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Pressure-induced superconductivity in the spin-ladder cuprate

N Fujiwara[1,6], **N Môri**[1,2], **Y Uwatoko**[1], **T Matsumoto**[3], **N Motoyama**[4] **and S Uchida**[5]

[1] Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan
[2] Department of Physics, Faculty of Science, Saitama University, 255 Simookubo, Saitama 338-8581, Japan
[3] National Institute for Materials Science, Tsukuba 305-0047, Japan
[4] College of Science and Engineering, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagamihara-shi 229-8558, Kanagawa, Japan
[5] Department of Physics, Faculty of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

E-mail: naokif@mbox.kudpc.kyoto-u.ac.jp (N Fujiwara)

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Abstract
Pressure-induced superconductivity in a spin-ladder cuprate $Sr_2Ca_{12}Cu_{24}O_{41}$ was investigated on a microscopic level by using ^{63}Cu nuclear magnetic resonance (NMR) under a pressure of 3.5 GPa. We found a fully gapped superconducting state, and the superconductivity is stable at magnetic fields close to the conventional Pauli limit. The superconducting gap was observed in addition to a spin gap which occurs in a separated temperature range.

1. Introduction

$Sr_{14-x}Ca_xCu_{24}O_{41}$ ($x = 11.5$–13.5) has attracted a number of researchers because the system is the only spin-ladder compound which exhibits superconductivity. However, superconductivity is only realized under high pressure above 3 GPa in highly doped compounds ($x \geqslant 10$) [1]. This fact has been the main hurdle in the detailed investigation of the superconductivity, although the superconductivity itself was discovered in 1996.

In the early stage superconductivity was studied only by resistivity and AC-susceptibility measurements using cubic and modified Bridgeman cells, respectively, because these measurements only need a small amount of sample [1–5]. The resistivity measurements have shown that the superconducting phase appears between 3 and 8 GPa with the optimum T_c being 10 K at 4 GPa [3]. It is found from the anisotropy of the transport properties that

[6] Present address: Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan.

pressure plays the role of stabilizing the metallic state within the ladder plane [3, 4]. The H_c–T_c characteristics have been determined by AC-susceptibility measurements and the results show a strong anisotropy with respect to the field direction [5]. For the field perpendicular to the ladder plane, the crystal *b*-axis, T_c is strongly suppressed at a fixed field, whereas in the case of the field being applied parallel to the plane, the superconducting state persists even above the conventional Pauli limit which is determined from T_c at zero field.

For other measurements in which a larger sample volume is needed, a clamp-type pressure cell is much more convenient and available. However, usual clamp cells are made of CuBe alloy and the maximum pressure is 3 GPa. Mayaffre and Piskunov *et al* made NMR measurements under high pressure above 3 GPa for the field (H) perpendicular to the plane [6, 7]. However, the measurements were not done on the superconducting phase with the strongly suppressed T_c but on the normal state.

Similar to high-T_c cuprates, the interplay between spin gap and superconductivity is an important problem as well as the determination of the pairing symmetry. The existence of the spin gap itself is much easier to understand compared to high-T_c cuprates [8] since the ground state of the undoped system is a quantum spin liquid and this state is expected to persist even in the highly doped region according to theoretical investigations [9–12]. In the present system the dopant hole dependence has been intensively studied at ambient pressure since it can be controlled over a wide range from 0.07 ($x = 0$) to 0.24 ($x = 14$) per ladder Cu [3]. The decrease of the spin gap for Ca substitution was observed in NMR measurements [13–15], whereas no change was observed in neutron scattering experiments [16]. In any case, the question whether the spin gap persists or not in the normal state above the superconducting phase is not resolved unless high pressures above 3 GPa are achieved and superconductivity is confirmed.

Our motivation to perform NMR under high pressure above 3 GPa arises from the following open questions: (1) What is the pairing symmetry? (2) Does the spin gap persist in the normal state above the superconducting state? To clarify these questions NMR measurements were performed using a clamp cell made of NiCrAl alloy for the field parallel to the leg direction, the crystal *c*-axis, where the superconducting state is expected to persist even at fairly high magnetic fields.

2. Experimental results

2.1. H_c–T_c characteristics

A single crystal of $Sr_2Ca_{12}Cu_{24}O_{41}$ with a volume of $4 \times 2 \times 1$ mm^3 was prepared for the measurements. A clamp-type pressure cell with an effective sample space of diameter 4×20 mm^2 was used for the measurement. The appearance of superconductivity was confirmed by measuring the resonance frequency of an NMR probe attached to the pressure cell. The resonance frequency is roughly given as $f \propto 1/\sqrt{LC}$ where L and C represent the inductance and variable capacitance of the NMR probe, respectively. The sample is contained in a coil and the onset of superconductivity is detected by the change of the resonant frequency, i.e. the change of L-value. This method corresponds to an AC-susceptibility measurement. The T-dependence of the frequency at several fields is shown in figure 1.

The value of T_c at $P = 3.5$ GPa is 4.7 K, which is consistent with that obtained from the resistivity measurement shown in figure 2. If we probe the temperature at which the resonance frequency starts to change against H, this gives H_{c2} versus T_c characteristics as shown in the inset of figure 1.

For high-T_c cuprates, the temperature has often been identified as the irreversibility temperature T_{irr}. T_{irr} gives a borderline between creeping and freezing of flux lines (FL)

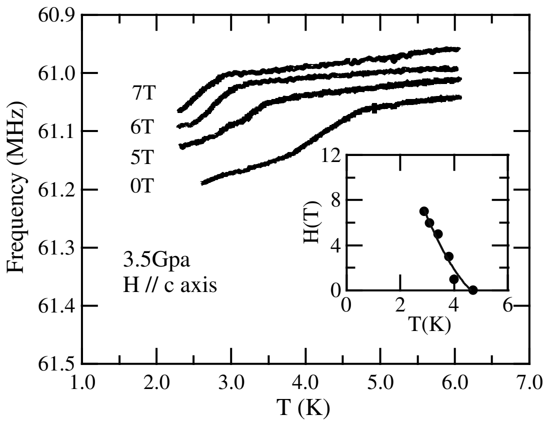

Figure 1. Resonance frequency of an NMR probe attached to a pressure cell at $P = 3.5$ GPa. The frequency changes at the superconducting state. The onset corresponds to the upper critical field. The inset shows the H_c–T_c curve obtained from the onset of the frequency at each field. The solid line is a guide for the eyes.

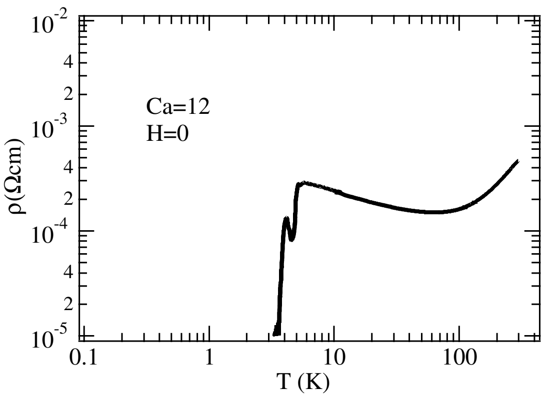

Figure 2. The resistivity measurement at a pressure of 3.5 GPa [5].

which are formed through the planes for the H perpendicular to the plane. In the present case, flux lines are self-trapped between the planes since the field is applied parallel to the plane, and thus such a creep is hardly expected. It should be remarked that the conventional Pauli limit is calculated from $T_c = 4.7$ K to be 8.65 T. The experimental results show that superconductivity remains stable even at high field close to the Pauli limit. The results are consistent with those obtained from AC-susceptibility measurement [5]. The fact implies that superconductivity in this system is anomalous compared to the conventional one.

2.2. NMR spectra

NMR spectra at 2 GPa and ambient pressure that were measured using the NiCrAl pressure cell are shown in figures 3(a) and (b), respectively, together with the spectra measured without the pressure cell (figure 3(c)). The NMR spectra at 3.5 GPa were almost the same as those at 2 GPa. As is seen from the figure, the spectra at 2 GPa are almost the same as those at ambient pressure as far as the splitting due to the quadrupole effect is concerned. The linewidth shows no remarkable increase around 2 K where antiferromagnetic ordering is expected according to neutron scattering experiments [16]. As far as the NMR results are concerned, such an

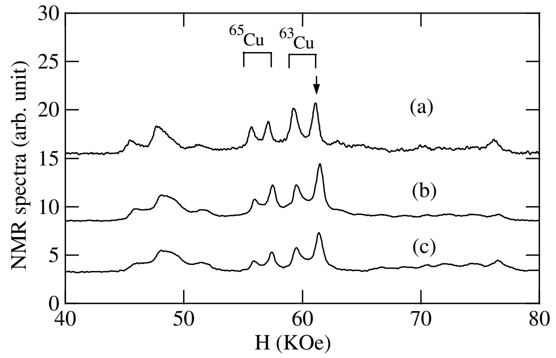

Figure 3. NMR spectra measured at 70 MHz at 4.2 K. Spectra (a) and (b) were measured by using the clamp cell at 2 GPa and ambient pressure, respectively. Spectra (c) were measured at ambient pressure without the clamp cell. The signal from the ladder sites appears at higher fields compared to that from the chain sites. The arrow in the figure represents the ^{63}Cu signal from the ladder sites.

ordering was not observed at the ladder sites. If the ordering is realized at the ladder sites, the intensity of the NMR spectra should drastically decrease at the critical regime coinciding with a drastic broadening of the linewidth. In fact, the T-dependence contrasts with that of 2%-Zn doped $SrCu_2O_3$ which includes no chain sites [17].

2.3. T_1^{-1}

^{63}Cu-NMR signals for the ladder site can be separated from those for the chain site since the nuclei of these sites possess a different quadrupole coupling as is shown in figure 3 [14, 18]. The measurements of the relaxation rate (T_1^{-1}) were performed for the central transition ($I = -1/2 \Leftrightarrow 1/2$) of ^{63}Cu nuclei at 70.0 MHz which corresponds to 6.2 T. T_c at this field is about 2.8 K, as is seen from the inset of figure 1. The T-dependence of T_1^{-1} is shown in figure 4. The spin gap is observed even under high pressure as an activated T-dependence of T_1^{-1} at temperatures higher than 30 K, i.e.,

$$T_1^{-1} \propto \exp(-\Delta_{\mathrm{spin}}/T). \tag{1}$$

The value of Δ_{spin} is estimated to be 173 K. It should be noted that the spin gap is seen in the state in which the charge transport is metallic [3].

By contrast, T_1^{-1} below 30 K is dominated by a term showing a T-linear dependence followed by a peak developed below T_c. The onset and the position of the peak shift to higher temperatures when decreasing the magnetic field to 5.0 T (open squares in figure 4). If the T-linear component originates from an extrinsic source, it should be persistent in the superconducting state. However, T_1^{-1} measured at low temperatures obviously goes below the T-linear line shown in figure 4, thus excluding this interpretation. The possibility of vortex motion might be pointed out as the origin of the peak: vortex motion has been observed in T_1^{-1} of ligand sites in high-T_c cuprates such as $YBa_2Cu_4O_8$ (YBCO) [19] or $HgBa_2CuO_{4+\delta}$ (HBCO) [20] when the H is applied perpendicular to the plane. The FL is self-trapped between the planes for H parallel to the plane, and thus the effect is hardly expected in the present case. In fact in the HBCO system [20] the effect disappears when H is applied parallel to the planes. Furthermore, T_1^{-1}/γ_N^2 (γ_N = nuclear gyromagnetic ratio) at the peak is 80 or 25 times larger than the values for YBCO or HBCO, respectively. The value observed in our experiments is too large to explain the peak as a result of vortex motion. Hence, we conclude that the peak in T_1^{-1} and the T-linear component have the same origin in the electric state and/or spin fluctuations.

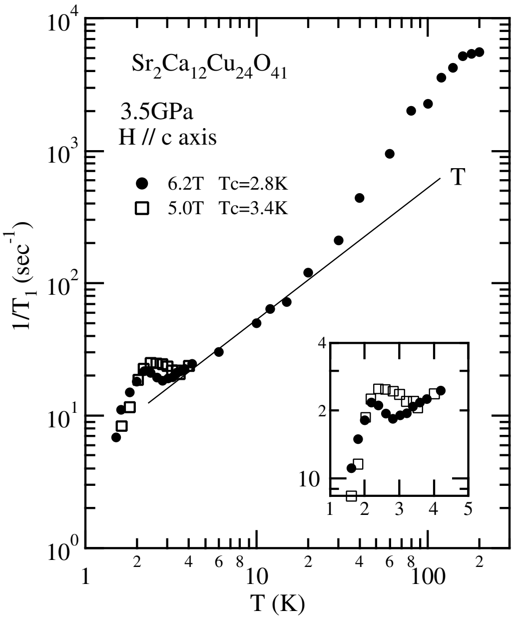

Figure 4. Nuclear lattice relaxation rate $1/T_1$ for ^{63}Cu nuclei. The solid line shows the Korringa relation expressed by equation (2). $1/T_1$ at low temperatures around T_c is expanded in the inset.

The T-linear dependence of T_1^{-1} can be assigned as a Korringa-type behaviour,

$$T_1^{-1} \propto bT \tag{2}$$

where the value of b is about 6.1 (s^{-1} K^{-1}). The peak on the other hand reminds one of the so-called coherence peak from conventional s-wave superconductors. However, our peak is anomalous: in the case of a conventional one, the peak disappears at high magnetic fields. The values of $1/TT_1$ normalized by those at the normal state are shown in figure 5. The observation of the clear peak at high field implies that superconductivity with a full gap is realized and is stable even at high magnetic fields close to the Pauli limit. This fact is consistent with the results of H_c–T_c characteristics determined from the resonant frequency of the NMR probe.

2.4. NMR shift

The spin gap is also observed in the ^{63}Cu-NMR shift (K) at relevant temperatures. The raw data of K show H^{-2}-linear dependence because of the large quadrupole effect acting on the ^{63}Cu nuclei. The values free from the quadrupole effect are obtained by plotting K versus H^{-2} and extrapolating to zero [21]. The values after the extrapolating process are shown in figure 6. The shift is given as a sum of two components, the orbital and the spin parts ($K = K_{orb} + K_{spin}$) and the spin part is proportional to the spin susceptibility. The T-dependence of K at high temperatures fits well the theoretical curve for a spin-ladder system [22],

$$K(T) = K_0 + \frac{K_1}{\sqrt{T}} \exp(-\Delta_{spin}/T). \tag{3}$$

The gap Δ_{spin} obtained from the fit is 217 K and is comparable with that estimated from T_1^{-1}. K_0 is given as a sum of K_{orb} and K_{para} which is related with the Korringa relation ($T_1T \propto K_{para}^2$). The value of K_0 is estimated to be 0.25%. The main contribution of K_0 would come from K_{orb} which is comparable with that for high-T_c cuprates (K_0 of YBCO, for example, is 0.28% [23]). However, the paramagnetic contribution corresponding to the Korringa term in T_1^{-1} (equation (2)) should be finite.

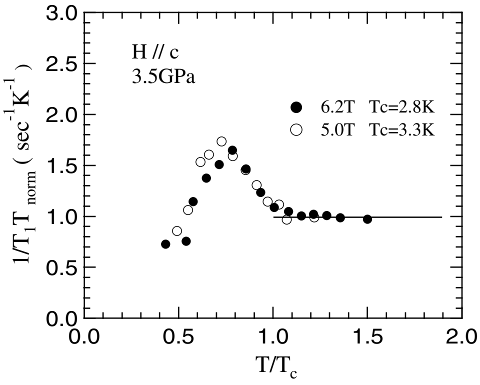

Figure 5. $1/TT_1$ normalized by that of the normal state. A solid line shows the relation expressed by equation (2).

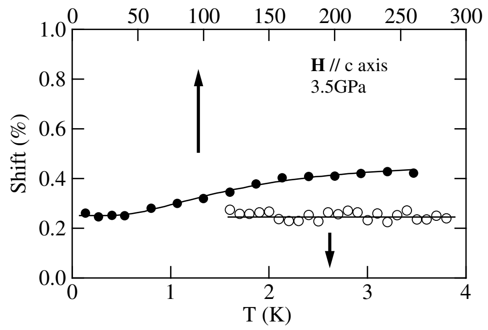

Figure 6. NMR shift of ^{63}Cu nuclei for the ladder sites. Closed and open circles represent the data for the high and low T range, respectively. The solid curve represents values calculated by equation (3) in the text.

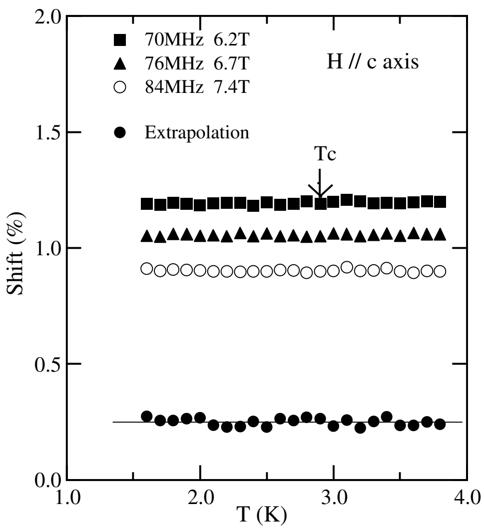

Figure 7. NMR shift of ^{63}Cu nuclei for the ladder sites at low temperatures around T_c. The raw data which show the H^{-2}-linear dependence due to the quadrupole effect are plotted in the figure. The data of figure 6 after extrapolation are also plotted in the figure.

The raw data before the extrapolating process are plotted in figure 7 as well as the data after the extrapolating process since the extrapolated data scatters due to the extrapolation process and T_c also depends on the value of the applied fields. As is seen from figure 7, no appreciable change occurs at T_c.

3. Discussion

3.1. Spin gap and superconductivity

We have observed unexpected features in both the normal and superconducting states in T_1^{-1} and K. At a pressure of 3.5 GPa we observed two excitation modes in the normal metallic state: one gives rise to the gapless T-linear component in T_1^{-1} ($T_1^{-1} \propto bT$) which is directly correlated to superconductivity, and the other activation-type component which is expressed in equation (1). The persistence of the spin gap at high pressures suggests that

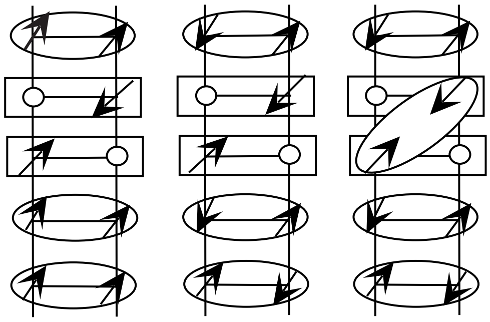

Figure 8. (A) Illustration of spin and charge configuration at high temperatures. The ellipses show spin dimmers on the rung. Some of them are in the triplet states at high temperatures. A rectangles imply the holon–spinon bound states. They move independently in the ladder. (B) Illustration at intermediate temperatures. A spin within the holon–spinon bound state is free and paramagnetic. Spin dimmers in the ellipses are in the singlet state at this temperature region. (C) Illustration at the superconducting state. Two spins within the bound state form the pairing.

quasi-one-dimensional spin-charge dynamics is preserved in the normal state although pressure increases coupling or hopping between the ladders. In the case of conventional metals the gapless T-linear component arises from paramagnetic free electrons and such a feature is also observed at low temperature in this system. The ladder system is characterized by the appearance of both features.

The problem is how to understand the peculiarity of this system. Since the system is metallic under high pressure, the system should be treated in k-space. However, a microscopic snapshot in real space helps to understand the existence of the T-linear component as well as the activation-type component. The snapshot in real space can be described as follows. The ground state of the undoped ladders is understood as overlap of spin dimmers on the rung [4]. Hole doping implies breaking of the spin dimmers on the rung and gives rise to a holon–spinon bound state [24]. At high temperatures singlet–triplet spin excitation in the spin dimmers away from the bound state dominates, which causes the activated behaviour of T_1^{-1} as is illustrated in figure 8(A). At intermediate temperatures the majority of the spin dimmers fall into the singlet ground state, but the spins in the bound states move freely and contribute to the gapless T-linear component in T_1^{-1} (figure 8(B)). Superconductivity would be realized by the pairing of two bound states as illustrated in figure 8(C). It should be noted that the normal state in the present system is free from large antiferromagnetic fluctuations unlike high-T_c cuprates. T_1^{-1} in typical high-T_c cuprates such as the YBCO system is expressed as $a + bT$ above T_c where the T-independent term a represents the antiferromagnetic fluctuations ($a \sim 3 \times 10^3$ (s^{-1}) and $b \sim 6$ (s^{-1} K^{-1}) for YBCO) [25]. In the present system, antiferromagnetic fluctuations are extremely suppressed due to the existence of the spin gap, which might explain why no high-T_c is realized in this system although the structure is quite similar to high-T_c cuprates.

3.2. Pairing symmetry

In the present work, we found that superconductivity with a full gap is realized and is quite stable even at high field close to Pauli limit excluding the possibility of conventional s-wave superconductivity. As for the existence of a full gap, both singlet and triplet Cooper pairings are possible if there are no nodes across the Fermi surface. However, in the case of singlet superconductivity two questions arise: one is why the NMR shift remains unchanged below

T_c, and the other is why singlet pairing occurs again at low temperatures below T_c although spin-singlet pairing is already formed at high temperatures. As far as the NMR results are concerned, a p-wave with a full gap may be preferred.

4. Conclusion

We found that superconductivity with a full gap is realized in $Sr_2Ca_{12}Cu_{24}O_{41}$ and that the superconductivity is quite stable even at high fields. The spin gap remains in the normal state even in conditions where superconductivity is realized.

Acknowledgments

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References

[1] Uehara M *et al* 1996 *J. Phys. Soc. Japan* **65** 2764
[2] Osafune T *et al* 1997 *Phys. Rev. Lett.* **78** 1980
[3] Nagata T *et al* 1998 *Phys. Rev. Lett.* **81** 1091
[4] Motoyama N *et al* 1997 *Phys. Rev.* B **55** R3386
Motoyama N *et al* 2002 *Eur. Phys. Lett.* **58** 758
[5] Nakanishi T *et al* 2000 *Physica* B **281/282** 957
[6] Mayaffre H *et al* 1998 *Science* **279** 345
[7] Piskunov Y *et al* have recently extended the work of [6]. They measured NMR under high pressure up to 3.6 GPa for the field parallel to the *b*-axis
Piskunov Y *et al* 2000 *Eur. Phys. J.* B **13** 417
Piskunov Y *et al* 2001 *Eur. Phys. J.* B **24** 443
[8] See for example
Yasuoka H *et al* 1989 *Strong Correlation and Superconductivity* vol 89 (Berlin: Springer) p 254
Rossat-Mignod *et al* 1990 *Dynamics of Magnetic Fluctuations in High T_c Materials* (New York: Plenum) p 35
[9] Dagotto E, Riera J and Scalapino D 1992 *Phys. Rev.* B **45** 5644
[10] Rice T M, Gopalan S and Sigrist M 1993 *Europhys. Lett.* **23** 445
[11] Sigrist M, Rice T M and Zhang F C 1994 *Phys. Rev.* B **49** 12058
[12] Kontani H and Ueda K 1998 *Phys. Rev. Lett.* **80** 5619
[13] Kumagai K *et al* 1997 *Phys. Rev. Lett.* **78** 1992
[14] Magishi K *et al* 1998 *Phys. Rev.* B **57** 11533
[15] Imai T *et al* 1998 *Phys. Rev. Lett.* **81** 220
[16] Katano S *et al* 1999 *Phys. Rev. Lett.* **82** 636
[17] Fujiwara N *et al* 2002 *J. Phys. Chem. Solids* B **63** 1103
[18] Takigawa M *et al* 1998 *Phys. Rev.* B **57** 1124
[19] Corti M *et al* 1996 *Phys. Rev.* B **54** 9469
[20] Suh B J *et al* 1996 *Phys. Rev. Lett.* **76** 1928
[21] Kohen M H and Rief F 1957 *Solid State Phys.* **5** 321
[22] Troyer M *et al* 1994 *Phys. Rev.* B **50** 13515
[23] Barrett S E *et al* 1990 *Phys. Rev.* B **41** 6283
[24] Tsunetsugu H *et al* 1994 *Phys. Rev.* B **49** R16078
[25] See, for example, Ginsberg D M 1990 *Physical Properties of High Temperature Superconductors II* vol 5 (Singapore: World Scientific) p 269