Anomalous Peak in the Superconducting Condensate Density of Cuprate High-T_c Superconductors at a Unique Doping State

C. Bernhard,[1] J. L. Tallon,[2] Th. Blasius,[3] A. Golnik,[4] and Ch. Niedermayer[3]

[1]*Max-Planck-Institut für Festkörperforschung Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

[2]*Industrial Research Ltd., P.O. Box 31310, Lower Hutt, New Zealand*

[3]*Universität Konstanz, Fakultät für Physik, D-78434 Konstanz, Germany*

[4]*Institute of Experimental Physics, Warsaw University, Hoża 69, 00-681 Warsaw, Poland*

(Received 30 May 2000)

The doping dependence of the ratio of the superconducting condensate density to the effective mass, n_s^o/m_{ab}^*, was studied in detail by muon-spin rotation for $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-z}Zn_z)_3O_{7-\delta}$ and $Tl_{0.5-y}Pb_{0.5+y}Sr_2Ca_{1-x}Y_xCu_2O_7$. Our data show that n_s^o/m_{ab}^* exhibits a peak at a unique doping state in the overdoped regime. Its position coincides with the critical doping state, where the normal state pseudogap was reported to appear and to deplete the electronic density of states. This finding implies that the pseudogap primarily arises from a change in the electronic ground state rather than from thermal fluctuations.

DOI: 10.1103/PhysRevLett.86.1614 PACS numbers: 74.72.Jt, 74.25.Ha, 76.75.+i

The superconducting (SC) condensate density, n_s, is proportional to the squared amplitude of the macroscopic wave function which describes the SC charge carriers. It is thus a fundamental parameter whose variation as a function of temperature (T) and of carrier doping provides important information about the SC state. From early on in the investigation of the cuprate high-T_c superconductors (HTSC), the absolute value of n_s/m^* was studied by transverse-field muon-spin-rotation (TF-μSR) measurements on polycrystalline samples. By using this technique, a linear relationship between the low-T value, n_s^o/m^*, and the critical temperature, T_c, was established in underdoped HTSC (so-called "Uemura line") [1]. This finding has stimulated the development of the precursor pairing model. Its basic idea is that the low value of n_s allows for large thermal phase fluctuations which can suppress the formation of a macroscopically coherent SC state over a significant T interval below the mean-field transition temperature, $T_c^{\rm macr} \ll T_c^{\rm mf}$ [2]. The precursor pairing model can also explain the pseudogap effect, which manifests itself as a partial suppression of the low-energy charge and spin excitations in the normal state (NS) of underdoped HTSC. Within this model the pseudogap state is thought of as the macroscopically incoherent SC state within the range $T_c^{\rm macr} < T < T_c^{\rm mf}$ [2]. Many more models were introduced in an effort to understand the phenomenology of the pseudogap [3]. In particular, some models associate the pseudogap effect with additional electronic correlations which appear below a critical doping state and compete with SC [4,5]. It was shown that the combined suppression of T_c and n_s^o in underdoped HTSC can be equally well explained in terms of the depletion of the density of states near the Fermi level, $N(\epsilon_F \pm \Delta)$, brought about by competing correlations which rapidly grow in strength on the underdoped side [6]. The question as to the origin of the NS pseudogap is presently vigorously debated and is considered as an important key to resolve the mystery of HTSC.

In this paper we report extensive TF-μSR studies on the evolution of n_s^o/m_{ab}^* as a function of hole doping, p, for series of polycrystalline $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-z}Zn_z)_3O_{7-\delta}$ (Y,Ca-123) and $Tl_{0.5-y}Pb_{0.5+y}Sr_2Ca_{1-x}Y_xCu_2O_7$ (Tl-1212). Our new data complement previous less detailed studies [7–10] and highlight that n_s^o/m_{ab}^* exhibits a pronounced peak at a unique doping state in the slightly overdoped region. We emphasize that the observed peak in n_s^o/m_{ab}^* versus doping is indicative of a sudden change in the SC ground state. Most remarkably, we find that the location of this change coincides with the critical doping state where previously a rapid suppression of $N(\epsilon_F \pm \Delta)$ was observed signaling the onset of competing pseudogap correlations [4,6]. This finding is in contrast to models which relate the pseudogap effect to thermal fluctuations, such as the precursor pairing model.

A series of under- to overdoped polycrystalline samples of $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-z}Zn_z)_3O_{7-\delta}$, with $z = 0$, 0.02, and 0.04, and $Tl_{0.5-y}Pb_{0.5+y}Sr_2Ca_{1-x}Y_xCu_2O_7$, with $y \leq 0.15$ and $x \leq 0.4$, was prepared following previously described procedures [8,9,11]. The T_c values were determined by resistivity and dc susceptibility measurements. The hole doping of the CuO_2 planes, p, was deduced from measurements of the room-temperature thermoelectric power (RT-TEP) [12]. Alternatively, p was estimated from the ratio of $T_c/T_{c,\max}$ (knowing, e.g., from the RT-TEP, whether the sample is underdoped or overdoped) by assuming the approximate parabolic p dependence in which $p = 0.16 \pm \sqrt{(1 - T_c/T_{c,\max})/82.6}$ [11,13]. Good agreement was obtained between both estimates.

The TF-μSR experiments at 3 kOe were performed at the πM3 beam line of the Paul-Scherrer-Institut in Villigen, Switzerland. A detailed description of the TF-μSR technique and its use in determining n_s/m^* for polycrystalline HTSC samples is given in Ref. [14]. A Gaussian relaxation function was used to fit the measured time spectra. From the obtained depolarization rate, σ, we deduced

 0031-9007/01/86(8)/1614(4)$15.00

the magnetic penetration depth, λ_{ab}, and n_s/m^*_{ab} using the established relationship [8,14]: $\sigma[\mu s^{-1}] = 7.086 \times 10^4 \lambda_{ab}^{-2}[\mathrm{nm}] = 2.51 \times 10^{-21} m_e n_s/m^*_{ab}[\mathrm{cm}^{-3}]$.

Figure 1(a) displays the evolution of the low-T depolarization rate, $\sigma_o \sim n_s^o/m^*_{ab}$, as a function of hole doping per CuO_2 plane, p, for under- to overdoped $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-z}Zn_z)_3O_{7-\delta}$. Figure 1(b) shows the evolution of T_c with p. It is evident from Fig. 1(a) that σ_o exhibits a pronounced peak in the slightly overdoped regime. For all three series it occurs at a similar doping state of $p \approx 0.19$ (in the following we call it "critical doping," p_{crit}). At optimum doping of $p_{\mathrm{opt}} \approx 0.16$, where the highest T_c value of $T_{c,\mathrm{max}} = 85.5$ K is observed for the Zn-free series, σ_o is already reduced by 25%–30% as compared to critical doping. Note that for these Y,Ca-123 samples the contribution of the CuO chains to n_s^o should be much weaker than in $YBa_2Cu_4O_8$ (Y-124) or in fully oxygenated Y-123 since the CuO chains are significantly deoxygenated, except for the strongly overdoped regime, and even there the Ca substitution leads to chain disorder by occupation of the O(5) off-chain position [8,9,13]. The difference between optimum doping (highest T_c value) and critical doping (highest n_s^o/m^* value) is largest for the pure series, but it is reduced for the Zn-substituted series. At high Zn content, SC survives only in the vicinity of the critical doping state, i.e., $p_{\mathrm{opt}} \rightarrow p_{\mathrm{crit}}$. This effect was previously explained in terms of the suppression of $N(\varepsilon_F \pm \Delta)$ due to the opening of the pseudogap below p_{crit} which, for impurity scattering in the unitarity limit, enhances the suppression of T_c and n_s^o [15]. The other remarkable feature is the plateau in n_s^o/m^*_{ab} versus p centered around 1/8 doping which appears far more pronounced in n_s/m^* than in T_c. The p dependence of n_s^o/m^*_{ab} in Y,Ca-123 therefore is characterized by two marked features, a plateau around 1/8 doping (likely associated with the tendency for the formation of static stripes) and the peak near critical doping (due to some yet unknown correlations which compete with SC—stripes are a likely candidate). In the following, we focus on the critical doping region at about $p \sim 0.19$.

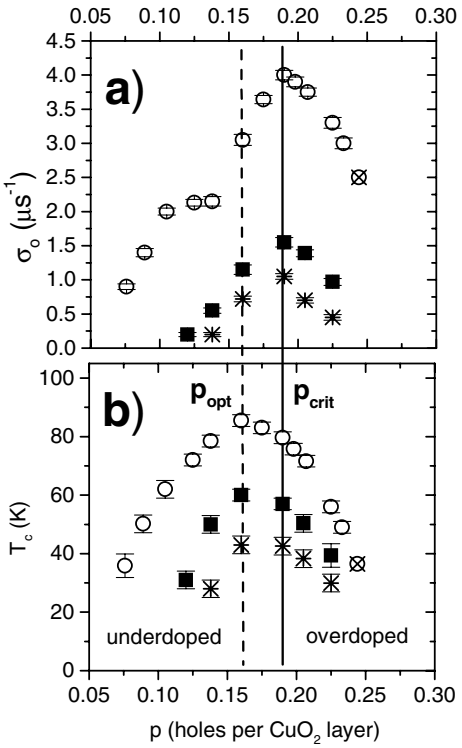

FIG. 1. (a) Low-T depolarization rate $\sigma_o \sim n_s^o/m^*_{ab}$ as a function of hole doping for under- to overdoped $Y_{0.8}Ca_{0.2}Ba_2Cu_{3-z}Zn_zO_{7-\delta}$ with $z = 0$ (open circles), $z = 0.02$ (solid squares), and $z = 0.04$ (stars). The crossed circle shows σ_o for strongly overdoped $Lu_{0.7}Ca_{0.3}Ba_2Cu_3O_{6.95}$. Critical (optimum) doping is marked by the solid (dotted) line. (b) Doping dependence of the critical temperature shown by the same symbols.

In order to confirm that the peak of n_s^o/m^*_{ab} at $p_{\mathrm{crit}} \approx 0.19$ is a common feature of the hole-doped HTSC we also investigated a series of under- to overdoped Tl-1212 ($T_{c,\mathrm{max}} = 107$ K). Figure 2 shows the evolution of $\sigma_o \sim n_s^o/m^*_{ab}$ as a function of p. It is evident that σ_o follows a very similar p dependence as in Y,Ca-123 and that, in particular, it also exhibits a peak at about $p_{\mathrm{crit}} \approx 0.19$. The present Tl-1212 series contains only one sample near 1/8 doping. We cannot therefore decide whether the plateau in n_s^o/m^*_{ab} is a common feature of HTSC. Note that the significantly larger electronic anisotropy of Tl-1212, as compared to Y,Ca-123, does not lead to any noticeable difference in the evolution of σ_o vs p. This confirms our previous finding that the relationship $\sigma_o \sim n_s^o/m^*_{ab}$ is valid for a variety of HTSC, the only exception being the most extremely anisotropic compound Bi-2212 [8].

It is remarkable that the same critical doping state was previously identified based on specific heat, susceptibility and NMR data as the point where the NS pseudogap first appears and starts to deplete $N(\epsilon_F \pm \Delta)$ [4,6,16]. In Fig. 3 the solid line marked by the crosses shows the p dependence of the ratio of the electronic entropy divided by the temperature, $(S/T)_{T_c} = (\int^{T_c} \gamma(T')\,dT')/T_c$ (normalized to its value at critical doping), as obtained by Loram *et al.* from specific heat data for Y,Ca-123 [6,17] The Y,Ca-123 sample used for the specific heat measurements originates in fact from the same batch as the majority of the samples used in our μSR study. $(S/T)_{T_c}$ is the average of γ between $T = 0$ and T_c and is a measure of the average density of states within an energy window of $\sim(2-3)k_BT_c$ and thus proportional to $N(\epsilon_F \pm \Delta)$ just above T_c. It is almost constant on the strongly overdoped side while it exhibits a steady decrease below critical doping due to the opening of the pseudogap. A very similar p dependence was also obtained from optical measurements for the plasma frequency, $\omega_{\mathrm{pl}}^n \sim n_n/m^*_{ab}$, of the normal carriers [18]. Shown by the dotted line and marked by the stars is the condensation energy

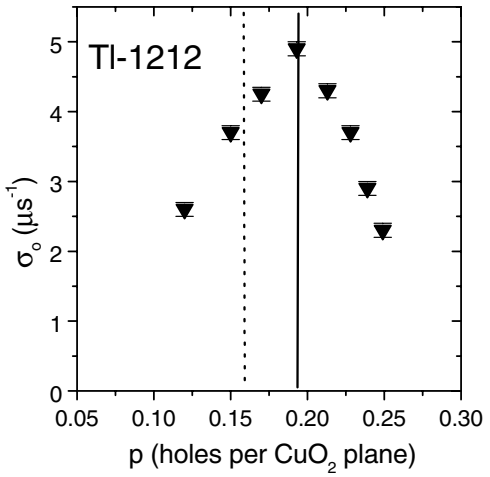

FIG. 2. Doping dependence of the low-T depolarization rate σ_o for under- to overdoped $Tl_{1-y}Pb_ySr_2Ca_{1-x}Y_xCu_2O_7$. The solid (dotted) line marks critical (optimum) doping.

$U_o = \int^{T_c}(S_n - S_s)\,dT'$ normalized to its value at critical doping [6,17]. Finally, the normalized value of $\sigma_o \sim n_s^o/m_{ab}^*$ for pure Y,Ca-123 and Tl-1212 is shown by the open circles and solid triangles, respectively. Once more it becomes apparent that n_s^o/m_{ab}^* follows very similar doping dependency in Y,Ca-123 and Tl-1212. Another striking result which becomes evident from Fig. 3 is the similar doping dependence of n_s^o/m_{ab}^* and U_o , both of which exhibit a pronounced peak around critical doping and decrease rather steeply on the underdoped as well as on the overdoped sides. Such a correlation is expected on the underdoped side due to the decreasing density of states. In fact, $(S/T)_{T_c}$ and n_s^o/m_{ab}^* match rather well below $p_{\rm crit}$. Also, the decrease of U_o on the overdoped side can be understood within a Bardeen-Cooper-Schrieffer (BCS) model due to the decreasing size of T_c and the concomitant decrease of the size of the SC energy gap (such as observed

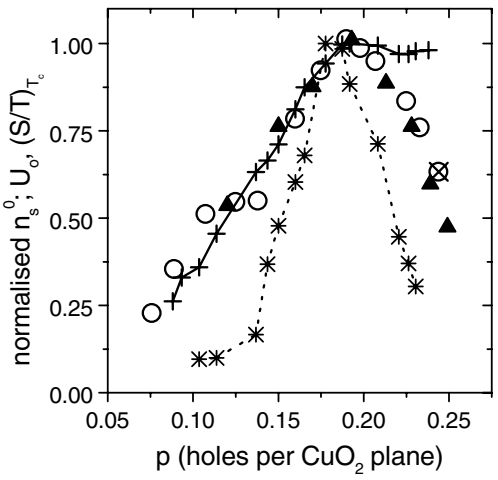

FIG. 3. Doping dependence of the normalized values of $(S/T)_{T_c}$ (solid line and crosses) and of U_o (dotted line and stars) for Y,Ca-123 as deduced from specific heat [6,17] and of n_s^o/m_{ab}^* for Y,Ca-123 (open circles) and Tl-1212 (solid triangles) deduced from TF-μSR.

by spectroscopic techniques [19,20]). In clear contrast, the strong decrease of n_s^o/m_{ab}^* on the overdoped side is unexpected since the electronic density of states $\sim(S/T)_{T_c}$ or likewise the plasma frequency of the normal carriers $\omega_{\rm pl}^n \sim n_n/m_{ab}^*$ [18] remain almost constant on the overdoped side. We return to this important point later and focus first on the observed behavior on the underdoped side. Below critical doping it is evident that all three quantities which are displayed in Fig. 3 follow a common doping dependence, i.e., below $p_{\rm crit}$ they suddenly start to decrease. It was pointed out earlier that this circumstance of a steady reduction of $N(\varepsilon_F \pm \Delta)$ for $p < p_{\rm crit}$, accompanied by a sharp reduction in the condensation energy U_o and n_s^o/m_{ab}^*, is precisely what is expected with the onset of an electronic correlation competing with SC [4,6]. It is important to note that n_s^o/m_{ab}^* characterizes the SC ground state. Our new μSR data therefore highlight a sudden change in the SC ground state which occurs at the same critical doping level for which the onset of the pseudogap phase was reported. This finding suggests that the pseudogap effect is associated with a change of the electronic ground state and thus cannot be explained solely in terms of thermal fluctuations, such as in the precursor pairing model.

The argument against the precursor pairing model can be further substantiated by examples which show that for underdoped samples T_c is not uniquely determined by n_s^o/m_{ab}^*. $YBa_2Cu_4O_8$ (Y-124) is underdoped with $T_c = 80$ K and exhibits clear signatures of the pseudogap. It has, besides the superconducting CuO_2 bilayers, metallic CuO chains that become superconducting, most likely due to proximity coupling and lead to a significant enhancement of n_s^o/m_{ab}^* with $\sigma_o = 3.3\ \mu s^{-1}$ as compared to $\sigma_o \sim 2.2 - 2.3\ \mu s^{-1}$ in similarly underdoped Y-123 or Y,Ca-123 with $T_c \approx 80$ K [8,9]. If T_c of underdoped samples was indeed uniquely determined by n_s^o, then T_c should exceed 100 K in Y-124. Another counterexample is underdoped Zn-substituted Y-123. It has been shown that, upon Zn substitution, n_s^o/m_{ab}^* is even more rapidly suppressed than T_c. This behavior was explained in terms of the d-wave symmetry of the superconducting OP and elastic scattering in the unitarity limit on Zn impurities [10]. Such compounds thus can lie far to the left of the Uemura line. For $Y_{0.8}Ca_{0.2}Ba_2Cu_{2.94}Zn_{0.06}O_{6.45}$ with $T_c = 31$ K we obtained $\sigma_o \approx 0.2\ \mu s_s^{-1}$ which, according to the Uemura relation, should result in $T_c \leq 10$ K, i.e., one-third the observed value [10]. Finally, there is the surprising result that n_s^o/m_{ab}^* decreases rapidly also on the overdoped side [7,21], yet no clear pseudogap effect was observed for such strongly overdoped samples.

Now we focus on the TF-μSR data on the strongly overdoped side past critical doping. Our measurements confirm previous reports that n_s^o/m_{ab}^* is dramatically reduced on overdoping. This surprising result was first obtained by TF-μSR on $Tl_2Ba_2CuO_{6+\delta}$ (Tl-2201) [7] and later on (Y,Ca)-123 [8,9]. Subsequently, it was confirmed by other experimental techniques [22]. It was previously

pointed out that the strong suppression of n_s^o/m_{ab}^* for heavily overdoped samples cannot be understood within a BCS model, unless one assumes that pair breaking correlations become increasingly important [7,10]. This earlier proposal of strong pair breaking on the overdoped side, however, is not supported by recent specific heat [6] or ^{89}Y-NMR and ^{17}O-NMR data [23] which give no clear indication for a growing density of unpaired carriers within the SC gap. These data also do not support the scenario that overdoped materials are inhomogeneous with only a small SC volume fraction [21]. The BCS model predicts that n_s^o/m_{ab}^* should follow the same p dependence as the normal state plasma frequency, $\omega_{\rm pl}^n \sim n_n/m_{ab}^*$, deduced from optical experiments [18], or $(S/T)_{T_c}$, obtained from the specific heat [4,17], which both remain almost constant on the overdoped side. Note that this inconsistency cannot be explained by a change of the effective mass m_{ab}^* which enters all three quantities in the same way, namely in the denominator. In this context we emphasize once more the surprising similarity between the p dependences of n_s^o/m_{ab}^* and the condensation energy U_o. This effect cannot easily be understood within BCS theory, where U_o is determined by the change in potential energy due to the attractive pairing interaction times the density of states $N(\varepsilon_F \pm \Delta)$, while n_o^s/m_{ab}^* should be determined by the kinetic energy of the carriers times $N(\varepsilon_F \pm \Delta)$. This apparent inconsistency of the experimental data on the overdoped side with the prediction of the BCS model is especially important in light of the indication that competing electronic correlations are at work below critical doping. This should mean that the intrinsic properties of the SC state are best seen for overdoped materials. Yet it is this very region which cannot be described by the BCS model and therefore suggests an unconventional SC state. As one example of an unconventional model which explains the correlation between U_o and n_s^o we only mention here the so-called spin-charge separation model. Superconductivity can only occur here if both holons and spinons condense resulting in a total condensate density of $1/n_s = 1/n_s^{\rm holon} + 1/n_s^{\rm spinon}$ [24]. On the overdoped side the diminishing spinon density would therefore lead to the dramatic reduction of n_s^o. As a final remark we note that a similar TF-μ SR study was recently performed on $La_{2-x}Sr_xCuO_4$ (La-214) [25]. For La-214 the maximum in σ_o versus p is significantly broader than the one reported here for Y,Ca-123 and Tl-1212. The reason for this probably lies in the fact that $N(\varepsilon_F \pm \Delta)$ for La-214 goes on increasing with overdoping [17]. What is important is that while $n_s^o/(S/T)_{T_c}$ for La-214 remains constant below $p_{\rm crit}$, this ratio decreases sharply for $p > p_{\rm crit}$, just as shown in Fig. 3. Moreover, the peak in U_o for La-214 is also significantly broadened as compared with the one in Y,Ca-123 [17]. This finding supports our suggestion that n_s^o/m_{ab}^* and U_o may be correlated in the HTSC.

In summary, we have presented TF-μSR measurements which establish that a unique critical doping state exists in the slightly overdoped regime, where the ratio of the superconducting condensate density to the effective mass, n_s^o/m_{ab}^*, exhibits a pronounced maximum. This unexpected sudden change of n_s^o/m_{ab}^* highlights a corresponding change in the electronic ground state properties. Its coincidence with the onset of the pseudogap implies that the pseudogap effect originates from a change in the electronic ground state rather than from thermal phase fluctuations such as predicted by the precursor pairing model [2]. The rapid decrease of n_s^o/m_{ab}^* on the strongly overdoped side cannot be easily understood within a conventional BCS model since the normal state carrier density remains almost constant here. Even more surprisingly, n_s^o/m_{ab}^* is found to exhibit a similar doping dependence such as the condensation energy U_o obtained from specific heat [6,17]. This correlation suggests unconventional behavior even in the overdoped region.

We acknowledge A. Amato and D. Herlach (PSI) for technical support. C. B. and J. L. T thank J. W. Loram for providing the specific heat data. C. B. and J. L. T. appreciate the financial support of the Marsden Fund of New Zealand. J. L. T. thanks the Royal Society of New Zealand for financial support.

[1] Y. J. Uemura *et al.,* Phys Rev. Lett. **62**, 2317 (1989).
[2] V. J. Emery and S. A. Kivelson, Phys. Rev. Lett. **74**, 3253 (1995); Nature (London) **374**, 434 (1995).
[3] For a review, see T. Timusk and B. Statt, Rep. Prog. Phys. **62**, 61 (1999).
[4] J. W. Loram and K. A. Mirza, J. Supercond. **7**, 243 (1994).
[5] See, for example, C. Castellani, C. DiCastro, and M. Grilli, Phys. Rev. Lett. **75**, 4650 (1995); C. M. Varma, Phys. Rev. Lett. **83**, 3538 (1999).
[6] J. W. Loram *et al.,* Physica (Amsterdam) **282C–287C**, 1405 (1997); J. Phys. Chem. Solids **59**, 2091 (1998).
[7] Ch. Niedermayer *et al.,* Phys. Rev. Lett. **71**, 1764 (1993).
[8] C. Bernhard *et al.,* Phys. Rev. B **52**, 10 488 (1995).
[9] J. L. Tallon *et al.,* Phys. Rev. Lett. **74**, 1008 (1995).
[10] C. Bernhard *et al.,* Phys. Rev. Lett. **77**, 2304 (1996).
[11] M. Presland *et al.,* Physica (Amsterdam) **176C**, 95 (1991).
[12] S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 14 928 (1992).
[13] J. L. Tallon *et al.,* Phys. Rev. B **51**, R12911 (1996).
[14] B. Pümpin *et al.,* Phys. Rev. B **42**, 8019 (1990).
[15] J. L. Tallon *et al.,* Phys. Rev. Lett. **79**, 5294 (1997).
[16] J. L. Tallon *et al.,* Physica (Amsterdam) **235C**, 1821 (1994).
[17] J. W. Loram *et al.,* Annual Report, IRC, Cambridge, 1998.
[18] A. V. Puchkov *et al.,* Phys. Rev. Lett. **77**, 1853 (1996).
[19] P. J. White *et al.,* Phys. Rev. B **54**, 15 669 (1996).
[20] C. Bernhard *et al.,* Phys. Rev. B **59**, 6631 (1999).
[21] Y. I. Uemura *et al.,* Nature (London) **364**, 605 (1993).
[22] J. P. Locquet *et al.,* Phys. Rev. B **54**, 7481 (1996); G. Villard *et al.,* Phys. Rev. B **58**, 15 231 (1998).
[23] G. V. M. Williams *et al.,* Phys. Rev. B **57**, 8696 (1998).
[24] N. Nagaosa and P. A. Lee, Phys. Rev. B **45**, 966 (1992); S-S. Lee and S-H. S. Salk, cond-mat/0005120.
[25] C. Panagopoulos *et al.,* Phys. Rev. B **60**, 14 617 (1999).