PHYSICAL REVIEW B **81**, 220501(R) (2010)

Line nodes in the energy gap of superconducting $BaFe_2(As_{1-x}P_x)_2$ single crystals as seen via penetration depth and thermal conductivity

K. Hashimoto,[1,2] M. Yamashita,[1] S. Kasahara,[3] Y. Senshu,[1] N. Nakata,[1] S. Tonegawa,[1] K. Ikada,[1] A. Serafin,[2] A. Carrington,[2] T. Terashima,[3] H. Ikeda,[1] T. Shibauchi,[1] and Y. Matsuda[1]

[1]*Department of Physics, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan*

[2]*H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, United Kingdom*

[3]*Research Center for Low Temperature and Materials Sciences, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*

(Received 13 May 2010; published 1 June 2010)

We report magnetic penetration depth and thermal-conductivity data for high-quality single crystals of $BaFe_2(As_{1-x}P_x)_2$ (T_c=30 K) which provide strong evidence that this material has line nodes in its energy gap. This is distinctly different from the nodeless gap found for $(Ba,K)Fe_2As_2$ which has similar T_c and phase diagram. Our results indicate that repulsive electronic interactions play an essential role for Fe-based high-T_c superconductivity but that uniquely there are distinctly different pairing states, with and without nodes, which have comparable T_c.

DOI: 10.1103/PhysRevB.81.220501 PACS number(s): 74.70.Xa, 74.20.Rp, 74.25.N−, 74.25.F−

The most important question concerning the Fe-based high-temperature superconductors[1] is what is the interaction that glues the electrons into Cooper pairs. Conventional phonon-mediated pairing leads to the superconducting gap opening all over the Fermi surface, while unconventional pairing mechanisms, such as spin fluctuations, can lead to a gap which has opposite signs on some regions of the Fermi surface. The sign change is a result of the anisotropic pairing interaction which is repulsive in some momentum directions. In high-T_c cuprate superconductors, where the electronic structure is essentially described by a single quasi-two-dimensional Fermi surface, the sign change in order parameter inevitably produces line nodes in the gap function. In Fe pnictides, however, the Fermi surface has disconnected hole and electron sheets and so the condition for a sign-changing gap can be fulfilled without nodes. In fact, a simple picture based on spin fluctuations predicts a distinct type of unconventional order parameter with sign change between the sheets, known as an $s_{\pm}$ state.[2,3] In this case, each Fermi surface is fully gapped, preventing low-energy excitation of quasiparticles.

Many experimental studies of high-T_c Fe-arsenides indicate a fully gapped superconducting state.[1,4–9] However, some measurements have suggested the existence of low-lying quasiparticle excitations[1,10,11] which is consistent with a strongly disordered fully gapped $s_{\pm}$ or a nodal state.[7,12,13] Strong evidence for gap nodes in the clean limit has been reported for LaFePO.[14–16] However, this material has a low T_c and has no nearby magnetic phases and so it is unclear whether it is representative of the higher-T_c Fe-based superconductors.

Recently, high-quality single crystals of the isovalent pnictogen substituted system $BaFe_2(As_{1-x}P_x)_2$ with T_c as high as 30 K have been grown.[17] As with the electron- and hole-doped materials, superconductivity with similar maximum T_c appears in close proximity to the spin-density-wave phase boundary ($x \approx 0.3$), where the presence of the strong antiferromagnetic fluctuations has been detected by NMR measurements.[9,18] It has been suggested from the spin-fluctuations theory[3] that the superconducting gap structure can depend sensitively on the pnictogen height from the Fe plane. The substitution of P for As reduces this pnictogen height,[17] which is not the case for the hole doping by K substitution for Ba. A comparison of the gap structure in $BaFe_2(As_{1-x}P_x)_2$ and $(Ba,K)Fe_2As_2$ with similar T_c should then give important insight into the pairing mechanism of high-T_c superconductivity in Fe pnictides.

Here we report low-temperature measurements of the magnetic penetration depth λ and thermal conductivity κ in high-quality crystals of $BaFe_2(As_{1-x}P_x)_2$(x=0.33) with optimum T_c=30 K. Both λ and κ are particularly good probes of the gap structure of superconductors. λ is related to the superfluid density $n_s \propto \lambda^{-2}$, whose temperature dependence is directly determined by the gap function. κ probes low-energy delocalized quasiparticles carrying entropy, which extend over the whole crystal. Both measurements probe the bulk superconducting properties. Our results provide strong evidence for line nodes in the energy gap in this system. The presence of nodes is in sharp contrast to the fully gapped superconducting state deduced from similar measurements of $(Ba,K)Fe_2As_2$ having similar T_c, and points toward a electronic repulsive pairing interaction in high-T_c Fe-pnictide superconductors.

Our $BaFe_2(As_{0.67}P_{0.33})_2$ crystals were grown using a self-flux method[17] and were characterized using x-ray diffraction and energy dispersion. No impurity phases were detected within experimental limits of $\lesssim$1%. The samples exhibit excellent sharp bulk superconducting transitions (see Fig. 1) at T_c=30 K in both the dc resistivity ρ as well as the specific heat. Importantly for studies of the gap structure, these samples are relatively free from disorder, as demonstrated by the observation of quantum oscillations.[19] The temperature dependence of penetration depth $\lambda(T)$ in $BaFe_2(As_{0.67}P_{0.33})_2$ was measured by a megahertz tunnel-diode oscillator down to ~0.15 K (Ref. 14) and by a microwave superconducting cavity resonator down to ~1.6 K.[4,7] In both measurements, a weak ac magnetic field is applied along the c axis, generating supercurrents in the ab plane. In the microwave measurements with angular frequency ω, the absolute values of both the real (R_s) and imaginary (X_s) parts of surface impedance can be determined by using the relation $R_s=X_s=\sqrt{\mu_0\omega\rho/2}$.[4,7] This allows us to estimate $\lambda(0)=X_s(0)/\mu_0\omega$

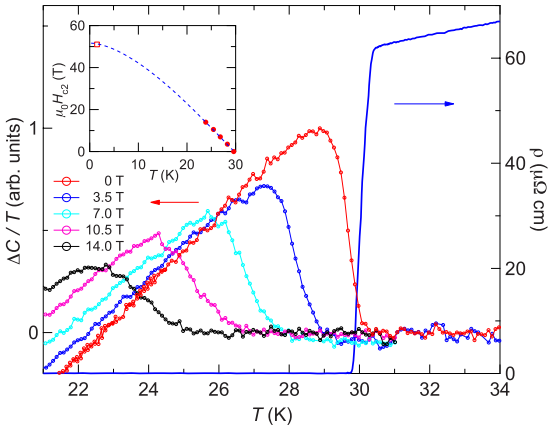

FIG. 1. (Color online) Relative change in the electronic specific heat $\Delta C/T$ of single crystal $BaFe_2(As_{0.67}P_{0.33})_2$ measured using an ac technique under magnetic fields applied along the c axis. A smooth background determined from an extrapolation of the 14 T data has been subtracted. Temperature dependence of the in-plane resistivity ρ of a crystal from the same batch is also shown. Inset shows the upper critical field $H_{c2}(T)$ determined from the midpoint of the specific-heat jump at each field (closed circles) and the irreversibility field measured by torque measurements (open square) (Ref. 19). The dashed line is a fit to the Wertharmer-Helfand-Hohenberg formula.

$=200\pm30$ nm, which is consistent with the recent μSR results of $\lambda(0)\approx170$ nm.[20] The $\lambda(T)$ results obtained by the two techniques at different frequencies show excellent agreement [inset of Fig. 2(a)]. Thermal conductivity was measured in a dilution refrigerator with the heat current applied in the ab plane.[16]

Figure 2(a) shows the normalized change in the penetration depth $\Delta\lambda(T)/\lambda(0)$ in $BaFe_2(As_{0.67}P_{0.33})_2$, compared with previous results for a clean $(Ba_{0.45}K_{0.55})Fe_2As_2$ crystal.[7] In sharp contrast to the flat behavior observed in the K-doped crystal, $\Delta\lambda(T)$ in the P-substituted crystal exhibits a strong quasilinear temperature dependence at low temperatures. The T-linear dependence of $\Delta\lambda(T)$ is a strong indication of line nodes in the superconducting gap. The normalized superfluid density $\lambda^2(0)/\lambda^2(T)$ in Fig. 2(b) also clearly demonstrates the fundamental difference between P- and K-doped samples. The low-temperature data of $BaFe_2(As_{0.67}P_{0.33})_2$ can be fitted to $1-\alpha(T/T_c)^n$ with the exponent $n=1.13(\pm0.05)$ close to unity. This is completely incompatible with the flat exponential dependence observed in the fully gapped superconductors, and immediately indicates low-lying quasiparticle excitations in this system. This behavior is fundamentally different from the power-law dependence of superfluid density with powers varying $n\sim2.0$ to ~2.4 found for other Fe arsenides.[7,10,11] In the fully gapped unconventional $s_\pm$ state, it has been suggested that substantial impurity scattering may induce in-gap states that change the exponential superfluid density to a power-law dependence but the exponent is expected to be not smaller than ~2.[12,13] However, the present results with exponent significantly smaller than 2 and much closer to 1 as expected for clean superconductors with line nodes, cannot be explained by these modifications of a full-gap state but is indicative of well-developed line nodes in the gap. We note that our data

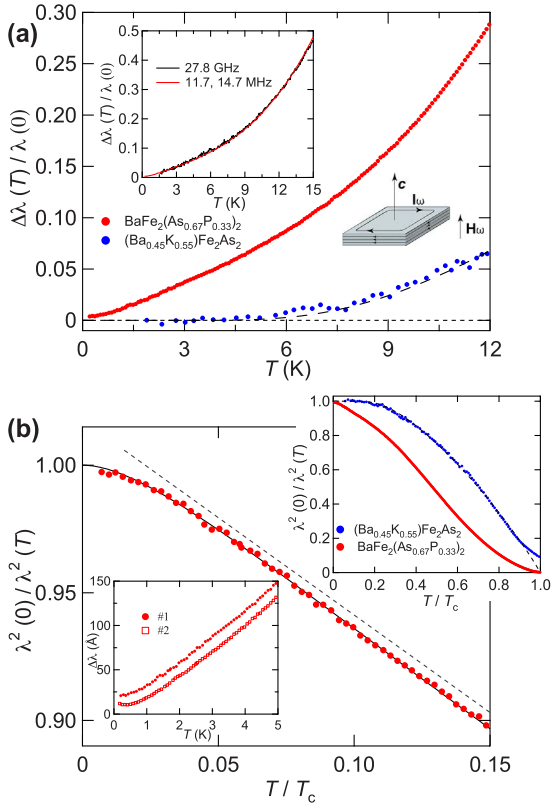

FIG. 2. (Color online) (a) The change $\Delta\lambda(T)\equiv\lambda(T)-\lambda(0)$ in the penetration depth of $BaFe_2(As_{0.67}P_{0.33})_2$ along with the data for $(Ba_{0.45}K_{0.55})Fe_2As_2$ ($T_c\simeq33$ K) (Ref. 7). Inset compares the results obtained by the microwave and rf techniques. (b) Normalized superfluid density $\lambda^2(0)/\lambda^2(T)$ as a function of T/T_c. The data follow a T-linear dependence (dashed line) down to $T/T_c\sim0.05$. The deviation at lower T/T_c can be fitted to the dependence for a gap with line nodes with disorder (solid line). The upper inset is the data up to T_c. The tail near T_c in $(Ba_{0.45}K_{0.55})Fe_2As_2$ is due to the skin depth effect at microwave frequencies (Ref. 7). The lower inset shows $\Delta\lambda(T)$ at low temperatures in two samples (shifted vertically for clarity).

do not exclude the possibility that some of the bands being fully gapped. Indeed, the higher-temperature behavior of the superfluid density is different to that expected for a single band with line nodes and instead suggests that some sheets of Fermi surface have a maximum gap below the weak-coupling value, as was found for MgB_2.[21]

The fact that the experimental value of n is slightly larger than unity may result from impurity scattering. In the limit of high levels of disorder, a general gap with line nodes gives $\Delta\lambda(T)\sim T^2$, and the following formula is often used to interpolate between the clean and dirty limits, $\Delta\lambda(T)\propto T^2/(T+T^*)$.[22] The disorder parameter T^* is related to the impurity band width γ_0. If we use this formula to fit our data [solid line in Fig. 2(b)], we get $T^*=1.3$ K$\approx0.04T_c$, which shows we are close to the clean nodal limit. A small variable-sized upturn in $\Delta\lambda(T)$ is observed at the lowest temperatures [inset of Fig. 2(b)]. This probably originates from amounts (on the order of 0.1% in volume) of paramagnetic impurities. This effect is negligible for $T>0.5$ K$(\sim0.017T_c)$, and is very small in sample 1 so this does not affect our conclusion of

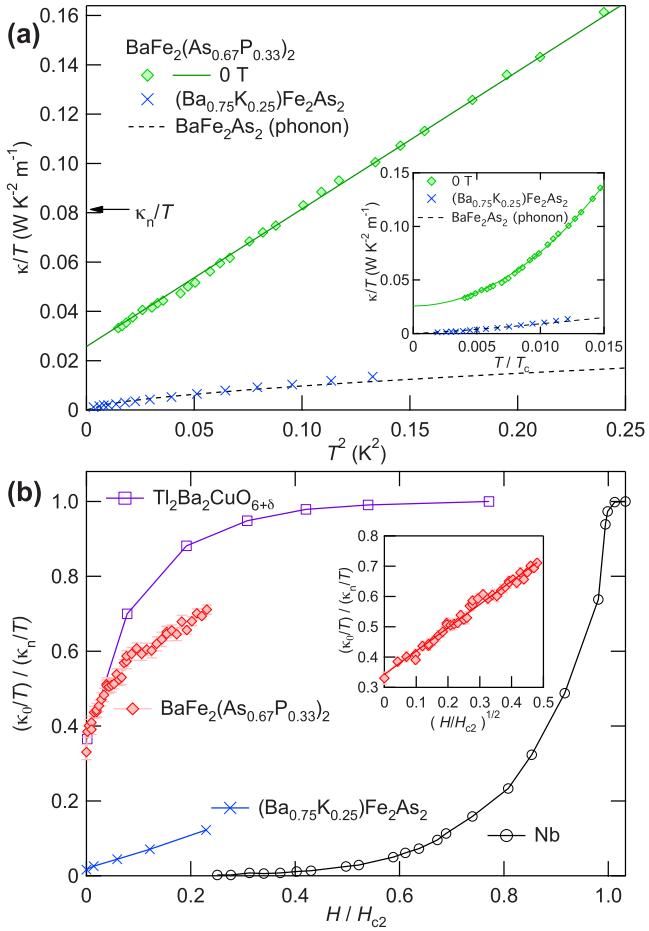

FIG. 3. (Color online) (a) Thermal conductivity divided by temperature κ/T is plotted against T^2 at zero field (main panel) and on a linear T axis (inset). The solid lines are the fit to the T^2 dependence. The reported data of $(Ba_{0.75}K_{0.25})Fe_2As_2$ ($T_c \simeq 30$ K) (Ref. 8) and the phonon contribution estimated in $BaFe_2As_2$ (Ref. 23) are also shown. (b) Residual $\kappa_0(H)/T$ vs H/H_{c2}. Also shown are the results for $Tl_2Ba_2CuO_{6+\delta}$ (Ref. 27), $(Ba_{0.75}K_{0.25})Fe_2As_2$ (Ref. 8), and Nb (Ref. 28). The gradual increase in $\kappa(H)/T$ in $(Ba_{0.75}K_{0.25})Fe_2As_2$ has been attributed to the slight modulation of the gap value (Ref. 8). Inset shows the same data in $BaFe_2(As_{0.67}P_{0.33})_2$ plotted against $(H/H_{c2})^{1/2}$. The line represents the $\sqrt{H}$ dependence.

the existence of low-lying quasiparticle excitations.

Thermal conductivity also provides a probe for the presence of line nodes. First we address the temperature dependence of κ/T in zero field [Fig. 3(a)]. In hole-doped $(Ba_{0.75}K_{0.25})Fe_2As_2$,[8] κ/T is nearly identical to the phonon contribution $\kappa_{ph}(T)$ obtained from nonsuperconducting $BaFe_2As_2$,[23] consistent with fully gapped superconductivity, in which very few quasiparticles are excited at $T \ll T_c$. In spite of similar values of residual electrical resistivity in the normal state,[17,8] the magnitude of κ/T in $BaFe_2(As_{0.67}P_{0.33})_2$ is strongly enhanced from that in $(Ba_{0.75}K_{0.25})Fe_2As_2$. At low temperature, the data are well fitted by $\kappa/T = aT^2 + b$. The presence of a sizeable residual value $b \simeq 25$ mW/K^2 m is clearly resolved.

It has been shown that the quasiparticle thermal conductivity in superconductors with sign-changing line nodes is given by

$$\kappa/T = \kappa_0/T(1 + O[T^2/\gamma_0^2]) \quad (1)$$

in the range $k_BT < \gamma_0$, where γ_0 is the impurity bandwidth.[24] In this case, κ_0/T is independent of the impurity content and depends only on the Fermi-surface parameters and the slope of the gap near the nodes. A rough estimation using parameters for the present material gives $\kappa_0/T \approx 22$ mW/K^2 m,[25] which reasonably coincides with the observed value. The T^2 term in Eq. (1) arises from the thermally excited quasiparticles around the nodes. For $BaFe_2(As_{0.67}P_{0.33})_2$, we find that this term is one order of magnitude larger than κ_{ph}/T. Recently calculations of $\kappa(T)$ for various candidate gap functions for the Fe-based superconductors have been reported by Mishra *et al.*[26] For the $s_{\pm}$ state without sign-changing nodes a sizeable value of κ_0/T is predicted only for very strong pair-breaking scattering (with accompanying strong reduction in T_c) which is incompatible with the low value of T^* found in the $\lambda(T)$ measurements. For the case of sign-changing nodes in one or more of the Fermi-surface sheets a sizeable κ_0/T is predicted in the low scattering limit, which is consistent with our experimental results.

Next we discuss the field dependence of κ_0/T, which is another independent test of the gap structure. The most distinguished feature in Fig. 3(b) is that $\kappa_0(H)/T$ increases steeply at low fields and attains nearly 70% of the normal-state value κ_n/T even at $0.2H_{c2}$ [where $\kappa_n/T \sim 81$ mW/K^2 m is estimated from the Wiedemann-Franz law by using the residual resistivity $\rho_0 \approx 30$ $\mu\Omega$ cm and H_{c2} was estimated from heat capacity and torque measurement (inset of Fig. 1)]. Such a field dependence is quite similar to that in $Tl_2Ba_2CuO_{6+\delta}$ with line nodes[27] but is in dramatic contrast to that in fully gapped superconductors such as Nb.[28] In fully gapped superconductors, quasiparticles excited by vortices are localized and unable to transport heat at low fields. In sharp contrast, the heat transport in superconductors with nodes is dominated by contributions from delocalized quasiparticles outside vortex cores. In the presence of line nodes where the density of states has a linear energy dependence $N(E) \propto |E|$, $N(H)$ increases steeply in proportion to $\sqrt{H}$ because of the Doppler shift of the quasiparticle energy.[29] This is consistent with the field dependence of $\kappa_0(H)/T$ in $BaFe_2(As_{0.67}P_{0.33})_2$ shown in the inset of Fig. 3(b).

The present results, (i) the T-linear penetration depth, (ii) the large value of κ_0/T at zero field, (iii) the T^2 dependence of κ/T, and (iv) the $\sqrt{H}$ field dependence of κ/T, all indicate that sign-changing line nodes exist in the gap function of $BaFe_2(As_{0.67}P_{0.33})_2$. An important question is then to answer how distinctly different gap structures (with and without nodes) can exist in a $BaFe_2As_2$-based family of Fe pnictides and have comparable transition temperatures. Although the Fermi-surface topology is similar in these two systems,[17,19,30] slight differences in the size and corrugation of hole surfaces may give rise to the dramatic change in the nodal topology. One possibility is that both systems have a *nodal s*-wave gap function but that the nodes in the electron band are lifted by disorder in the K-doped system.[31] However, as these K- and P-doped samples have very similar normal-state residual resistivities[8,17] as well as similar enhancements in the micro-

wave conductivity below T_c,[32] this suggests that they have similar levels of disorder, which makes this scenario unlikely. According to band-structure calculations,[3] the orbital character of one of the hole sheets is very sensitive to the pnictogen height which changes as As is substituted by P. This can cause significant changes in the spin-fluctuation spectrum and hence can change the pairing state.[3] This is consistent with the observation of a nodal pairing state in the Fe-phosphide superconductor LaFePO.[14–16] However, the nodal gap functions are expected to give a much lower T_c (as in LaFePO where $T_c \sim 6$ K) (Ref. 3) so the high T_c of $BaFe_2(As_{1-x}P_x)_2$ remains puzzling. A recent theory suggested that a competition between orbital and spin fluctuations may lead to line nodes,[33] which needs further investigations.

In summary, from the penetration depth and heat transport measurements, we demonstrate that the high-T_c superconductor $BaFe_2(As_{0.67}P_{0.33})_2$ has sign-changing line nodes, in sharp contrast to other Fe-based superconductors which appear to have a fully gapped pairing state. The presence of nodes is strong evidence for a repulsive pairing interaction such as that provided by antiferromagnetic spin fluctuations. Understanding the microscopic origin of these different behaviors remains a challenge for a complete theory of superconductivity in these materials.

We thank H. Takeya and K. Hirata for the early-stage collaboration on the crystal growth, and K. Ishida, H. Kontani, K. Kuroki, and R. Prozorov for helpful discussion. This work is partially supported by KAKENHI, Grant-in-Aid for GCOE program "The Next Generation of Physics, Spun from Universality and Emergence" from MEXT, Japan, and EPSRC in the U.K.

[1] K. Ishida, Y. Nakai, and H. Hosono, J. Phys. Soc. Jpn. **78**, 062001 (2009).
[2] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, Phys. Rev. Lett. **101**, 057003 (2008).
[3] K. Kuroki, H. Usui, S. Onari, R. Arita, and H. Aoki, Phys. Rev. B **79**, 224511 (2009).
[4] K. Hashimoto, T. Shibauchi, T. Kato, K. Ikada, R. Okazaki, H. Shishido, M. Ishikado, H. Kito, A. Iyo, H. Eisaki, S. Shamoto, and Y. Matsuda, Phys. Rev. Lett. **102**, 017002 (2009).
[5] L. Malone, J. D. Fletcher, A. Serafin, A. Carrington, N. D. Zhigadlo, Z. Bukowski, S. Katrych, and J. Karpinski, Phys. Rev. B **79**, 140501(R) (2009).
[6] H. Ding, P. Richard, K. Nakayama, K. Sugawara, T. Arakane, Y. Sekiba, A. Takayama, S. Souma, T. Sato, T. Takahashi, Z. Wang, X. Dai, Z. Fang, G. F. Chen, J. L. Luo, and N. L. Wang, EPL **83**, 47001 (2008).
[7] K. Hashimoto, T. Shibauchi, S. Kasahara, K. Ikada, S. Tonegawa, T. Kato, R. Okazaki, C. J. van der Beek, M. Konczykowski, H. Takeya, K. Hirata, T. Terashima, and Y. Matsuda, Phys. Rev. Lett. **102**, 207001 (2009).
[8] X. Luo, M. Tanatar, J. Reid, H. Shakeripour, N. Doironleyraud, N. Ni, S. Budko, P. Canfield, H. Luo, Z. Wang, H. Wen, R. Prozorov, and L. Taillefer, Phys. Rev. B **80**, 140503(R) (2009).
[9] M. Yashima, H. Nishimura, H. Mukuda, Y. Kitaoka, K. Miyazawa, P. Shirage, K. Kiho, H. Kito, H. Eisaki, and A. Iyo, J. Phys. Soc. Jpn. **78**, 103702 (2009).
[10] R. T. Gordon, C. Martin, H. Kim, N. Ni, M. A. Tanatar, J. Schmalian, I. I. Mazin, S. L. Budko, P. C. Canfield, and R. Prozorov, Phys. Rev. B **79**, 100506(R) (2009).
[11] C. Martin, R. T. Gordon, M. A. Tanatar, H. Kim, N. Ni, S. L. Budko, P. C. Canfield, H. Luo, H. H. Wen, Z. Wang, A. B. Vorontsov, V. G. Kogan, and R. Prozorov, Phys. Rev. B **80**, 020501(R) (2009).
[12] A. B. Vorontsov, M. G. Vavilov, and A. V. Chubukov, Phys. Rev. B **79**, 140507(R) (2009).
[13] Y. Bang, EPL **86**, 47001 (2009).
[14] J. D. Fletcher, A. Serafin, L. Malone, J. G. Analytis, J. H. Chu, A. S. Erickson, I. R. Fisher, and A. Carrington, Phys. Rev. Lett. **102**, 147001 (2009).
[15] C. Hicks, T. Lippman, M. Huber, J. Analytis, J. Chu, A. Erickson, I. Fisher, and K. Moler, Phys. Rev. Lett. **103**, 127003 (2009).
[16] M. Yamashita, N. Nakata, Y. Senshu, S. Tonegawa, K. Ikada, K. Hashimoto, H. Sugawara, T. Shibauchi, and Y. Matsuda, Phys. Rev. B **80**, 220509(R) (2009).
[17] S. Kasahara, T. Shibauchi, K. Hashimoto, K. Ikada, S. Tonegawa, R. Okazaki, H. Ikeda, H. Takeya, K. Hirata, T. Terashima, and Y. Matsuda, Phys. Rev. B **81**, 184519 (2010).
[18] Y. Nakai, T. Iye, S. Kitagawa, K. Ishida, S. Kasahara, T. Shibauchi, Y. Matsuda, and T. Terashima, Phys. Rev. B **81**, 020503(R) (2010).
[19] H. Shishido, A. F. Bangura, A. I. Coldea, S. Tonegawa, K. Hashimoto, S. Kasahara, P. M. C. Rourke, H. Ikeda, T. Terashima, R. Settai, Y. Ōnuki, D. Vignolles, C. Proust, B. Vignolle, A. McCollam, Y. Matsuda, T. Shibauchi, and A. Carrington, Phys. Rev. Lett. **104**, 057008 (2010).
[20] C. Bernhard *et al.* (unpublished).
[21] J. D. Fletcher, A. Carrington, O. J. Taylor, S. M. Kazakov, and J. Karpinski, Phys. Rev. Lett. **95**, 097005 (2005).
[22] P. J. Hirschfeld and N. Goldenfeld, Phys. Rev. B **48**, 4219 (1993).
[23] N. Kurita, F. Ronning, C. F. Miclea, E. D. Bauer, J. D. Thompson, A. S. Sefat, M. A. McGuire, B. C. Sales, D. Mandrus, and R. Movshovich, Phys. Rev. B **79**, 214439 (2009).
[24] M. J. Graf, S.-K. Yip, J. A. Sauls, and D. Rainer, Phys. Rev. B **53**, 15147 (1996).
[25] κ_0/T is estimated for a state with line nodes (Ref. 24) on all Fermi-surface sheets by $\frac{\kappa_0}{T} \simeq \frac{\pi\hbar k_B^2}{3e^2\mu_0\lambda(0)^2\Delta_0}$, where Δ_0 is the maximum gap amplitude which we take equal to $1.7k_BT_c$.
[26] V. Mishra, A. Vorontsov, P. J. Hirschfeld, and I. Vekhter, Phys. Rev. B **80**, 224525 (2009).
[27] C. Proust, E. Boaknin, R. W. Hill, L. Taillefer, and A. P. Mackenzie, Phys. Rev. Lett. **89**, 147003 (2002).
[28] J. Lowell and J. B. Sousa, J. Low Temp. Phys. **3**, 65 (1970).
[29] G. E. Volovik, JETP Lett. **58**, 469 (1993).
[30] H. Luo, Z. Wang, H. Yang, P. Cheng, X. Zhu, and H.-H. Wen, Supercond. Sci. Technol. **21**, 125014 (2008).
[31] V. Mishra, G. Boyd, S. Graser, T. Maier, P. J. Hirschfeld, and D. J. Scalapino, Phys. Rev. B **79**, 094512 (2009).
[32] S. Tonegawa *et al.* (unpublished).
[33] H. Kontani and S. Onari, Phys. Rev. Lett. **104**, 157001 (2010).