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Evidence for Nodal Superconductivity in LaFePO from Scanning SQUID Susceptometry

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We measure changes in the penetration depth λ of the $T_c \approx 6$ K superconductor LaFePO. In the process scanning SQUID susceptometry is demonstrated as a technique for accurately measuring *local* temperature-dependent changes in λ, making it ideal for studying early or difficult-to-grow materials. λ of LaFePO is found to vary linearly with temperature from 0.36 to ~2 K, with a slope of 143±15 Å/K, suggesting line nodes in the superconducting order parameter. The linear dependence up to $\sim T_c/3$ is similar to the cuprate superconductors, indicating well-developed nodes.

Research on the iron pnictide superconductors has been intense over the past year. Most attention has focused on arsenic-based materials, which have the highest transition temperatures, but which only superconduct at ambient pressure when doped, resulting in intrinsic disorder. Superconductivity in LaFePO was announced in 2006 [1]. Most likely it is the fully stoichiometric compound that superconducts, with $T_c \approx 6$ K; very clean residual resistivities below 0.1 mΩ-cm have been obtained [2]. How similar LaFePO will prove to be to the higher-T_c arsenide compounds is not clear; although LaFePO does not show the magnetic order found in the arsenide compounds, its electronic structure has been found to be very similar [3].

The temperature dependence of the penetration depth provides information on the superconducting order parameter (OP). OPs with line nodes are known to result in a T-linear dependence of $\Delta\lambda(T) \equiv \lambda(T) - \lambda(0)$ at low T [4]. Scattering modifies this dependence to T^2 [5]. A fully-gapped OP results in an exponential dependence $\Delta\lambda \quad T^{-1/2}\exp(-T_0/T)$ [6]. For the iron pnictide superconductors, proposed OPs include nodal and nodeless s [7–11], $s+d$ [12], p [13, 14] and d [8, 14–16]. Most of these predictions are based on calculations in an unfolded, 1 Fe per unit cell Brillouin zone, which neglects the avoided crossings between the electron pockets in the true zone [3]. These avoided crossings could significantly alter the nodal structure of the OP. It is also a possibility that different pnictide superconductors, although electronically similar, have different OPs [17].

Radio-frequency tunnel diode resonator and microwave cavity perturbation measurements on iron arsenide superconductors have shown both power-law and exponential temperature dependences of $\Delta\lambda$. Power-law dependence has been found in $Ba(Fe_{1-x}Co_x)_2As_2$ [18], with the exponent n varying between 2.0 and 2.6 with doping. $n \approx 2$ has been found in $Ba_{1-x}K_xFe_2As_2$ [19], $NdFeAsO_{0.9}F_{0.1}$ [20] and $LaFeAsO_{0.9}F_{0.1}$ [20]. Exponential behavior has been found in $Ba_{1-x}K_xFe_2As_2$ [21], $PrFeAsO_{1-y}$ [22] and $SmFeAsO_{0.8}F_{0.2}$ [23].

In LaFePO, nearly linear dependence of $\Delta\lambda$ on T to below 150 mK has been reported by Fletcher *et al* [24], using an RF tunnel diode circuit. However early LaFePO samples have had irregular shapes, which complicate RF and microwave measurements: to isolate λ_{ab} the magnetic field of the excitation must be specifically oriented relative to the crystal axes, and at lower frequencies knowledge of the sample size is necessary to extract $\Delta\lambda$. Fletcher *et al* report these slopes $d\lambda/dT$ on three samples: 412, 436 and 265 Å/K (over $0.7 < T < 1.0$ K). The magnitude of $d\lambda/dT$ constrains the number and opening angle of nodes, so confirmation with additional measurement is desirable.

SQUID susceptometry has been demonstrated as a technique for observing superconducting transitions [25], and has been used to determine the Pearl length Λ of thin superconducting films, for $\Lambda \sim$10–100 μm [26]. We extend this technique to measurement of nm-scale changes in local λ with varying sample temperature. Our susceptometer is a niobium-based design [28]; its front end is shown in Fig. 1. The pick-up loop is part of a SQUID, and an excitation current (in this work, at 1071 Hz) is applied to the field coil. What is measured is the field coil–pick-up loop mutual inductance M. The susceptometer chip is polished to a point, aligned at an angle relative to the sample (in this work, $\approx 16°$), and mounted onto a 3-axis scanner. The Meissner response of superconducting samples partially shields the field coil, so M decreases as the susceptometer approaches the sample.

The schematic in Fig. 1 shows a model of the susceptometer. The field coil is taken as a wire loop of radius R at a height h above the superconductor surface, and

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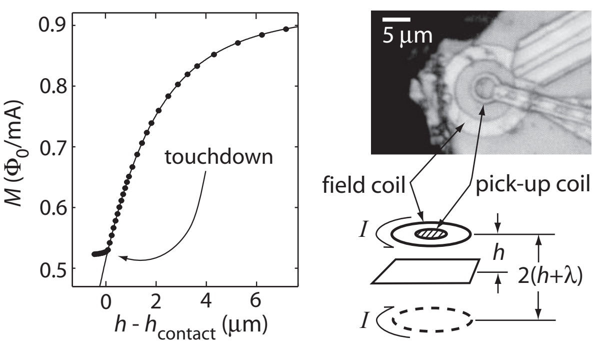

FIG. 1: Left: Field coil–pick-up loop mutual inductance M against height above the sample; $h_{\rm contact}$ is the height at which the corner of the susceptometer chip contacts the sample. The line is a fit of eq. 1. Right: photograph of the front end of the susceptometer, and a schematic of the susceptometer-sample geometry. The dashed loop is the image field coil.

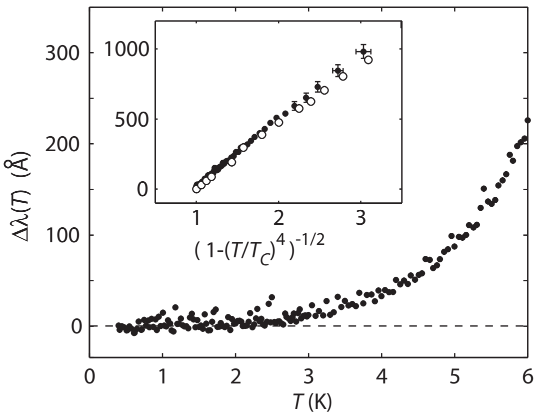

FIG. 2: $\Delta\lambda(T) \equiv \lambda(T) - \lambda(0)$ of Pb. A drift has been subtracted as described in the text. Inset: Open symbols: measurement of Gasparovic and McLean [29]. Filled: present data; the vertical error bars are the systematic ±5% error on all $\Delta\lambda$ data in this Letter.

the superconductor response field as an image coil placed a height $2h_{\rm eff}$ beneath the field coil, where the effective height $h_{\rm eff} = h + \lambda$. The flux through the pick-up coil (radius a) is taken as the field at its center times its area. All coils are taken parallel to the surface, neglecting the alignment angle. These approximations give a conversion between M and $h_{\rm eff}$:

$$M = \frac{\mu_0}{2}\pi a^2 \left(\frac{R^2}{(R^2 + 4h_{\rm eff}^2)^{3/2}} - \frac{1}{R} \right). \qquad (1)$$

To measure changes in λ the susceptometer is placed in contact with a flat *ab*-plane area of the sample, and the sample temperature T is varied. The contact is sufficient to overcome system vibration but weak enough to avoid excessive thermal coupling (the susceptometer is maintained at $\approx$ 0.3 K). The contact keeps h constant, so changes to $h_{\rm eff}$ are changes in λ_{ab}: we are using the fact that, for $h \gg \lambda$, the response field of the superconductor is a function of $h_{\rm eff}$ alone [27]. In this sense, the physical origin of eq. 1 is irrelevant as long as it accurately models the dependence of M on h, which Fig. 1 shows to be the case. R and a are fitting parameters; they approximately match the actual dimensions of the susceptometer, but with precise values that vary with alignment angle and sample surface orientation; R and a are obtained separately for each sample. Crucial to this measurement, if the susceptometer is over a flat ab surface then the relevant penetration depth is λ_{ab} alone, even with nonzero alignment angle [27]. Due to the alignment angle, the minimum h is $h_{\rm contact} \approx 3$ μm.

What is the accuracy of measurement of $\Delta\lambda$? The fit to eq. 1 returns R and a consistent with a particular conversion constant, in μm/V, between h and applied voltage to the scanner, which is measured separately, in this work with ±5% accuracy. All $\Delta\lambda$ quoted in this work have this ±5% systematic uncertainty. Also, deviations from the fit give errors on $\Delta\lambda$ up to 1.5%. At large λ the assumption that the response field is a function of $h + \lambda$ breaks down; numerical simulation shows that, at $h = 3$ μm and $\lambda(0) = 5000$ Å, this assumption leads $\Delta\lambda$ to be underestimated by 1% at $\Delta\lambda = 5000$ Å and 4% at 10,000 Å. Thermal gradients from the susceptometer-sample contact have minimal effect: control tests on sapphire show that the change in $h_{\rm eff}$ attributable to these gradients is no more than $\sim$ 20 Å for T varying between 1 and 8 K. By tracking T_c of LaFePO, we determine that contact locally cools the sample by only ∼40 mK at $T = 6$ K.

As a test we measure the penetration depth of a lump of industrial-grade lead; the results and comparison with an earlier measurement are shown in Fig. 2. A $\sim$ 100 Å-scale downward drift of $h_{\rm eff}$, due to the sensor gradually pressing a dent into the soft lead surface, is subtracted from our data. The drift rate is T-independent and was measured separately from the data in Fig. 2, so the flatness of $\Delta\lambda$ at low T is real.

Fig. 3 shows the main result of this work: $\Delta\lambda_{ab}$ vs. T for two LaFePO crystals (at the points indicated in Fig. 4(e) and (f)). For both data sets $\Delta\lambda$ was recorded over multiple temperature sweeps, both warming and cooling, and found to follow the same path. λ is seen to vary nearly linearly with temperature. Fitting $\Delta\lambda = A + BT^n$ over $0.7 < T < 1.6$ K, from top to bottom n=1.22(4), 1.13(10) and 0.97(5) are obtained for the three curves in Fig. 3(a).

Photographs of the two LaFePO specimens are shown in Fig. 4. An example of a susceptibility scan (a scan of the spatial variation in M) is shown in Fig. 4(c). Because M varies strongly with h, features in individual scans mainly reflect surface topography. More useful is comparison of scans at different T: *e.g.* Fig. 4(d) shows a map of $h_{\rm eff}(3\ {\rm K}) - h_{\rm eff}(0.4\ {\rm K})$ on sample #2, which

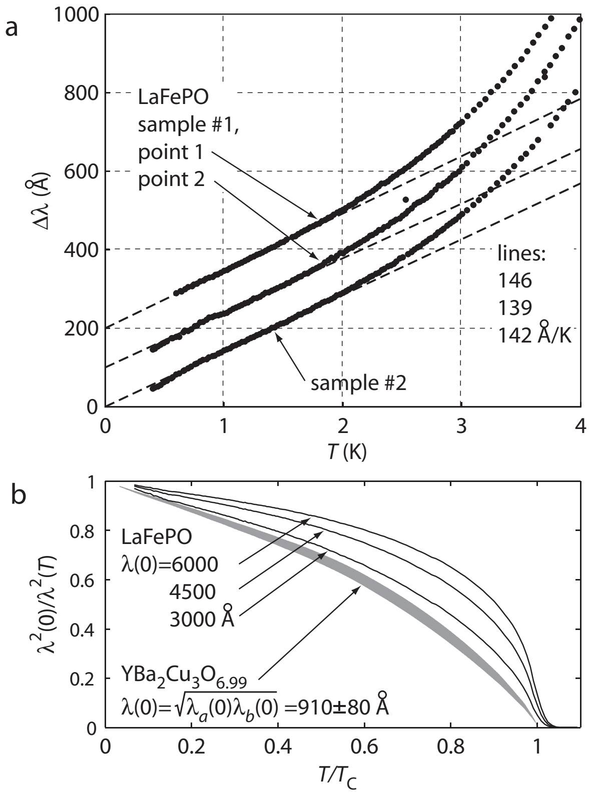

FIG. 3: Top: $\Delta\lambda$ of two LaFePO specimens, at the points indicated in Fig. 4. The lines were fit over $0.7 < T < 1.6$ K. Bottom: black lines are possible superfluid densities for LaFePO sample #1, point 2, with different $\lambda(0)$. Shaded area: superfluid density of $YBa_2Cu_3O_{6.99}$ $(1/(\lambda_a\lambda_b))$, from [30] and [31]; the width of the shaded area reflects uncertainty in $\lambda(0)$.

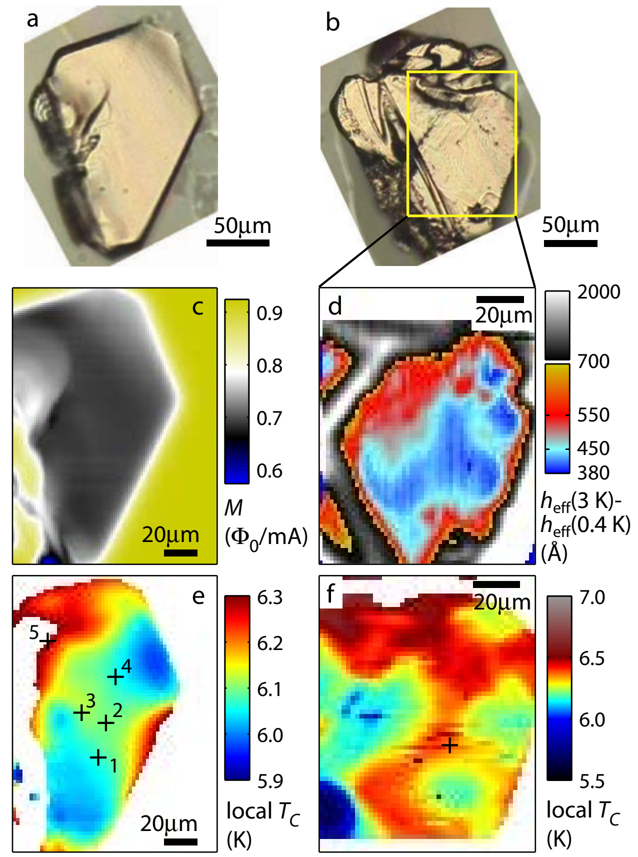

FIG. 4: (a,b) LaFePO specimens #1 and #2. (c) Susceptibility scan of #1 at $T = 0.4$ K. Over the superconductor M is reduced from its vacuum level by the Meissner response. (d) Change in $h_{\rm eff} = h+\lambda$ between 0.4 and 3 K over specimen #2. (e,f) Maps of local T_c, over the same areas as in (c) and (d). The crosses indicate the points where $\Delta\lambda(T)$ data were collected.

reveals two useful facts: (1) Where the sample surface is not flat λ_c mixes in strongly and $\Delta h_{\rm eff}$ is large; one needs to be at least ~ 10 μm from an edge to measure λ_{ab}. (2) Where the sample is flat, and $\Delta h_{\rm eff} = \Delta\lambda_{ab}$, $\Delta\lambda_{ab}$ is homogeneous to within $\sim 5\%$; areas of moderately increased $\Delta h_{\rm eff}$ are areas where the surface is pitted.

Maps of local T_c, shown in Fig. 4(e) and (f), are made by performing susceptibility scans at various T and extracting $\Delta h_{\rm eff}(T)$. Most areas of the samples show weak tails of superfluid density persisting a few 0.1 K beyond the dominant local T_c (and in places beyond 7 K), which give uncertainty to estimates of the dominant T_c. Our criterion for determining local T_c is based on superfluid density: the $\lambda(0) = 4500$ Å superfluid density curve in Fig. 3(b) is taken as a reference, and in the scans the local $\Delta h_{\rm eff}$ is taken as $\Delta\lambda$. The local $\lambda(0)$ (which varies with topography) and T_c are varied to obtain the best fit to the reference. Varying the reference $\lambda_{ab}(0)$ by 1000 Å varies the calculated T_c's by ~ 0.1 K.

$\lambda(0)$ could in principle be extracted from the geometry of the susceptometer and its contact with the sample surfaces; however the uncertainties are large. From the variation of M with surface orientation and SEM images of the susceptometer a plausible contact point on the susceptometer can be identified, and comparison with the lead specimen indicates that $\lambda_{ab}(0)$ of LaFePO likely falls in the range 3500–5500 Å.

At the five points on sample #1 indicated in Fig. 4(e), $d\lambda/dT$ over the linear portion of $\Delta\lambda$ is 146, 139, 136, 150 and 205 Å/K, and at the single measurement point on sample #2, 142 Å/K. The 205 Å/K measurement was at a point with significant topography and can be excluded. Taking into account the 5% and 1.5% uncertainties, $d\lambda/dT$ is 143±15 Å/K.

The superfluid densities $\rho_S \equiv 1/\lambda^2$ of LaFePO and $YBa_2Cu_3O_{6.99}$ are compared in Fig. 3. The linear portion of ρ_S persists to a similar fraction of T_c in both materials, indicating that the nodes in LaFePO must be well-formed, as in $YBa_2Cu_3O_{6.99}$— the magnitude of the gap on either side of the nodes must be similar. In contrast, accidental nodes in nodal s orders may result in very asymmetric + and − lobes [32]. Also apparent in Fig. 3

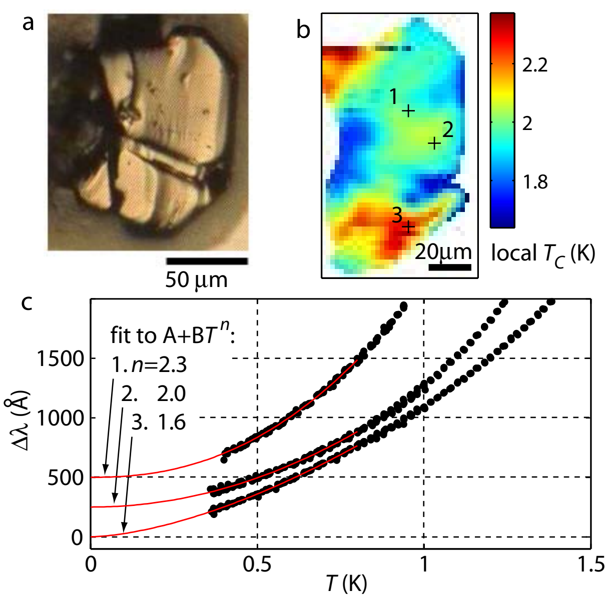

FIG. 5: (a) Photograph and (b) map of local T_c of a $T_c \approx$ 2 K specimen. The relative error on local T_c's is $\sim$ 0.1 K. (c) $\Delta\lambda(T)$ at the three points indicated in (b). Because the sample surface is not flat, these measured $\Delta\lambda$ include some fraction of λ_c.

is that ρ_S of LaFePO rises very sharply on cooling just below T_c. If the pairing is mediated by magnetic fluctuations then such a sharp rise may result from a gapping-out of low-frequency, pair-breaking fluctuations [33].

An intriguing possibility of highly asymmetric nodal s orders is that scattering might lift the nodes altogether, resulting in exponential rather than T^2 dependence of $\Delta\lambda$ at low T [32]. In this work we also studied a $T_c \approx$ 2 K LaFePO specimen. The reason for the anomalously low T_c is unclear; electron probe microanalysis shows no impurities (to the $\frac{1}{2}$% level), and no anomalies in the La, Fe and P concentrations (to within $\frac{1}{2}$, $\frac{1}{2}$, and 2%).

Fig. 5 a shows the 2 K specimen. Compared with the 6 K samples T_c varies more widely both on large and small length scales: at each point studied strong tails of superfluid density extend well above the dominant local T_c. $\Delta\lambda$ versus temperature was recorded at three locations. Fitting to a power law over $T < 0.8$ K, exponents n=2.3±0.1, 2.0±0.1 and 1.6±0.1 are obtained. The dominant local T_c's at these three locations are 2.1±0.2, 2.0±0.1 and 2.5±0.1 K, respectively; deviations from n=2 may in part reflect variation in the local T_c (or local T_c distribution). On data up to 0.8 K, power law fits perform better than exponential fits. Within our precision and temperature limits, $\Delta\lambda(T)$ is consistent with dirty nodal superconductivity, and with many of the measurements on As-based materials.

In conclusion, we have observed a linear temperature dependence of $\Delta\lambda_{ab}(T)$ below $\sim T_c/3$ in LaFePO and accurately measured its slope, 143±15 Å/K, using a local technique. The large temperature range of linear $\lambda_{ab}(T)$ indicates well-formed nodes.

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