PHYSICAL REVIEW B VOLUME 56, NUMBER 2 1 JULY 1997-II

Electronic structure of CuO_2 planes: From insulator to superconductor

S. LaRosa, I. Vobornik, F. Zwick, H. Berger, M. Grioni, and G. Margaritondo
Institut de Physique Appliquee, Ecole Politechnique Federale, Lausanne, Switzerland

R. J. Kelley and M. Onellion
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

A. Chubukov
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706
and P.L. Kapitza Institute for Physical Problems, Moscow, Russia

(Received 9 July 1996; revised manuscript received 14 February 1997)

Using angle-resolved photoemission and linearly polarized synchrotron radiation, we measured the electronic band structure of electronic states of CuO_2 plane materials ranging from insulators ($Sr_2CuO_2Cl_2$) to overdoped superconductors ($Bi_2Sr_2CaCu_2O_{8+x}$). We report three results: (i) The CuO_2 containing insulator possesses a spin-density-wave (SDW) ground state; (ii) there are precursors of the SDW state for underdoped $Bi_2Sr_2CaCu_2O_{8+x}$; (iii) an extended saddle-point-type van Hove singularity is neither a necessary nor a sufficient condition for a high superconducting transition temperature, T_c. [S0163-1829(97)50226-8]

How the electronic structure of cuprates changes with doping is of intense current interest. In this paper, we concentrate on two of the several reasons for this interest. First is how the electronic band structure evolves in changing from an antiferromagnetic insulator to an overdoped superconductor. To address this issue, we performed angle-resolved photoemission measurements on a prototypical antiferromagnetic insulator $Sr_2CuO_2Cl_2$ with $T_N=256$ K, and on $Bi_2Sr_2CaCu_2O_{8+x}$ samples ranging from underdoped to overdoped. The second issue on which we concentrated is the relation between the extended van Hove singularity observed near optimal doping and a high value of T_c. We find that underdoped cuprates with T_c values as high as 60 K do not exhibit such a van Hove singularity. We argue below that by itself a van Hove singularity is neither a necessary nor a sufficient condition for a high value of T_c.

We have recently succeeded in fabricating $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals that span the entire underdoped part of the phase diagram and extend far into the overdoped region as to reach $T_c=52$ K.[1] These samples were crucial to the complete photoemission study from insulator to overdoped superconductor. The overdoped $Bi_2Sr_2CaCu_2O_{8+x}$ exhibit a number of properties typical of a Fermi liquid: a large, Luttinger-type Fermi surface,[2–4] and a sizable T^2 term in the in-plane resistivity.[1] On the contrary, the underdoped and optimally doped samples exhibit predominantly linear in-T resistivity. Susceptibility measurements indicated that underdoped samples exhibit broad superconducting transition widths (8–10 K), while optimally doped and overdoped samples exhibit narrow widths (0.5 K). X-ray diffraction indicates no second phase material for underdoped or overdoped samples, with an experimental lower limit of 1%. As Ref. 5 recently noted, there is virtually no indication of bilayer interaction affecting the band structure, so each CuO_2 plane can be taken as approximately independent.

We also fabricated single crystals of $Sr_2CuO_2Cl_2$.[6] Transmission electron microscopy measurements indicated that the structure of oxychloride is tetragonal ($a=b$ to better than 0.1%) [Ref. 7(a)] and resistivity measurements confirmed the insulating character of the samples.[7(b)] Clean surfaces of all samples were prepared by *in situ* cleaving in a residual vacuum better than 10^{-10} torr, and the crystal orientation was determined by low-energy electron diffraction. Photoemission measurements were performed using a 50 mm mean radius hemispherical electrostatic energy analyzer, mounted on a two-axis goniometer.[4] The angular acceptance of the analyzer was 1.8°. Monochromatic radiation from the 4 m NIM beamline at the Aladdin storage ring of the Wisconsin Synchrotron Radiation Center was used. The light was $>95\%$ linearly polarized. The combined (photon plus electron) energy resolution was 25 meV.

We first report the photoemission results for the insulating oxichloride $Sr_2CuO_2Cl_2$. Photoemission on this compound measures a dispersion of a single hole in a square-lattice spin-1/2 quantum antiferromagnet.[8] Photoemission measurements on $Sr_2CuO_2Cl_2$ have recently been performed by Wells *et al.*[9] We found similarities, but also discrepancies, with their results. Figure 1 illustrates our photoemission spectra of the valence-band dispersion in $Sr_2CuO_2Cl_2$ along the $(0,\pi)$ and (π,π) high-symmetry directions. In both series of spectra a broad but still clearly visible *dispersing* quasiparticle peak is observed. Our data in the (π,π) direction and also along the magnetic Brillouin zone boundary from $(0,\pi)$ to $(\pi,0)$ are consistent with Ref. 9. Namely, we found that the valence-band dispersion has a single maximum located near $(\pi/2,\pi/2)$. The dispersion near the maximum is quadratic, and the two effective masses, along and perpendicular to the (π,π) direction, are nearly equal. The experimental bandwidth of 300 meV is considerably smaller than that predicted by band-structure calculations. To within the experimental error, the bandwidth is $(2.0–2.2)J$, where $J\sim 0.13$ eV is the nearest-neighbor antiferromagnetic exchange.

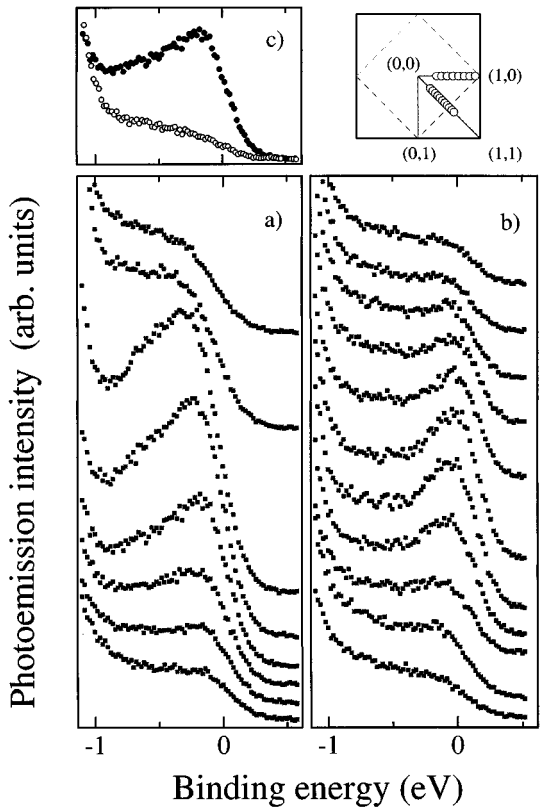

FIG. 1. Photoemission data for $Sr_2CuO_2Cl_2$ along (a) $(0,\pi)$ and (b) (π,π) directions in the momentum space. The incident photon energy is 25 eV. The zero of energy corresponds to the top of the valence band. The k points for which the data have been collected are shown in the inset. The bottom curves are for the k values closest to (0,0); (c) quasiparticle peak along $(0,\pi)$ for two different polarizations of light. The peak is observed for the photon field nearly perpendicular to the $(0,\pi)$ direction.

We next consider the $(0,\pi)$ direction. Here our data differ from those of Ref. 9. Contrary to their findings, we observe a strong quasiparticle dispersion in this direction [Figs. 1(a) and 1(c)]. The peak of Figs. 1(a) and 1(c) was reproducibly observed (five times) whenever states of even reflection symmetry were probed. We also found that the peak amplitude is very sensitive to the direction of the photon electric field, and the peak exists only for fields nearly perpendicular to the $(0,\pi)$ direction ($\phi=\pi/2$). The angular variation of the peak intensity is definitely much stronger that $\cos\phi$, and, as Fig. 1(c) illustrates, for $\phi=\pi/4$, the peak intensity is already extremely small. This, we believe, may explain why the peak has not been observed in Ref. 9 where measurements were done with unpolarized light, i.e., one measured the intensity averaged over ϕ. The reason for this strong angular dependence is, however, presently not known to us.

We now turn to the discussion of these results. At half-filling, the system is a Heisenberg antiferromagnet, and it possesses a commensurate antiferromagnetic order in the ground state. In this situation, a quantitative description of the electronic states is expected to be provided by a large U spin-density-wave (SDW) theory which adequately describes a Heisenberg antiferromagnet.[10] The point of departure for the theoretical considerations is the one-band Hubbard model with the hopping between nearest (t) and next-nearest (t') neighbors. The presence of an antiferromagnetic order in the ground state splits the fermionic dispersion into two subbands (valence and conduction fermions) with the dispersion $E^{c,v}=\Delta+J(\cos k_x+\cos k_y)^2\mp 4t'\cos k_x\cos k_y$, where $J=4t^2/U$ and $\Delta=U/2$. For comparison with the data, we need to know the value of t'. It was estimated in Ref. 11 by comparing the low-energy levels of the underlying three-band model for CuO_2 and of the effective one-band model. This comparison yielded $t'\approx -0.07$ eV, i.e., t' is negative and its absolute value is about half of J. For this t', the valence-band dispersion takes a particularly simple form

$$E^d=\Delta+J(\cos^2 k_x+\cos^2 k_y). \tag{1}$$

Though appealing due to its simplicity, the mean-field SDW dispersion is an approximate one and can only be rigorously justified if one artificially extends the Hubbard model to a large number of orbitals at a given site, $n=2S$, and considers a limit $S\to\infty$.[12] This corresponds to a large spin description of a Heisenberg antiferromagnet. For the physical case of $n=1$, the fluctuation corrections to the mean-field quasiparticle dispersion are not small. However, both numerical[13(a)] and analytical[13(b)] studies have demonstrated that the dominant effect of fluctuations is to reduce nearly homogeneously the spectral weight of the coherent part of the dispersion, which still holds up to $2J$, and transform this spectral weight to the incoherent background which stretches up to a few t. In practice, this implies one can still use Eq. (1) for the dispersion, but the excitations acquire a substantial width. Moreover, the calculations beyond mean-field have demonstrated[14,15] that the near-SDW form of the electronic dispersion extends well above T_N, up to temperatures $T\sim J$.

We now list the specific features of the valence-band quasiparticle dispersion of Eq. (1). They are (i) the maximum of the valence band dispersion is at $(\pi/2,\pi/2)$; (ii) the dispersion near the maximum is quadratic in momentum, and the two effective masses in the direction along and perpendicular to (π,π) are equal to each other, $m_1=m_2=1/2J$; (iii) the quasiparticle energies at (0,0) and $(0,\pi)$ are both equal to $E^d=\Delta+2J$; (iv) the width of the valence band is $2J$. All four of these results agree with our data and the data of Ref. 9.

The apparent absence of the quasiparticle dispersion along the $(0,\pi)$ direction, reported in Ref. 9, was the key difficulty in earlier attempts to apply an SDW formalism to $Sr_2CuO_2Cl_2$. Several groups suggested that in order to find agreement with the data of Ref. 9 along the $(0,\pi)$ direction, one has to introduce a substantial third-neighbor hopping.[17] Our experimental finding of the dispersion in the $(0,\pi)$ direction yields much better agreement with the simplest t-t' model [see Fig. 3(a)].

We also find, consistent with Ref. 9, that the quasiparticle residue along the (π,π) direction is much stronger from (0,0) to $(\pi/2,\pi/2)$ than from $(\pi/2,\pi/2)$ to (π,π). This result is again consistent with the SDW calculation that relates the quasiparticle residue Z to the coherence factors:[10] $2Z=1-\epsilon_k^-/[\Delta^2+(\epsilon_k^-)^2]^{1/2}$, where $\epsilon_k^-=-2t(\cos k_x+\cos k_y)$. Between (0,0) and $(\pi/2,\pi/2)$, ϵ_k^- is negative, while between $(\pi/2,\pi/2)$ and (π,π) it is positive, which obviously yields a difference in Z, consistent with our experimental results.

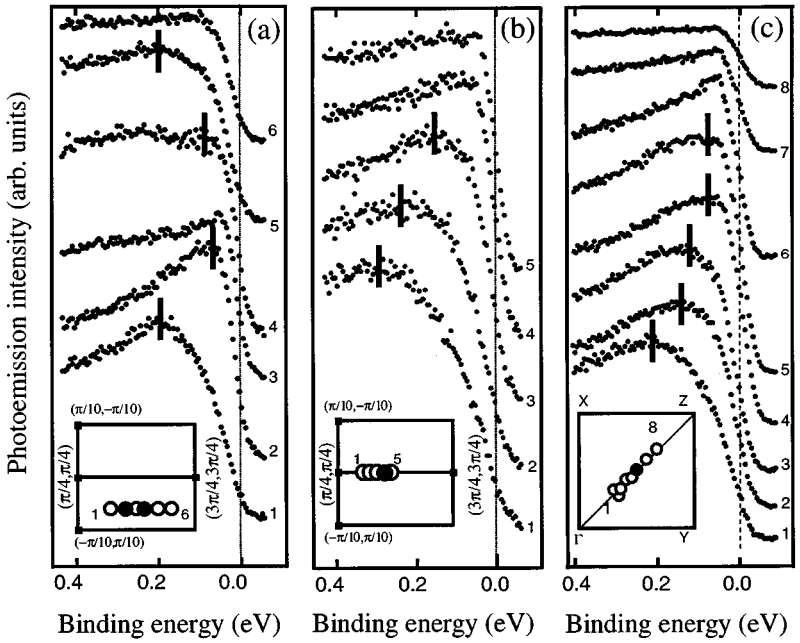

FIG. 2. Photoemission data for Bi2212: (a) for a 30 K superconductor along the (π,π) direction, (b) for a 60 K superconductor along the (π,π) direction, and (c) for a 60 K superconductor along the $(0,\pi)$ direction. The location of the k points in the Brillouin zone is shown in the inset. The peak positions are indicated by vertical bars. The black dots indicate the crossing of the Fermi surface.

The bandwidth of around $2J$ is also consistent with theoretical predictions based on a model that exhibits spin-charge separation.[18] In fact, the difference between the two scenarios is not that large: in both theories, the electron spectral function has a wide $(\sim 6-8t)$ featureless incoherent part, and some dispersion on a scale of J. The only real difference between the two theoretical predictions is for the momentum range near $(\pi/2,\pi/2)$ where the SDW scenario predicts, at $T=0$, a Fermi-liquid dispersion with $G(k,\omega)=Z/[\omega - J(k-\pi/2)^2+i\gamma\omega^2]$, where $Z\propto J/t$ and $\gamma\propto 1/J$, while the model with spin-charge separation yields a branch cut behavior of $G(k,\omega)$ with the maximum of the spectral function at $\omega\propto|k-\pi/2|$. Experimentally, it is difficult to make a precise conclusion about the shape and width of the dispersion right near $(\pi/2,\pi/2)$ in the zero-temperature limit because experiments are done at only one temperature.

We now proceed to the results at finite doping. Figure 2 contains our experimental results for a heavily underdoped cuprate with T_c 30 K and a less underdoped cuprate with T_c 60 K. The dispersion relation which emerges from these data is shown in Fig. 3(b) (triangles for 30 K material and black dots for 60 K material) together with the data for the insulator $Sr_2CuO_2Cl_2$ (open circles), and optimally doped cuprates (dashed line). The zero of energies coincides with the Fermi energy in the superconductors, and with the top of the valence band in the oxychloride. Several noteworthy points emerge directly from the data. First, the data taken along the (π,π) direction are very similar to the data obtained in the insulating $Sr_2CuO_2Cl_2$ [cf. Figs. 1(b) and 2(a)]. In both cases the photoemission intensity has a relatively sharp maximum between (0,0) and $(\pi/2,\pi/2)$ which approaches zero energy and eventually disappears as k approaches $(\pi/2,\pi/2)$. This maximum can naturally be identified as a quasiparticle peak. For larger k, however, the maximum in the intensity reappears and shifts towards higher energies as k moves towards (π,π). In the insulating $Sr_2CuO_2Cl_2$ this second maximum was interpreted by Wells *et al.* as a second quasiparticle peak which obviously should be present due to antiferromagnetism. Similarity between the data for the insulator and 30 K $Bi_2Sr_2CaCu_2O_{8+x}$ material then suggests that the latter also possesses electronic states between $(\pi/2,\pi/2)$ and (π,π) (black triangles in Fig. 3). This dispersion is in full agreement with the idea[14–16] that underdoped cuprates develop the precursors of the SDW state even before the system actually becomes magnetically ordered.

We caution, however, that the peak between $(\pi/2,\pi/2)$

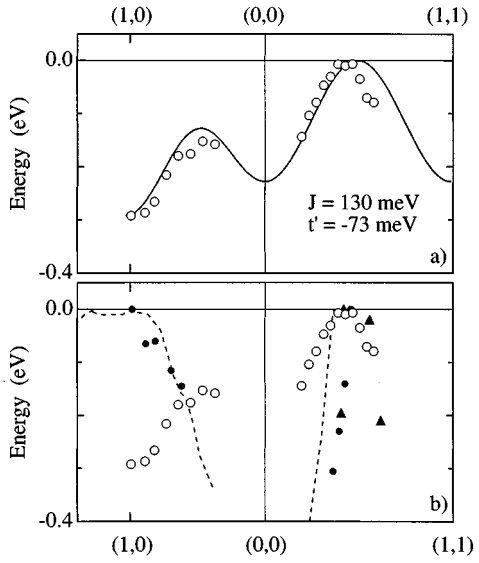

FIG. 3. (a) Valence-band quasiparticle energy for $Sr_2CuO_2Cl_2$ measured from the top of the valence band. Solid line: mean-field SDW result. (b) Quasiparticle dispersion as a function of doping. Open circles: the data for $Sr_2CuO_2Cl_2$, triangles, closed circles, and dashed line: the data for T_c 30 K, T_c 60 K, and optimally doped $Bi_2Sr_2CaCu_2O_{8+x}$, respectively. The zero of energies coincides with the Fermi energy in the superconductors, and with the top of the valence band in the oxychloride. The error bars for the data can be extracted directly from the data sets in Figs. 1 and 2.

and (π,π) is rather broad so it is not completely clear whether it corresponds to a true quasiparticle state or just to an enhancement of the intensity at the early stages of the development of the SDW precursors.

Further, we found that the overall width of the dispersion gradually increases with doping, and the electronic states observed above $(\pi/2,\pi/2)$ for 30 K superconductors are no longer observed for less underdoped 60 K superconductors and for optimally doped material. This is consistent with the model calculations of Ref. 15 which show that the electronic states between $(\pi/2,\pi/2)$ and (π,π) lose their spectral weight and eventually disappear with increased doping. Simultaneously, the overall width of the electronic dispersion increases from $2J\sim 0.3$ eV to roughly $\sim 4t=1$ eV which is the half bandwidth for noninteracting quasiparticles.

We also found that the Fermi surface at optimally doped $Bi_2Sr_2CaCu_2O_{8+x}$ is located (for $k_x=k_y$) slightly further away from $(\pi/2,\pi/2)$ than in underdoped samples. This is consistent with the recent data by Marshall *et al.*[19] However, even at optimal doping, the Fermi surface is still located very close to $(\pi/2,\pi/2)$. Combining this result with our earlier data which show that the Fermi surface crosses the Brillouin zone boundary near $(0,\pi)$ and symmetry related points, we conclude that even at optimal doping, a substantial portion of the quasiparticle Fermi surface is located close to the magnetic Brillouin zone boundary. This proximity is essential for theoretical considerations as, e.g., it is a key ingredient for the calculations which yield linear in T in-plane resistivity in a nearly antiferromagnetic Fermi-liquid model.[20]

We now turn to dispersion along the $(0,\pi)$ direction. Here the evidence in favor of precursors of the SDW state is less clear: for a 30 K superconductor, we do not have conclusive data at the moment. For a less underdoped 60 K superconductor we observed a broad quasiparticle peak which disperses through the Fermi surface near $(0,\pi)$ (see Fig. 2). This behavior is similar to the one observed in optimally doped superconductors, though the width of the peak is larger for 60 K material than for optimally doped material (230 ± 20 meV compared to 175 ± 15 meV for 90 K material). The dispersion along the $(0,\pi)$ direction has been recently studied by Stanford and Argonne groups.[19,21] For optimally doped superconductors, our data and their data are consistent. For their 60 K superconductors, they found no Fermi-surface crossing but rather a broad maximum at about 150 meV consistent with the existence of the precursors to the SDW state. In addition, they also observed a shift of the leading edge of the photoemission curve to some finite frequency of ~ 25 meV. Our 60 K material, as we said, shows no SDW features along either the $(0,\pi)$ or (π,π) direction. Most likely, our 60 K material is actually more doped than the one studied by Stanford and Argonne groups.

Another issue which we studied in detail is the quasiparticle dispersion near $(0,\pi)$. It has been reported by a number of groups[22] that at optimal doping, the dispersion around $(0,\pi)$ is anomalously flat. Since the $(0,\pi)$ point is close to the Fermi surface, this anomalous dispersion was identified as an extended van Hove singularity. It has been argued that this flat dispersion is the necessary ingredient for superconductivity in cuprates. However, our results for a 60 K superconductor show no evidence for the flat dispersion (see Fig. 3). We therefore believe that an extended van Hove singularity by itself is not a necessary ingredient for a high transition temperature, though it may give rise to an extra increase in T_c.

In summary, our results indicate that the electronic band structure of a CuO_2 plane gradually changes upon doping from a semiconductorlike structure in a SDW insulator to a normal, Fermi-liquid-like metallic structure at optimal doping. We have presented extensive evidence for precursors of the SDW state persisting in the underdoped cuprates. This evidence is particularly strong along the (π,π) direction. We also found that an extended van Hove singularity, by itself, is not a necessary condition for a high T_c value.

We thank C. Beeli and L. Forro for providing their TEM and oxychloride resistivity data, respectively, prior to publication. We gratefully acknowledge stimulating conversations with E. Dagotto, F. Del Dongo, and D. Morr. Measurements were performed at the SRC, University of Wisconsin, which is supported by the NSF under Grant No. DMR-95-31009. The friendly support of the SRC staff was greatly appreciated. This work was supported by the NSF through the Wisconsin MRG in high-temperature superconductivity, by NSF Grant No. DMR-9629839, by NSF Grant No. DMR-9629839, and the A.P. Sloan Foundation (A.C.), by the Fonds National Suisse de la Recherche Scientifique, and by Ecole Polytechnique Federale Lausane.

[1] C. Kendziora *et al.*, Physica C **257**, 74 (1996).
[2] J. C. Campuzano *et al.*, J. Low Temp. Phys. **95**, 245 (1994).
[3] D. S. Dessau *et al.*, Phys. Rev. Lett. **71**, 2781 (1993).
[4] Jian Ma *et al.*, Phys. Rev. B **51**, 3832 (1995).
[5] H. Ding *et al.*, Phys. Rev. Lett. **76**, 1533 (1996).
[6] D. L. Novikov *et al.*, Phys. Rev. B **51**, 6675 (1995).
[7] (a) C. Beeli and (b) L. Forro *et al.* (private communications).
[8] See, e.g., D. J. Scalapino, Phys. Rep. **250**, 329 (1995); E. Dagotto *et al.*, Phys. Rev. Lett. **74**, 310 (1995), and references therein.
[9] B. O. Wells *et al.*, Phys. Rev. Lett. **74**, 964 (1995).
[10] J. R. Schrieffer *et al.*, Phys. Rev. B **39**, 11 663 (1989); A. Chubukov and D. Frenkel, *ibid.* **46**, 11 884 (1992); A. Chubukov and K. Musaelian, J. Phys., Condens. Matter. **7**, 133 (1995); Phys. Rev. B **50**, 6238 (1994).
[11] M. S. Hybertsen *et al.*, Phys. Rev. B **41**, 11 068 (1990).
[12] I. Affleck and F. D. M. Haldane, Phys. Rev. B **36**, 5291 (1987).
[13] (a) R. Preuss *et al.*, Phys. Rev. Lett. **75**, 1344 (1995); E. Dagotto *et al.*, *ibid.* **73**, 728 (1994); (b) C. Kane, P. Lee, and N. Read, Phys. Rev. B **39**, 6880 (1989); A. Chubukov and D. Morr (unpublished).
[14] A. Kampf and J. R. Schrieffer, Phys. Rev. B **42**, 7967 (1990); J. R. Schrieffer, J. Low Temp. Phys. **99**, 397 (1995).
[15] A. Chubukov *et al.*, Philos. Mag. A **74**, 563 (1996); A. Chubukov and D. Morr, Phys. Rep. (to be published).
[16] S. LaRosa *et al.* (unpublished).
[17] See, e.g., Andrey V. Chubukov and O. Starykh, Phys. Rev.B **53**, R14 729 (1995).
[18] R. B. Laughlin, J. Phys. Chem. Solids **56**, 1627 (1995).
[19] D. S. Marshall *et al.*, Phys. Rev. Lett. **76**, 4841 (1996).
[20] A. Chubukov *et al.*, J. Phys. Condens. Matter **8**, 10 017 (1996).
[21] H. Ding *et al.*, Nature (London) **382**, 51 (1996).
[22] K. Gofron *et al.*, Phys. Rev. Lett. **73**, 3302 (1994).