Evidence for nodal superconductivity in LaFePO

J.D. Fletcher, D. R. Serafin, L. Malone, J. Analytis, J.-H. Chu, A. S. Erickson, J. R. Fisher, and A. Carrington

1 H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, BS8 1TL, United Kingdom, and
2 Geballe Laboratory for Advanced Materials and Department of Applied Physics, Stanford University, Stanford, California 94305-4045

(Dated: December 19, 2008)

In several iron-arsenide superconductors there is strong evidence for a fully gapped superconducting state consistent with either a conventional $s$-wave symmetry or an unusual $s_\pm$ state where there the gap changes sign between the electron and hole Fermi surface sheets. Here we report measurements of the penetration depth $\lambda(T)$ in very clean samples of the related iron-phosphide superconductor, LaFePO, at temperatures down to $\sim 100$ mK. We find that $\lambda(T)$ varies almost perfectly linearly with $T$ strongly suggesting the presence of gap nodes in this compound. Taken together with other data, this suggests the gap function may not be generic to all pnictide superconductors.

A key question in understanding the physics of the recently discovered iron pnictide superconductors is the origin of the pairing interaction. Measurements of the symmetry and anisotropy of the superconducting energy gap are very useful for helping to decide between competing theories. Although several experiment designed to deduce the gap anisotropy have been performed a consensus has not yet been reached.

Several experiments indicate that the gap is finite at all points on the Fermi surface, however, others have suggested the presence of pronounced gap anisotropy or nodes. The presence of a fully gapped state is supported by point-contact tunneling spectroscopy measurements of SmFeAsO$_x$F$_{1-x}$ (Sm-1111) [1, 2, 3], penetration depth measurements of Pr-1111 [4], Sm-1111 [3], Nd-1111 [5], and Ba$_2$K$_y$Fe$_2$As$_2$ (Ba-122) [6] and angle resolved photoemission measurements of Ba-122 [7, 8, 9, 10]. Several of these measurements show evidence of two distinct gaps. On the other hand, some experiments suggest the presence of low energy excitations which could be indicative of nodes. These include nuclear magnetic resonance measurements of La-1111 [12, 13], and penetration depth measurements of Ba-122 [14, 15].

Theoretically, there is considerable debate about the nature of the gap anisotropy and symmetry. Band-structure calculations have indicated that both the 1111 and 122 materials have multiple quasi-two-dimensional sheets of Fermi-surface, hole-like close to the zone center and electron-like at the zone corner. At least for the undoped parent compounds these sheets are close to a nesting instability which can drive the system towards antiferromagnetism [15]. Several papers have argued that spin-fluctuations mediate the electron pairing and Mazin et al. [15] argued this favors an $s_\pm$ paring state where both the electron and hole Fermi surfaces are fully gapped but with gap-functions which are $\pi$ out of phase. Others however, have come to different conclusions. Most recently, Graser et al. [16] have calculated that the two lowest energy gap functions, one with $s$-symmetry and one with $d$ symmetry both have nodes on one or more of the Fermi surface sheets and are nearly degenerate.

The iron phosphide superconductor LaFePO, is isostructural with LaFeAsO (La-1111). Its relatively low $T_c \sim 6$ K [17] has been linked to the fact that the Fe-P bond angles depart substantially from those of a regular tetrahedron [18]. Unlike the corresponding As-based compound, nominally undoped LaFePO is non-magnetic and superconducting [19]. The electronic structure of LaFePO has recently been explored in some detail by de Haas-van Alphen (dHvA) measurements [20], which confirm the band-structure predictions of almost nested electron and hole pockets, a feature expected to be common to all Fe-pnictides not subject to antiferromagnetic Fermi surface reconstruction. The detailed knowledge of the electronic structure and availability of superconducting samples with very low levels of disorder makes LaFePO an ideal material in which to study order parameter symmetry. In this letter, we report measurements of the London penetration depth of LaFePO down to very low temperature $T < 0.02 T_c$. Our data show strong evidence for the presence of line-nodes in this compound.

Our samples were grown via a flux method which produces plate-like single crystals with typical dimensions 0.15 mm in the basal plane and <0.03 mm in the interlayer direction [19]. The samples measured in this study are from the same batch as those used for dHvA measurements where the mean free path was estimated to be $\gtrsim 1000$ Å for the electron sheets and $\sim 500$ Å for the hole sheets [20]. Heat capacity, measured using a modulated temperature technique, on the same single crystals used for the penetration depth measurements confirmed the bulk nature of the superconductivity. The data shown in Fig. 1 shows a sharp jump in $C$ at $T_c$ with the midpoint at $\approx 5.6$ K with width $\approx 0.25$ K.

Measurements of the temperature dependence of the London penetration depth were performed with a high resolution susceptometer based on a self-resonant tunnel...
diode circuit which was mounted in a dilution refrigerator. The circuit operates at \( \approx 14 \) MHz with an extremely small probe field \( (H_{ac} < 10\text{mOe}) \) so that the sample is always in the Meissner state \([21]\). Changes in the resonant frequency are directly proportional to changes in the magnetic penetration depth as the temperature of the sample is varied. The calibration factor is determined from the geometry of the sample, and the total perturbation to the resonant frequency due to the sample, found by withdrawing the sample from the coil at low temperature \([22]\). The sample is mounted on a sapphire rod, the other end of which is glued to a copper block on which the RuO\(_2\) thermometer is mounted. The sample and rod are placed inside a solenoid which forms part of the resonant tank circuit. The position of the sample within the solenoid could be varied in-situ allowing us to vary the RF field seen by the sample and hence check for RF heating which in-principle could cause the thermometer and sample to be out of equilibrium. The sapphire sample holder is of very high purity and has a very small paramagnetic background signal which was difficult to determine precisely and has not been subtracted. It corresponds to at most 20\( \lambda\) at the lowest temperature. Susceptibility measurements in this apparatus are shown in Fig. 1 in the region near \( T_c \). The mid point of the transition occurs at 5.6\( K\) consistent with the heat capacity measurement on the same sample. Other samples measured had \( T_c \) values in the range 5.4-5.9\( K\).

Fig. 2 shows the temperature dependence of the in-plane penetration depth, \( \Delta \lambda \), in three single crystals of LaFePO. The data for sample \#3 has been multiplied by 1.5. The curves are offset for clarity. Solid lines are power-law fits giving an exponent of \( 1.2 \pm 0.1 \). Curve (a) is an extrapolation of the two gap behavior found in Sm-1111 [2]. Curve (b) is the temperature dependence expected from weak coupling BCS behavior (i.e. \( \Delta = 1.76 \) \( T_c \)). We have used \( \lambda (0) \sim 2500\lambda\) in both cases and multiplied both curves by 50 to make them visible on this scale.

FIG. 1: (a) Heat capacity anomaly in a LaFePO single crystal. \( \Delta C \) is the difference between the heat capacity data in zero field and for \( B = 0.47 \) \( T \) (where \( T_c < 2 \) \( K \)). (b) RF susceptibility of the same sample close to \( T_c \).

FIG. 2: Temperature dependence of the in-plane penetration depth, \( \Delta \lambda \), in three single crystals of LaFePO. Data for sample \#3 has been multiplied by 1.5. The curves are offset for clarity. Solid lines are power-law fits giving an exponent of \( 1.2 \pm 0.1 \). Curve (a) is an extrapolation of the two gap behavior found in Sm-1111 [2]. Curve (b) is the temperature dependence expected from weak coupling BCS behavior (i.e. \( \Delta = 1.76 \) \( T_c \)). We have used \( \lambda (0) \sim 2500\lambda\) in both cases and multiplied both curves by 50 to make them visible on this scale.

measured with the ac field perpendicular to the conducting planes so only in-plane currents are induced. The temperature dependence is very similar in all three samples and is approximately linear. A variable power law fit, i.e. \( \Delta \lambda (T) \propto T^n \) for \( T < 1K \) gives \( n = 1.2 \pm 0.1 \). The close to linear temperature dependence of \( \lambda \) is strongly indicative of nodes in the order parameter.

The temperature dependence of \( \lambda \) arises from the depletion of the screening superfluid by thermal excitations. The superconducting energy gap, \( \Delta k \), dictates the spectrum of these excitations; if \( \Delta k \) is finite for all momentum wavevectors, an exponential temperature dependence of \( \lambda (T) \) is observed. By contrast, in a superconductor with an unconventional pairing symmetry the order parameter passes through zero for some wavevectors, leading to the presence of low energy excitations down to low temperatures and a power-law temperature dependence of the penetration depth. In a clean superconductor with line nodes on a quasi 2D fermi surface the angular averaged density of states has a linear energy dependence, leading to a linear behavior of \( \lambda (T) \) at low temperature.

The linear temperature dependence in LaFePO is in marked contrast with that observed in conventional superconductors, or those displaying anisotropic s-wave superconductivity, such as MgB\(_2\) or NbSe\(_2\) [23, 24], or the As-based 1111 compounds described in the introduction. In an s-wave multiband superconductor the low temper-
ature behavior is dominated by the smallest gap on the Fermi surface. We show in Fig. 2 the expected temperature dependence from gaps of 1.76 $T_c$ (the BCS weak coupling value) and 1.0 $T_c$ (similar to that found in Sm-1111 [3]). These show a clear exponential saturation which is not visible in our data. We find that if there is a small residual gap it at least 30 times smaller than the gap maximum. The presence of nodes is therefore much more likely.

The absolute values of $\Delta \lambda(T)$ are somewhat variable between samples. As shown in Fig.2 $d\lambda/dT \simeq 350 \text{Å}/\text{Hz}$ in samples #1 and #2 and smaller value of 220 Å/Hz in sample #3. This discrepancy in slope is likely to be due to uncertainties in the calibration factors relating the measured frequency shifts to $\Delta \lambda(T)$ arising from surface roughness. LaFePO has a mica-like morphology and samples #1 and #2 had visibly more flaky edges than sample#3, which had mirror like surface on all faces (a similar effect was observed in NbSe$_2$ [24]). Alternatively, it could result from intrinsic differences in the superfluid density as a function of doping i.e., slight changes in the oxygen stoichiometry (the samples had slightly different $T_c$).

In the usual weak-coupling theory for superconductors with line nodes, the superfluid density $\rho_s = [\lambda(0)/\lambda(T)]^2$ varies linearly over a much wider range of $T$ than $\lambda(T)$ (corrections to the former are $\mathcal{O}T^3$ whereas to the later they are of $\mathcal{O}T^2$). Muon spin relaxation measurements of polycrystalline samples [23] report a depolarisation rate of 1.2$\mu$m$^{-1}$, which corresponds to a penetration depth of $\lambda(0) \simeq 2400$ Å (we note that these authors indicate some uncertainty in this result due to a comparable anomalous contribution to the depolarisation rate in those samples). Measurements in the related materials La-1111 [26] and Sm-1111 [27] span the range 2000-3500 Å. Choosing a representative value of $\lambda(0)=2500$ Å we calculate the superfluid density as shown in Fig. 3. The figure shows that despite the uncertainties in the ratio $\Delta \lambda(T)/\lambda(0)$ the superfluid density varies almost perfectly linearly with $T$ from below $\sim 2$ K to around 100 mK. This key result is robust to the assumed value of $\lambda(0)$, so there is strong evidence for nodal excitations in the data regardless of this choice. In a nodal superconductor the low temperature behavior is dominated by the excitations near the gap nodes. For a superconductor with line-nodes $\lambda(T)$ is linear, with a slope determined by the rate at which the gap grows away from the nodes. In the simple d-wave case with $\Delta \lambda = \Delta_0 \cos(2\theta)$, $\Delta \lambda = \ln 2 \lambda(0) k_B T/\Delta_0$. For the weak coupling value $\Delta_0 \simeq 2.14 k_B T_c$ this predicts a value of around 100-200 Å/K (for $\lambda(0)$ in the range quoted above), somewhat smaller than the slope observed experimentally in sample #1 and #2, but close to the value seen in sample #3. As this calculation relies directly on $\lambda(0)$, better measurements of this parameter are required to make any precise comparisons to this or other candidate gap functions.

Differences in the temperature dependence of $\lambda_c$ and $\lambda_a$ can sometimes reveal information about gap symmetry. For example, in multi-band systems the c-axis response can also be different due to the presence of sheets with differing anisotropy and different gaps [24, 28]. For sample #1 measurements were also performed with the field parallel to the conducting planes. This induces a combination of in-plane and inter-plane currents and thus probes a mixture of $\Delta \lambda_a$ and $\Delta \lambda_c$. Sample #1 has a ratio of thickness to width of about $t/w \simeq 7$ which mixes

![FIG. 3: Low temperature normalized superfluid density for samples #1 and #3 using $\lambda(0) = 2500$ Å. Solid lines are linear fits to the data. Inset shows the superfluid density over the full temperature range. The dashed line shows the behavior found for Sm-1111 [3].](image)

![FIG. 4: Temperature dependence of the penetration depth, $\Delta \lambda_{\text{mix}}$, measured with $H \parallel ab$. Data for the same crystal with $H \parallel c$ are also shown for comparison.](image)
in a substantial component of $\lambda_c$. We denote this mixture $\Delta \lambda_{\text{mix}}$. This data is shown in Fig. 6 along with data from H$_c^a$ for comparison. The changes in $\lambda_{\text{mix}}$ are larger, with $d\lambda_{\text{mix}}/dT = 1300$ Å/Hz. Although the present crystals are not of sufficiently regular geometry to isolate the changes in $\lambda_c$ precisely, the data are consistent with $\lambda_c(T)$ also having a linear temperature dependence but with a much larger slope due to substantial electronic anisotropy. Measurements of the upper critical field at low temperature indicate an anisotropy $H_{c2}^{1a}/H_{c2}^{1c} \simeq 11$ consistent with the quasi-2D character of the Fermi surface [20]. When line nodes are present on a simply warped quasi-2D Fermi surface, as found in LaFePO, $\lambda_c(T)/\lambda_c(0)$ is expected to be similar to $\lambda_0(T)/\lambda_0(0)$. This is observed in the quasi-2D organic superconductors, where the in-plane and inter-plane penetration depth have a similar temperature dependence [21].

The importance of the observation of a linear $T$ dependence of the superfluid density over a wide range of temperature is that it is very difficult to produce this from extrinsic effects. The identification by Hardy et al. [20] of a similar predominately linear behavior of $\lambda(T)$ in YBa$_2$Cu$_3$O$_7$ was instrumental in identifying the $d_{x^2-y^2}$ state in the cuprates. Impurities will weaken any intrinsic linear temperature dependence, with $\lambda(T)$ varying like $T^2$ in the dirty limit [31]. However, power-laws with exponent close to two can result from, for example, a fully gapped $s_\pm$ state with impurities [32]. The impurities produce a non-zero energy density of states similar to that found in the $d$-wave case, and this has been shown to account well for the NMR data [33, 34]. Hence, although power-laws (with $n \sim 2$) point towards an unconventional gap symmetry they can be produced either with or without intrinsic nodes. However, the linear dependence observed here strongly points towards intrinsic nodes.

The observation of an exponential behavior of $\lambda(T)$ is also a robust feature which is not easily mimicked by extrinsic effects, so the different behavior found here for LaFePO compared to the As based 1111 compounds detailed above, probably points towards these compounds having intrinsically different gap symmetry / anisotropy. Just such a possibility was recently emphasized in the theoretical work of Graser et al. [16].

After completion of this work we learnt of local scanning SQUID susceptibility measurements in LaFePO crystals which also show a linear temperature dependence [23].

From precise measurements of the penetration depth in clean crystals we have shown strong evidence to suggest that the ferro pnictide superconductor LaFePO has nodes in its superconducting gap function. Combined with the detailed information about the full three dimensional electronic structure of this material derived from dHvA measurements, this should help to decide between competing theories for the origin of superconductivity in these materials.

We thank A. Chubukov, P. Hirschfeld and R. Prozorov for useful comments. Work at Bristol was supported by EPSRC. Work at Stanford was supported by the DOE, Office of Basic Energy Sciences under contract DE-AC02-76SF00515.

[1] T. Y. Chen, Z. Tesanovic, R. H. Liu, X. H. Chen, and C. L. Chien, Nature 453, 1224 (2008).
[2] D. Daghero, et al., arXiv:0812.1141 (Unpublished).
[3] R. S. Gonnelli, et al., arXiv:0807.3149 (Unpublished).
[4] K. Hashimoto, et al., arXiv:0806.3149 (Unpublished).
[5] L. Malone, et al., arXiv:0806.3908 (Unpublished).
[6] C. Martin, et al., arXiv:0807.0876 (Unpublished).
[7] K. Hashimoto, et al., arXiv:0810.3506 (Unpublished).
[8] K. Nakayama, et al., arXiv:0812.0663 (Unpublished).
[9] D. V. Evtushinsky, et al., arXiv:0809.4455 (Unpublished).
[10] H. Ding, et al., Europhys. Lett. 83, 47901 (6pp) (2008).
[11] L. Zhao, et al., Chin. Phys. Lett. 25, 4402 (2008).
[12] Y. Nakai, K. Ishida, Y. Kamihara, M. Hirano, and H. Hosono, J. Phys. Soc. Jpn 77, 073701 (2008).
[13] H.-J. Grafe, et al., Phys. Rev. Lett. 101, 047003 (2008).
[14] R. T. Gordon, et al., arXiv:0810.2295 (Unpublished).
[15] I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, Physical Review Letters 101, 057003 (2008).
[16] S. Graser, T. A. Maièr, P. J. Hirschfeld, and D. J. Scalapino, arXiv:0812.0343 (Unpublished).
[17] Y. Kamihara, et al., J. Amer. Chem. Soc. 128, 10012 (2006).
[18] C.-H. Lee, et al., J. Phys. Soc. Jap. 77, 083704 (2008).
[19] J. G. Analytis, et al., arXiv:0810.5368 (Unpublished).
[20] A. I. Coldea, et al., Phys. Rev. Lett. 101, 216402 (2008).
[21] A. Carrington, R. W. Giannetta, J. T. Kim, and J. Giaiaptzakis, Phys. Rev. B 59, 14173 (1999).
[22] R. Prozorov, R. W. Giannetta, A. Carrington, and F. M. Araujo-Moreira, Phys. Rev. B 62, 115 (2000).
[23] F. Manzano, et al., Phys. Rev. Lett. 88, 047002 (2002).
[24] J. D. Fletcher, et al., Phys. Rev. Lett. 98, 057003 (2007).
[25] Y. J. Uemura, arXiv:0811.1546 (Unpublished).
[26] R. Khasanov, et al., Phys. Rev. B 78, 092506 (2008).
[27] H. Luetkens, et al., Phys. Rev. Lett. 101, 097009 (2008).
[28] J. D. Fletcher, A. Carrington, O. J. Taylor, S. M. Kazarsov, and J. Karpinski, Phys. Rev. Lett. 95, 097005 (2005).
[29] A. Carrington, et al., Phys. Rev. Lett. 83, 4172 (1999).
[30] W. N. Hardy, D. A. Bonn, D. C. Morgan, R. Liang, and K. Zhang, Phys. Rev. Lett. 70, 3999 (1993).
[31] P. J. Hirschfeld and N. Goldenfeld, Phys. Rev. B 48, 4219 (1993).
[32] A. B. Vorontsov, M. G. Vavilov, and A. V. Chubukov, (Unpublished).
[33] A. V. Chubukov, D. E. Efremov, and I. Eremin, Phys. Rev. B 78, 134512 (2008).
[34] D. Parker, O. V. Dolgov, M. M. Korshunov, A. A. Golubov, and I. I. Mazin, Phys. Rev. B 78, 134524 (2008).
[35] K. Moler (private Communication).