Observation of Hexagonally Correlated Flux Quanta In $YBa_2Cu_3O_7$

P. L. Gammel, D. J. Bishop, G. J. Dolan, J. R. Kwo, C. A. Murray, L. F. Schneemeyer, and J. V. Waszczak
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 26 August 1987)

The high-resolution Bitter pattern technique has been used to reveal the magnetic structure of single-crystal samples of high-T_c superconductor $YBa_2Cu_3O_7$ at 4.2 K. Typical patterns consist of hexagonally correlated, singly quantized vortices of flux $hc/2e$. That is, the structures are comparable to those that would be observed in conventional type-II superconductors under similar conditions.

PACS numbers: 74.70.Ya, 74.60.Ge

The way in which a superconductor breaks into normal and superconducting regions when magnetic flux is admitted involves fundamental aspects of its superconducting properties and metallurgy. Abrikosov's prediction[1] of a triangular array of vortices in the mixed state of type-II superconductors was central to his landmark contribution to the understanding of those materials. These vortices, each corresponding to a quantum of magnetic flux, were shown explicitly in high-resolution Bitter patterns by Träuble and Essmann[2] and by Sarma.[3] Similar information should be of use in the investigation of the fundamental properties and difficult materials properties of the new high-T_c materials. Some emerging theories[4] allow for the possibility of a flux quantum of hc/e rather than $hc/2e$, for example, and many experiments are explained in terms of inhomogeneities in the materials[5] or intrinsic inhomogeneities of the superconducting state.[6,7] It is even in question whether the materials are completely superconducting since magnetization data are often described in terms of the fraction of flux excluded by a sample of inconvenient shape and incompletely described microstructure. Our Bitter pattern experiments on $YBa_2Cu_3O_7$ crystals at 4.2 K show the individual vortices and indicate a strong tendency toward hexagonal ordering in the predominant patterns.

The Bitter pattern technique uses very small magnetic particles to sense the field at the surface of a magnetic material. The particles ("smoke") are made by evaporation of a magnetic material in a background of inert gas. The particles drift to the sample surface and preferentially "decorate" regions where there is a magnetic field. A sketch of the apparatus is shown in Fig. 1. Once on the surface, the particles are found to be immobile, presumably held in place by van der Waals forces. The sample is warmed to room temperature and the particle pattern is examined by scanning electron microscopy. The technique is limited to low fields and by its nature senses only the magnetic structure at a sample surface. Details of the technique as we use it are described in previous work.[8]

About fifteen successful decoration experiments have been performed on bulk samples of $YBa_2Cu_3O_7$. The single-crystal samples were grown from partially melting Y_2O_3-BaO-CuO mixtures and annealed in oxygen as described previously.[9] The crystals are known to be single-phase material with composition near stoichiometry but with many twins, usually in the form of long "domains." The material is orthorhombic with a large (1.17 nm) spacing between the planes perpendicular to the c axis. Usually the samples were flat platelets $\simeq 1$ mm in size with the broad surface perpendicular to the c axis, i.e., parallel to the basal plane. The magnetic field was oriented perpendicular to this surface. For some platelets the surface appeared smooth but for others waves and spirals arising in the crystal growth were apparent. The crystals were part of batches having $T_c \approx 92$ K although measurements of T_c were not made on the specific crystals decorated. Usually several small crystals were picked from a batch and decorated at the same time. The patterns considered successful on the

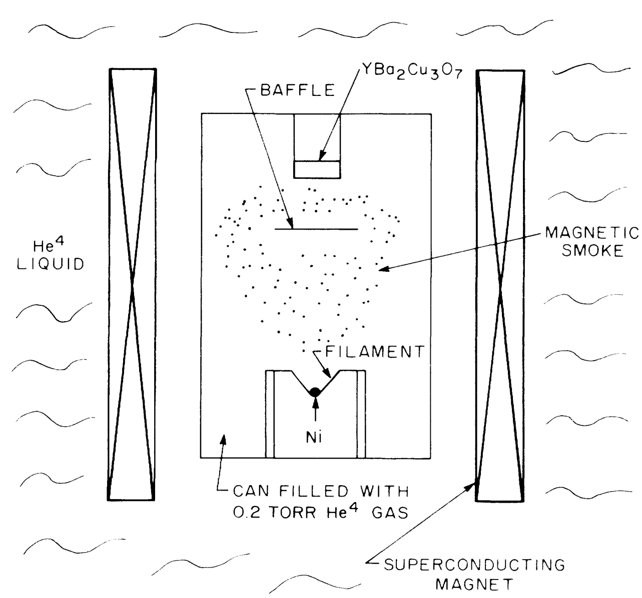

FIG. 1. Sketch of the decoration apparatus.

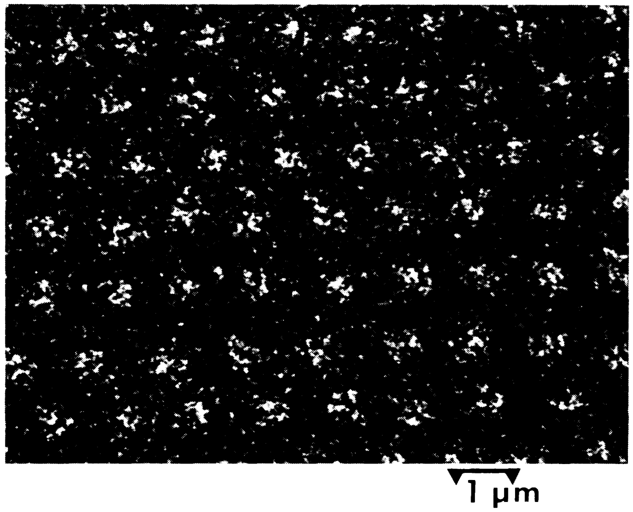

FIG. 2. Flux spots in a $YBa_2Cu_3O_7$ sample decorated after cooling in a field of 13 G.

different pieces were generally similar in character, implying a similarity in other properties. Experiments were conducted usually by cooling from room temperature in a fixed field, since this procedure gave the most uniform structures and seems *a priori* most likely to do so. A piece of Pb foil was decorated with the samples in many experiments. The observation of typical intermediate-state patterns implies that the temperature rise during decoration was modest (Pb has $T_c = 7.2$ K) and that the decoration procedure was effective. At 77 K we observed no flux-related patterns, and so our observations are directly pertinent only to low temperatures. We will discuss this further in our conclusion.

Figure 2 shows one of the patterns observed. The scanning electron microscope micrograph shows the particles as light on a dark background and is typical of the pattern observed everywhere on the sample and on another decorated at the same time. The sample was cooled to 4.2 K in a magnetic field of 13 G; this is also the local field within experimental error if the flux quantum is $hc/2e$. Figure 3(a) shows a similar pattern on one of the samples cooled in a 51-G field. The irregular shape of the spots in the figures is a consequence of interactions between the particles. Nevertheless, the spots are overall similar in spacing and brightness over the entire samples. Very similar patterns are observed in ordinary type-II superconductors, but highly ordered lattices are observed when flux pinning is small.[9] We conclude from the overall uniformity that the spots correspond to singly quantized vortices and that inhomogeneities on a scale at or near the vortex spacing must be small, i.e., that the samples are completely superconducting. The absence of a well defined lattice does imply some inhomogeneity or pinning, however, even in these crystal samples. Further, portions of many samples showed strong correlations to surface structures such as growth spirals and, possibly, to the twinning "domain" structure known to exist in the crystal. These pinning effects notwithstanding, we believe that the more regular patterns demonstrate that the Abrikosov lattice should be considered the equilibrium model state.

The vortices are clearly highly correlated in the small area shown in Fig. 2. Figure 3(a) shows a larger region of one of a set of samples cooled in a 52-G field. Computation[10] of the autocorrelation function, $G(\delta x, \delta y)$, of a digitized version of Fig. 3(a) shows the hexagonal trend more dramatically in Fig. 3(b). The pattern of brightness of Fig. 3(a) does not accurately replicate the shape

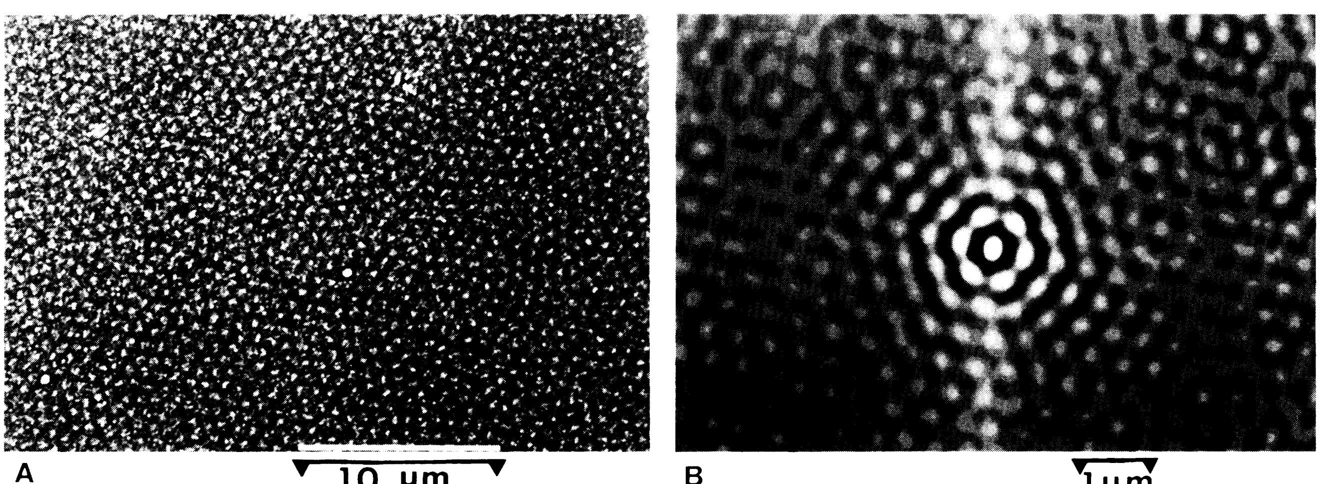

FIG. 3. (a) Typical area of a sample cooled in a 52-G field. (b) Central portion of the autocorrelation function of the pattern in (a).

and size of each vortex because of the large variations in size and shape of the magnetic particles, the bright patches in the micrograph. Even though the magnetic particles do not decorate each vortex in an identical manner, the underlying vortex structure determines on average the particle positions. The centers of intensity of each of the bright particles were located by a simple algorithm.[10] An autocorrelation function of the resulting image of particle centers produced an identical falloff of the central hexagonal region to that of Fig. 3(b). The autocorrelation function is defined as

$$G(\delta x,\delta y)=\int I(x+\delta x,y+\delta y)I(x,y)d(x)d(y),$$

where $I(x,y)$ is the image brightness. Essentially, $G(\boldsymbol{\delta})$ gives the probability of finding a similar degree of brightness in the image if one moves $\boldsymbol{\delta}=(\delta x,\delta y)$ from any point. The four rings of sixfold peaks near the center ($\delta x=\delta y=0$) of the figure indicate that one has high probability of finding another fluxoid if one moves the indicated direction and distance from any fluxoid site. The decay of intensity of the peaks as one moves larger distances confirms that the correlation length for hexagonal order is roughly 2.5 lattice parameters of the fluxoid lattice, a fact that is evident from the size of a hexagonal "grain" in the original image. The sixfold symmetry of the detail in Fig. 3(b) indicates a strong tendency towards local hexagonal ordering. In the low-field limit one would assume the ordering would become stronger for stronger fields, i.e., as the vortices become more compressed and interact more strongly. In our experiments, all patterns were qualitatively similar to the one discussed here. At the highest field attempted, the field was still only 170 G and vortices were resolved in only a few small areas. Elsewhere a distinct threefold symmetry was discernible in a noisy background but the evidence for a more nearly perfect lattice was inconclusive.

For samples with sufficiently uniform flux density, a sampling of the spot density in several sample regions was used to provide an estimate of the overall sample flux and an upper bound on the flux quantum. Since there is no general agreement at this time on the microscopic or phenomenological basis of superconductivity in the new compounds, the value of the flux quantum is still in question theoretically. But experiments based on Josephson effects[11,12] and on flux jumps in cylinders[13] show a flux quantum $hc/2e$. Our test is of a somewhat different nature but should confirm these proofs and assure that the mixed state consists of vortices of the same quantum. In principle, one could measure the local field of a specified region and then count the vortices in this region to measure Φ_0 in a decoration experiment. We have not attempted to do this but can use our knowledge of the field history to set a bound on Φ_0 and thereby distinguish between $hc/2e$ and hc/e as the fluxoid. If a sample is cooled in a constant field the total flux in the specimen must clearly be less than the applied flux since some flux will be expelled. Figure 4 shows the sampled flux line or spot density for several experiments as a function of the field in which the samples were cooled. If all of the applied flux were trapped in the specimens the density would be given by one of the dashed lines depending on whether Φ_0 is $hc/2e$ or hc/e. In each experiment the line density was less than that required if $\Phi_0=hc/2e$; that is the data are consistent with this value since some flux would be expelled. All of the points except one are inconsistent with $\Phi_0=hc/e$ since the line density would then correspond to larger flux than the applied value, i.e., flux would have to be absorbed when the samples became superconducting. The one marginal point is merely inconclusive. Therefore, $\Phi_0=hc/2e$.

Our failure to observe a pattern at 77 K suggests several possible interpretations. Negative results occur for a variety of reasons in this kind of experiment, so that such results are inconclusive ultimately. Nevertheless, we believe we should have observed a pattern in the several attempts had the structure been strictly analogous to the 4.2 K structure. Taking the observations at face value, the experiments indicated a homogeneous penetration of flux throughout the specimens. This may reflect a temporally unstable distribution of flux since T/T_c is high. However, we cannot rule out other possibilities: that the samples are not homogeneously superconducting so that flux enters on a scale finer than our resolution; that there is a fundamentally different kind of state at the high temperature; or that there is a surface

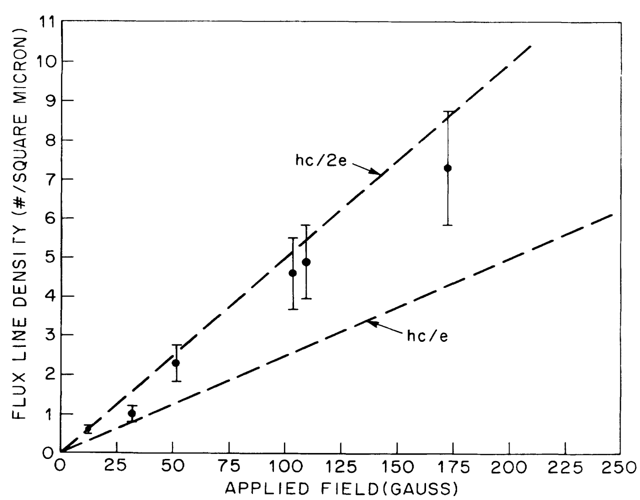

FIG. 4. Sampled flux-spot density on several samples plotted at the field in which the samples were cooled. The dashed lines are the densities which would be observed if all of the magnetic flux were trapped and if the flux quantum were either $hc/2e$ or hc/e. The data exclude hc/e as a possibility since the observed spot density would then correspond to a total sample flux greater than the applied value.

layer which has low T_c so that the bulk structure is masked. More difficult and comprehensive experiments are necessary to distinguish which, if any, of these is the case. Recently, Ourmazd *et al.*[14] reported dilute vortices and fine-scale magnetic structures of unusual character in polycrystalline, ceramic samples at 77 K. It is not implausible that the more disordered material with its stronger pinning would have a more stable flux structure. However, the patterns observed by Ourmazd *et al.* are rather unusual and the corroborative link to the applied field is weak. Also, we should point out the observation by us of some rather unusual patterns under decoration conditions where electrical rather than magnetic effects should dominate. We believe that at least some of the patterns reported by Ourmazd *et al.* are of this kind. These patterns may be of independent interest in understanding the new materials, but can have no direct relation to the magnetic structure of the superconducting state.

In conclusion, we have observed the magnetic structure in $YBa_2Cu_3O_7$ crystals at 4.2 K and found patterns strongly reminiscent of the analogous structures in low-T_c, type-II superconductors. The implications are that the crystals are uniform superconductors with a magnetic structure consisting of singly quantized vortices of quantum $hc/2e$ and with a tendency to form hexagonally ordered arrays. None of this can be shown to apply at 77 K, the only other temperature studied. It seems unlikely to us that this failure reflects anything exotic about the new superconductors since the low-temperature behavior is so ordinary.

We gratefully acknowledge technical discussions and assistance from P. W. Anderson, C. H. Chen, and D. Washington. We thank A. Ourmazd for showing and discussing his results and R. Wenk for assistance in the image-digitizing software.

[1]A. A. Abrikosov, Zh. Eksp. Teor. Fiz. **32**, 1442 (1957) [Sov. Phys. JETP **5**, 1174 (1957).

[2]H. Träuble and U. Essmann, J. Appl. Phys. **25**, 273 (1968).

[3]N. V. Sarma, Philos. Mag. **17**, 1233 (1968).

[4]P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987); Steven A. Kivelson, Daniel S. Rokhsar, and James P. Sethna, to be published.

[5]D. W. Johnson, Jr., E. M. Gyorgy, W. W. Rhodes, R. J. Cava, L. C. Feldman, and R. B. van Dover, Adv. Ceram. Mater. **2**, 364 (1987).

[6]B. Goldfarb, A. F. Clark, A. I. Braginski, and A. J. Panson, to be published.

[7]J. C. Phillips, to be published.

[8]G. J. Dolan and J. Silcox, Phys. Rev. Lett. **30**, 603 (1973), and J. Low Temp. Phys. **15**, 111,133 (1974); G. J. Dolan, thesis, Cornell University, 1973 (unpublished).

[9]L. S. Schneemeyer, J. V. Waszczak, T. Siegrist, R. B. van Dover, L. W. Rupp, B. Batlogg, R. J. Cava, and D. W. Murphy, Nature (London) **328**, 601 (1987).

[10]C. A. Murray and D. H. Van Winkle, Phys. Rev. Lett. **58**, 1200 (1987).

[11]W. R. McGrath, H. K. Olsson, T. Claeson, S. Eriksson, and L. G. Johansson, to be published.

[12]R. H. Koch, C. P. Umbach, G. J. Clark, P. Chaudhari, and R. B. Laibowitz, Appl. Phys. Lett. **51**, 200 (1987).

[13]C. E. Gough, M. S. Colclough, E. M. Forgan, R. G. Jordan, M. Keene, C. M. Muirhead, A. I. M. Rae, N. Thomas, J. S. Abell, and S. Sutton, Nature (London) **326**, 855 (1987).

[14]A. Ourmazd, J. A. Rentschler, W. J. Skocpol, and D. W. Johnson, Jr., to be published.

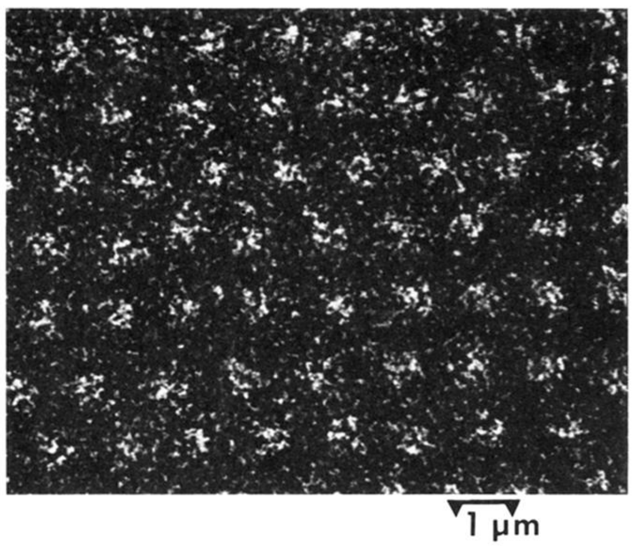

FIG. 2. Flux spots in a $YBa_2Cu_3O_7$ sample decorated after cooling in a field of 13 G.

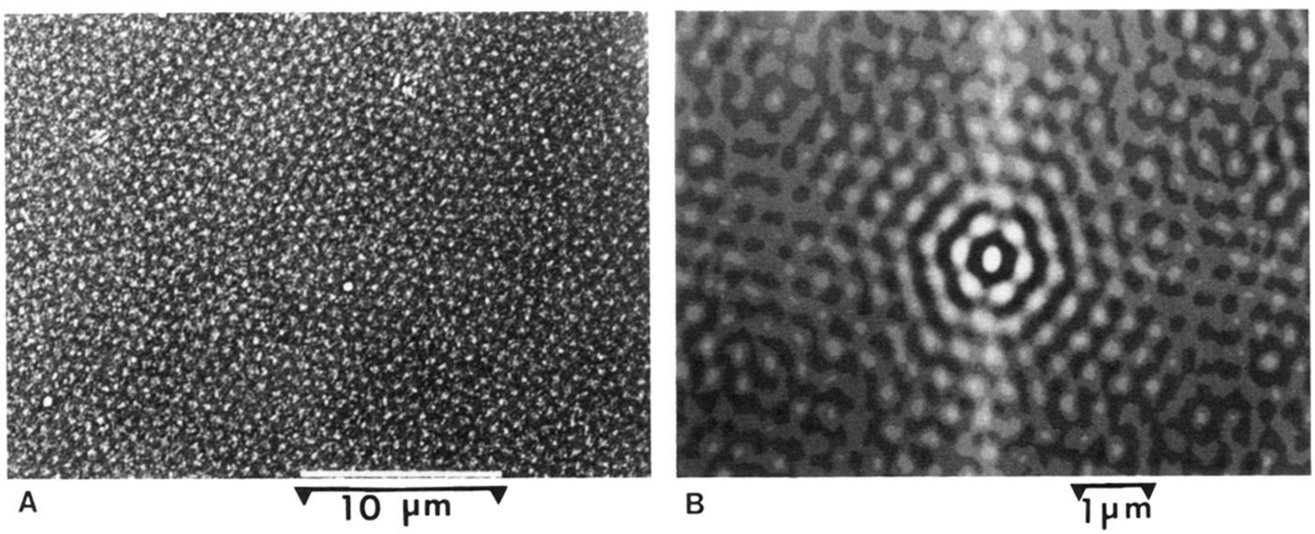

FIG. 3. (a) Typical area of a sample cooled in a 52-G field. (b) Central portion of the autocorrelation function of the pattern in (a).