Flux-Line Lattice Distortion in $PrOs_4Sb_{12}$

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We report that the flux-line lattice in the cubic superconductor $PrOs_4Sb_{12}$ is strongly distorted from an ideal hexagonal lattice at very low temperatures in a small applied field. We attribute this to the presence of gap nodes in the superconducting state on at least some Fermi-surface sheets.

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$PrOs_4Sb_{12}$ belongs to the structural family of filled skutterudites [1]. These structures have cubic lattices and tetrahedral (T_h) point group symmetry with threefold rotation symmetries along the cube diagonals, but no fourfold rotation axes. As a consequence, combinations of the principal directions that are not cyclical permutations are not equivalent ($xyz = yzx \neq yxz$). Thus, once a field is applied along one crystal axis, say the c axis, the a axis and the b axis are distinguishable.

An interesting feature of the fundamental physics of $PrOs_4Sb_{12}$ is its strongly-correlated itinerant-electron normal state implied by the large jump in its specific heat at the superconducting transition [2]. Also apparent in the specific heat is a broad peak at 2 K that is attributed to transitions between different local crystal field states of the Pr $4f^2$ electrons. A level crossing is then believed to explain an observed thermodynamic transition in a field of about 4.5 T at low temperature [3,4] to a field induced ordered phase (FIOP). Neutron scattering in a field applied parallel to c revealed a weak antiferromagnetic moment parallel to the b axis in the FIOP, consistent with an antiquadrupolar ordering with order parameter O_{bc} [4].

The strongly-correlated electronic state and the possible propensity of quadrupolar fluctuations raises the possibility that the superconductivity could be unconventional with the pairing eventually mediated by these fluctuations. The experimental evidence for an unconventional superconducting state has, however, been rather mixed. The sensitivity of the superconducting transition temperature, T_c, to disorder produced by doping is much less than the Abrikosov-Gorkov dependence expected for a one band unconventional superconductor [5]. In contrast with this, the magnitude of the jump in the specific heat at T_c is very sensitive to sample quality. The superconducting transition is split in samples with the lowest normal-state residual resistivity [6], and the double transition remains well resolved as a function of magnetic field, giving rise to two closely spaced almost parallel critical field curves [7]. The origin of the double transition, however, remains unresolved; it could be a signature of a multiple component order parameter or alternatively of some subtle phase segregation. For samples with a higher residual resistivity, the specific heat jump is smaller and only one transition is discernible. Another transition, in the anisotropy of the thermal conductivity [8], is seen at a lower field. Denoting $\kappa_i(H_j)$ to be the thermal conductivity parallel to the crystal i axis with the field applied along the j axis, the surprising result is that experimentally, $\kappa_c(H_a) \neq \kappa_c(H_b)$ or equivalently, $\kappa_a(H_c) \neq \kappa_b(H_c)$ at low field (breaking the point group symmetry at zero field); the transition occurs at a field $H^* \approx 0.8$ T, above which this anisotropy vanishes abruptly. It is then tempting to suggest that while the high field phase might correspond to a conventional isotropic superconducting state, a lower symmetry unconventional component of the order parameter appears below H^*. Possible theoretical order parameter symmetries have been discussed by Goryo [9], who concluded that the order parameter symmetry most compatible with the thermal conductivity is $s + id$, with a strongly anisotropic s-state gap having "accidental" point nodes (strong minima) along the crystal axes. All but two of these accidental nodes are removed when the d component appears below H^*. This is consistent with muon spin relaxation (μSR) experiments that show that the low field state breaks time reversal symmetry [10], and a careful study of the temperature dependence of the London penetration depth [11] that suggests that the superconducting gap has point nodes. A Ginzburg-Landau theory for this model order parameter has been developed by Matsunaga *et al.* [12]. In the limit of $T \approx T_c$ where such a theory is valid, the authors predict that the flux-line lattice (FLL) should also be deformed from an ideal hexagonal lattice.

Small angle neutron scattering (SANS) measures the Fourier components of the magnetic field distribution in a sample and thus is a direct probe of the FLL geometry in the bulk of a material. In general, deviations from an ideal hexagonal lattice arise due to both anisotropy of the

Fermi surface and anisotropy of the superconducting gap. With due care to distinguish between these two sources of deformation, SANS studies of the FLL are then a powerful probe of the symmetry of unconventional superconductivity as illustrated by recent studies of UPt_3 [13,14] and Sr_2RuO_4 [15]. In this Letter, we report the results of our study of the geometry of the FLL in $PrOs_4Sb_{12}$.

Measurements were performed on a large ($7 \times 8 \times 4$ mm) single crystal plate comprising of many faceted platelets of mm dimensions, grown at Tokyo Metropolitan University by the flux growth method [16,17], and spark cut along the crystal axes. The orientation and mosaic of the entire sample was measured on the D23 neutron diffractometer at the ILL (Institute Laue Langevin, Grenoble). The intensities of different diffraction peaks prove that the crystal was not twinned; the permutation "*abc*" of the crystal axes was the same throughout the specimen. The overall crystal mosaic was less than 1.5°. The specific heat measured on a small piece cut from the sample is comparable to that of the sample used in Ref. [8]. We note that the height of the Schottky peak at 2 K differs slightly between these and other samples, which could indicate the inclusion of up to 25% flux (principally Sb).

The SANS measurements were made with the D22 apparatus at the ILL. The neutron collimation and the sample-detector distances were 14.4 m and the mean neutron wavelength was 11 Å. The sample was tightly clamped to a thin copper plate bolted to the mixing chamber of a dilution refrigerator and aligned with its thickness parallel to the direction of an applied field. The sample and magnet could be rotated together through small "rocking" angles about the incident neutron beam direction to satisfy the Bragg condition for small wave vector transfers in the XY plane. The crystal had its c axis parallel to the field (Z), its a axis vertical (Y), and its b axis horizontal (X).

Figure 1(a) shows the difference in scattering seen on the XY detector at 0.2 T relative to that in zero field at a temperature of 100 mK. The image has been summed over several rocking angles chosen to satisfy the Bragg condition for scattering to the right hand and upper halves of the detector. Images obtained with the background scattering measured above $T_c = 1.85$ K at 0.2 T, or by forming the FLL following different field histories (cooling in a constant field, zero field cooling, and after oscillating the field) gave equivalent results. The positions of the peaks in intensity define a reciprocal lattice unit cell of area B/ϕ_0, confirming that the scattering is due to a FLL composed of singly quantized vortices (ϕ_0 is the flux quantum). Peaks in the lower left quadrant are weaker or not present because the sample and field were not rotated to the angles that fulfill the Bragg condition for diffraction in those directions. The intensity of the upper right peak as a function of the rocking angle is shown in Fig. 1(b). Assuming that 100% of the sample mass contributes to the integrated intensity we estimate [18] a

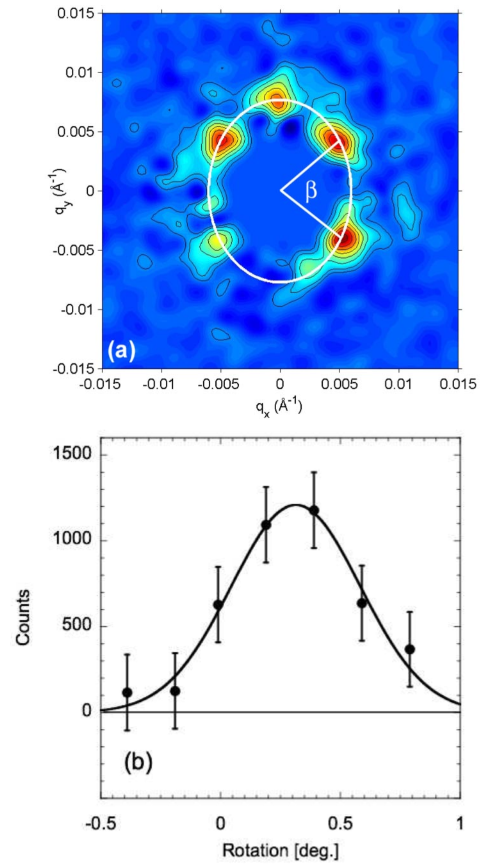

FIG. 1 (color online). Panel (a) shows the difference between the XY detector images recorded at 0.2 T and zero field, averaged over several rocking angles of the field and sample (contours are drawn at 0.25, 0.5, 1, 1.5, 2, 2.5, 3, and 3.5 counts/hour/pixel [1 detector pixel = (8 mm)^2]). The region immediately around the straight through beam is masked from the image. Panel (b) shows the integrated intensity of the upper right-hand peak as a function of the rotation angle of the sample and field about the vertical (Y) axis. The line is a Gaussian function.

value for the penetration depth, $\lambda = 3600 \pm 100$ Å (3350 Å, if only 75% of the sample contributes), in excellent agreement with the value obtained by μSR [19].

We now discuss the geometry of the FLL and its orientation with respect to the crystal lattice. For all the fields and temperatures studied, a unique orientation of the FLL was seen. The FLL geometry may be quantified by the angle between two reciprocal lattice vectors, β in Fig. 1(a), or equivalently the eccentricity, e, of the ellipse passing through the lowest order diffraction spots ($e^2 = 1 - \cot(\beta/2)^2/3$). In Fig. 2 we show the variation of β with field and temperature.

For a perfect lattice with no tilt mosaic and with only a few fortuitous choices of rocking angle, a deformation of the measured positions of maximum intensity on the detector can arise if the Bragg condition is satisfied only for neutron wavelengths in the tails of the incident intensity profile [20]. In the most extreme limit, this artifact can at most account for an apparent $e^2/2 \approx \delta\lambda/\lambda = 0.1$, where $\delta\lambda/\lambda$ is the fractional spread of incident wavelengths; this is significantly smaller than the deformation from a perfect hexagonal FLL observed. In the present experiment, any such artifact would be much smaller still because the range of rocking angles over which the Bragg condition is satisfied is large. Crystal defects can also impose a preferred orientation of the FLL as seen in $YBa_2Cu_3O_7$ [21]; however, they do not lead to a change in the eccentricity of the lattice. In the present case, the metallurgical scattering is anyway only weakly anisotropic and appears comparable along the a and b axes.

Theoretically, the FLL adopts the geometry and orientation with respect to the crystal axes that minimizes the free energy arising from the interactions between the vortices. This free energy can be calculated starting from London's theory that relates the current, $\vec{j}$, to the magnetic vector potential, $\vec{a}$, as $\frac{4\pi}{c}\vec{j} = -\frac{1}{\lambda^2}\vec{\vec{m}}_L^{-1}\vec{a}$ (where $\vec{\vec{m}}_L$ is a normalized London effective mass tensor, $\mathrm{Det}(\vec{\vec{m}}_L) = 1$). The vortex cores are included in the calculation by introducing an isotropic cutoff for the interaction at small distances. Nonlocal corrections to the London theory become increasingly important the smaller κ_{GL} (the Ginzburg-Landau parameter $\kappa_{GL} \approx 29$ for $PrOs_4Sb_{12}$). We consider first the theoretical effect on the FLL geometry of the nonlocal corrections to London's theory arising from fourfold and higher anisotropies of the Fermi surface. These corrections to the Free energy are proportional to the magnetic field to lowest order and their role in determining the geometry of the FLL has been well documented both theoretically [22] and experimentally [23] for the borocarbide superconductors. Although the FLL deformation has to be calculated numerically, in all the cases studied these terms resulted in a β that increased at least linearly with field from 60° at zero field up to a field at which the lattice becomes square. Since in our measurements β remains close to 80° as the field is decreased, such terms alone cannot explain the deformation we observe. However, if all else is equal, for the T_h crystal point group symmetry, we note that nonlocal terms could break any degeneracy between otherwise equivalent FLL orientations.

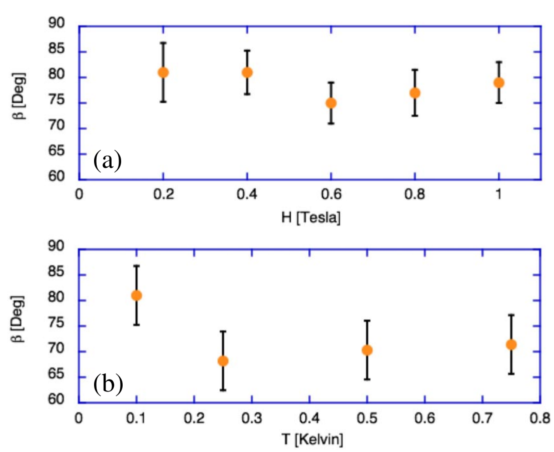

FIG. 2 (color online). The field and temperature dependence of β, the angle between two reciprocal lattice vectors of the FLL. The vertical bars through the points indicate half of the angular width (FWHM) of the peak intensities on the multidetector.

A field independent anisotropy would result from an anisotropic $\vec{\vec{m}}_L$ [24]. For an isotropic superconducting gap, $\vec{\vec{m}}_L$ is the same as the (normalized) normal-state mass tensor, $\vec{\vec{m}}_N$. To explain the observed anisotropy of the FLL, we require a mass anisotropy of $1 - (m_N)_b/(m_N)_a = e^2 \approx 0.5$. The T_h crystal symmetry of $PrOs_4Sb_{12}$, however, imposes that $\vec{\vec{m}}_N$ is isotropic in the limit of zero field. To be consistent with the field independence of e we observe, a large normal-state mass anisotropy would have to appear below 0.2 T and remain approximately unchanged up to at least 1 T. To our knowledge, no effective mass anisotropy has been reported in the low field normal-state properties of $PrOs_4Sb_{12}$. Further the cyclotron masses so far measured in quantum oscillation experiments under higher fields are found to be almost isotropic [25]. The FLL deformation we observe cannot therefore be attributed to a field induced anisotropy of the normal-state effective mass.

An anisotropic superconducting gap Δ gives a second cause of anisotropy. Specifically, in the Ginzburg-Landau region close to T_c, $\vec{\vec{m}}_L^{-1} \propto \langle v_{fi} v_{fj} |\Delta|^2 \rangle_{FS}$ (v_{fi} is the i^{th} component of the Fermi velocity and $\langle\rangle_{FS}$ denotes an average over the Fermi surface). However, for anisotropic conventional superconductivity, one again finds that $\vec{\vec{m}}_L = \vec{\vec{m}}_N$ in the limit of zero temperature ($k_B T < \Delta_{min}$, where Δ_{min} is the minimum gap). Thus, for a conventional but anisotropic order parameter, although a deformation of the FLL can occur at higher temperature, a perfect hexagonal FLL is expected at low temperatures and fields. In contrast to this, the deformation of the FLL we observe increases at the lowest temperature. Such a temperature dependence can however occur theoretically for an unconventional superconductor with symmetry enforced gap nodes. It arises since the coherence length is formally infinite along the node directions [26]. For equal nodes along both a and b directions, a deformed FLL is predicted with two equivalent FLL orientations. We find based on Ref. [26] that for nodes along only one of these directions that the predicted FLL is also deformed from hexagonal with a unique orientation having a reciprocal lattice vector along the major axis of the ellipse defining the lattice geometry and parallel to the node direction. Further, the deformation depends only weakly on the field. This could explain our data if $PrOs_4Sb_{12}$ has a gap node parallel to the crystal a axis in low fields.

For a pure unconventional order parameter, it is likely that a small concentration of defects (giving resonant scattering) would actually strengthen the deformation from a hexagonal FLL (of course, the scattering must not be so strong as to suppress the unconventional component of the superconductivity altogether). For an order parameter where the Fermi-surface average of the gap is zero ($\langle\Delta(\mathbf{k})\rangle_{FS} = 0$), impurities give rise to a finite density of states at zero energy at $T = 0$ [27]. If the order parameter has nonaccidental nodes, the superconducting gap can be suppressed completely over a small solid angle around the gap node directions [28], thus reinforcing the mechanism responsible the FLL distortion. For a gap with accidental nodes including the mixed state form proposed in Ref. [9], the effect of defect scattering is to reduce any anisotropy. When larger samples of better quality become available, a comparative SANS study would be highly worthwhile to distinguish between these possibilities.

The deformation of the FLL we observe could give rise directly to a small twofold symmetry of the thermal conductivity [8]. The thermal conductivity would also respond directly to the gap anisotropy of an unconventional superconducting order parameter. In the thermal conductivity measurements, the *ab* anisotropy, however, disappeared abruptly above $H^* = 0.8$ T, while above this field a fourfold anisotropy appeared. No significant change in the FLL geometry was found up to 1 T (the maximum measurement field available). One possible explanation is that nonlocal corrections at high field (where a fourfold anisotropy appears in the thermal conductivity) compensate the reduced deformation due to the disappearance of the twofold anisotropy. However, it is also possible that H^* is sample dependent and is simply higher than 1 T in the present sample: transitions at slightly above 1 T [29] and at 1.5 T [30] have been reported in different samples in independent magnetization studies.

To conclude, we have found that the FLL in $PrOs_4Sb_{12}$ is deformed from a perfect hexagonal lattice in the limit of low temperature. The weak field dependence of the deformation means that it cannot be explained by nonlocal corrections arising from an anisotropy of the Fermi surface alone, and a substantial part of the distortion must be due to an anisotropic superconducting state. In detail, this requires that the gap minima are indistinguishable from zero on an energy scale corresponding to 100 mK ($k_B T_c/20$). This strongly suggests that the gap contains nodes on some Fermi-surface sheets that are rigorously enforced by symmetry and are not just accidental, more so if the sample quality is less than perfect. This requires a pure unconventional order parameter on these sheets rather than a mixed state such as $s + id$ that might describe the superconductivity on other sheets. In this sense, our interpretation departs from the model put forward in Ref. [9].

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[1] B. C. Sales, *Handbook on the Physics and Chemistry of Rare Earth*, edited by K. A. Gschneidner, Jr., C. G. Bunzli, and V. K. Pecharsky (Elsevier Science, Amsterdam, 2003), Vol. 33, Chap. 211.
[2] E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple, Phys. Rev. B **65**, 100506(R) (2002).
[3] Y. Aoki, T. Namiki, S. Ohsaki, S. R. Saha, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **71**, 2098 (2002).
[4] M. Kohgi, K. Iwasa, M. Nakajima *et al.*, J. Phys. Soc. Jpn. **72**, 1002 (2003).
[5] N. A. Frederick, T. D. Do, P.-C. Ho, N. P. Butch, V. S. Zapf, and M. B. Maple, Phys. Rev. B **69**, 024523 (2004).
[6] R. Vollmer, A. Faißt, C. Pfleiderer *et al.*, Phys. Rev. Lett. **90**, 057001 (2003).
[7] M.-A. Measson, D. Braithwaite, J. Flouquet *et al.*, Phys. Rev. B **70**, 064516 (2004).
[8] K. Izawa, Y. Nakajima, J. Goryo *et al.*, Phys. Rev. Lett. **90**, 117001 (2003).
[9] J. Goryo, Phys. Rev. B **67**, 184511 (2003).
[10] Y. Aoki, A. Tsuchiya, T. Kanayama *et al.*, Phys. Rev. Lett. **91**, 067003 (2003)
[11] Elbert E. M. Chia, M. B. Salamon, H. Sugawara, and H. Sato, Phys. Rev. Lett. **91**, 247003 (2003)
[12] Y. Matsunaga, M. Ichioka and K. Machida, Phys. Rev. Lett. **92**, 157001 (2004).
[13] A. Huxley, P. Rodière, D. M. Paul, N. van Dijk, R. Cubitt, and J. Flouquet, Nature (London) **406**, 160 (2000).
[14] A. Huxley, *Vortices in Unconventional Superconductors and Superfluids.*, edited by G. Volovik and N. Schopohl (Springer-Verlag, Berlin, 2001), p. 301.
[15] P. G. Kealey, T. M. Riseman, E. M. Forgan *et al.*, Phys. Rev. Lett. **84**, 6094 (2000).
[16] N. Takeda and M. Ishikawa, Physica B (Amsterdam) **259-261**, 92 (1999).
[17] E. D. Bauer, A. Slebarski, E. J. Freeman, C. Sirvent, and M. B. Maple, J. Phys. Condens. Matter **13**, 4495 (2001).
[18] E. H. Brandt, Phys. Rev. Lett. **78**, 2208 (1997).
[19] D. E. MacLaughlin, J. E. Sonier, R. H. Heffner *et al.*, Phys. Rev. Lett. **89**, 157001 (2002).
[20] R. Cubitt, E. M. Forgan, D. McK. Paul *et al.*, Physica B (Amsterdam) **180-181**, 377 (1992).
[21] S. T. Johnson, E. M. Forgan, S. H. Lloyd *et al.*, Phys. Rev. Lett. **82**, 2792 (1999).
[22] V. G. Kogan, M. Bullock, B. Harmon *et al.*, Phys. Rev. B **55**, R8693 (1997).
[23] D. McK. Paul, C. V. Tomy, C. M. Aegerter *et al.*, Phys. Rev. Lett. **80**, 1517 (1998).
[24] L. J. Campbell, M. M. Doria and V.G. Kogan, Phys. Rev. B **38**, 2439 (1988).
[25] H. Sugawara, S. Osaki, S. R. Saha *et al.*, Phys. Rev. B **66**, 220504(R) (2002).
[26] M. Franz, I. Affleck and M. H. S. Amin, Phys. Rev. Lett. **79**, 1555 (1997).
[27] G. Preosti, H. Kim, and P. Muzikar, Phys. Rev. B **50**, 13638 (1994).
[28] Yu. S. Barash, A. A. Svidzinski, and V. P. Mineev, JETP Lett. **65**, 638 (1997).
[29] S. Drobnik, K. Grube, C. Pfleiderer *et al.*, International Conference on Strongly Correlated Materials, Karlsruhe, Germany, 2004 [Physica B (to be published)].
[30] T. Tayama, T. Sakakibara, H. Sugawara, Y. Aoki, and H. Sato, J. Phys. Soc. Jpn. **72**, 1516 (2003).