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Disappearance of superconductivity in overdoped $La_{1.15-x}Pr_{0.85}Sr_xCuO_4$ and the orthorhombic-tetragonal phase boundary

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A study of the structural and electronic phase diagram of Pr-doped $La_{2-x}Sr_xCuO_4$ is presented in order to investigate whether there is an influence of the high-temperature tetragonal-to-orthorhombic phase transition on the disappearance of superconductivity in the overdoped region. We find that Pr doping shifts the structural phase boundary to higher Sr concentrations, but that superconductivity occurs in the same Sr-concentration range as in "pure" $La_{2-x}Sr_xCuO_4$. Thus, the disappearance of superconductivity is not related to the high-temperature structural transition, but is determined predominantly by the hole concentration in the CuO planes.

The generic phase diagram of the copper oxide superconductors as a function of the hole doping is believed to consist of three fundamental phases, the antiferromagnetic insulator for small doping, the high-T_c superconductor, and the nonsuperconducting metal for large hole concentration in the Cu-O planes. Among the high-T_c superconductors these phases can easily be realized by doping La_2CuO_4 with Sr.[1] The disappearance of superconductivity in the metallic overdoped region in $La_{2-x}Sr_xCuO_4$ has been studied frequently.[1,2] This phase boundary between the superconductor and a nonsuperconducting metal has been attributed to a crossover from an unusual metal towards a Fermi liquidlike metal with increasing hole doping of the Cu-O planes, signaled by the concentration dependence of the transport properties and the magnetic susceptibility.[1]

Recently the electronic and structural phase diagram of heavily doped $La_{2-x}Sr_xCuO_4$ has been reexamined.[2] It has been found that the disappearance of superconductivity seems to be correlated with a structural phase boundary. From the Meissner flux expulsion and from x-ray diffraction spectra of long-time annealed samples Takagi *et al.* find that (i) the superconducting phase is confined to a much narrower composition range than previously believed and that (ii) the disappearance of superconductivity and the phase boundary of the high-temperature tetragonal to orthorhombic structural (HT) transition coincide at a Sr concentration of $x \simeq 0.21$. According to Takagi *et al.* superconductivity observed for Sr concentrations $x > 0.21$ can be attributed to local variations of the Sr content. Quite similarly Jorgensen *et al.* argue that the disappearance of superconductivity is correlated to a change from a locally orthorhombic structure towards a tetragonal structure at a Sr concentration of $x \simeq 0.24$.[3]

According to these studies one may ask the following. (1) Does the disappearance of superconductivity in overdoped $La_{2-x}Sr_xCuO_4$ reflect the dependence of the electronic properties on the hole doping of the Cu-O planes, i.e., is the metallic nonsuperconducting phase in the overdoped region a characteristic feature of the doped Cu-O planes and is $La_{2-x}Sr_xCuO_4$ a prototype system for the high-T_c superconductors? (2) Is a (local) structural deformation of the planar and square Cu-O planes a requirement for superconductivity in the cuprates?

In this paper we present a study of the structural and electronic phase diagram of $(La,Pr)_{2-x}Sr_xCuO_4$, i.e., Pr-doped $La_{2-x}Sr_xCuO_4$. We find that Pr doping shifts the phase boundary of the high-temperature structural transition towards much higher temperatures at fixed hole concentration. On the other hand, superconductivity occurs in the same range of Sr concentrations as in $La_{2-x}Sr_xCuO_4$. This demonstrates that the disappearance of superconductivity with increasing Sr concentration is not related to the high-temperature structural transition, but is mainly determined by the hole concentration.

Sample preparation and characterization as well as the experimental techniques have been described elsewhere.[4,5] The oxygen content of the samples as determined by iodometric titration was proved to be 4.000(5).

We have previously reported several studies of rare earth (RE) doped $La_{2-x}Sr_xCuO_4$.[5,4] The main results with respect to the structural properties are the following. (1) With increasing RE concentration, the high-temperature tetragonal-orthorhombic transition temperature T_{HT} is shifted towards higher temperatures. This shift scales well with the mean ionic (La/RE) radius. (2) RE doping induces an additional low-temperature structural phase transition for all RE's *with the exception of Pr.* The influence of both RE doping and hole doping on T_{HT} can be attributed to a change of the bondlengths mismatch between La-O and Cu-O layers.[4]

On the other hand, RE doping has no significant influence on the hole concentration as found from iodometric titration and, more importantly, from Hall effect and thermopower, whose absolute values are independent of the RE content.[4] Thus, RE doping allows us to change the structural properties at fixed hole concentration, or, equivalently, to shift the hole concentra-

tion at the HT structural phase boundary. In particular, Pr-doped compounds are well suited to investigate a correlation between the HT structural transition and the disappearance of superconductivity, since no additional low-temperature structural transition occurs.[6] One should mention that the magnetic susceptibility, transport properties, inelastic neutron diffraction data[7] and the influence of the Pr doping on the superconductivity shown below do not give any evidence for tetra- or mixed valent Pr or for a strong hybridization between the Pr $4f$ electrons and the electronic states within the Cu-O planes in $(La,Pr)_{2-x}Sr_xCuO_4$.

The influence of Pr doping on the structural transition can be extracted from the x-ray diffraction data. In the left panel of Fig. 1 we show the orthorhombic strain (a-b) measured at room temperature as a function of the Sr concentration in $La_{1.15-x}Pr_{0.85}Sr_xCuO_4$. The orthorhombic strain strongly decreases with increasing Sr concentration similar as in pure $La_{2-x}Sr_xCuO_4$. The Sr concentration at the HT phase boundary at *room temperature* in $La_{1.15-x}Pr_{0.85}Sr_xCuO_4$ is found at $x \approx 0.21$. In "pure" $La_{2-x}Sr_xCuO_4$ this phase boundary is observed at $x \sim 0.1$.[1,4] The temperature dependence of the orthorhombic strain for samples with a higher Sr concentration, i.e., for compositions with a tetragonal room temperature structure is shown in the right panel of Fig. 1. For the samples with Sr concentrations 0.23, 0.25, and 0.28 the HT structural transitions are observed at 250, 200, and 100 K, respectively. There is no hint on an additional low-temperature transition. Similar results are obtained for samples with other Sr and Pr concentrations. The Sr concentration dependence of T_{HT} does not change due to Pr doping, i.e., $\Delta T_{HT}/\Delta x \approx -25$ K/0.01 is found for both $La_{2-x}Sr_xCuO_4$ and $La_{1.15-x}Pr_{0.85}Sr_xCuO_4$. Both the room temperature and the temperature-dependent data shown in Fig. 1 clearly demonstrate that doping with $Pr_{0.85}$ leads to a shift Δx of the $T_{HT}(x)$ curve to higher Sr concentrations by about $\Delta x \simeq 0.1$ at a given temperature, or, alternatively to an increase of T_{HT} by about 270 K at fixed Sr concentration.

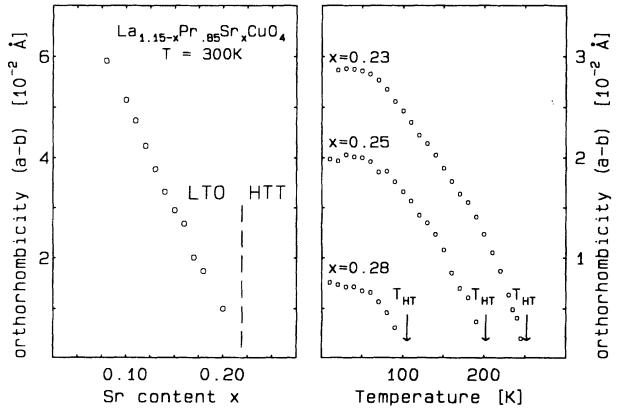

FIG. 1. Left panel: Orthorhombic splitting (a-b) at room temperature as a function of the Sr concentration in $La_{1.15-x}Pr_{0.85}Sr_xCuO_4$. Right panel: Orthorhombic splitting (a-b) as a function of temperature for samples with various Sr concentrations.

We turn now to the superconducting transition. In Fig. 2 we show the ac susceptibility of $La_{1.15-x}Pr_{0.85}Sr_xCuO_4$ measured in an external field $H = 1$ G as a function of temperature. Since weak intergranular coupling can lead to an ideal diamagnetic signal in the ac susceptibility or in the zero field cooled (ZFC) dc susceptibility even for samples with small superconducting volume fractions, the data shown in Fig. 2 were measured for powdered samples. The typical size of the single grains was in the order of several μm. As shown in the inset of Fig. 2(b) the ac susceptibility does not change by changing the external fields between 0.03 and 8 G. Thus the data in Fig. 2 reflect the magnetic properties of small isolated particles.

In the underdoped region ($x < 0.15$) the diamagnetic response of the Pr-doped samples is significantly smaller than for higher Sr concentrations quite similar to the findings in pure $La_{2-x}Sr_xCuO_4$.[1] For higher Sr concentrations, on which we shall focus in the following, the field cooled (fc) dc susceptibility [inset of Fig. 2(a)] shows bulk superconductivity with a Meissner fraction comparable to that in $La_{2-x}Sr_xCuO_4$.[1] The reduction of the di-

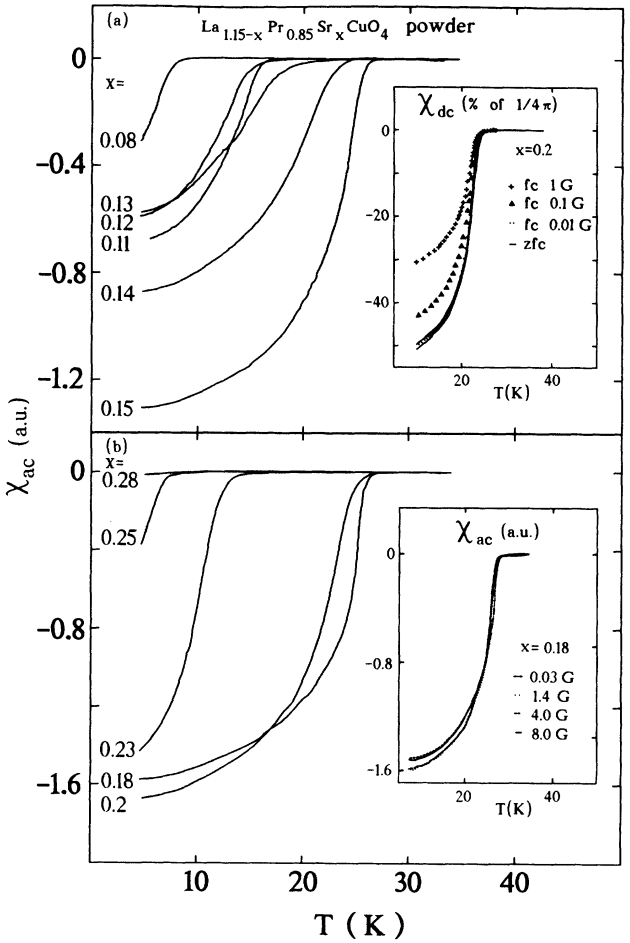

FIG. 2. Temperature dependence of the ac susceptibility ($H = 1$ G) for samples with various Sr concentrations in $La_{1.15-x}Pr_{0.85}Sr_xCuO_4$. Insets: Field cooled (fc) and zero field cooled (zfc) dc susceptibility for a sample with $x = 0.2$ in external fields between 0.01 and 1 G (a) and ac susceptibility for a sample with $x = 0.18$ in external fields between 0.03 and 8 G (b).

amagnetism compared to the ideal value [inset of Fig. 2(a)] as well as the broadening of the transition is mainly due to the small size of the particles and pinning of flux lines (fc susceptibility). However, there is also some evidence for inhomogeneities of the samples. For compositions away from optimal Sr doping ($x \sim 0.15$) a broad onset of the diamagnetic response is found. This indicates a small spatial variation of the hole concentration, again quite similar to the findings in pure $La_{2-x}Sr_xCuO_4$.[2,1]

The temperatures at the midpoint of the magnetic transitions in $La_{1.15-x}Pr_{0.85}Sr_xCuO_4$ together with the $T_c(x)$ curve of pure $La_{2-x}Sr_xCuO_4$ are shown in the inset of Fig. 3. Pr doping leads to a small reduction of T_c, which is somewhat stronger in the underdoped region ($x < 0.15$). It is apparent that the overall behavior of $T_c(x)$, i.e., the nonsuperconducting-superconducting boundary in the underdoped region, the dip in $T_c(x)$ at $x \sim 0.12$, the highest transition temperatures for $x \sim 0.15$, and *the Sr concentration at the superconducting-nonsuperconducting phase boundary in the overdoped concentration range is very similar in both cases.*

We note that the results shown in Figs. 2 and 3 clearly demonstrate that magnetic moments and disorder in the (La, RE) layer caused by the Pr doping do not influence the superconductivity in the Cu-O layers significantly. This is in striking contrast to the behavior of Pr-doped Y 1:2:3 and Nd (Sm, Eu, Gd, . . .)-doped $La_{2-x}Sr_xCuO_4$.[5] The different behavior of Pr-doped $YBa_2Cu_3O_7$ (Ref. 9) and Pr-doped $La_{2-x}Sr_xCuO_4$ may be attributed to a smaller hybridization between the Pr $4f$ electronic states and the holes in the Cu-O layers. On the other hand, the different behavior of Pr- and Nd (Sm, Eu, Gd, . . .)-doped $La_{2-x}Sr_xCuO_4$ is due to the influence of the low-temperature structural transition on the electronic properties, which is induced by doping with smaller RE only.[6]

The main result of our study is summarized in the phase diagram displayed in Fig. 3, where we show T_c and T_{HT} as a function of the Sr concentration for pure $La_{2-x}Sr_xCuO_4$ and $La_{1.15-x}Pr_{0.85}Sr_xCuO_4$. There is obviously no correlation between the high-temperature structural phase boundary and superconductivity in the Pr-doped compounds, i.e., superconductivity disappears without a qualitative change of the structure. Moreover, the $T_c(x)$ curves of pure and Pr-doped $La_{2-x}Sr_xCuO_4$ are very similar in the concentration range of 0.2 to 0.25, irrespective of the position of the structural phase boundary. We conclude from these results that the disappearance of superconductivity in overdoped $La_{2-x}Sr_xCuO_4$ is not caused by the structural transition. In other words, there is no bulk superconductivity in doped La_2CuO_4 for hole concentrations $x > 0.25$, disregarding whether the structure is high-temperature tetragonal ($La_{2-x}Sr_xCuO_4$), orthorhombic (Pr-doped $La_{2-x}Sr_xCuO_4$) or low-temperature tetragonal (Nd, Sm, Eu, Gd, . . . doped $La_{2-x}Sr_xCuO_4$).[10] The data shown in Fig. 3 give strong evidence that the overall behavior of T_c as a function of the Sr concentration in $La_{2-x}Sr_xCuO_4$ including the disappearance of superconductivity in the overdoped composition range is predominantly determined by the hole content in the Cu-O layers.

From our measurements we cannot prove the existence of superconductivity in the high-temperature tetragonal phase. Such a proof requires to shift the $T_{HT}(x)$ curve towards lower concentrations, which is not possible via RE doping. However, the phase diagram in Fig. 3 indicates that the proximity of the HT phase boundary and the disappearance of superconductivity in overdoped $La_{2-x}Sr_xCuO_4$ is accidental. Moreover, to our knowledge there is no further experimental evidence for a suppression of superconductivity in the high-temperature tetragonal phase or for the importance of an orthorhombic distortion for superconductivity in $La_{2-x}Sr_xCuO_4$. Vice versa, investigations of the pressure dependence of both, T_{HT} and T_c, which have recently been carried out by Yamada and Ido,[11] show that T_c increases due to the suppression of the HT transition by applying external pressure. From their measurements they conclude that T_c decreases with increasing orthorhombic distortion, which is in qualitative agreement with the findings from the thermal expansion and neutron diffraction measurements[8] and the small suppression of superconductivity by Pr doping shown in Figs. 2 and 3.

In conclusion we have shown that doping of $La_{2-x}Sr_xCuO_4$ with Pr leads to a decoupling of the high-temperature structural phase boundary and the disappearance of superconductivity in the overdoped concentration range. Our measurements give strong evidence that the overall Sr concentration dependence of T_c in $La_{2-x}Sr_xCuO_4$ including the suppression of supercon-

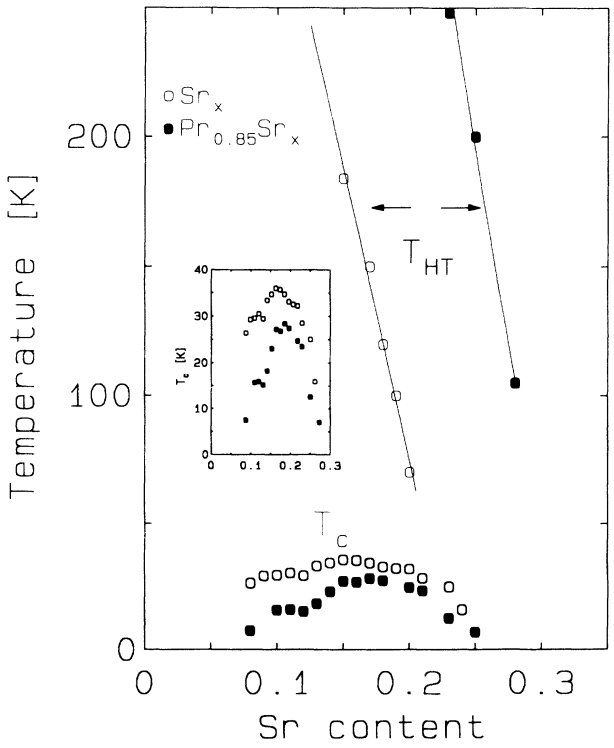

FIG. 3. Structural and superconducting phase diagram of $La_{1.15-x}Pr_{0.85}Sr_xCuO_4$ (filled symbols) and pure $La_{2-x}Sr_xCuO_4$ (open symbols) as a function of the Sr concentration. Inset: T_c defined at the midpoint of the magnetic transitions as a function of the Sr concentration in both series of samples.

ductivity in the overdoped concentration range is mainly determined by the hole content of the Cu-O layers and does not depend sensitively on the small structural changes associated with the high-temperature structural transition.

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[1]J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin, Phys. Rev. Lett. **61**, 1127 (1988); H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Ushida, and Y. Tokura, Phys. Rev. B **40**, 2254 (1989); J. B. Torrance, A. Bezinge, A. I. Nazzal, T. C. Huang, S. S. P. Parkin, D. T. Keane, S. J. LaPlaca, P. M. Horn, and G. A. Held, *ibid.* **40**, 8872 (1989); K. Yoshimura, Y. Nishizawa, Y. Ueda, and K. Kosuge, J. Phys. Soc. Jpn. **59**, 3073 (1990); M. Oda, T. Nakano, Y. Kamada, and M. Ido, Physica C **183**, 234 (1991); M. Oda, T. Ohguro, N. Yamada, and M. Ido, J. Phys. Soc. Jpn. **58**, 1137 (1989).

[2]H. Takagi, R. J. Cava, M. Marezio, B. Batlogg, J. J. Krajewski, W. F. Peck, P. Bordet, and D. E. Cox, Phys. Rev. Lett. **68**, 3777 (1992).

[3]J. D. Jorgensen, D. G. Hinks, B. A. Hunter, R. L. Hitterman, A. W. Mitchell, P. G. Radaelli, B. Dabrowski, J. L. Wagner, H. Takahashi, and E. C. Larson, in *Lattice Effects in High-T_c Superconductors,* edited by Y. Bar-Yam, T. Egami, J. Mustre-de Leon, and A. R. Bishop (World Scientific, Singapore, 1992), p. 84; T. R. Sendyka and T. Egami, *ibid.*, p. 111.

[4]M. Breuer, B. Büchner, R. Müller, M. Cramm, O. Maldonado, A. Freimuth, B. Roden, R. Borowski, B. Heymer, and D. Wohlleben, Physica C **208**, 217 (1993).

[5]B. Büchner, M. Braden, M. Cramm, W. Schlabitz, W. Schnelle, O. Hoffels, W. Braunisch, R. Müller, G. Heger, and D. Wohlleben, Physica C **185–189**, 903 (1991); B. Büchner, M. Cramm, M. Braden, W. Braunisch, O. Hoffels, W. Schnelle, J. Harnischmacher, R. Borowski, A. Gruetz, B. Heymer, C. Hohn, R. Müller, O. Maldonado, A. Freimuth, W. Schlabitz, G. Heger, D. I. Khomskii, and D. Wohlleben, in *Physics and Materials Science of High Temperature Superconductors-II,* Vol. 209 of *NATO Advanced Study Institute Series E,* edited by R. Kossowsky, B. Raveau, D. Wohlleben, and S. Patapis (Kluwer Academic, Dordrecht, 1992), p. 349; B. Büchner, M. Cramm, M. Braden, W. Braunisch, O. Hoffels, W. Schnelle, R. Müller, A. Freimuth, W. Schlabitz, D. Heger, D. I. Khomskii, and D. Wohlleben, Europhys. Lett. **21**, 953 (1993).

[6]B. Büchner, M. Cramm, M. Breuer, R. Borowski, A. Gruetz, and W. Schlabitz, *Proceedings of the Beijing International Conference on High T_c Superconductivity* (World Scientific, Singapore, 1993), p. 309.

[7]E. Holland-Moritz, M. Breuer, and A. Gruetz (unpublished).

[8]M. Braden, O. Hoffels, W. Schnelle, B. Büchner, G. Heger, B. Hennion, I. Tanaka, and H. Kojima, Phys. Rev. B **47**, 12 288 (1994).

[9]e.g. J. T. Markert, Y. Dalichaouch, and M. B. Maple, in *Physical Properties of High Temperature Superconductors I,* edited by D. M. Ginsberg (World Scientific, Singapore, 1989), p. 265.

[10]M. Breuer *et al.* (unpublished).

[11]N. Yamada and M. Ido, Physica C **203**, 240 (1992).