RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 14 1 OCTOBER 1991-II

Lattice instabilities and the effect of copper-oxygen-sheet distortions on superconductivity in doped La_2CuO_4

M. K. Crawford, R. L. Harlow, E. M. McCarron, and W. E. Farneth
Central Research and Development, Du Pont Experimental Station, P.O. Box 80356, Wilmington, Delaware 19880-0356

J. D. Axe and H. Chou
Brookhaven National Laboratory, Upton, New York 11973

Q. Huang
National Institute of Standards and Technology, Reactor E151, Gaithersburg, Maryland 20899
(Received 2 May 1991)

Synchrotron x-ray and neutron-diffraction measurements demonstrate that Nd^{3+} substitution at the La^{3+} site in both metallic and insulating $La_{2-x}Sr_xCuO_4$ induces low-temperature structural instabilities which reorient the tilting of the copper-oxygen octahedra. These structural transformations strongly affect superconductivity. In addition, there is a bicritical point involving phases of *Bmab*, *Pccn*, and $P4_2/ncm$ space-group symmetries in the structural phase diagram of $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ at $x\sim0.15$. There are also anomalies in the structural transformation temperatures and the superconducting transition temperatures when $x\sim\frac{1}{8}$, providing evidence for an electronic instability at this doping level.

One of the many interesting aspects of the high transition temperature (T_c) copper-oxide superconductors is the presence of lattice instabilities which involve distortions of the copper-oxygen layers. For example, La_2CuO_4 has orthorhombic symmetry (space group *Bmab*) as a direct result of a second-order structural phase transition involving cooperative tilting of the copper-oxygen octahedra about either the (110) or ($1\bar{1}0$) axes, referred to the tetragonal $I4/mmm$ (HTT denotes high-temperature tetragonal) structure.[1] The temperature at which this phase transition occurs[2] is strongly dependent upon the doping level of holes in the Cu-O sheets, tending toward 0 K as the hole content approaches 0.2 per Cu^{2+}. Although bulk superconductivity and long-range orthorhombic distortion both disappear near this hole concentration, transport measurements do not indicate any notable coupling of this transformation to the charge carriers in the Cu-O layers.[2]

This situation has been greatly altered by the recent discovery[3] of a second structural phase transition in $La_{1.88}Ba_{0.12}CuO_4$ at about 70 K. This phase transition, from *Bmab* (LTO denotes low-temperature orthorhombic) to $P4_2/ncm$ (LTT denotes low-temperature tetragonal) space-group symmetry, has a strong effect both upon superconductivity and normal-state transport properties in this material.[3,4] Furthermore, the oxygen isotope effect on T_c also exhibits great sensitivity to this instability.[5] Motivated by these developments, we have examined the substitution of smaller rare-earth ions (for example, Nd^{3+} or Gd^{3+}) for La^{3+} in $La_{1.88}Sr_{0.12}CuO_4$, and discovered that these substitutions produce similar lattice instabilities. We have, therefore, studied the compositions $La_{1.88-x}Nd_xSr_{0.12}CuO_4$ and $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$, all of which have the $I4/mmm$ structure at high temperatures, but undergo various structural transformations involving tilting of the CuO_6 octahedra upon cooling. These materials permit us to study the interplay among structural instability, doping, and superconductivity. Our results also address the long-standing question[6] concerning the reason for the depression of T_c in $La_{2-x}Sr_xCuO_4$ when La^{3+} is partially substituted with smaller rare-earth ions.

The synthesis of the materials studied has been described previously.[5] Synchrotron x-ray-diffraction data were obtained at beamlines X7A and X3A at the National Synchrotron Light Source, Brookhaven National Laboratory. Typical x-ray wavelengths used were between 0.7 and 1.2 Å. The powder diffractometers in each case were set up in a high-resolution, parallel beam mode with double Si(111) monochromators and a Ge(220) or (111) analyzing crystal.[7] Low-temperature data were obtained using a closed cycle He refrigerator. The neutron-diffraction measurements were made with the high-resolution, five-counter diffractometer (BT-1, wavelength of 1.553 Å) at the National Institute of Standards and Technology reactor.[8] Samples were placed in a 10-mm vanadium can and cooled in a helium cryostat. Superconducting transition temperatures were determined from Meissner data obtained using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. A magnetic field of 3G was used.

In Fig. 1 we show x-ray-diffraction data at various temperatures for a $La_{1.68}Nd_{0.2}Sr_{0.12}CuO_4$ sample. From 300 to about 55 K the orthorhombic distortion, represented by the splitting of the (200) and (020) reflections, increases smoothly. Beginning with data at 50 K, however, these two reflections broaden and nearly coalesce in a continuous manner as temperature decreases. The low-temperature (16 K) structure is orthorhombic with space group *Pccn*. For comparison, Fig. 2 shows similar data for a $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ sample. In this case the structural transformation is clearly underway at 70 K. Two phases coexist at 65 K, one LTO and the other with *Pccn* symmetry, suggesting that the transformation is discon-

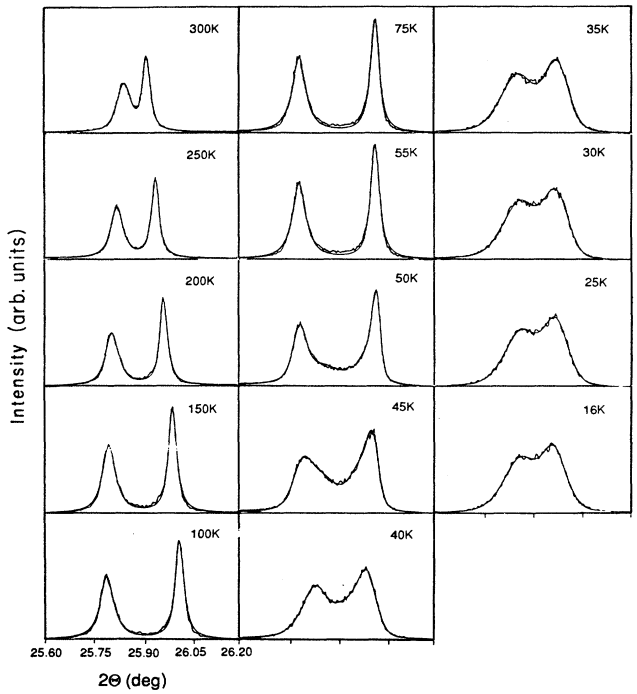

FIG. 1. Synchrotron x-ray-diffraction data for $La_{1.68}Nd_{0.2}Sr_{0.12}CuO_4$ at different temperatures. The peaks correspond to the $(110)_{HTT}$ Bragg reflection. Below 55 K the material undergoes a second-order LTO→ *Pccn* structural transformation. Fits to the line profiles are superimposed on the data. The x-ray wavelength was 1.19754(3) Å.

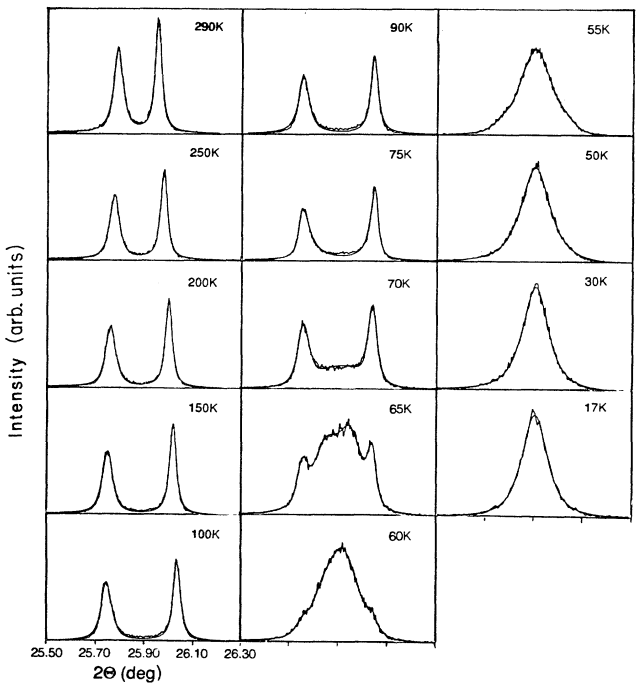

FIG. 2. Synchrotron x-ray-diffraction data for $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ at different temperatures. The peaks correspond to the $(110)_{HTT}$ Bragg reflection. The material undergoes a first-order LTO→ *Pccn* phase transition at about 70 K, and then a second-order Pccn→ LTT transformation at lower temperature. Fits to the line profiles are superimposed on the data. The 17 K linewidth deduced from the fit implies LTT domain sizes of 400–500 Å. The x-ray wavelength was 1.19754(3) Å.

tinuous. At low temperature (17 K) there is only one reflection, consistent with the material having the LTT structure. These space-group assignments are consistent with synchrotron x-ray and neutron-diffraction structural refinements which will be described in detail elsewhere.[9]

Axe and others[3] have developed a Landau theory for octahedra tilt instabilities in materials with the K_2NiF_4 structure. By expanding the Landau free energy to eighth order in the order parameters Q_1, Q_2 which describe the tilts around the (110) and $(1\bar{1}0)$ axes of the $14/mmm$ or HTT structure (Fig. 3), they find that the following structural phases can occur: HTT ($Q_1=Q_2=0$); LTO ($Q_1\neq0$, $Q_2=0$, or $Q_1=0$, $Q_2\neq0$); LTT ($|Q_1|=|Q_2|\neq0$); and *Pccn* ($Q_1\neq0$, $Q_2\neq0$, $Q_1\neq Q_2$). The appearance in a given system of an intermediate *Pccn* phase, which interpolates smoothly between the LTO and LTT structures, depends upon the sign of the relevant eight-order term. The second-order LTO→ *Pccn* phase transition we observe in $La_{1.68}Nd_{0.2}Sr_{0.12}CuO_4$ can be understood within this framework. On the other hand, we propose that $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ goes through the transformation sequence HTT→ LTO→ *Pccn*→ LTT, with the successive transitions being second, first, and (probably) second order. A first-order LTO→ *Pccn* transformation, rather than a continuous one as allowed by symmetry, requires the addition of terms higher than eighth order (for example, twelfth order) in the Landau free-energy expansion.

Our structural studies of the $La_{1.88-x}Nd_xSr_{0.12}CuO_4$ system are summarized in the phase diagram shown in Fig. 4. One interesting feature is the decrease of the superconducting transition temperature (T_c) in the structural sequence LTO to *Pccn* to LTT symmetry, that is, as $|Q_2|\rightarrow|Q_1|$. Previous[6] studies of rare-earth-substituted $La_{2-x}Sr_xCuO_4$ have concluded that the decrease of T_c induced by the substitution is not a result of magnetic pair breaking. Furthermore, we have titrated each sample and find the hole concentration to be independent of the Nd^{3+} content and equal, within 0.01, to the nominal Sr^{2+} content. This demonstrates that the Nd^{3+}-substituted samples are not oxygen deficient. Thus the decrease of T_c as x increases in Fig. 4 is most likely a direct manifestation of the changes in structure which we observe.

The structural phase diagram for the $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ system is shown in Fig. 5. The T_c values for the $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ samples and a similar series of $La_{2-x}Sr_xCuO_4$ samples[5] are also plotted versus x. $La_{1.6}Nd_{0.4}CuO_4$, a composition near the T-T' phase boundary,[10] transforms from LTO to *Pccn* symmetry at about 60 K. As the Sr^{2+} content is increased, the *Pccn* phase evolves into the LTT phase at low temperatures. Indeed, for Sr^{2+} contents of $x\sim0.15$ or greater we see no evidence for the *Pccn* phase, but rather observe a direct LTO→ LTT transformation. Thus there is a bicritical point in the phase diagram when $x\sim0.15$, the point at which the *Pccn* phase disappears. There may be a second bicritical point, involving HTT, LTO, and LTT phases, between $x=0.25$ and 0.30. We also observe that both

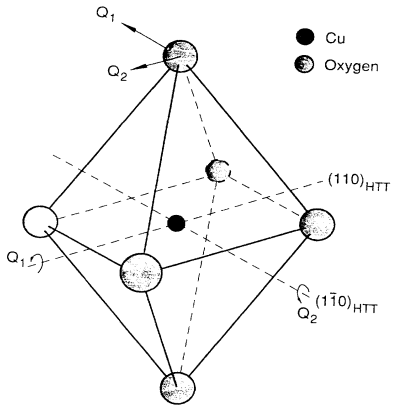

FIG. 3. Schematic diagram of a copper-oxygen octahedron. The Q_i represent the order parameters in the Landau theory describing the various tilt structures in, for example, La_2CuO_4. The Q_i have the following values for the four tilt structures discussed in the text: HTT ($Q_1=Q_2=0$); LTO ($Q_1\neq0$, $Q_2=0$, or $Q_1=0$, $Q_2\neq0$); *Pccn* ($Q_1\neq0$, $Q_2\neq0$, $Q_1\neq Q_2$); LTT ($|Q_1|=|Q_2|\neq0$).

$T_c(x)$ curves exhibit minima at $x=0.12$ ($\sim\frac{1}{8}$), while the LTO→ *Pccn* and *Pccn*→ LTT phase boundaries have local maxima near this doping level. This may indicate that an electronic instability,[5,11] which competes with superconductivity for the Fermi surface, is coupled to the LTO→ LTT structural transformation. The rational fraction $\frac{1}{8}$ suggests that some commensurability exists between the Fermi surface and the LTT structure which could, for example, be associated with a charge[12] or spin[13]

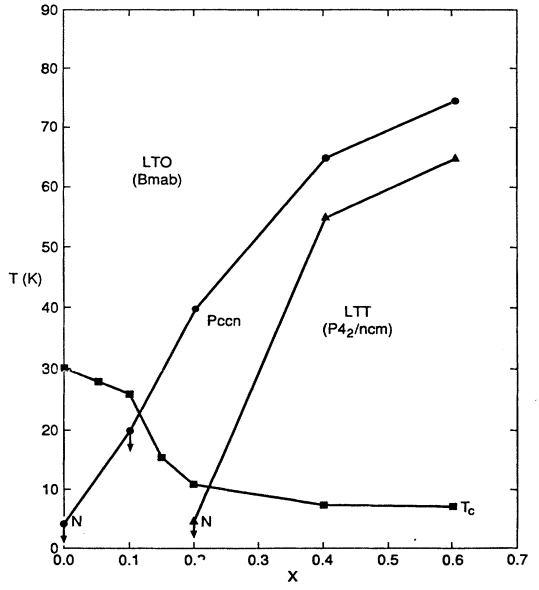

FIG. 4. Structural phase diagram for $La_{1.88-x}Nd_xSr_{0.12}CuO_4$ determined from synchrotron x-ray and neutron-diffraction data. Note that $La_{1.88}Sr_{0.12}CuO_4$ (that is, $x=0$) has the LTO structure for temperatures down to 4 K. Points with an arrow attached indicate upper limits for the phase-transition temperatures. Points labeled with an *N* are the results of neutron-diffraction measurements.

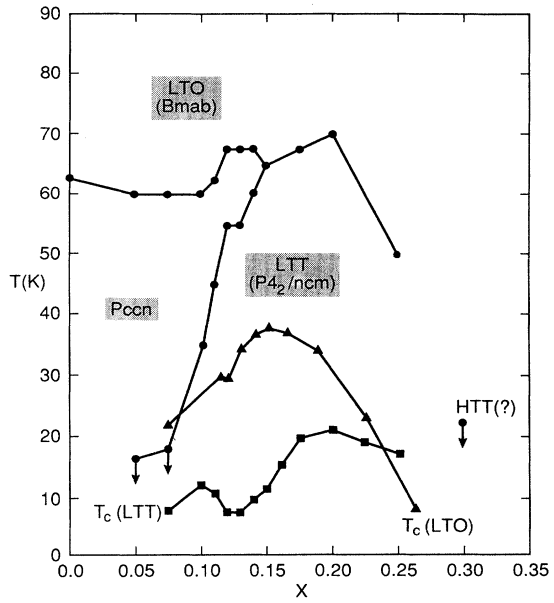

FIG. 5. Structural phase diagram for $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ determined from synchrotron x-ray and neutron-diffraction data. Note the anomalies at $x\sim\frac{1}{8}$. T_c values are for $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ (solid squares) and $La_{2-x}Sr_xCuO_4$ (solid triangles). The latter data are from Ref. 5. The points with arrows attached indicate upper limits for the phase-transition temperatures.

density wave. A partially gapped Fermi surface has been predicted for the LTT phase by band-structure calculations,[14] and these predictions are supported by our infrared spectroscopic measurements which indicate that the LTT phases remain metallic to temperatures as low as 10 K. The presence of commensurability at $x\sim\frac{1}{8}$ could further gap the Fermi surface in the LTT phase and produce a local minimum in the superconducting T_c. Such minima are seen in Fig. 5 for LTT $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ and LTO $La_{2-x}Sr_xCuO_4$ at $x\sim\frac{1}{8}$, with the minimum clearly more pronounced in the LTT phase.

While it is clear[3] that the sequence of transformations HTT→ LTO→ LTT can occur naturally from a Landau-type analysis of a free-energy function with the requisite two-component x-y symmetry and quartic anisotropy, the temperature-dependent sign reversal of the effective quartic anisotropy term, which leads to the LTO→ LTT transformation, is not explained by this analysis. An effort to discover the simplest true statistical-mechanical model which shows these effects led to an investigation of a four-state vector Potts model with quadratic (harmonic) and biquadratic (anharmonic) exchange. Let states 1 and 3 represent LTT-like tilts in the positive or negative sense about one axis, while states 2 and 4 represent tilts about the orthogonal axis. If the n_i represent the average occupancies of the four possible states, a mean-field free energy with the permutation symmetry appropriate to the symmetric HTT phase is of the form

$$F=J[(n_1-n_3)^2+(n_2-n_4)^2]+K[(n_1-n_3)^4+(n_2-n_4)^4]+kT\sum_{n_i}\ln n_i\,. \quad (1)$$

For $K=0$ (no anharmonic exchange) and $J<0$, there is a single continuous transformation from a disordered high-temperature HTT-like phase (all $n_i=\frac{1}{4}$) to an ordered low-temperature LTT-like phase, for example, $n_1 \neq n_3$, $n_2=n_4=\frac{1}{2}(1-n_1-n_3)$. Including anharmonic exchange, a LTO-like ordered phase, for example, $n_1=n_2$, $n_3=n_4=\frac{1}{2}(1-2n_1)$, is stable at intermediate temperatures between the HTT- and LTT-like phases when $\frac{1}{3}<-(K/J)<\frac{7}{4}$ and $J<0$. If Eq. (1) is developed in a Landau-like expansion near $kT_c=-J$, it is seen that the temperature dependence of the effective quartic Landau parameters results from a competition between energy and entropy. That such a simple model shows the full transformation sequence suggests that this behavior is generic, and helps to explain why it is seen in such a wide range of compounds with the prototypical K_2NiF_4 structure.[15-17]

Finally, we describe a plausible relationship between the LTO→LTT instability and the T (La_2CuO_4) and T' (Nd_2CuO_4) structures. It is fairly well established[18] that the T to T' structure change produces a change in the sign of the majority charge carrier in the Cu-O layers from p type (hole conduction) to n type (electron conduction). Perhaps the most important difference between the two structures is the position of the O(2) atoms.[18,19] The LTO→LTT phase transition moves the O(2) (apical) oxygen atoms about 10% of the way toward the sites they occupy in the T' structure. Furthermore, transport measurements[4,11] (Hall effect, thermopower) across the LTO→LTT transition in $La_{1.88}Ba_{0.12}CuO_4$ may be interpreted to indicate that there is a change in the relative conductivities due to charge carriers of opposite sign (two-band model) associated with this structural transformation. Thus we suggest that the LTO→LTT transition may be thought of as a "partial" $T\rightarrow T'$ phase transition in both a structural and an electronic sense.

In conclusion, we have demonstrated that structural phase transitions in La_2CuO_4-type superconductors can be controlled by chemical substitution at the La^{3+} site. Utilizing this control, we observe that at fixed hole concentration superconducting T_c decreases in the structural sequence LTO→*Pccn*→LTT. Furthermore, $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ has a bicritical point in its structural phase diagram at $x\sim 0.15$. The behavior of T_c vs x in $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$, where bulk superconductivity occurs in the LTT phase, furnishes evidence for an electronic instability at $x=\frac{1}{8}$. It seems likely that these phenomena are related to the unusual normal state and superconducting properties of the copper oxides.

The authors thank W. Dolinger, D. Groski, R. J. Smalley, and M. W. Sweeten for technical assistance, and D. Cox (Brookhaven) and A. Santoro (NIST) for helpful discussions. We also thank N. Herron and J. Jensen (Du Pont) for performing the iodometric titrations. This research was carried out, in part, at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

[1] P. Boni *et al.*, Phys. Rev. B **38**, 1985 (1988); T. R. Thurston *et al.*, *ibid.* **39**, 4327 (1989); R. J. Birgeneau *et al.*, Phys. Rev. Lett. **59**, 1329 (1987).

[2] R. M. Fleming *et al.*, Phys. Rev. B **35**, 7191 (1987); J. B. Torrance *et al.*, *ibid.* **40**, 8872 (1989); H. Takagi *et al.*, *ibid.* **40**, 2254 (1989).

[3] J. D. Axe *et al.*, Phys. Rev. Lett. **62**, 2751 (1989); A. R. Moodenbaugh *et al.*, Phys. Rev. B **38**, 4596 (1988); D. E. Cox *et al.*, Mater. Res. Soc. Symp. Proc. **156**, 141 (1989).

[4] M. Sera *et al.*, Solid State Commun. **69**, 851 (1989).

[5] M. K. Crawford *et al.*, Phys. Rev. B **41**, 282 (1990); M. K. Crawford *et al.*, Science **250**, 1390 (1990).

[6] G. W. Crabtree *et al.*, Phys. Rev. B **36**, 5258 (1987); H. Takagi *et al.*, J. Appl. Phys. **63**, 4009 (1988); J. M. Tarascon *et al.*, Solid State Commun. **63**, 499 (1987); G. Xiao, M. Z. Cieplak, and C. L. Chien, Phys. Rev. B **40**, 4538 (1989).

[7] D. E. Cox, B. H. Toby, and M. M. Eddy, Aust. J. Phys. **91**, 117 (1988).

[8] E. Prince, in *NBS Reactor: Summary of Activities, July 1978–June 1979,* edited by F. Shorten, Natl. Bur. Stand. No. 1117 (U.S. GPO, Washington, DC, 1980).

[9] R. L. Harlow *et al.* (unpublished).

[10] J. F. Bringley, S. S. Trail, and B. A. Scott, J. Solid State Chem. **86**, 310 (1990).

[11] Y. Maeno *et al.*, Physica B **165-166**, 1689 (1990); S. Shamoto, M. Sera, and M. Sato, Solid State Commun. **76**, 923 (1990); Y. Koike *et al.*, *ibid.* **79**, 155 (1991).

[12] S. Barisic and J. Zelenko, Solid State Commun. **74**, 367 (1990).

[13] J. C. Phillips and K. M. Rabe, Phys. Rev. B **44**, 2863 (1991).

[14] W. E. Pickett, R. E. Cohen, and H. Krakauer, in *Proceedings of the International Conference on the Manifestations of Electron-Phonon Interaction in Cu-O Superconductors,* edited by R. Baquero and J. Carbotte (World Scientific, Singapore, 1991); Phys. Rev. Lett. **67**, 228 (1991).

[15] D. E. Rice *et al.*, Phys. Rev. B **42**, 8787 (1990); G. Burns *et al.*, *ibid.* **42**, 10777 (1990); G. H. Lander *et al.*, *ibid.* **40**, 4463 (1989).

[16] J. Rodriguez-Carvajal *et al.*, Europhys. Lett. **11**, 261 (1990).

[17] K. Yamada *et al.*, Phys. Rev. B **39**, 2336 (1989).

[18] Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989); M. B. Maple, Mater. Res. Soc. Bull. **15**, 60 (1990).

[19] H. Muller-Buschbaum and W. Wollschläger, Z. Anorg. Allg. Chem. **414**, 76 (1975).