

Hole depletion and localization due to disorder in insulating $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$: A Compton scattering study

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The (mostly) insulating behavior of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is still unexplained and even more interesting due to the occasional appearance of superconductivity in this material. Since $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is nominally isostructural and always superconducting, we have measured the electron momentum density in these materials. We find that they differ in a striking way, the wave function coherence length in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ being strongly suppressed. We conclude that Pr on Ba-site substitution disorder is responsible for the metal-insulator transition. Preliminary efforts at growth with a method to prevent disorder yield 90 K superconducting $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystallites. [S0163-1829(99)02517-5]

The peculiar case of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ stands out in the $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ family (R for rare earth or Y) because it is the only easily fabricated member which until recently was consistently insulating in the normal state *and* nonsuperconducting (for a review see Refs. 1,2). Superconducting samples have since been fabricated,^{3,4} some of which show metallic behavior in the normal state, akin to that seen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The nonsuperconducting behavior has been attributed to various causes: (1) +4 valence for Pr leading to hole filling in the Cu-O layers, (2) hybridization between the Pr 4f and O 2p orbitals⁵, leading to hole localization in these layers, (3) a chain-based model for superconductivity and magnetic pair breaking induced by Pr on the Ba site.³ The first possibility has been invalidated on the grounds that Pr on the rare-earth site is essentially trivalent^{7,8} while the last is unlikely if only because it fails to explain why nonsuperconducting $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ should be insulating in the normal state.

The Fehrenbacher-Rice model of hole-localization in its various forms^{5,6} remains a possible explanation, and to get further insight into this matter we have measured the electron momentum density in both $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ using Compton scattering of high energy x rays. This is the first high statistics and high resolution measurement in these materials, which are difficult candidates for such experiments given the problems related to fluorescence background from heavy atoms and low count rates due to absorption. These problems have been overcome thanks to high-energy synchrotron radiation and dedicated instrumentation at ID15B at the ESRF.^{9,10} Our measurements show that the experimental momentum density is similar to that given by local density approximation (LDA) band-structure calculations for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. However, in

$\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, a striking difference is seen between measurement and calculation. Simple models show that Pr on Ba site defects (labeled Pr_{Ba} hence-forward) and a lack of hole doping in the Cu-O planes probably lead to this difference. These facts are interpreted in the light of other experiments^{7,8,11-24} in the $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system.

The experiments were performed on crystals grown by the flux method in the nonreactive crucible material BaZrO_3 , known to give uncontaminated, high-purity samples.²⁵ The $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals were annealed under 1 bar of oxygen at 530 °C for 170 h yielding a T_c of 91.3 K and an oxygen content of 6.89.²⁶ The $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals were annealed under 1 bar of oxygen at 500 °C for 200 h yielding an oxygen content of 6.92,²⁷ and were insulating and nonsuperconducting. Both exhibited uniform twins in the a - b plane, as is usually observed after such a treatment. These twinned crystals were used for the experiment.

Compton scattering, or inelastic scattering with very high momentum and energy transfer is a probe of the ground state, one-electron properties of the system.^{28,29} The measured quantity $J(p_z)$, the Compton profile, is a projection onto the z direction (parallel to the scattering vector) of the three-dimensional electronic momentum density $\rho(\mathbf{p})$: $J(p_z) = \int_{-\infty}^{\infty} \rho(\mathbf{p}) dp_x dp_y$. Compton profiles were measured using the high-resolution scanning spectrometer at ID15B. A cylindrically bent focusing Si(311) Bragg monochromator provided an incident energy of 55.91 keV for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and 57.78 keV for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, respectively. The radiation scattered at an angle of 159° was analyzed by a cylindrically bent Ge(440) analyzer. For both compounds three twinned single crystals were stacked to use the full beam size of 0.2×5 mm. Compton profiles were measured for the

[100/010] and [110] directions, in symmetric reflection geometry at room temperature with high statistics [5×10^6 counts in a 0.05 a.u. bin at $p_z=0$; 1 atomic unit (a.u.) of momentum $\cong 1.89 \text{ \AA}^{-1}$]. The effective resolution was 0.15 a.u. (full width at half maximum). The incident beam was monitored using a Si PIN diode and this was used to normalize the scanned profiles. The raw profiles were further corrected for geometrical effects, for absorption in air and in the sample and for the analyzer reflectivity. The background was measured separately and subtracted. Finally after ensuring that the features in the measured anisotropy were symmetric with respect to momentum transfer the profiles were symmetrized to increase statistics and normalized appropriately.

In the following we shall discuss the anisotropy of the Compton profiles, that is, the difference between Compton profiles measured in two crystallographic directions ($J_{[100/010]} - J_{[110]}$). This procedure has the advantage of getting rid of the isotropic contribution of the core electrons as well as residual background. Since both measured directions are in the a - b plane, the structure in the anisotropy originates essentially in this plane, but includes contributions from all entities of the unit cell, the Cu-O chains, the Ba-O and Y/Pr planes, as well as the Cu-O layers. However, from earlier momentum density measurements¹¹ as well as other experiments¹²⁻¹⁴ it has been established that the Cu-O chains are identical in both materials, being locally metallic with a corresponding Fermi surface (even in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$). Thus, any differences between the two originate in the remaining entities, the Cu-O layers or the Ba-O and Y or Pr planes.

For comparison with experiment we have computed theoretical Compton profiles based on the LDA band structure. A full potential linear augmented plane wave (FLAPW) (Ref. 30) calculation was performed for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. For $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, earlier studies have shown that two of the three Pr- f electrons can actually be considered as core states³¹ since treating them as band electrons does not modify the density of states significantly,³² implying that theory predicts little change with respect to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The expected difference in the anisotropy in going from $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is due to the hybridization of Pr- f electrons with O-2 p electrons which even in LDA calculations produces some hole depletion in the Cu-O layers similar to the Fehrenbacher-Rice model.³³ However, LDA calculations are known to work reasonably well only for the metallic phase and not for undoped insulating Cu-O layers in these materials. To estimate this difference due to hybridization we used the linear muffin-tin orbital (LMTO) (Ref. 34) method to calculate the anisotropy for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (with the Pr- f electrons considered as valence electrons), from which the LMTO anisotropy for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was subtracted. This difference should give us an upper bound on the expected change since LDA is known to overestimate the effect of hybridization of localized f -orbitals (see, for example, Ref. 35). This difference was then added to the FLAPW anisotropy for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to give an estimation of the theoretical anisotropy for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Liechtenstein and Mazin⁶ have included Coulomb correlations in their LDA+U, LMTO calculations for $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and find that in $R=\text{Pr}$, with respect to $R=\text{Y}$, an additional band

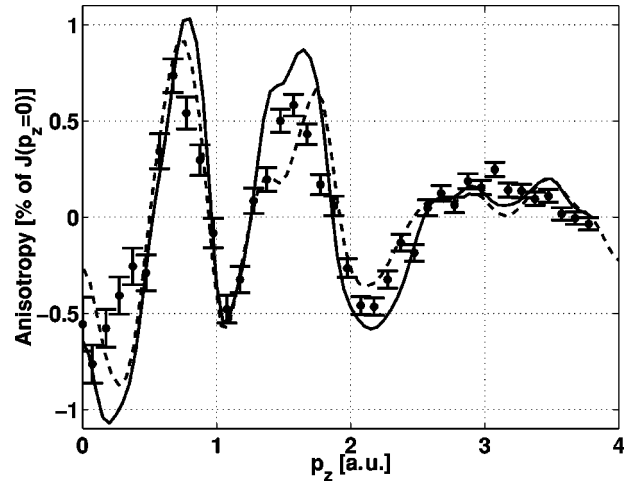


FIG. 1. Anisotropy ($J_{[100/010]} - J_{[110]}$) in the electron momentum density of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Note the good agreement between the experiment and the LDA calculations ($\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$: solid line $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$: dashed line). Calculations are scaled to the experimental variation.

crosses the Fermi level trapping holes and changing their nature, but with negligible impact on the Compton profile according to our estimations.

The anisotropy is shown as a percentage of the peak value of the Compton profile. The amplitude of the anisotropy in the theory is about 40% larger than in the experiment. This tendency is commonly observed, even in simple metals, and attributed to correlation effects underestimated by LDA.^{36,37} However the shape of the anisotropy, which is what we use in our analysis, is generally very well described by LDA, even in highly correlated electron systems containing f electrons, such as CeCu_2Si_2 .³⁵ In the figures shown we have scaled the theoretical anisotropy to the experimental one by a factor of 1.4 to ease comparison. Figure 1 shows the measured and calculated (solid line) anisotropy for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The two are remarkably alike, showing that the overall description of the electronic structure is satisfactory. We also show the calculated (as detailed above) anisotropy for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (dashed line), which, despite Pr-O hybridization, shows little change with respect to the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ calculation. Figure 2 shows the measured anisotropy for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which is strikingly different than the one predicted by theory.

When $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is synthesized it is known that Ba-rich or Pr-rich, off-stoichiometric phases ($\text{Pr}_{1\pm x}\text{Ba}_{2\mp x}\text{Cu}_3\text{O}_{7-\delta}$) may be produced. There is however substantial evidence that even in globally stoichiometric samples substitution disorder concerning the Pr and Ba sites (spinodal decomposition for example) exists locally,^{3,15-17} especially if growth is followed by slow cooling. Such disorder, due to the large size of Pr ions has also been observed in the case of similar sized Nd (Ref. 17) and La (Ref. 3,18) ions. The amount of this substitution has been estimated to be a maximum of about 8%.^{2,15} If such disorder were present, one effect would be to diminish the contribution of the Pr and Ba-O planes to the total anisotropy due to the absence of long-range order in these planes. Since accounting for such disorder in the theory is not trivial, for qualitative analysis we have used a simple model within the LMTO

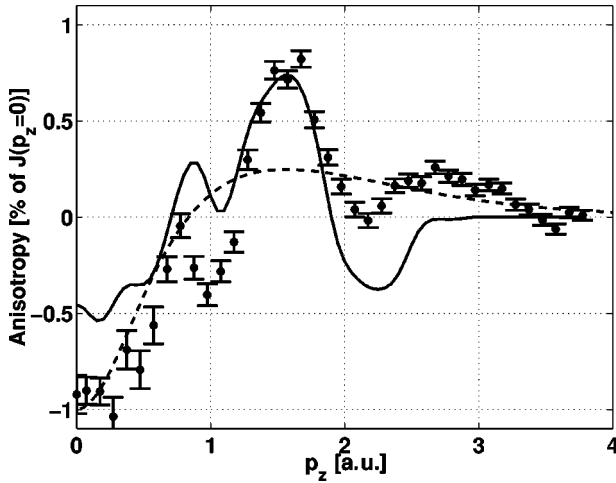


FIG. 2. Anisotropy ($J_{[100/010]} - J_{[110]}$) in the electron momentum density of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The experiment differs remarkably from the LDA calculation (Fig. 1). Two simple theoretical models accounting for Pr_{Ba} disorder (solid line) and undoped Cu-O planes (dashed line) are also shown.

method, where we have neglected the contribution of Pr and Ba-O planes to the total anisotropy (solid line in Fig. 2). In the same figure we also show a molecular orbital calculation (dashed line) of the anisotropy due to a hole in the $\text{Cu}3d_{x^2-y^2}$ state corresponding to Cu-O layers in undoped insulating $\text{RBa}_2\text{Cu}_3\text{O}_6$. Again we are limited to a qualitative approach because LDA predicts an incorrect metallic ground-state for $\text{RBa}_2\text{Cu}_3\text{O}_6$ with anisotropy similar to that for $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The calculation accounting for disorder mimics the strong suppression of the first peak in the measured anisotropy for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which also tends towards the behavior calculated for undoped Cu-O layers. We argue below how Pr_{Ba} disorder could in fact lead to a situation where carriers are not doped in to the Cu-O layers, effectively killing both metallic behavior and superconductivity in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

The charge-transfer model for the effect of oxygen doping in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Refs. 19,20) is well established, and describes the mechanism of transfer of positive charge from the Cu-O chains to the Cu-O layers as oxygen is added to the chains. Two possible mechanisms may exist to block or modify this charge transfer. The first that we propose, supposes that if Pr is present at the Ba site, the needed charge is supplied by Pr_{Ba} (possibly in a 4+ oxidation state because the chemical environment on this site is different), inhibiting hole creation in the layers. However, the chains would maintain their microscopic metallic character as has been experimentally observed and mentioned above. It is significant that according to Cava *et al.*¹⁹ the total charge transfer associated with T_c going from 0 to 90 K is $0.08e/\text{Cu-O}$ layer in the unit cell. Knowing that the concentration of Pr_{Ba} defects is a few percent, we have here a hole-depleting mechanism which is of the same magnitude as the hole-creating mechanism of charge transfer. Experimental observations of hole-depletion in the Cu-O layers include optical conductivity,¹³ NMR,²¹ Hall-effect,²² and transport²³ measurements. Most experimental evidence favors a valence for Pr close to +3 (compatible, in our model, with Pr on the rare-earth site) but also indicates the probable presence of a small fraction of +4

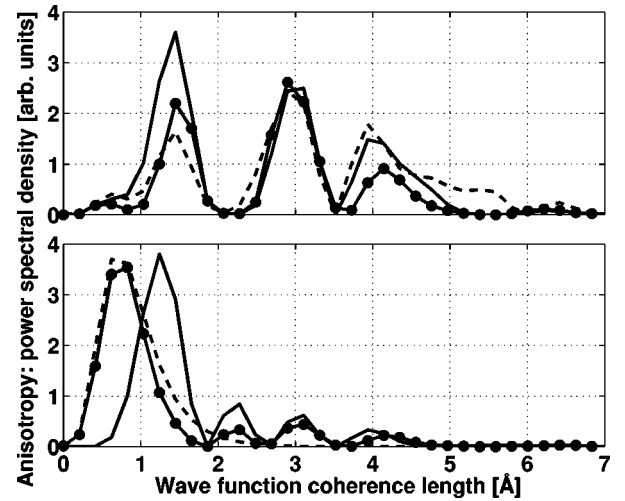


FIG. 3. Power spectral densities of anisotropies. The peaks indicate characteristic distance scales over which wave functions are coherent. Top panel: Experiment (solid line with dots) and theory (solid line) for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$; theory for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (dashed line). Bottom panel: In $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the experiment (solid line with dots) shows a strong suppression of the longer range coherence peaks as in the disordered model (solid line) as well as a shifting of the remaining coherence peak to shorter length scales similar to the model for insulating, undoped Cu-O layers (dashed line).

valent Pr ,^{2,8,18,23} which can be explained if Pr_{Ba} had a valence of +4. It is known that Pr_6O_{11} , used in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ preparation, is actually a mixture of two oxides Pr_2O_3 (+3 Pr) and PrO_2 (+4 Pr). The ratio of these two oxides depends on temperature and oxygen partial pressure and at high temperature or low oxygen partial pressure the PrO_2 oxide is unstable and decomposes to Pr_2O_3 . Thus at the moment of substitution onto the Ba site the Pr ion is +3 valent but at some moment during the cooling phase of the “standard” fabrication method probably changes to +4 valent and stays “trapped” at the Ba site. As mentioned earlier, large sized 3+ ions (Nd, La), though known to substitute on the Pr site and magnetic (in the case of Nd) do not interfere with superconductivity. Neither Nd or La are known to exist in the 4+ state. Studies on the influence of ion size in $\text{R}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ show that at constant Pr concentration, T_c decreases while the antiferromagnetic ordering temperature of Pr ions, T_N , increases with the ionic radius of R.²⁴ It is reasonable to assume that the larger the ionic radius of the host rare earth R, the easier its substitution by Pr, leading also to the higher T_N . Lastly, Zou *et al.*⁴ found an anomalously short c lattice parameter in nonsuperconducting $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, which could be due to the smaller size of the Pr^{4+} ion.

We have further analyzed the anisotropies shown in Figs. 1 and 2 by computing the power spectral density $|\int_{-\infty}^{\infty} [J_{100/010}(p) - J_{110}(p)] \exp\{-ipr\} dp|^2$. Compton profiles, and hence anisotropies, are modulated with oscillations corresponding to characteristic distances over which wave functions are coherent in given crystallographic directions.^{28,38} Peaks in the power spectral density then indicate these characteristic distance scales as shown in Fig. 3. Only the positions and relative intensities of the peaks

in each spectrum are significant since the theoretical anisotropies have been scaled. The top panel shows that experiment (solid line with dots) and theory (solid line) for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as well as theory for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (dashed line) are in agreement and that the charge carriers are of a delocalized nature. The periodic structure of the anisotropy shown in Fig. 1 and the corresponding peaks in the power spectral density in Fig. 3 are directly related to the phases of the wave function associated with the four O atoms surrounding a given Cu atom in the Cu-O layers.³⁹ In the bottom panel the experiment for $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (solid line with dots) shows both a tendency for strong suppression of the longer range coherence peaks as in the disordered model (solid line), as well as a shifting of the remaining coherence peak to shorter length scales similar to the simple model of insulating, undoped Cu-O planes (dashed line). This is a clear indication of hole wave function localization in the Cu-O layers and of the disorder on the Pr and Ba sites. Ongoing experiments in underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ confirm the possibility to monitor wave function coherence length behavior near the metal-insulator transition using Compton profiles anisotropies.

With these arguments in mind we can state that superconductivity in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ appears with decreasing Pr_{Ba} defects and that this is also the reason for the scatter in the measured T_c values which correspond to varying degrees of such disorder, dependent on the method and particular conditions of sample fabrication. Mazin⁶ has independently come to a similar conclusion arguing, however, that disorder effectively localizes holes in the Cu-O layers in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ which are of a different nature with respect to $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ due to hybridization. This possible second mechanism for hole depletion would also lead to a metal-insulator transition in the Cu-O layers and therefore to similar results for the anisotropy. One or both of these mecha-

nisms may be active and we point out that disorder-induced disruption of charge transfer would provoke insulating behavior independently of the precise nature of the holes which would have been created in the absence of disorder. Further support for this picture is provided by the fact that by using a combined strategy of minimizing substitution disorder by quenching the melt from high temperatures after crystal growth *and* avoiding tetravalent Pr_{Ba} , by using very low oxygen partial pressures during growth, we have succeeded in obtaining small flux-grown crystallites of $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with a T_c of 90 K and a bulk Meissner effect.^{17,40} The oxygenation used for these samples was the same as for 90 K superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ implying similar, optimal doping in both. We expect the electron momentum density in superconducting $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to be similar, but at the moment such samples are much too small for Compton profile measurements.

In conclusion we provide a consistent explanation of the observed behavior in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Our data explicitly shows a strong suppression of the wave function coherence length in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ due to disorder in the Ba and Pr planes and the metal-insulator transition of the Cu-O layers. The presence of some Pr on the Ba site, probably in a 4+ oxidation state, while maintaining the carrier concentration in the Cu-O chains, inhibits hole doping in the Cu-O planes and/or localizes doped carriers. We further propose that superconductivity appears if this substitution is suppressed and our preliminary experiments yielding superconducting $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ strongly support this model.

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- ¹H. B. Radousky, *J. Mater. Res.* **7**, 1917 (1992).
²C. H. Booth, F. Bridges, J. B. Boyce, T. Claeson, Z. X. Zhao, and P. Cervantes, *Phys. Rev. B* **49**, 3432 (1994).
³H. A. Blackstead, J. D. Dow, D.B. Chisey, J. S. Horwitz, M. A. Black, P. J. McGinn, A. E. Klunzinger, and D. B. Pulling, *Phys. Rev. B* **54**, 6122 (1996).
⁴Z. Zou, J. Ye, K. Oka, and Y. Nishihara, *Phys. Rev. Lett.* **80**, 1074 (1998).
⁵R. Fehrenbacher and T. M. Rice, *Phys. Rev. Lett.* **70**, 3471 (1993).
⁶A. I. Liechtenstein and I.I. Mazin, *Phys. Rev. Lett.* **74**, 1000 (1995); I.I. Mazin, cond-mat/9806246 (unpublished).
⁷L. Soderholm, C.-K. Loong, G. L. Goodman, and B. D. Dabrowski, *Phys. Rev. B* **43**, 7923 (1991).
⁸H.-D. Jostarndt, U. Walter, J. Harnischmacher, J. Kalenborn, A. Severing, and E. Holland-Moritz, *Phys. Rev. B* **46**, 14 872 (1992).
⁹S. Manninen, V. Honkimäki, K. Hämäläinen, J. Laukkanen, C. Blaas, J. Redinger, J. McCarthy, and P. Suortti, *Phys. Rev. B* **53**, 7714 (1996).
¹⁰P. Suortti, T. Buslaps, P. Fajardo, V. Honkimäki, M. Kretzschmer, U. Lienert, J. E. McCarthy, M. Renier, A. Shukla, T. Tschentscher, and T. Meinander, *J. Synchrotron Rad.* (to be published).
¹¹L. Hoffmann, A. A. Manuel, M. Peter, E. Walker, M. Gauthier, A. Shukla, B. Barbiellini, S. Massidda, Gh. Adam, S. Adam, W. N. Hardy, and R. Liang, *Phys. Rev. Lett.* **71**, 4047 (1993).
¹²A. Shukla, L. Hoffmann, A. A. Manuel, E. Walker, B. Barbiellini, and M. Peter, *Phys. Rev. B* **51**, 6028 (1995).
¹³K. Takenaka, Y. Imanaka, K. Tamamsaku, T. Ito, and S. Uchida, *Phys. Rev. B* **46**, 5833 (1992).
¹⁴Y. Suzuki, J.-M. Triscone, C. B. Eom, M. R. Beasley, and T. H. Geballe, *Phys. Rev. Lett.* **73**, 328 (1994).
¹⁵M. P. Nutley, A. T. Boothroyd, and G. J. McIntyre, *J. Magn. Magn. Mater.* **104-107**, 623 (1992).
¹⁶K. Kinoshita, A. Matsuda, H. Shibata, T. Ishi, T. Watanabe, and T. Yamada, *Jpn. J. Appl. Phys., Part 2*, **27**, L1642 (1988).
¹⁷A. Erb, E. Walker, and R. Flükiger, *Inst. Phys. Conf. Ser.* **58**, 1109 (1997).
¹⁸M. Guillaume, P. Allenspach, J. Mesot, B. Roessli, U. Staub, P. Fischer, and A. Furrer, *Z. Phys. B* **90**, 13 (1993).
¹⁹R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck, Jr., and L. W. Rupp, Jr., *Physica C* **165**, 419 (1990).

- ²⁰J. D. Jorgensen, S. Pei, P. Lightfoot, H. Shi, A. P. Paulikas, and B. W. Veal, *Physica C* **167**, 571 (1990).
- ²¹A.P. Reyes, D. E. MacLaughlin, M. Takigawa, P. C. Hammel, R. H. Heffner, J. D. Thompson, and J. E. Crow, *Phys. Rev. B* **43**, 2989 (1991).
- ²²A. Matsuda, K. Kinoshita, T. Ishii, H. Shibata, T. Watanabe, and T. Yamada, *Phys. Rev. B* **38**, 2910 (1988).
- ²³J. Neumeier and M. Maple, *Physica C* **191**, 158 (1992).
- ²⁴W. Guan, Y. Xu, S. R. Sheen, Y. C. Chen, J. Y. T. Wei, H. F. Lai, and M. K. Wu, *Phys. Rev. B* **49**, 15 993 (1994); W. J. Zhu, P. Liu, and Z. X. Zhao, *Physica C* **199**, 285 (1992).
- ²⁵A. Erb, E. Walker, and R. Flükiger, *Physica C* **9**, 258 (1996); A. Erb, E. Walker, J.-Y. Genoud, and R. Flükiger, *ibid.* **89**, 282 (1997).
- ²⁶T. B. Lindemer, J. F. Hunley, J. E. Gates, Jr., A. L. Sutton, J. Brynstad, C. R. Hubbard, and P. K. Gallagher, *J. Am. Ceram. Soc.* **72**, 1775 (1989).
- ²⁷T. B. Lindemer and E. D. Specht, *Physica C* **268**, 271 (1996).
- ²⁸M. J. Cooper, *Rep. Prog. Phys.* **48**, 415 (1985).
- ²⁹E. Isaacs and P. Platzman, *Phys. Today* **49** (2), 40 (1996).
- ³⁰S. Massidda, J. Yu, A. J. Freeman, and D. D. Koelling, *Phys. Lett. A* **122**, 198 (1987).
- ³¹M. Biagini, C. Calandra, and S. Ossicini, *Europhys. Lett.* **31**, 317 (1995).
- ³²C. Ambrosch-Draxl, P. Blaha, and K. Schwarz, *J. Phys.: Condens. Matter* **43**, 2347 (1994).
- ³³D. J. Singh, *Phys. Rev. B* **50**, 4106 (1994).
- ³⁴B. Barbiellini, P. Genoud, J. Y. Henry, L. Hoffmann, T. Jarlborg, A. A. Manuel, S. Massidda, M. Peter, W. Sadowski, H. J. Scheel, A. Shukla, A. K. Singh, and E. Walker, *Phys. Rev. B* **43**, 7810 (1991).
- ³⁵D. Vasumathi, B. Barbiellini, A. A. Manuel, L. Hoffmann, T. Jarlborg, R. Modler, C. Geibel, F. Steglich, and M. Peter, *Phys. Rev. B* **55**, 11 714 (1997).
- ³⁶M. Y. Chou, P. K. Lam, M. L. Cohen, G. Louprias, J. Chomilier, and J. Petiau, *Phys. Rev. Lett.* **49**, 1452 (1982).
- ³⁷J. R. Schneider and F. Bell, *Europhys. News* **23**, 10 (1992); Y. Kubo, *J. Phys. Soc. Jpn.* **66**, 2236 (1997).
- ³⁸P. Pattison, W. Weyrich, and B. G. Williams, *Solid State Commun.* **21**, 967 (1977).
- ³⁹B. Barbiellini and P. Platzman, *Mater. Sci. Forum* **255-257**, 189 (1997).
- ⁴⁰A. Erb (unpublished).