

Anisotropic optical spectrum of untwinned $\text{PrBa}_2\text{Cu}_3\text{O}_7$: Persistence of the charge-transfer insulating state of the CuO_2 plane against hole doping

K. Takenaka, Y. Imanaka, K. Tamasaku, T. Ito, and S. Uchida

Faculty of Engineering, The University of Tokyo, Yayoi 2-11-16, Bunkyo-ku, Tokyo 113, Japan

(Received 26 May 1992)

Polarized optical reflectivity spectra of untwinned $\text{PrBa}_2\text{Cu}_3\text{O}_7$ are reported. The spectra show a large ab -plane anisotropy in the infrared region with higher reflectivity along the chain direction. For the a polarization, the spectrum is similar to that of deoxygenated tetragonal $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$, with an optical energy gap of about 1.5 eV, indicating that it is difficult to dope holes into the CuO_2 planes by the addition of oxygen. The holes are doped onto the CuO chains and probably also into Pr atoms. The difficulty of hole doping into the planes may be related to the relatively small charge-transfer energy gap.

$\text{PrBa}_2\text{Cu}_3\text{O}_7$ is an exception among rare-earth (L) substituted $\text{YBa}_2\text{Cu}_3\text{O}_7$ compounds, which are all 90-K-class superconductors.¹ Electrically $\text{PrBa}_2\text{Cu}_3\text{O}_7$ is a semiconductor, and using this electric property, $\text{YBa}_2\text{Cu}_3\text{O}_7/\text{PrBa}_2\text{Cu}_3\text{O}_7$ superlattices²⁻⁴ or $\text{YBa}_2\text{Cu}_3\text{O}_7/\text{PrBa}_2\text{Cu}_3\text{O}_7/\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor-insulator-superconductor junctions⁵ have been fabricated, with the aim of extracting a minimum structural element exhibiting superconductivity or to develop novel high- T_c devices.

However, although several explanations have been proposed,⁶⁻¹¹ the absence of superconductivity and the electronic structure in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ are not fully understood yet. An apparent inconsistency exists concerning the valence of the Pr ion. Magnetic-susceptibility measurements suggest a tetravalent (Pr^{4+}) ionic state which would lead to compensation or back filling of the holes introduced by oxygenation.⁶ On the other hand, high-energy spectroscopies⁹⁻¹¹ indicated a Pr valence close to $3+$. In this case one supposes that the extended f shell of Pr changes the electronic structure of the CuO_2 plane by hybridization with the in-plane O $2p$ level, which may lead to localization of the mobile holes in the CuO_2 plane.

In this paper we show the result of an optical study on an untwinned $\text{PrBa}_2\text{Cu}_3\text{O}_7$ single crystal, which enables us to isolate the contribution of the CuO_2 planes from that of CuO chains. The result clearly demonstrates that the CuO_2 planes are not highly doped with holes even under full oxygenation and preserve the electronic structure of the undoped CuO_2 plane with a charge-transfer (CT) energy gap. Holes are introduced into the CuO chains and perhaps also (from charge neutrality considerations) into Pr atoms. The holes doped into the chains are highly mobile at high frequencies but show a trend for localization at low frequencies.

$\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were grown by the self-flux method using a Pt crucible. Typical crystal size was $1.0 \text{ mm} \times 0.6 \text{ mm} \times 0.06 \text{ mm}$. In order to obtain single-domain crystals we applied uniaxial stress ($\sim 10^2 \text{ kg/cm}^2$) on the crystal under flowing oxygen gas at 450°C . This procedure was successful in producing a single-domain crystal of $\text{YBa}_2\text{Cu}_3\text{O}_7$. However, in the

case of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ it was much more difficult to obtain a single-domain crystal. The best crystal so far obtained consisted of several domains, the largest one of which was $0.2 \text{ mm} \times 0.2 \text{ mm}$. The domain size was sufficient for optical measurements when we used microscopes specially designed for infrared and visible-ultraviolet spectrometers.

Near-normal-incident reflectivity measurements were made with polarized light using a rapid scanning Fourier-type interferometer (0.030–1.0 eV), a grating spectrometer (0.6–6.0 eV), and a Seya-Namioka-type spectrometer for vacuum-ultraviolet synchrotron radiation (4.0–40 eV) at the Institute for Solid State Physics, The University of Tokyo. All the data were taken at 300 K.

The reflectivity spectra of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ for two polarizations are shown in Fig. 1 below 5 eV. Anisotropy is

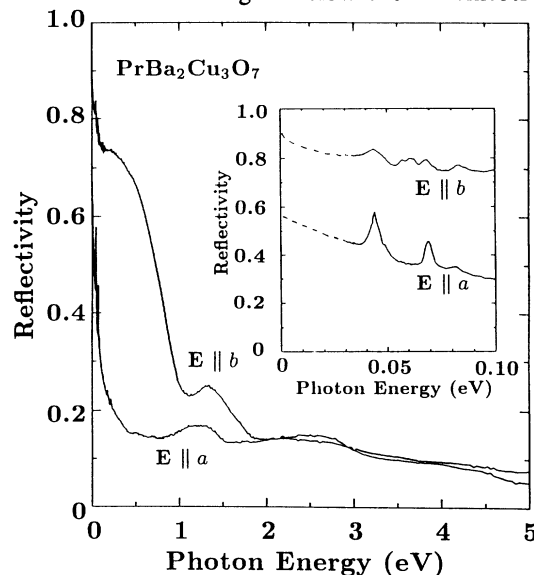


FIG. 1. Reflectivity spectra of untwinned $\text{PrBa}_2\text{Cu}_3\text{O}_7$ at 300 K with polarization parallel ($E||b$) and perpendicular ($E||a$) to the CuO chain direction. The inset shows the spectra in the low-energy region in an expanded energy scale where the dashed parts are extrapolations to $\omega=0$ in order to make Kramers-Kronig (KK) transformation.

particularly pronounced in the infrared region. The spectrum for $E \parallel b$ contains contributions from both planes and chains and exhibits a steep rise below 1 eV, reminiscent of a free-carrier plasma, but the optical phonons in the far-infrared region are not completely screened by the carriers. By contrast, the spectrum for $E \parallel a$ is typical of a semiconductor with low reflectivity and manifests optical phonons. Therefore, the reflectivity edge at 1 eV in the b spectra is ascribed to the carriers (excitations) associated with chains. In the higher-energy region the difference becomes small and both spectra are characterized by a peak at about 1.4 eV.

The implications of the data become clearer when the reflectivity spectrum is transformed to the optical conductivity by the Kramers-Kronig (KK) transformation. To do this appropriate extrapolation procedures are necessary. Since the experiment covers the region up to 40 eV, which includes the contributions from almost all the valence electrons in the material, extrapolation to a higher-energy region is not a concern. An example for reasonable extrapolation to energies below 30 meV is shown by the dashed curves in the inset of Fig. 1. For $E \parallel a$ a smooth extrapolation to $R = 1$ at $\omega = 0$ is difficult because of low reflectivities, which implies $\sigma_a(0) \approx 0$. On the other hand, there is some room for various extrapolated reflectivities in the $E \parallel b$ case. It is not possible to make a smooth extrapolation by using a single Drude (or Hagen-Rubens) term. To do that we need to fit the reflectivity by a Lorentz oscillator term plus a weak Drude term. Differences in extrapolation, under the condition of reasonably smooth extrapolation, lead to variation of $\sigma_b(0)$ in the range $0 \leq \sigma_b(0) \leq 600 \Omega^{-1} \text{cm}^{-1}$, but this ambiguity does not affect the result for $\hbar\omega > 0.1$ eV. A preliminary dc resistivity measurement along the b direction of untwinned $\text{PrBa}_2\text{Cu}_3\text{O}_7$ gives $\sigma_b(0) \sim 100 \Omega^{-1} \text{cm}^{-1}$ at room temperature, which incidentally coincides with the result in Fig. 2 based on the low-energy extrapolation shown in the inset of Fig. 1.

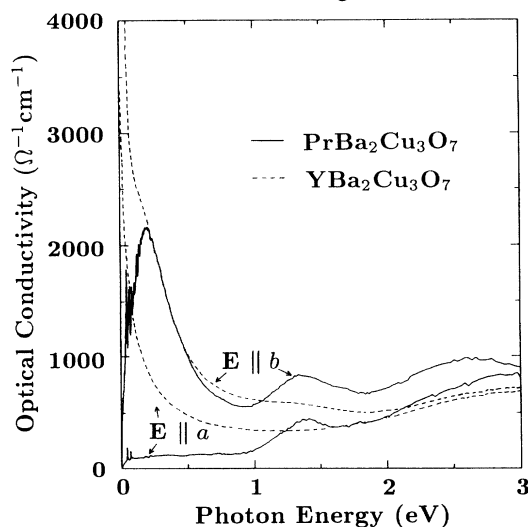


FIG. 2. Optical conductivity spectra of untwinned $\text{PrBa}_2\text{Cu}_3\text{O}_7$ for two polarizations calculated via the KK transformation of the reflectivity spectra. For comparison the spectra of untwinned $\text{YBa}_2\text{Cu}_3\text{O}_7$ are shown by the dashed curves.

The optical conductivity in the b direction, $\sigma_b(\omega)$, is higher than σ_a in the spectral region shown in Fig. 2 and the difference $\sigma_b - \sigma_a$, or σ_{chain} , should be a contribution for the CuO chains. The σ_b spectrum is characterized by a broad peak at 0.2 eV and associated Drude-like tail in the higher-energy region. As compared with the result on untwinned $\text{YBa}_2\text{Cu}_3\text{O}_7$ (shown by the dashed curves, which agree exactly with the earlier results¹²⁻¹⁴), σ_b of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ nearly coincides with that of $\text{YBa}_2\text{Cu}_3\text{O}_7$ above 0.2 eV. A distinct feature in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ is that σ_b steeply decreases below 0.2 eV, a decrease that does not depend on the low-energy extrapolation as described above, in contrast to the steeper rise observed in $\text{YBa}_2\text{Cu}_3\text{O}_7$. This decrease is indicative of localization of carriers moving along the chains owing to disorder existing in the chains and is consistent with the observed semiconductive resistivity. One would note that the amount of disorder in the chains of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ should not be larger than that in $\text{YBa}_2\text{Cu}_3\text{O}_7$, since disorder arises mostly from oxygen deficiencies in the CuO chains. The fact that the carriers in the $\text{PrBa}_2\text{Cu}_3\text{O}_7$ chains are localized, while those in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ chains are not, is suggestive of either weaker coupling between CuO chains or stronger one-dimensionality of the chain in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ or the presence of weak coupling between chains and planes in the 1:2:3 compound. In the latter case conduction along the chains may be affected by metallicity or nonmetallicity of the adjacent planes. The coupling might be responsible for the apparently metallic conduction along the c axis observed in fully oxygenated $\text{YBa}_2\text{Cu}_3\text{O}_7$.¹⁵

Although a very weak mid-infrared absorption band is seen, the σ_a spectrum is basically similar to that observed in undoped cuprates such as $\text{YBa}_2\text{Cu}_3\text{O}_6$ (Ref. 16) or La_2CuO_4 .¹⁷ The peak at 1.4 eV, which is also observed in the σ_b spectrum, can be regarded as the fundamental absorption of the CT insulating CuO_2 plane, corresponding to the $\text{O } 2p \rightarrow \text{Cu } 3d$ (upper Hubbard) excitations. Note that the 1.4-eV CT excitation energy is considerably smaller than 1.7 eV in $\text{YBa}_2\text{Cu}_3\text{O}_6$.¹⁶

This assignment is confirmed in Fig. 3, where the spectrum for deoxygenated $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ ($y \sim 0.7$) is shown together with the σ_a spectrum of $\text{PrBa}_2\text{Cu}_3\text{O}_7$. The reduced crystal is tetragonal and its spectrum has no polarization dependence. Two pronounced peaks at about 1.5 and 4.1 eV are seen in the spectrum. The latter is specifically observed in every deoxygenated 1:2:3 compound and has been plausibly attributed to intra-atomic excitations on the Cu(1) site of oxygen-free chains.¹⁸ The Cu(1) atom of the $\text{YBa}_2\text{Cu}_3\text{O}_6$ compound is supposed to be monovalent (Cu^+), so that transitions from occupied $3d$ ($3d_{z^2}$ and $3d_{x^2-y^2}$) to unoccupied $4p$ levels are possible. The 4.1-eV feature is sensitive to the introduction of oxygen into chains. The absence of this feature in the spectra shown in Fig. 1 is evidence for CuO chain formation in oxygenated $\text{PrBa}_2\text{Cu}_3\text{O}_7$.

In $\text{YBa}_2\text{Cu}_3\text{O}_6$ the absorption associated with the 1.7-eV CT excitations is also sensitive to oxygen addition corresponding to hole doping into the CuO_2 planes, which transfers the CT oscillator strength to low-energy excita-

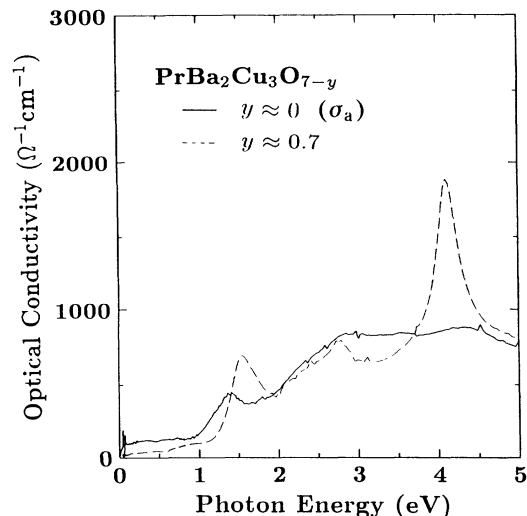


FIG. 3. Optical conductivity spectra of oxygenated $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ ($y \sim 0$) for a polarization and of reduced (tetragonal) $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ ($y \sim 0.7$).

tions.^{16,17} By contrast the corresponding CT peaks in $\text{PrBa}_2\text{Cu}_3\text{O}_6$ behaves quite differently on oxygen addition. The peak position slightly shifts to lower energy but the oscillator strength of the CT excitation remains large even in the oxygenated compound. This is convincing evidence for the fact that holes are not significantly doped into the CuO_2 planes of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ and is in agreement with the NMR and μSR results which indicated antiferromagnetic order of the planar Cu sites below 280 K in $\text{PrBa}_2\text{Cu}_3\text{O}_7$.^{19,20} One should note again that the 1.4–1.5-eV CT energy is the smallest among those of the known parent compounds of high- T_c cuprates and is by 0.3 eV smaller than that in isostructural $\text{YBa}_2\text{Cu}_3\text{O}_6$. It is pointed out that the CT gap Δ_{CT} is sensitive to the presence or absence of apical oxygen atoms and typically $\Delta_{\text{CT}} \sim 2.0$ eV for octahedral configuration (two apical oxygens above and below Cu), ~ 1.7 eV for pyramidal configuration (one apical oxygen), and ~ 1.5 eV for the square planar case (no apical oxygen).²¹ For single-CuO-layer systems, they correspond to the T , T^* , and T' phases, respectively. The magnitude of Δ_{CT} is related to the difference in Madelung energy ΔV_M between Cu and O sites in the CuO_2 plane and therefore related, more or less, with facility or difficulty in hole doping.²² In fact, the facility of hole doping decreases in the order of $T \rightarrow T^* \rightarrow T'$ and the T' compound, Nd_2CuO_4 , cannot be doped with holes. The difficulty in hole doping into $\text{PrBa}_2\text{Cu}_3\text{O}_6$ with small Δ_{CT} might be understood in this context.

The reason for the small Δ_{CT} is not clear, but there seems a general trend that in the series of cuprates with the same crystal structure containing different rare-earth elements (L) the CT gap energy decreases as the ionic radius of the rare-earth element increases. In the series of T' compounds, $L_2\text{CuO}_4$, Δ_{CT} , defined as the peak position in the $\sigma(\omega)$ spectrum, decreases from 1.65 eV for $L = \text{Gd}$ to 1.55 eV for Pr .^{23,24} The ionic radius of Y^{3+} is

in between Dy^{3+} and Er^{3+} , so the smaller Δ_{CT} in Pr 1:2:3 than that in Y 1:2:3 agrees with this trend. Addition of oxygen to chain sites seems to change the Madelung potentials at Cu and O sites of the CuO_2 plane, leading to further reduction of Δ_{CT} in $\text{PrBa}_2\text{Cu}_3\text{O}_7$.

Finally, we consider the valence state of Pr in $\text{PrBa}_2\text{Cu}_3\text{O}_7$. The valence of Pr in the undoped $\text{PrBa}_2\text{Cu}_3\text{O}_6$ is apparently 3+ because the Cu atoms of the two inequivalent sites, Cu(1) and Cu(2), are the 1+ and 2+ valence states, respectively, as in $\text{YBa}_2\text{Cu}_3\text{O}_6$. In $\text{YBa}_2\text{Cu}_3\text{O}_7$, the addition of oxygen formally increases the valence of both plane and chain Cu; since the Y stays in the 3+ valence state, the most likely valences are $\text{Cu}(2)^{2.25+}$ and $\text{Cu}(1)^{2.5+}$ in $\text{YBa}_2\text{Cu}_3\text{O}_7$ so that with respect to Cu^{2+} about 50% of the holes go into the CuO_2 planes and the remaining 50% into CuO chains by the addition of oxygen. This estimate is justified quantitatively by examining the integrated spectral weight given as

$$N_{\text{eff}}^*(\omega) = \frac{2m_0V}{\pi e^2} \int_0^\omega \sigma(\omega') d\omega'$$

where the effective number of holes (electrons) per unit cell is defined with the bare electron mass m_0 and the unit-cell volume V . The chain contribution, $\sigma_{\text{chain}} \equiv \sigma_b - \sigma_a$, shown in Fig. 4, integrated up to 1.5 eV gives $N_{\text{eff}}^*(\omega) \approx 0.5$ in agreement with the above estimate, as also pointed out by the previous works.^{13,14}

The chain contribution in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ is also plotted in Fig. 4. While the chain conductivity is depressed below 0.1 eV, it is compensated by the enhanced conductivity in the higher-energy region over that in $\text{YBa}_2\text{Cu}_3\text{O}_7$. $N_{\text{eff}}^*(\omega)$ at 1.0 eV, the integrated spectral weight below the gap, is about 0.5, in coincidence with that in $\text{YBa}_2\text{Cu}_3\text{O}_7$. Thus, we may conclude that equal amounts of holes are introduced into the chain Cu site. The charge neutrality then requires that remaining holes

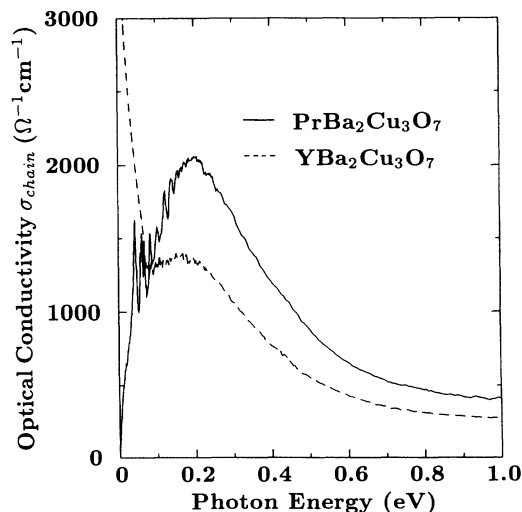


FIG. 4. Difference optical conductivity spectra, $\sigma_b(\omega) - \sigma_a(\omega)$, of $\text{PrBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$, representing the chain contribution, $\sigma_{\text{chain}}(\omega)$.

have to go mainly into Pr, changing the formal Pr valence state from $3+$ to about $3.5+$. This might be plausible since Pr is stable in both trivalent and tetravalent states and in this regard supports the view that "hole filling" or compensation is responsible for the absence of superconductivity in $\text{PrBa}_2\text{Cu}_3\text{O}_7$.⁶ The present result is based upon a rather low-energy spectrum but the optical spectrum in the high-energy region suggests trivalent Pr.²⁵ So, the apparent inconsistency in the Pr valence may arise from different energy scales among various experimental techniques.

We have shown by polarized optical spectra on detwinned $\text{PrBa}_2\text{Cu}_3\text{O}_7$ single crystal that the absence of superconductivity in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ is due to the difficulty in the hole doping into the CuO_2 plane. The electronic structure of the CuO_2 plane does not change with addition of oxygen to $\text{PrBa}_2\text{Cu}_3\text{O}_6$ and thus preserves the CT insulating state with $\Delta_{\text{CT}} \approx 1.4$ eV. Doped holes go into the CuO chains and partly into Pr atoms, which is possible because two valence states, Pr^{3+} and Pr^{4+} , are stable. The density of holes in CuO chains is approximately 0.5

per unit cell, the same as that in the chains of $\text{YBa}_2\text{Cu}_3\text{O}_7$. These holes exhibit a tendency for localization at low energies and at low temperatures, which appears to be related to the presence of adjacent insulating CuO_2 planes due to weak interlayer coupling or to the stronger one-dimensionality of the CuO chain. The difficulty in hole doping into the CuO_2 plane in $\text{PrBa}_2\text{Cu}_3\text{O}_7$ may be connected to the relatively small CT energy gap corresponding to the smaller Madelung energy difference between in-plane Cu and O sites.

The authors would like to thank T. Arima for the help in the optical measurement in the visible and ultraviolet regions. We are also grateful to M. Fujisawa at Synchrotron Radiation Laboratory of the Institute for Solid State Physics, The University of Tokyo, for the skillful technical assistance to use vacuum-ultraviolet radiation. The present work was supported partly by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

-
- ¹L. Soderholm *et al.*, Nature (London) **328**, 604 (1987); S. Kambe *et al.*, Jpn. J. Appl. Phys. Suppl. **1**, 11 (1988).
²J.-M. Triscone *et al.*, Phys. Rev. Lett. **64**, 804 (1990).
³Q. Li *et al.*, Phys. Rev. Lett. **64**, 3086 (1990).
⁴D. H. Lownders, D. P. Norton, and J. D. Budai, Phys. Rev. Lett. **65**, 1160 (1990).
⁵C. T. Rogers *et al.*, Appl. Phys. Lett. **55**, 2032 (1989).
⁶D. P. Norton *et al.*, Phys. Rev. Lett. **66**, 1537 (1991); Y. Dalichaouch *et al.*, Solid State Commun. **65**, 1001 (1988).
⁷J. L. Peng *et al.*, Phys. Rev. B **42**, 4517 (1989).
⁸C. R. Fincher, Jr. and Graciela B. Blanchet, Phys. Rev. Lett. **67**, 2902 (1991).
⁹J. Fink *et al.*, Phys. Rev. B **42**, 4823 (1990).
¹⁰L. Soderholm and G. L. Goodman, J. Solid State Chem. **81**, 121 (1989).
¹¹J. S. Kang *et al.*, J. Less-Common Met. **24**, 25 (1989).
¹²B. Koch, H. P. Gessrich, and Th. Wolf, Solid State Commun. **71**, 495 (1989).
¹³Z. Schlesinger *et al.*, Phys. Rev. Lett. **65**, 801 (1990); L. D. Rotter *et al.*, *ibid.* **67**, 2741 (1991).
¹⁴S. L. Cooper *et al.*, Phys. Rev. B **45**, 2549 (1992).
¹⁵T. Ito, H. Takagi, T. Ido, S. Ishibashi, and S. Uchida, Nature (London) **350**, 596 (1991).
¹⁶J. Orenstein *et al.*, Phys. Rev. B **42**, 6342 (1990).
¹⁷S. Uchida *et al.*, Phys. Rev. B **43**, 7942 (1991).
¹⁸J. Kircher *et al.*, Phys. Rev. B **44**, 217 (1991).
¹⁹D. W. Cooke *et al.*, Phys. Rev. B **41**, 4801 (1990).
²⁰A. P. Reyes *et al.*, Phys. Rev. B **42**, 2688 (1990).
²¹Y. Tokura *et al.*, Physica C **162-164**, 1231 (1990).
²²J. Kondo, J. Phys. Soc. Jpn. **58**, 2884 (1989); Y. Ohta, T. Tohyama, and S. Maekawa, Phys. Rev. Lett. **66**, 1228 (1991).
²³S. L. Cooper *et al.*, Phys. Rev. B **42**, 10785 (1990).
²⁴T. Arima *et al.*, Phys. Rev. B **44**, 917 (1991).
²⁵J. Kircher *et al.*, Phys. Rev. B **44**, 2410 (1991).