Low Energy Excitations in Superconducting $La_{1.86}Sr_{0.14}CuO_4$

T. E. Mason,[1,2,*] G. Aeppli,[1,2] S. M. Hayden,[3] A. P. Ramirez,[2] and H. A. Mook[4]
[1] *Risø National Laboratory, 4000 Roskilde, Denmark*
[2] *AT&T Bell Laboratories, Murray Hill, New Jersey 07974*
[3] *H.H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, United Kingdom*
[4] *Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*
(Received 19 April 1993)

We present magnetic neutron scattering and specific heat data on the high-T_c superconductor $La_{1.86}Sr_{0.14}CuO_4$. Even when the samples are superconducting and the magnetic response, χ'', is suppressed, there are excitations with energies well below $3.5k_BT_c$. The wave-vector dependence of χ'' is identical to that for the normal state, which implies that the low frequency excitations in our crystals are not those associated with the nodes of a clean d-wave superconductor. However, the data are consistent with gapless superconductivity induced by localized magnetic impurities, clearly observed in the specific heat measurements.

PACS numbers: 74.72.Dn, 61.12.Ex

One signature of unconventional superconductivity is a gap function with nodes on the Fermi surface. In a clean BCS superconductor, such nodes do not occur and the low energy quasiparticle excitations are absent for energies $\hbar\omega < 2\Delta$. Pairing due to antiferromagnetic spin fluctuations tends to favor "d-wave" superconductivity with a gap vanishing at points or lines on the Fermi surface [1]. Another well-known way to generate a superconductor with vanishing gap is to introduce magnetic impurities [2], in which case the low energy excitations exist everywhere on the Fermi surface. Thus, a direction-dependent probe should be able to distinguish between "conventional gapless" and symmetry reducing d-wave superconductivity. For the cuprate superconductors the primary evidence for a d-wave gap has been from relatively indirect measurements of the (scalar) density of states [3]. These experiments are insensitive to the most characteristic feature of the d-wave state, namely, that the gap vanishes at particular points or lines on the Fermi surface. There have also been NMR and photoemission experiments designed to examine the direction-dependent properties of the superconducting states of cuprates [4]. While intriguing, the results call for independent verification because of the well-known limitations of these techniques.

With its good energy (~ 1 meV) and momentum resolution, nonperturbing nature (experiments can be performed in zero applied field), as well as simple cross section, magnetic neutron scattering is an excellent bulk probe of the wave-vector dependence of the superconducting gap function [5]. This follows because the generalized magnetic susceptibility, $\chi''(\mathbf{Q},\omega)$, probed by neutrons is associated with electron-hole pairs formed by transitions across the Fermi surface. In a perfect BCS superconductor such transitions become disallowed for all wave vectors, $\mathbf{Q}$ (provided $\hbar\omega < 2\Delta$). On the other hand, for an anisotropic superconductor, the degree of suppression will depend on $\mathbf{Q}$. For example, in the case of a $d_{x^2-y^2}$ gap function and the Fermi surface commonly associated [6,7] with $La_{1.86}Sr_{0.14}CuO_4$ [see Fig. 1(a)], the low ω magnetic response at the wave vector closest to nesting, $\mathbf{Q}_\delta$, should be eliminated, while that at $\mathbf{Q}_\gamma$ [along (π,π)] should survive [7]. In this paper we present specific heat and neutron scattering data which demonstrate that the low energy excitations in one high-T_c material, $La_{1.86}Sr_{0.14}CuO_4$, are not those associated with a clean $d_{x^2-y^2}$ superconductor. Instead, they are consistent with gapless superconductivity induced by magnetic impurities revealed in the magnetic-field dependent heat capacity.

For the present study we used three crystals of $La_{1.86}Sr_{0.14}CuO_4$, fabricated as described in Ref. [8]. The first (volume is 0.7 cm^3) was one employed in earlier measurements [8,9] while the second (0.7 cm^3) and third (0.2 cm^3) were used to augment the neutron scattering sample and for specific heat measurements, respectively. The latter two samples have the same lattice constants as the first and, more importantly, when investigated separately by inelastic neutron scattering, exhibit the same incommensurate magnetic response and suppression of low frequency fluctuations below $T_c = 35 \pm 1$ K as the first [8,9].

The specific heat data, obtained using a standard heat pulse method and shown in Fig. 2, provide the most precise definition of sample quality. There are two indications of quality, the first being a slightly smeared jump (right panel) in C/T between 34 and 36 K, with an amplitude comparable to that found in optimized powder samples [10]. The second is a residual constant contribution to C/T at low temperatures (left panel). This corresponds to a constant density of states near zero energy and is not expected for clean BCS superconductors. At 1.3 mJ/mole K^2, it represents $\sim 20\%$ of the normal state Sommerfeld constant and is slightly less than the residual C/T reported for samples of $La_{2-x}Sr_xCuO_4$ with

0031-9007/93/71(6)/919(4)$06.00

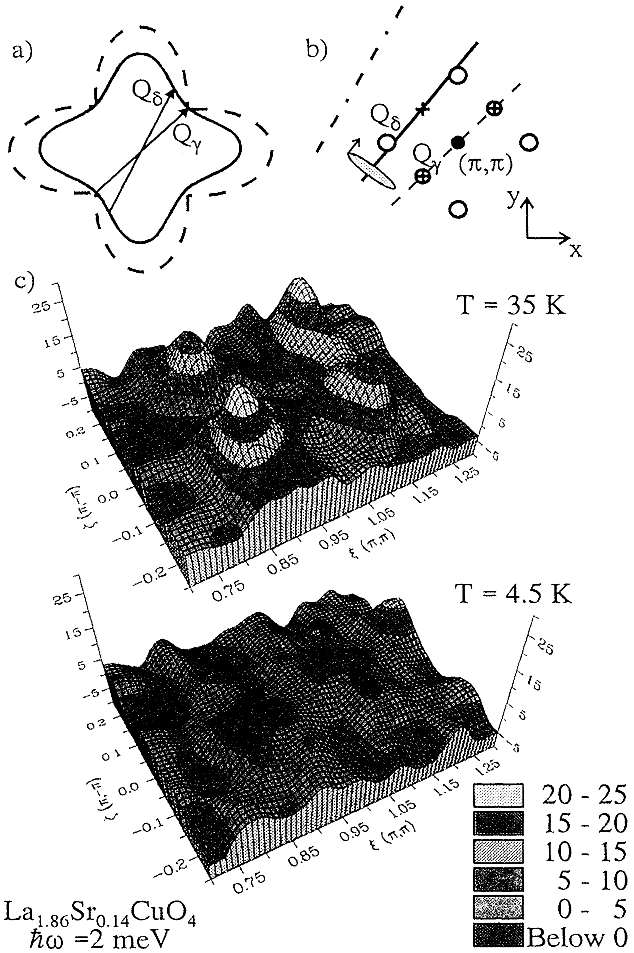

FIG. 1. (a) Schematic Fermi surface for $La_{1.86}Sr_{0.14}CuO_4$. (b) Map of reciprocal space probed in this experiment. (c) Contour plot of the magnetic intensity in the region of **Q** space shown in (b) for $\hbar\omega = 2$ meV for $T = 35$ K and $T = 4.5$ K.

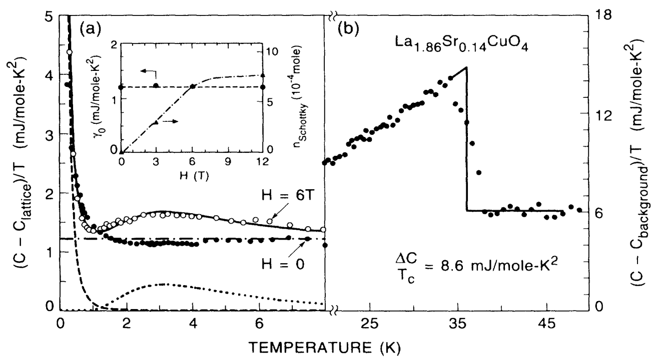

FIG. 2. Temperature dependence of the nonphonon part of the specific heat of $La_{1.86}Sr_{0.14}CuO_4$ below (left panel) and near (right panel) T_c. The concentration of impurities is found to be 0.07%/Cu from the size of the Schottky anomaly in a magnetic field (open circles); the inset shows the field dependence of this contribution, along with the estimated linear contribution.

$x = 0.15$ [10] as well as $YBa_2Cu_3O_7$ [11]. In addition to the constant term, there are contributions to the $H = 0$ C/T which appear to diverge as $T \to 0$. Some of these are associated with local electronic moments, as demonstrated by the Schottky anomaly observed in an external field. Indeed, following Ref. [11], we can determine both the concentration and moment of the relevant impurities from the size and position of the Schottky peak. In our samples this corresponds to spin 1/2 (assuming $g = 2$) moments with a concentration of 0.7×10^{-3}/Cu, or 0.5×10^{-2}/Sr acceptor.

Having established that our samples have a constant density of excited states at energies well below $3.5k_BT_c$, we measured the dynamical structure factor at such frequencies using magnetic neutron scattering. Our inelastic measurements were performed with the TAS VI cold neutron spectrometer at the DR3 reactor, Risø National Laboratory. We label points in reciprocal space using the usual square lattice notation where (π,π) is the location of the lowest order antiferromagnetic Bragg point in pure La_2CuO_4 [12]. Figure 1(b) depicts the 0.6×0.6 Å^{-2} region of reciprocal space probed here. The open circles at $(\pi,\pi) \pm \delta(\pi,0)$ and $(\pi,\pi) \pm \delta(0,\pi)$ ($\delta = 0.245 \pm 0.004$) are the four equivalent locations of the maxima in $\chi''(\mathbf{Q},\omega)$ for $\omega \to 0$, and correspond to the wave vectors closest to nesting, $\mathbf{Q}_\delta$, for the Fermi surface of Fig. 1(a) [6]. The crossed open circles, at $(\pi,\pi) \pm \delta/2(\pi,\pi)$, correspond to the minimal vector, $\mathbf{Q}_\gamma$, spanning opposite sides of the Fermi surface. They are equivalent to the points $(\pi,\pi) \pm \delta/2(\pi,-\pi)$ marked by crosses.

The previous experiments on the effects of superconductivity on $\chi''(\mathbf{Q},\omega)$ for $La_{2-x}Sr_xCuO_4$ [9,13] focused on the behavior for $\mathbf{Q} \approx \mathbf{Q}_\delta$. In view of the possibility that new structures in $\chi''(\mathbf{Q},\omega)$ might emerge below T_c, we have performed a complete survey of the two-dimensional Brillouin zone near (π,π) with a fixed final energy of 8.09 meV and 70′-58′-81′-180′ collimation. Figure 1(c) shows the outcome at $\hbar\omega = 2$ meV (= 20% of $3.5k_BT_c$) for $T \cong T_c$ and 4.5 K. It is clear that cooling from T_c to 4.5 K greatly suppresses the magnetic scattering at all wave vectors. Also, it yields no detectable new peaks in $\chi''(\mathbf{Q},\omega)$. Having established these important conclusions at the rough level allowed by our large coverage of reciprocal space, we made a more detailed study of $\chi''(\mathbf{Q},\omega)$ for $\mathbf{Q}$'s along the dashed and solid trajectories in Fig. 1(b). A somewhat higher $\hbar\omega$, 3.5 meV, for which the $n(\omega) + 1$ temperature factor is less significant, was selected to increase our sensitivity to changes in χ''. The results are shown in Fig. 3. As found previously [9,13] and in agreement with the specific heat data, there is still a response at low temperatures. However, χ'' clearly remains peaked at the $\mathbf{Q}_\delta$ positions. The solid lines in Fig. 3 are derived from fits to a modified

Lorentzian squared,

$$S(\mathbf{Q},\omega) = [n(\omega)+1]\chi''(\mathbf{Q},\omega) = [n(\omega)+1]\frac{\omega\chi^0/A^2}{[\kappa_\omega^2 + R(\mathbf{Q})]^2}$$

convolved with the spectrometer resolution function [shown as a dotted line in the top panel and as a grey ellipse in Fig. 1(b)]. This is the zero frequency limit of the form employed in Ref. [9] (the line shape is only weakly frequency dependent at low frequencies) where

$$R(\mathbf{Q}) = \frac{[(q_x - q_y)^2 - (\pi\delta)^2]^2 + [(q_x + q_y)^2 - (\pi\delta)^2]^2}{2(2a_0\pi\delta)^2}$$

and κ_ω is a width parameter. The transition to a superconducting state yields an isotropic suppression of χ^0/A^2 to 0.62 ± 0.05 times the value at 35 K. Otherwise the scattering is unchanged. The intensity at the $\mathbf{Q}_\gamma$ positions in the two scans is different due to the orientation of the resolution ellipse with respect to the crystal lattice and, more particularly, the neighboring $\mathbf{Q}_\delta$ peaks. The intensity in the center of the uppermost scan of Fig. 3 most accurately reflects the magnitude of the response at $\mathbf{Q}_\gamma$; it is 0.18 ± 0.03 times that at $\mathbf{Q}_\delta$.

Figure 4 summarizes how the response varies with temperature. Panel (a) shows the imaginary part of the dynamic susceptibility at $\mathbf{Q}_\delta$, obtained from the raw data by subtracting the background and dividing out the $n(\omega)+1$ temperature factor, for several energies. For $\hbar\omega \lesssim 6$ meV the susceptibility is reduced to approximately 60% of the value just above T_c. The extent of the reduction does not vary appreciably with frequency for $1.2 \le \hbar\omega \le 4$ meV, which demonstrates that at $\mathbf{Q}_\delta$, a gaplike structure does not fall within this frequency range. This validates the choice of $\hbar\omega = 2$ and 3.5 meV in our searches for ($\mathbf{Q}$ space) anisotropy in $\chi''(\mathbf{Q},\omega)$ induced by $d_{x^2-y^2}$ pairing: the $d_{x^2-y^2}$ gap structure [Fig. 1(a)], which is at $\omega = 0$ for $\mathbf{Q} = \mathbf{Q}_\gamma$ and clearly above 4 meV for $\mathbf{Q} = \mathbf{Q}_\delta$, must necessarily pass through $\hbar\omega = 2$ and 3.5 meV for $\mathbf{Q}$'s intermediate between $\mathbf{Q}_\delta$ and $\mathbf{Q}_\gamma$, thereby significantly altering the shape of $\chi''(\mathbf{Q},\omega)$. At energies (such as 15 meV) much greater than 6 meV, the evolution of the intensity continues through T_c unchanged. Panel (b) of Fig. 4 shows the width parameter, κ_ω, for $\hbar\omega = 3.5$ meV extracted from fits to the line shape described above convolved with the spectrometer resolution. Neither κ_ω nor δ (not shown) changes on passing through the superconducting transition, confirming that the line shape of the low frequency response is unaffected by the superconductivity. Panel (c) shows the intensities, measured at $\mathbf{Q}_\delta$ and the two $\mathbf{Q}_\gamma$ positions for $\hbar\omega = 3.5$ meV, relative to their values just above T_c (at 38.6 K). The results for the three wave vectors fall onto a common curve. Any new anisotropy introduced by a $d_{x^2-y^2}$ superconducting gap would result in different temperature dependences for $\mathbf{Q}_\delta$ and $\mathbf{Q}_\gamma$ below T_c. An indication of the extent to which the line shape remains unchanged in the superconducting state may be obtained by comparing the ratio, $R = I(Q_\gamma)/I(Q_\delta)$, above T_c to that below T_c.

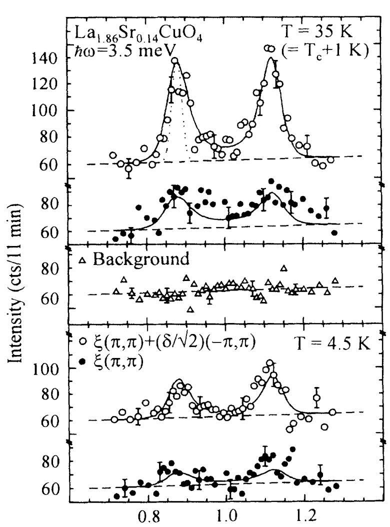

FIG. 3. The $\mathbf{Q}$ dependence of the neutron intensity for $La_{1.86}Sr_{0.14}CuO_4$ above (upper panel) and below (lower panel) T_c for $\hbar\omega = 3.5$ meV. The open (closed) circles correspond to the scan indicated by a solid (dashed) line in Fig. 1(b). The lines are the results of fits described in the text. The straight dashed lines indicate the measured background, shown as triangles in the middle panel.

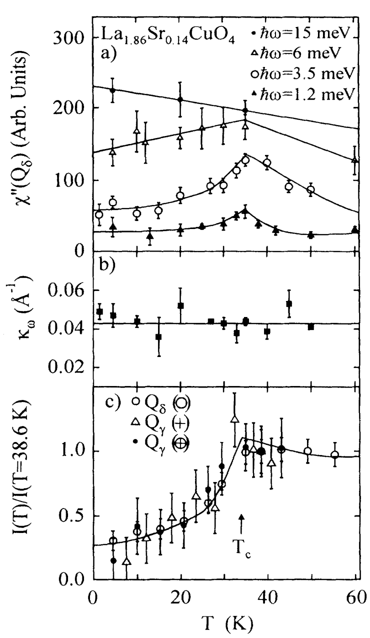

FIG. 4. (a) Temperature dependence of $\chi''(Q_\delta)$ for four frequencies. (b) The width parameter, $\kappa_\omega(\hbar\omega = 3.5$ meV), as a function of temperature. (c) The intensity of the response for $\hbar\omega = 3.5$ meV at the $\mathbf{Q}_\delta$ and $\mathbf{Q}_\gamma$ positions (see Fig. 1). The lines are guides to the eye.

The value at $\hbar\omega = 3.5$ meV for the low temperature data is 0.9 ± 0.3 times that above T_c, a result indistinguishable from isotropic suppression which would give one. The corresponding number at $\hbar\omega = 1.5$ meV is 0.4 ± 0.8, also indistinguishable from unity. A clean $d_{x^2-y^2}$ gap would have an infinite ratio as ω and $T \to 0$. At intermediate ω, R at $T = 0$ would still be larger than at T_c, and the line-shape parameters δ and κ_ω would change considerably. One expects similar behavior for a $d_{x^2-y^2}$ state weakly perturbed by impurities, especially in a sample such as ours where the half-width of the incommensurate peaks (and hence the inverse quasiparticle mean free path) is smaller than $|Q_\delta - Q_\gamma|$.

In conclusion, the specific heat and inelastic neutron scattering experiments show a considerable suppression of electronic excitations on going through the superconducting transition of $La_{1.86}Sr_{0.14}CuO_4$. At the same time, even at the lowest frequencies and temperatures probed, such excitations continue to exist in our samples. However, the wave-vector dependence of the magnetic response due to these states is incompatible with currently available predictions for a clean $d_{x^2-y^2}$ superconductor [7]. In particular, there is no anisotropy in the suppression of the response as would be the case if there were sharp (on the scale of the separation between the Fermi surface spanning vectors Q_δ and Q_γ) nodes in the gap function near (π, π). The present results, which are the first such measurements on any superconductor, therefore represent a significant constraint on theories of high temperature superconductivity.

The isotropic, but incomplete, suppression of the susceptibility below T_c, energy dependence of the response, and residual linear specific heat are all consistent with a gapless s-wave superconductor, perhaps not as envisaged by Abrikosov and Gor'kov [2], but similar to what is observed in conventional superconductors with comparable levels of magnetic impurities [14]. Of course consistency is not the same as unambiguous proof: it may be possible to concoct a more complicated $s + id$ or dirty d-wave account of the data. In any case, for our samples the gapless behavior is most likely due to $S = 1/2$ impurities not introduced deliberately, but nonetheless obvious in the field dependent heat capacity. Presumably the impurity density varies between different sample types, being highest in the Zn-doped samples displaying virtually no signature of the superconducting transition in their magnetic response [15], intermediate in the work of Thurston *et al.* [13] which merely showed a flattening of $\chi''(Q_\delta, \omega)$ below T_c, and smallest, but still non-negligible, in our crystals. Several open questions remain, most notably the extent to which paramagnetic centers can be removed from $La_{2-x}Sr_xCuO_4$ which, after all, is a random alloy not very far from a metal-insulator transition. Based on experience with doped Si [16], a certain number of such centers could well be intrinsic for $La_{2-x}Sr_xCuO_4$, but not for fully ordered, stoichiometric $YBa_2Cu_3O_7$.

We are grateful to E. Abrahams, B. Batlogg, Z. Fisk, P. B. Littlewood, C. Varma, D. J. Scalapino, R. Schrieffer, and A. -M. Tremblay for stimulating discussions and to B. Chakoumakous and B. Sales for invaluable assistance with the crystal preparation. Work carried out at Risø and Oak Ridge was supported by the Danish Natural Science Research Council, the European Commission through the EC Large Installation Program, and the Division of Materials Sciences, U.S. DOE under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. T.E.M. and S.M.H. acknowledge the support of the C.I.A.R. and the United Kingdom SERC.

* Present address: Department of Physics, University of Toronto, Toronto, Ontario, Canada M5S 1A7.

[1] K. Miyake *et al.*, Phys. Rev. B **34**, 6554 (1986); D. J. Scalapino *et al.*, *ibid.* **34**, 8190 (1986).
[2] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1961) [Sov. Phys. JETP **12**, 1243 (1961)].
[3] W. Hardy *et al.*, Phys. Rev. Lett. **70**, 3999 (1993); D.A. Bonn *et al.*, *ibid.* **68**, 2390 (1992); P.C. Hammel *et al.*, *ibid.* **63**, 1992 (1989).
[4] M. Takigawa *et al.*, Phys. Rev. B **44**, 7764 (1991); N. Bulut and D. J. Scalapino, Phys. Rev. Lett. **68**, 706 (1992); Z. X. Shen *et al.*, *ibid.* **70**, 1553 (1993).
[5] R. Joynt and T. M. Rice, Phys. Rev. B **38**, 2345 (1988).
[6] P. B. Littlewood *et al.*, Phys. Rev. B **48**, 487 (1993); P. Bénard *et al.*, *ibid.* **47**, 589 (1993); Q. Si *et al.*, *ibid.* **47**, 9055 (1993). For convenience and simplicity we ignore less conventional pictures and discuss our data in terms of the Fermi surface shown in Fig. 1(b). However, whatever description is chosen, $\chi''(\mathbf{Q}, \omega)$ is always ultimately derived from electron-hole pairs and its $\mathbf{Q}$ dependence will correspondingly reflect the $\mathbf{Q}$ dependence of the gap function.
[7] Y. Zha *et al.*, Phys. Rev. B **47**, 9124 (1993); J. P. Lu, Phys. Rev. Lett. **68**, 125 (1992).
[8] S. W. Cheong *et al.*, Phys. Rev. Lett. **67**, 1791 (1991).
[9] T. E. Mason *et al.*, Phys. Rev. Lett. **68**, 1414 (1992).
[10] N. E. Phillips *et al.*, Physica (Amsterdam) **148B**, 360 (1987); D. Eckert, Ph.D. thesis, University of Geneva, 1989; J. W. Loram *et al.*, Physica (Amsterdam) **162-164C**, 498 (1989).
[11] N. E. Phillips *et al.*, Phys. Rev. Lett. **65**, 357 (1990).
[12] D. Vaknin *et al.*, Phys. Rev. Lett. **58**, 2802 (1987).
[13] T. R. Thurston *et al.*, Phys. Rev. B **46**, 9128 (1992).
[14] C. A. Luengo *et al.*, Solid State Commun. **11**, 1445 (1972); A. S. Edelstein, Phys. Rev. Lett. **19**, 1184 (1967).
[15] M. Matsuda *et al.*, J. Appl. Phys. (to be published).
[16] M. Paalanen *et al.*, Phys. Rev. Lett. **57**, 2061 (1986); M. Lakner and H. v. Löhneysen, *ibid.* **63**, 648 (1989).

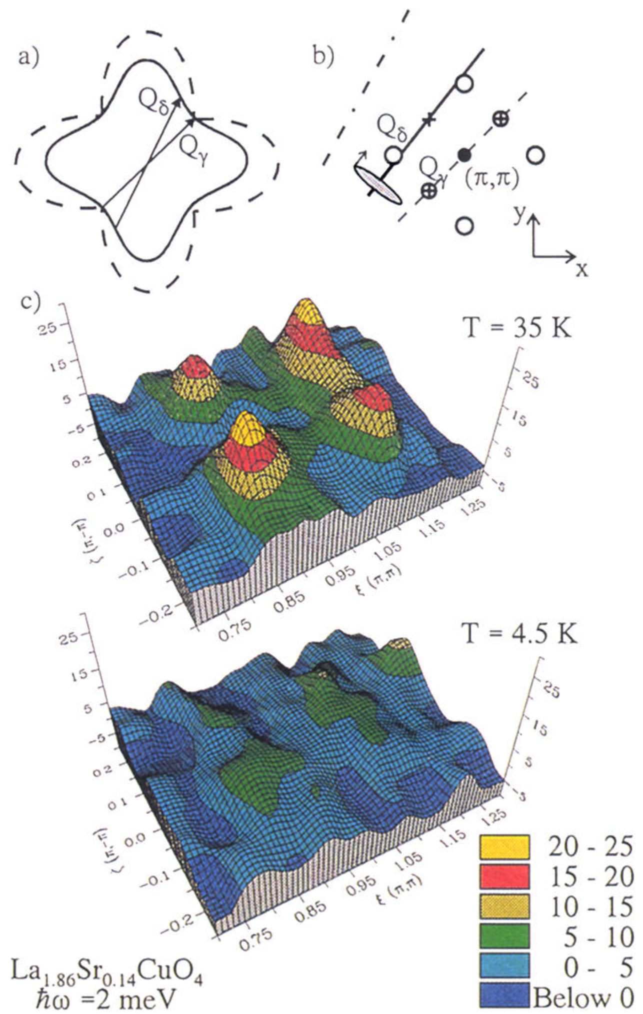

FIG. 1. (a) Schematic Fermi surface for $La_{1.86}Sr_{0.14}CuO_4$. (b) Map of reciprocal space probed in this experiment. (c) Contour plot of the magnetic intensity in the region of **Q** space shown in (b) for $\hbar\omega = 2$ meV for $T = 35$ K and $T = 4.5$ K.