PHYSICAL REVIEW B **88**, 184507 (2013)

Superconducting energy gap versus pseudogap in hole-doped cuprates as revealed by infrared spectroscopy

T. Dong, F. Zhou, and N. L. Wang
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

(Received 29 August 2013; revised manuscript received 30 October 2013; published 13 November 2013)

We present in-plane infrared reflectance measurement on two superconducting cuprates with relatively low T_c: nearly optimally doped $Bi_2Sr_{1.6}La_{0.4}CuO_{6+\delta}$ with $T_c = 33$ K and underdoped $La_{1.89}Sr_{0.11}CuO_4$ with $T_c = 30$ K. The measurement clearly reveals that the superconducting energy gap is distinct from the pseudogap. They have different energy scales and appear at different temperatures. The results suggest that the pseudogap is not a precursor to the superconducting state. The data also challenge the longstanding and predominant viewpoint that the superconductivity within the *ab* plane is in the clean limit and the superconducting pairing energy gap could not be detected by in-plane infrared spectroscopy.

DOI: 10.1103/PhysRevB.88.184507 PACS number(s): 74.25.Gz, 74.72.−h

I. INTRODUCTION

The energy gap created by the pairing of electrons is the most important parameter of a superconductor. Probing the pairing energy gap is crucial for elucidating the mechanism of superconductivity. For conventional superconductors, infrared spectroscopy is a standard technique to probe the superconducting energy gap, as the electromagnetic radiation below the gap energy 2Δ could not be absorbed.[1] For high-temperature superconductors (HTSCs), however, the situation is rather unclear. A predominant view is that the superconducting energy gap could not be detected from the *ab*-plane infrared spectra because the HTSCs are in the clean limit.[2] Although some features were actually seen in the low-frequency reflectance and conductivity spectra, they were widely ascribed to either the onset of a mid-infrared component or the coupling effect of electrons with some bosonic excitations.

Another factor that complicates the identification of the superconducting energy gap is the presence of the pseudogap. The pseudogap was observed for almost all underdoped high-T_c cuprates,[3] and many optimally doped systems, including the most commonly studied $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212),[4] and $Bi_2Sr_2CuO_{6+\delta}$ (Bi2201).[5] Early angle-resolved photoemission (ARPES)[6–8] and scanning tunneling microscopy (STM) experiments[9,10] on underdoped samples indicated that the superconducting gap smoothly evolves into the pseudogap state with increasing temperature. The lack of any obvious change at T_c for the gap amplitude has been taken as important evidence for the one-gap picture that the pseudogap is a precursor to the superconducting state but lacks its pairing phase coherence. However, in recent years, several ARPES measurements on underdoped Bi2212,[4,11] optimally doped Bi2201,[5] and $La_{2-x}Sr_xCuO_4$ (LSCO),[12] as well as Raman,[13] STM[14] and high field[15,16] studies, revealed a second energy gap forming abruptly at T_c on the Fermi arc near the nodal region. This gap has a canonical BCS-like temperature dependence and is accompanied by the appearance of Bogoliubov quasiparticles.[4] So it represents the order parameter of the superconducting state, whereas the pseudogap near the antinodal region is an energy scale associated with a different mechanism. Recently, a number of experimental investigations indicated that the pseudogap is associated with the charge-density-wave order, and it competes with the superconductivity.[17–23] It is noted that the superconducting gaps are close or comparable to the pseudogaps for systems with relatively higher T_c's [for example, in not heavily underdoped Bi2212 or $YBa_2Cu_3O_{6+\delta}$ (YBCO)]. On the other hand, for optimally doped Bi2201,[5] LSCO,[12] or heavily underdoped Bi2212,[11] the gaps formed at the Fermi arc, including their simple extrapolation to the antinodal position, are significantly smaller than the antinodal pseudogaps.

It is important to reconcile the infrared spectroscopy measurement with other experimental probes on the gap issue in cuprates. It is worth noting that, in the literature, a few studies on optimally doped or overdoped electron-type cuprates $Pr_{2-x}Ce_xCuO_4$ indicated that the superconducting energy gap could be actually detected by infrared spectroscopy.[24,25] More recently, it was reported that the formation of the superconducting energy gap on a hole-doped $La_{2-x}Ba_xCuO_4$ system could also be seen by infrared measurement.[26] Nevertheless, the relation between the superconducting energy gap and the pseudogap was not addressed in those studies. In fact, the pseudogap does not exist in optimally doped or overdoped electron-type cuprates.

To avoid possible complication arising from similar gap amplitudes between the superconducting gap and the pseudogap, here we study two different systems with relatively low T_c: a nearly optimally-doped $Bi_2Sr_{1.6}La_{0.4}CuO_{6+\delta}$ (La-doped Bi2201 with $T_c = 33$ K) and underdoped $La_{1.89}Sr_{0.11}CuO_4$ (LSCO, $T_c = 30$ K). We observed an abrupt spectral change at low frequency directly associated with the superconducting transition in both cuprate systems. We elucidate that those changes are caused by the formation of a *d*-wave superconducting gap below T_c. At higher frequencies, another shoulder feature is present in reflectance and shows little change across T_c. It is caused by the partial energy gap in the Fermi surface. Our study reveals that the superconducting gap and pseudogap are two distinct energy gaps. They have different energy scales and appear at different temperatures.

II. EXPERIMENTS AND RESULTS

High-quality single crystals in both systems were grown by the floating zone method.[27] The near-normal incident reflectances were measured using both Bruker 66v/s and

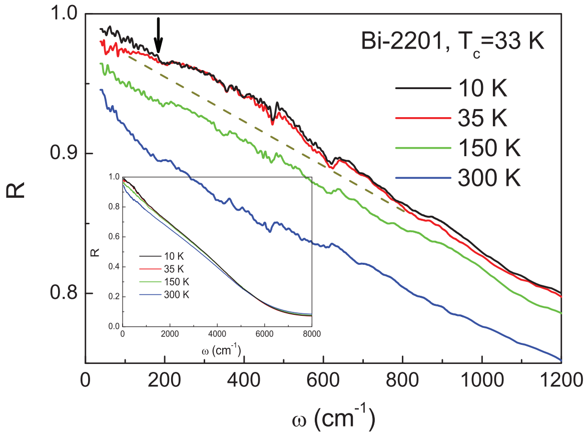

FIG. 1. (Color online) The temperature-dependent reflectance $R(\omega)$ for Bi2201 below 1200 cm^{-1}. An upward deviation from linear-ω dependence below roughly 800 cm^{-1} is seen in $R(\omega)$ at 10 and 35 K. The dashed straight line is a guide for the eyes. This gives a weak shoulder at around 400–800 cm^{-1} in $R(\omega)$. Below T_c, a further upturn is observed at lower frequency as indicated by an arrow. The inset shows the data taken over broad frequencies.

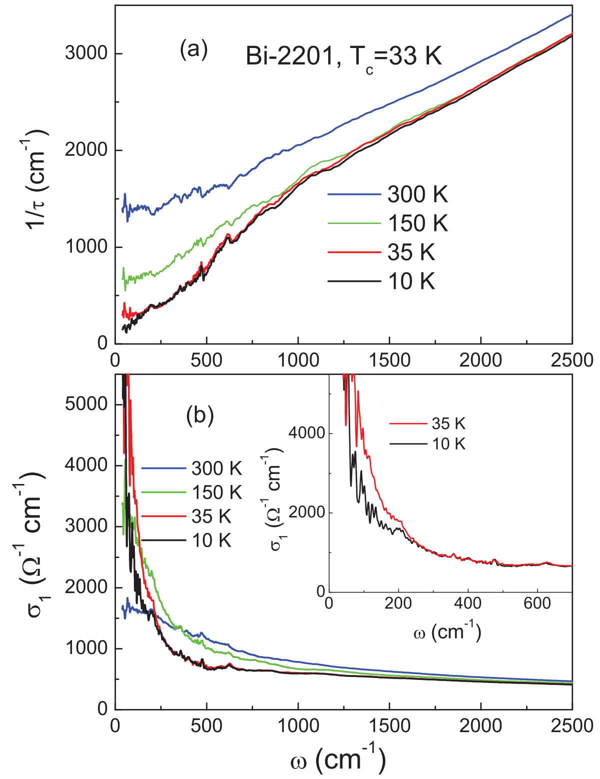

FIG. 2. (Color online) (a) The scattering rate and (b) the optical conductivity spectra for Bi2201 at different temperatures. The inset shows the conductivity spectra in the superconducting state and the normal state just above T_c.

113v spectrometers with an *in situ* overcoating technique. The optical conductivity was obtained by performing a Kramers-Kronig transformation.

Let us first look at the data collected on the La-doped Bi2201 crystal. Figure 1 shows the temperature-dependent reflectance $R(\omega)$ below 1200 cm^{-1}. The inset shows the data taken over broad frequencies. We notice that $R(\omega)$ roughly displays the well known linear-ω dependence over broad frequencies at high temperatures, i.e., 300 or 150 K. This gives rise to the approximately linear frequency dependent optical scattering rate, as shown in Fig. 2(a), in terms of the extended Drude model $1/\tau(\omega) = (\omega_p^2/4\pi)\,\mathrm{Re}[1/\sigma(\omega)]$, where ω_p is the overall plasma frequency and can be obtained by summarizing optical conductivity up to the reflectance edge frequency. Its line shape looks just like an upside-down plot of $R(\omega)$. However, at low temperatures, e.g., at 10 and 35 K, the $R(\omega)$ curves apparently deviate upward from the linear-ω dependence below roughly 800 cm^{-1}. A curvature is seen very clearly for the $R(\omega)$ curves in the main panel. The dashed straight line is a guide for the eyes. This curvature is essentially the same as the prominent shoulder features observed in other systems with relatively higher T_c's, such as YBCO,[28] Bi2212,[29] or Tl-based systems,[30] although it is much weaker here. In the $1/\tau(\omega)$ spectrum, the low-temperature scattering rate shows a downward suppression at low frequencies. Those spectral features were taken as the optical signature of the pseudogap state, but later were frequently assigned to the coupling effect of electrons with a certain bosonic mode.[28,29] According to previous optical studies on electronic systems with partial energy gaps formed on the Fermi surface, for example, in the two-dimensional (2D) transitional-metal dichalcogenide charge density wave (CDW) system[31] or the electron-doped cuprate system $Nd_{2-x}Ce_xCuO_4$,[32] such spectral structures could be unambiguously caused by the partial energy gaps.

The most important observation in this work is that a further spectral change occurs below the superconducting transition. The reflectance at 10 K below 200 cm^{-1} shows a clear further upturn from the $R(\omega)$ curve at 35 K (above T_c). This spectral change was repeatedly observed in different pieces of crystals from the same crystal rod. A similar spectral change is also seen in underdoped LSCO below superconducting transitions, as we shall present below. Thus it represents a new energy scale associated with the superconducting transition. The spectral change is not significant, and the low-ω reflectance at the temperature far below T_c does not approach unity abruptly. This could be attributed to the d-wave energy gap. The low-energy quasiparticle excitations are still present due to the presence of nodes. It is worth remarking that, in earlier optical studies on underdoped high-temperature superconductors with relatively higher T_c, including commonly studied Bi2212,[29] $YBa_2Cu_3O_{7-\delta}$,[28] and $YBa_2Cu_4O_8$,[33] this second abrupt spectral change below T_c was not observed. In those systems, no qualitative difference in the spectra between the pseudogap state and the superconducting state was seen in infrared experiments, similar to the observations in earlier ARPES[6–8] and tunneling measurements.[9,10] This leaded to the conclusion that the pseudogap state was already a lot like the superconducting state. We note that this statement is only true for the spectra taken above 200 cm^{-1} at 10 and 35 K here, suggesting that the spectral structure related to the pseudogap energy does not change across T_c; in contrast, the spectral change in $R(\omega)$ below 200 cm^{-1} is directly caused by the d-wave superconducting pairing. It leads to a reduction of the spectral weight in optical conductivity at very low energies, as shown in Fig. 2(b). The missing spectral weight is transferred to the strength of the delta function at zero frequency, representing the superconducting condensate.

It is worthwhile to compare the optical data with the result obtained from the ARPES measurement on a similar La-doped Bi2201 crystal with approximately the same T_c.[5] The ARPES study clearly revealed the existence of a gapless Fermi arc near the nodal region and an energy gap of about 40 meV near the antinodal region (π, 0) above T_c (but below the pseudogap closing temperature T_{PG}). The antinodal energy gap does not show much difference as the sample becomes superconducting; however, a second energy gap opens up on the Fermi arc only below T_c. Its energy scale is about 10–15 meV, being distinct from the magnitude of the pseudogap.[5] We find that our optical data are in very good agreement with the ARPES experiment, considering that the optical gap should double the ARPES measurement, being relative to the Fermi energy. The weak shoulder in $R(\omega)$ between 600 and 800 cm^{-1} is associated with the partial energy gap, i.e., the pseudogap, near the antinodal region, while the new energy scale below 200 cm^{-1} is associated with the d-wave pairing gap that opened up on the nodal Fermi arc. Above 150 K, the spectral feature linked with the pseudogap could not be well resolved in our infrared data; this is also consistent with the ARPES measurement that the pseudogap is already closed at 150 K.[5] Our experiment strongly suggests that the spectral change caused by the pairing gap below T_c could be detected with infrared spectroscopy.

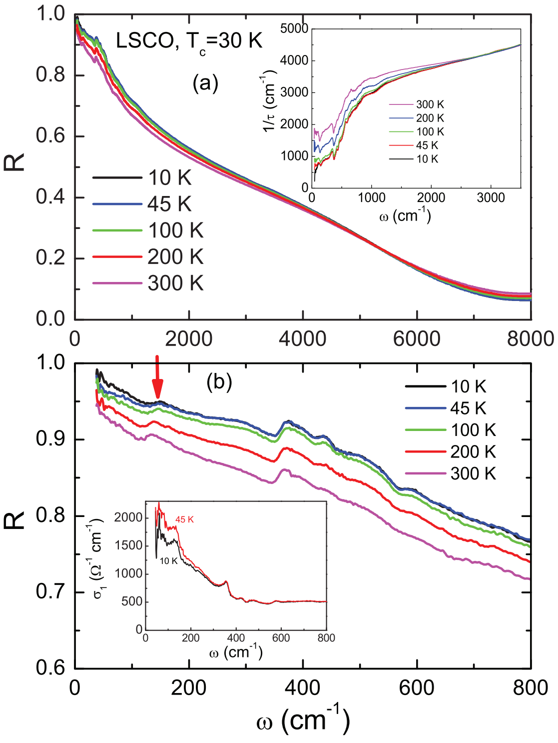

FIG. 3. (Color online) The temperature-dependent reflectance $R(\omega)$ for La$_{1.89}$Sr$_{0.11}$CuO$_4$ (a) over broad frequencies, and (b) below 800 cm^{-1}. The arrow indicates the frequency below which a further upturn appears below T_c. The insets show the scattering rate and the conductivity spectra above and below T_c, respectively.

Figure 3 shows the measured in-plane reflectance data for an underdoped La$_{1.89}$Sr$_{0.11}$CuO$_4$ crystal with $T_c = 30$ K: (a) the data over broad frequencies up to 8000 cm^{-1}; (b) the data at low frequencies, below 800 cm^{-1}. As the sample is rather underdoped, the reflectance does not show a linear frequency dependence. A pronounced shoulder is seen near 500–700 cm^{-1} for spectra at all measured temperatures. The reversed S-like shape is a strong indication for the presence of a partial energy gap in the Fermi surface.[32] In the scattering rate spectra shown in the inset of Fig. 3(a), the strong suppression below 700 cm^{-1} is seen for all curves. Like the case of La-doped Bi2201, those features could be ascribed to the partial energy gaps at the antinodal region which should be persistent even above room temperature in LSCO. In the expanded plot of $R(\omega)$ at low frequencies [Fig. 3(b)], a further upturn is observed in the curve at 10 K only below 150 cm^{-1} from the normal state $R(\omega)$ at 45 K. Similar to La-doped Bi2201, this spectral change is linked with the superconducting gap below T_c. It causes a small missing area at low frequencies in optical conductivity, as shown in the inset of Fig. 3(b).

Summarizing our infrared measurement on two different superconducting systems with relatively lower T_c, we find two major structures in the optical spectra. One is a shoulder feature at relatively higher energy scale in $R(\omega)$, roughly 600–800 cm^{-1}. The feature is rather weak in the Bi2201 sample, and not visible above 150 K. In underdoped LSCO, the feature is strong, and persistent above room temperature. The other one, which is more important and not resolved in earlier optical studies on systems with relatively higher T_c, is the identification of a second energy scale about 150–200 cm^{-1} directly associated with the superconducting transition.

III. DISCUSSIONS

It is highly interesting to discuss the origin of the second energy scale which is directly associated with the superconducting transition. Although it is very natural to assign it to the formation of the superconducting energy gap, one may argue that this kind of spectral change may originate from the coupling effect of electrons with a certain bosonic mode.[28,29] Let us discuss this possibility first. In high-T_c cuprates, two candidates for a sharp bosonic mode could exist: a phonon and magnetic excitation [with a resonance at (π,π)]. Since the phonon mode could not disappear suddenly above $T_c \sim 30$ K, and furthermore the frequency is already much lower than any known phonon mode involved in in-plane Cu-O vibrations, the phonon mode could be ruled out. As for the magnetic resonance mode, neutron studies on bilayer cuprates YBCO and BSCCO revealed that the mode occurs only below T_c at optimal doping. For underdoped samples, a broad mode feature could be observed above T_c, but it locates at the same energy scale as below T_c.[34] Here the LSCO crystal is substantially underdoped; however, the feature is only observed below T_c. Additionally, the magnetic resonance at (π,π) was not observed in the single-layered compound. Therefore it is very unlikely that the feature is linked with magnetic excitations. Then we are left with the sole possibility: that is, gap formation caused by the superconducting pairing.

Our experiment severely challenges the point of view that the superconducting gap in high-T_c cuprates could not be

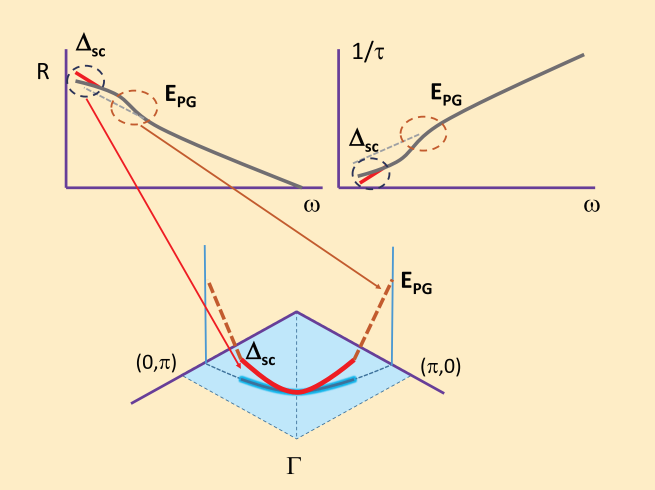

FIG. 4. (Color online) A schematic picture showing the relation between the gap features in the infrared reflectance spectrum and the two distinct gaps seen in ARPES.

observed in infrared spectroscopy. Such a statement was made based on the assumption that the superconductivity in the *ab* plane was in the clean limit.[2] In this case, the quasiparticle mean free path is much longer than the coherence length $l \gg \xi$, or equivalently the normal-state scattering rate is much smaller than the superconducting gap amplitude $1/\tau \ll \Delta$. However, this clean-limit scenario is under intense debate.[35] In many earlier studies on this issue, the anisotropic nature of the gap, the scattering rate, and the Fermi velocity were not sufficiently considered. We argue that this clean-limit criteria could not be fulfilled in the *d*-wave superconductivity in cuprates. In the nodal region, although the scattering rate is small, leading to large value of the mean-free-path, the gap amplitude is also very small (it is virtually zero at the nodal point, thus leading to divergence of the coherence length). In the antinodal region, the gap is large, but the quasiparticles experience very strong scattering, or they even could be not well defined in the underdoped case. Thus, generally the clean-limit criteria $1/\tau \ll \Delta$ could not be fulfilled over the entire Fermi surface. On this basis, the pairing energy gap is expected to be observed by infrared spectroscopy. As mentioned in the introduction, in optimally doped and overdoped electron-type cuprates as well as in a certain composition of $La_{2-x}Ba_xCuO_4$, the superconducting gap was also observed.[24–26] Our results and analysis provide further support for the findings of those works.

The comparison between our data and ARPES as we presented above strongly suggests that the low-frequency spectral change in $R(\omega)$ below T_c probes the superconducting gap formed on the Fermi arc near the nodal region, while the shoulder feature in $R(\omega)$ at higher frequencies is associated with the antinodal gap near $(\pi, 0)$. A schematic picture for the relation between the structures seen in the infrared spectrum and ARPES is shown in Fig. 4. We note that our experiment is not consistent with the one-gap scenario that the pseudogap is a precursor to the superconducting state. On the contrary, our work provides an optical evidence for two energy gaps for the superconducting state. It supports the picture that the gap near the antinodal region is associated with the nonsuperconducting order parameter, e.g., the CDW order as evidenced by a number of recent experimental probes,[17–23] while the gap which opens on the Fermi arc is associated with the superconductivity. The present work enables us to reconcile the optical spectroscopy probe with other experimental measurements on the observation of two distinct energy gaps.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China, and the 973 Project of the Ministry of Science and Technology of China (2011CB921701, 2012CB821403).

---

[1] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).

[2] K. Kamaras, S. L. Herr, C. D. Porter, N. Tache, D. B. Tanner, S. Etemad, T. Venkatesan, E. Chase, A. Inam, X. D. Wu, M. S. Hegde, and B. Dutta, Phys. Rev. Lett. **64**, 84 (1990); **64**, 1692(E) (1990).

[3] T. Timusk and B. Statt, Rep. Prog. Phys. **62**, 61 (1999).

[4] W. S. Lee, M. Vishik, K. Tanaka, D. H. Lu, T. Sasagawa, N. Nagaosa, T. P. Devereaux, Z. Hussain, and Z. X. Shen, Nature (London) **450**, 81 (2007).

[5] T. Kondo, T. Takeuchi, A. Kaminski, S. Tsuda, and S. Shin, Phys. Rev. Lett. **98**, 267004 (2007).

[6] H. Ding, T. Yokoya, J. C. Campuzano, T. Takahashi, M. Randeria, M. R. Norman, T. Mochiku, K. Kadowaki, and J. Giapintzakis, Nature (London) **382**, 51 (1996).

[7] A. G. Loeser, Z.-X. Shen, D. S. Dessau, D. S. Marshall, C. H. Park, P. Fournier, and A. Kapitulnik, Science **273**, 325 (1996).

[8] J. C. Campuzano, H. Ding, M. R. Norman, H. M. Fretwell, M. Randeria, A. Kaminski, J. Mesot, T. Takeuchi, T. Sato, T. Yokoya, T. Takahashi, T. Mochiku, K. Kadowaki, P. Guptasarma, D. G. Hinks, Z. Konstantinovic, Z. Z. Li, and H. Raffy, Phys. Rev. Lett. **83**, 3709 (1999).

[9] C. Renner, B. Revaz, J.-Y. Genoud, K. Kadowaki, and Ø. Fischer, Phys. Rev. Lett. **80**, 149 (1998).

[10] M. Kugler, Ø. Fischer, C. Renner, S. Ono, and Y. Ando, Phys. Rev. Lett. **86**, 4911 (2001).

[11] K. Tanaka, W. S. Lee, D. H. Lu, A. Fujimori, T. Fujii, Risdiana, I. Terasaki, D. J. Scalapino, T. P. Devereaux, Z. Hussain, and Z. X. Shen, Science **314**, 1910 (2006).

[12] K. Terashima, H. Matsui, T. Sato, T. Takahashi, M. Kofu, and K. Hirota, Phys. Rev. Lett. **99**, 017003 (2007).

[13] M. Le Tacon, A. Sacuto, A. Georges, G. Kotliar, Y. Gallais, D. Colson, and A. Forget, Nat. Phys. **2**, 537 (2006).

[14] M. C. Boyer, W. D. Wise, K. Chatterjee, M. Yi, T. Kondo, T. Takeuchi, H. Ikuta, and E. W. Hudson, Nat. Phys. **3**, 802 (2007).

[15] F. Rullier-Albenque, H. Alloul, and G. Rikken, Phys. Rev. B **84**, 014522 (2011).

[16] S. Kawasaki, C. T. Lin, P. L. Kuhns, A. P. Reyes, and G. Q. Zheng, Phys. Rev. Lett. **105**, 137002 (2010).

[17] G. Ghiringhelli, M. Le Tacon, M. Minola, S. Blanco- Canosa, C. Mazzoli, N. B. Brookes, G. M. De Luca, A. Frano, D. G. Hawthorn, F. He, T. Loew, M. M. Sala, D. C. Peets, M. Salluzzo, E. Schierle, R. Sutarto, G. A. Sawatzky, E. Weschke, B. Keimer, and L. Braicovich, Science **337**, 821 (2012).

[18] J. Chang, E. Blackburn, A. T. Holmes, N. B. Christensen, J. Larsen, J. Mesot, R. Liang, D. A. Bonn, W. N. Hardy, A. Watenphul, M. v. Zimmermann, E. M. Forgan, and S. M. Hayden, Nat. Phys. **8**, 871 (2012).

[19] E. Blackburn, J. Chang, M. Hucker, A. T. Holmes, N. B. Christensen, R. Liang, D. A. Bonn, W. N. Hardy, U. Rütt, O. Gutowski, M. v. Zimmermann, E. M. Forgan, and S. M. Hayden, Phys. Rev. Lett. **110**, 137004 (2013).

[20] S. Blanco-Canosa, A. Frano, T. Loew, Y. Lu, J. Porras, G. Ghiringhelli, M. Minola, C. Mazzoli, L. Braicovich, E. Schierle, E. Weschke, M. Le Tacon, and B. Keimer, Phys. Rev. Lett. **110**, 187001 (2013).

[21] T. Wu, H. Mayaffre, S. Kramer, M. Horvatic, C. Berthier, W. N. Hardy, R. Liang, D. A. Bonn, and M.-H. Julien, Nature (London) **477**, 191 (2011).

[22] D. LeBoeuf, S. Kramer, W. N. Hardy, R. Liang, D. A. Bonn, and C. Proust, Nat. Phys. **9**, 79 (2012).

[23] D. H. Torchinsky, F. Mahmood, A. T. Bollinger, I. Bosovic, and N. Gedik, Nat. Mater. **12**, 387 (2013).

[24] A. Zimmers, R. P. S. M. Lobo, N. Bontemps, C. C. Homes, M. C. Barr, Y. Dagan, and R. L. Greene, Phys. Rev. B **70**, 132502 (2004).

[25] C. C. Homes, R. P. S. M. Lobo, P. Fournier, A. Zimmers, and R. L. Greene, Phys. Rev. B **74**, 214515 (2006).

[26] C. C. Homes, M. Hucker, Q. Li, Z. J. Xu, J. S. Wen, G. D. Gu, and J. M. Tranquada, Phys. Rev. B **85**, 134510 (2012).

[27] F. Zhou, P. H. Hor, X. L. Dong, W. X. Ti, J. W. Xiong, and Z. X. Zhao, Physica C **408**, 430 (2004).

[28] J. Hwang, J. Yang, T. Timusk, S. G. Sharapov, J. P. Carbotte, D. A. Bonn, R. Liang, and W. N. Hardy, Phys. Rev. B **73**, 014508 (2006).

[29] J. Hwang, T. Timusk, and G. D. Gu, J. Phys. Cond. Matter **19**, 125208 (2007).

[30] Y. C. Ma and N. L. Wang, Phys. Rev. B **72**, 104518 (2005).

[31] W. Z. Hu, G. Li, J. Yan, H. H. Wen, G. Wu, X. H. Chen, and N. L. Wang, Phys. Rev. B **76**, 045103 (2007).

[32] N. L. Wang, G. Li, Dong Wu, X. H. Chen, C. H. Wang, and H. Ding, Phys. Rev. B **73**, 184502 (2006).

[33] D. N. Basov, R. Liang, B. Dabrowski, D. A. Bonn, W. N. Hardy, and T. Timusk, Phys. Rev. Lett. **77**, 4090 (1996).

[34] Pengcheng Dai, H. A. Mook, G. Aeppli, S. M. Hayden, and F. Dogan, Nature (London) **406**, 965 (2000).

[35] C. C. Homes, S. V. Dordevic, T. Valla, and M. Strongin, Phys. Rev. B **72**, 134517 (2005).