. Uwatoko, T. Matsumoto, N. Motoyama and S. Uchida, Phys. Rev. Lett. **90**, 137001 (2003).
[37] G. Grüner, Rev. Mod. Phys. **60**, 1129 (1988).
[38] A. Maeda, R. Inoue, H. Kitano, N. Motoyama, H. Eisaki and S. Uchida, Phys. Rev. B **67**, 115115 (2003).
[39] M. Tsuchiizu and Y. Suzumura, J. Phys. Soc. Jpn. **73**, 804 (2004).
[40] M. Tsuchiizu and Y. Suzumura, Phys. Rev. B **72**, 075121 (2005).