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Triangular to Square Flux Lattice Phase Transition in $YBa_2Cu_3O_7$

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We have used the technique of small-angle neutron scattering to observe magnetic flux lines directly in a $YBa_2Cu_3O_7$ single crystal at fields higher than previously reported. For field directions close to perpendicular to the CuO_2 planes, we find that the flux lattice structure changes smoothly from a distorted triangular coordination to nearly perfectly square as the magnetic induction approaches 11 T. The orientation of the square flux lattice is as expected from recent *d*-wave theories but is 45° from that recently observed in $La_{1.83}Sr_{0.17}CuO_{4+\delta}$.

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The technique of small-angle neutron scattering (SANS) from flux lines has a long and honorable record in measuring the properties of flux lines in superconductors. However, it continues to bring new dividends, especially in unconventional superconductors, since important information about the nature of the superconducting state is often revealed by the flux line lattice (FLL) structure, for example [1–4]. The diffraction pattern not only reveals the coordination and perfection of the FLL, and its correlation with the crystal lattice, but also the absolute intensity may be used to determine the actual spatial variation of the magnetic field within the mixed state and the values of the coherence length and penetration depth [1,5,6]. In the simplest approximation, flux lines would order in a regular triangular FLL; however, anisotropy of the Fermi surface or of the superconducting order parameter can cause distortions of the triangular lattice or transitions to other structures. The simplest situation in a high-κ material is anisotropy of the magnetic penetration depth associated with effective mass anisotropy [7]; for example, the anisotropy in the *ab* plane of $YBa_2Cu_3O_{7-\delta}$ (YBCO) leads at low values of field to a corresponding distortion of triangular FLLs [8]. At lower values of κ, "nonlocal" effects are expected [9] and observed to give a variety of FLL distortions and transitions in, e.g., the borocarbides [4,10] and V_3Si [11,12]. If the superconducting order parameter has a different symmetry from that of the crystal, this can again be revealed via its effects on the FLL structure, for instance, in the *p*-wave superconductor Sr_2RuO_4 [6,13]. In general in *d*-wave superconductors [14–16], there is expected to be a tendency towards a square FLL as the field is increased and the anisotropic flux line cores overlap. This may be the cause of the FLL phase transition recently observed in overdoped $La_{1.83}Sr_{0.17}CuO_{4+\delta}$ (LSCO) at the comparatively low field of 0.4 T [2]. According to [14,15], the FLL nearest-neighbor directions should lie along the directions of the nodes of the order parameter, which would be at 45° to the Cu-O bonds in the superconducting layers. This is not, however, the orientation of the square FLL observed in LSCO [2]. The *orientation* may instead be controlled by band structure effects [17], even if the *symmetry* of the FLL is controlled by *d*-wave effects. It has been suggested that a peak effect in magnetization measurements on overdoped YBCO may be a signature of a continuous triangular-to-square FLL transition in this material at high fields [18]. However, others have suggested that there is a glass transition in this region [19]. Only by *direct* measurements may such suggestions be tested and the correlation between FLL and crystal lattice (or superconducting order parameter) be determined.

Our experiments were performed on the SANS-I instrument at SINQ, Paul Scherrer Institut, Switzerland. Cold neutrons (8 to 14 Å, with a FWHM wavelength spread of 10%) were collimated over distances from 4.5 to 15 m, depending on the field and hence q range required. The diffracted neutrons were registered on a $128 \times 128 \times 7.5\ \mathrm{mm}^2$ multidetector, which was similarly adjustable in distance from the sample. The undiffracted main beam was intercepted by a cadmium beamstop. A magnetic field of up to 11 T applied approximately parallel to the neutron beam, was provided by a cryomagnet with a field uniformity of 0.2% over a 1 cm sphere. A variable temperature insert containing He heat exchange gas allowed sample temperatures from 1.5 to 300 K. The sample was a 40 mg low–twin-density (a fully detwinned crystal of this size was not available) high-purity single crystal of YBCO grown in a $BaZrO_3$ crucible [20] and oxygenated close to O_7 by high-pressure oxygen treatment in order to reduce pinning by oxygen vacancies in the Cu-O chains [21]. It was therefore overdoped and had a T_c of 86 K. It was initially mounted with its **c** axis parallel to the field direction. In order to satisfy the Bragg condition for each diffraction spot in turn and hence establish the FLL structure, the cryomagnet and sample together

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could be rotated or tilted to bring the FLL Bragg planes to the appropriate small angles (~1°) to the incident neutron beam.

In Fig. 1 is shown the FLL diffraction pattern obtained at the low field of 1 T. The most obvious feature of this pattern is its fourfold symmetry which reflects the average fourfold symmetry of the twinned orthorhombic structure of our YBCO sample. However, the FLL structure itself has *triangular* coordination, and the symmetry of Fig. 1 arises from four orientations of distorted triangular FLLs, present in different domains in the sample, as was first observed by Keimer *et al.* [22]. The diffraction spots arising from these four triangular lattices are represented in Fig. 2. It appears that the *distortion* of the individual lattices arises mainly from the a/b anisotropy present in each orthorhombic domain in the crystal [23,24]. This interpretation was confirmed by measurements on an untwinned sample [8] which show diffraction spots distributed around an *ellipse* aligned with the **a** and **b** axes. The ratio of the principal axes of the ellipse should represent the anisotropy of the London penetration depth for $B_{c1} \ll B \ll B_{c2}$ [7]. The value we observe for the anisotropy ratio, γ_{ab}, in our sample is 1.28(1), whereas many estimates of this quantity are rather larger [25]. However, comparable values to ours were obtained by measurements on a separate untwinned sample using neutrons [8] and muons and torque magnetometry [26]. Our results are also corroborated by recent surface-sensitive measurements using a novel atomic-beam magnetic-resonance technique [27]. It seems likely that the precise value of γ_{ab} depends on the degree of perfection of the Cu-O chains along the **b** direction [28]. The *orientation* of the triangular FLLs has been ascribed to pinning of a pair of spots, and hence planes of flux lines, to the twin planes [23,24]. However, results reported later in this Letter also support the existence of a correlation between the nearest-neighbor FLL directions and the directions of zeros of the d-wave order parameter.

In Fig. 3, we show diffraction patterns taken at higher fields. The data taken at 7 T show a distortion of the triangular FLLs so that some of the weaker spots are closer to the strong spots, and others have moved towards the diagonals. There is clearly another source of distortion than pure a/b anisotropy. Finally at 11 T, the FLL has become almost exactly square, with the weak corner spots now playing the role of second order $\{1, 1\}$ spots of a square FLL instead of first order spots from a distorted triangular FLL. In order to investigate this steady change in the FLL structure with field, we rotated the crystal about the vertical axis in Fig. 3, so that the field was 5° from the **c** axis. This was done in order to break the degeneracy between those FLL structures giving strong vertical diffraction spots [Figs. 2(a) and 2(c)], and those giving strong horizontal spots [Figs. 2(b) and 2(d)]. Within anisotropic London theory, this small angle of rotation should make a negligible change to the FLL distortion. As shown in Fig. 4, we found that at high fields the FLL structures giving horizontal spots were suppressed and instead only the structures depicted in Figs. 2(a) and 2(c) were observed. The advantage of this

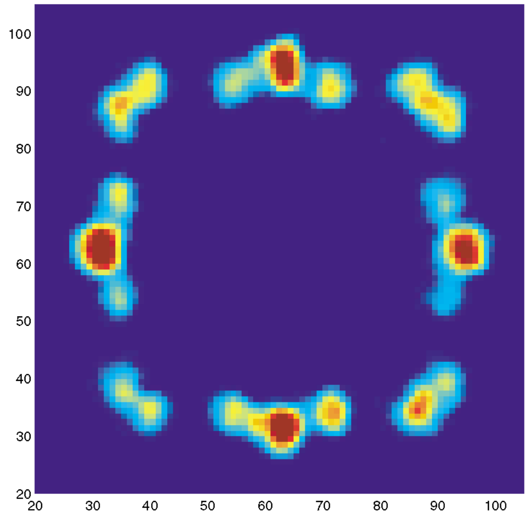

FIG. 1 (color). FLL diffraction pattern at 1 T. The figure shows the counts on the SANS multidetector at 4 K (minus backgrounds obtained above T_c) summed over a range of angles between the field direction and the neutron beam. Noise at the center of the picture has been masked. The cryostat was rocked by ±1° about horizontal and vertical axes, ensuring that all spots in the diffraction pattern from the sample are detected. The {110} directions, corresponding to twin plane directions, are vertical and horizontal in this picture. In all cases, the FLL was formed by applying the field above T_c and cooling.

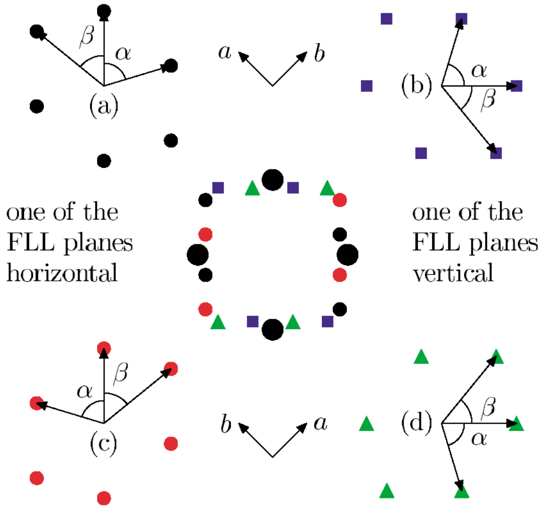

FIG. 2 (color). Schematic of diffraction patterns from four distorted triangular FLLs that together account for the pattern in Fig. 1. In each orthorhombic domain in the twinned crystal, there are two orientations of FLL [e.g., (a) and (b)], derived by taking a regular hexagonal pattern and distorting it by the a/b anisotropy [7]. The more intense pair of spots in each pattern is aligned with one of the {110} directions. The center figure is the superposition of the four FLL domains (a), (b), (c), and (d), which gives rise to the pattern in Fig. 1. The angles between reciprocal lattice vectors, α and β, are defined for use in Fig. 5.

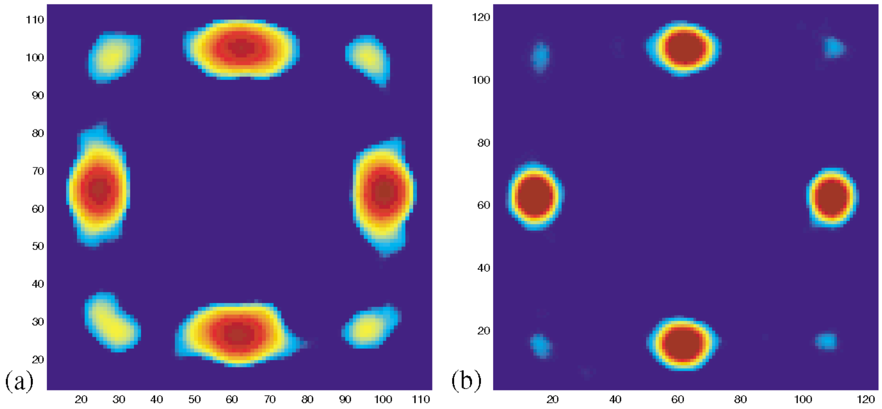

FIG. 3 (color). FLL diffraction patterns, as in Fig. 1 (but with a logarithmic intensity scale and smoothed to make the weaker spots more clearly visible), (a) at $B = 7$ T, (b) at $B = 11$ T, showing the change in position of the weaker spots as the field is increased.

arrangement is that the pairs of spots *near* the horizontal axis in Fig. 4 could be observed easily, without being overlaid by the strong ones *on* the axis. This allowed us to measure accurately the spot positions and hence the FLL distortion. Nevertheless, at high field, this pair of spots overlaps, but by assuming that the spot size is independent of field, we may estimate the angle between them even when they overlap. Further measurements of spot positions allow us to give a complete description of the FLL distortions versus field in terms of the angles between the FLL reciprocal lattice vectors. The results of this analysis are shown in Fig. 5. It is clear that the low field structure progressively changes with increase of field, although in our available field range the FLL never exactly reaches a perfectly square shape. This may partly be because the phase transition is at the extreme of our available field range, but it is also clearly a result of the orthorhombic structure of YBCO. As depicted in the inset to Fig. 5, the a/b anisotropy of each domain must, on symmetry grounds, distort a square lattice to a rectangular one, causing a slight splitting of the "square" spots from a twinned crystal such as ours.

We have further investigated [29] the temperature dependence of the FLL distortion shown in Fig. 5. We find that with increasing temperature, the FLL structure changes more towards triangular. Thus the boundary between square and triangular phases must curve up in field as temperature is increased. We would expect this if the triangular to square transition is due to d-wave effects, as the nature of the pairing becomes less important as k_BT becomes comparable with the magnitude of the gap. The shape of the phase boundary is similar to that seen in an overdoped sample by macroscopic measurements [19], but not the same as that proposed in Ref. [18]. Unlike LSCO [2], the *orientation* of the FLL that we observe is aligned as expected from d-wave theories [15,16]. It may be argued that twin planes, which are present in LSCO and YBCO are controlling the FLL orientation. To rule this out, measurements were also taken with the field at an angle to both sets of twin planes in our sample and the shape and orientation of the FLL was essentially unchanged. One should also note that the predicted difference in free energy between the two orientations of a square FLL is much larger than that between any triangular and the lower energy square orientation [15]. We also note that a similar correlation between FLL orientation and probable direction of d-wave nodes has recently also been observed in $CeCoIn_5$ [30]. Further

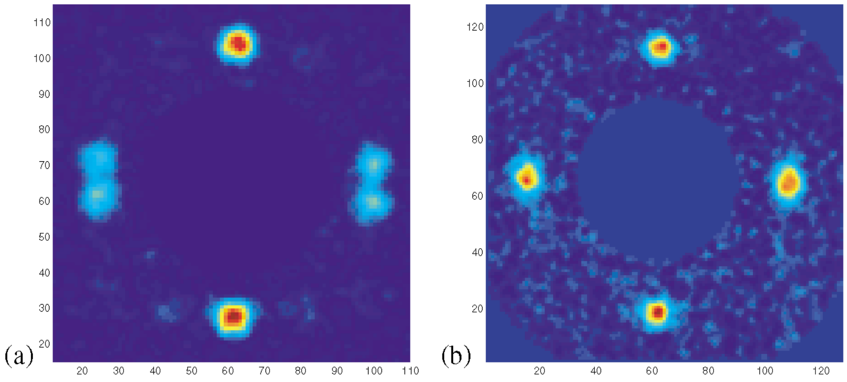

FIG. 4 (color). FLL diffraction patterns with the field rotated 5° from the **c** axis, to give only two FLL domains: (a) at $B = 7$ T and (b) at $B = 10.8$ T.

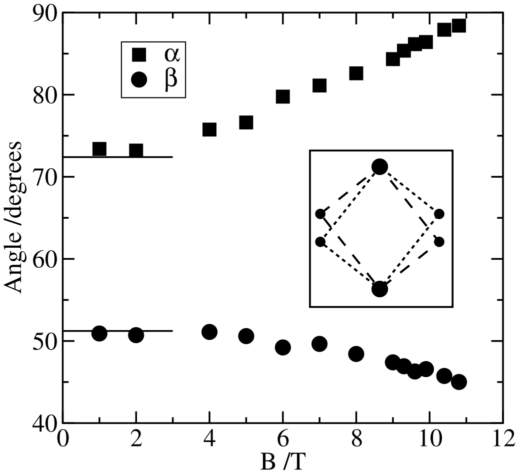

FIG. 5. Field variation at 5 K of two of the angles between reciprocal lattice vectors, α and β, depicted in Fig. 2. (Errors are comparable with the marker size.) All data were obtained with **B** parallel to the crystal **c** axis except the data for α at fields greater than 6 T, which were taken with **B** at 5° to **c** in order to resolve this angle more clearly (see text). A *regular* hexagonal lattice would have $\alpha = \beta = 60°$, and an exactly square one $\alpha = 90°$ and $\beta = 45°$. Also marked by horizontal lines are predictions of anisotropic London theory [7] for α and β, using a basal plane anisotropy, $\gamma_{ab} = 1.28$, and assuming that one pair of spots is tied to the $\{110\}$ directions. In the inset is shown the orthorhombic distortion from an exactly square pattern (exaggerated for clarity), expected in the two orthorhombic domains present in our crystal.

support of the *d*-wave origin of the triangular-square transition in YBCO is the value of the transition field, which is a similar order of magnitude to the predicted $0.15B_{c2}$ [15]. It should also be noted that a triangular to square transition in the FLL is predicted by the nonlocal London theory of Kogan *et al.* [9], in which an isotropic *s*-wave gap is assumed and is therefore not directly applicable to the FLL in YBCO. Furthermore, in a *d*-wave superconductor *s*-wave components of the order parameter are induced near the vortex core, resulting in a four-lobe structure [31] that cannot be predicted from Fermi surface anisotropy alone. Nevertheless, nonlocal and *d*-wave origins of the triangular to square transition are clearly related, since both result in core anisotropy, which becomes more important for intervortex interactions with increasing field. Finally, we note that our *bulk* observations of FLL structure are not in complete agreement with surface measurements by STM techniques [32,33].

In conclusion, using small-angle neutron scattering, we have directly observed a change from triangular to square coordination of the flux line lattice as a function of magnetic field in fully oxygenated $YBa_2Cu_3O_7$. This phase transition is most naturally interpreted as a consequence of the *d*-wave character of the order parameter, which is expected to be more prominent at high magnetic fields, where the flux line cores begin to overlap. The *orientation* of the FLL, with nearest neighbors along nodal directions is as expected from *d*-wave theory [15,16], unlike that in LSCO [2]. It appears that further investigation of these phenomena will allow stringent tests of theories of the order parameter in the mixed state of high-T_c materials as a function of angle of field and doping.

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