Field-Induced Orientation of Nonlevitated Microcrystals of Superconducting $YBa_2Cu_3O_{7-x}$

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X-ray diffraction patterns of superconducting $YBa_2Cu_3O_{7-x}$ particles which have typical dimensions $D < 5$ μm and do not levitate in an inhomogeneous magnetic field at $T < T_c$ show marked evidence of particle alignment when powder specimens are subjected to a 0.5-T field at $T < T_c$, but reveal random orientation for $T > T_c$. A majority of the particles align preferentially with their antiphase twin boundary planes and *a-b* planes along the applied field, but a minority align with their *b* axes along the field.

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Following the discovery of high-temperature superconductivity (HTSC) in oxides with perovskitelike structures[1] the focus of scientific interest has been $YBa_2Cu_3O_{7-x}$ for which $T_c \gtrsim 90$ K.[2] Even though large single crystals of this material have recently become available for physical measurements,[3] it is important to understand the physics of collections of microscopic particles of $YBa_2Cu_3O_{7-x}$. Such particles dominate the morphology and influence the behavior of technologically relevant polycrystalline forms such as sinters and thin films. However, the intrinsically interesting anisotropy of the HTSC's is normally masked by the quasirandom orientation of the grains in sinters or bulk powders. This disadvantage can be partially overcome with thin films, the *c*-axes of which are preferentially oriented perpendicular to the substrate surface,[4] and with oriented arrays of small particles embedded in an epoxy matrix.[5]

All reports to date of the preparation of oriented polycrystalline specimens[4-7] have focused upon magnetic torque while magnetic forces have been ignored. Therefore the interplay between superconductivity (SC), levitation, and orientation could not be directly probed. In this Letter we report the first preparation of oriented bulk polycrystalline specimens aligned at $T < T_c$ and prepared from particles which do not levitate in an inhomogeneous magnetic field. We show that both the preferred orientation which the HTSC particles adopt and their levitation properties cannot be readily accounted for by current models of the SC mechanism in $YBa_2Cu_3O_{7-x}$.

Modest quantities ($\simeq 2$ g) of $YBa_2Cu_3O_{7-x}$ were prepared according to the usual recipes.[2] Resistivity measurements of sintered pellets yielded $T_c \simeq 92$ K. Following Vieira *et al.*[8] ground powders immersed in liquid nitrogen were dropped at 77 K into a transverse magnetic field whose height-dependent strength varied from 0 to 0.6 T. Most of the particles levitated (L) but those that did not (NL) were collected for further study. Electron micrographs revealed that the NL and L particles had typical dimensions < 20 μm (single grains) and > 50 μm (multigrained), respectively. The NL material was fractionated by sieving and only the 2% fraction containing particles with $D < 5$ μm was used in the studies described below. Larger quantities of loose randomly oriented powders of these particles acquired by grinding in a ball mill were entirely of the NL variety and confirmed, by the field-cooling and zero-field-cooling susceptibility data shown in Fig. 1, to exhibit a Meissner effect of 72% in agreement with previous measurements of pure-phase material.[9] Unsintered compacted pellets of these particles levitated under the same conditions in which the free powders did not.

Powdered specimens of gross dimension 5.0×0.1 mm² were kinematically mounted in an x-ray powder

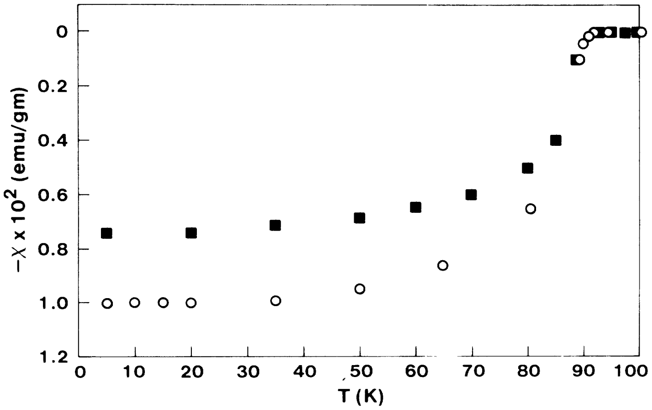

FIG. 1. Temperature dependence of the magnetic susceptibility of small ($D < 5$ μm) nonlevitating particles of $YBa_2Cu_3O_{7-x}$ recorded with fields below $H_{c1}^{\parallel,\perp}$. Squares, field cooling at 18 G; circles, zero-field cooling then field heating at 25 G.

diffractometer to provide accurate repositioning after exposure to the orienting field of a SQUID susceptometer. The small samples required by the susceptometer opening gave rise to a reduced x-ray intensity which was compensated for by an increase in slit width at some expense of resolution. The x-ray intensities were found to be reproducible to within 5%–10%.

Consider the x-ray patterns in Figs. 2(a)–2(c) which are indexed on an orthorhombic *Pmmm* cell.[10] The pattern of Fig. 2(a) was acquired from a randomly oriented powder. It is to be compared with Fig. 2(b) which was acquired from the same specimen after it had been zero-field cooled and exposed at 200 K for 45 min to a field of 0.5 T perpendicular to the specimen surface which was mechanically vibrated in order to aid orientation. To within experimental error, Figs. 2(a) and 2(b) are identical and indicate that mechanical agitation did not induce alignment.

In Fig. 2(c) is shown the pattern acquired under conditions which were *identical* to those used for Fig. 2(b) except that the alignment procedure was carried out at $T=65$ K. Note from Fig. 2(c) that the (110), (020)+(006), and (200) reflections grow in absolute intensity while the relative intensities of all other reflections referenced to the (110)+(103) peak decrease (see e.g., inset Fig. 2). The data of Fig. 2 were quite reproducible. For instance, consecutive measurements in which the specimen was randomized, oriented, rerandomized, and reoriented yielded relative intensity ratios of the (110)+(103) peak of the oriented to that of the random sample of 0.63 and 0.64.

One can, in principle, determine the orientational distribution (OD) of grains in a powder by measuring the full rocking curve of any observable reflection provided there is sufficient intensity to examine a very thin rod-shaped specimen.[11] This was not possible in our case and so the rocking curve of the most intense reflection of the oriented sample, the (110) reflection, was measured over the maximum available range $-\theta_B < \phi < \theta_B$ where the Bragg angle $\theta_B(110)=16.4°$ for Cu $K\alpha$ radiation. The results of this measurement, corrected for absorption,[11] are shown in Fig. 3 as a heavy line and clearly indicate a nonrandom OD.

The shape of the OD for angles in excess of 16.4° can

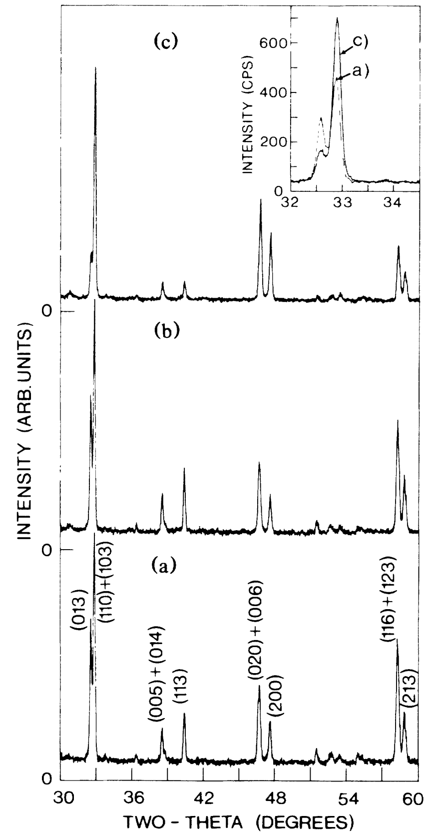

FIG. 2. Room-temperature Cu $K\alpha$ x-ray diffraction patterns of (a) a randomly oriented specimen, (b) after exposure to a 0.5-T field at $T=200$ K, and (c) at $T=65$ K. The patterns are normalized on the (110)+(103) reflection. Inset: Absolute intensity scale.

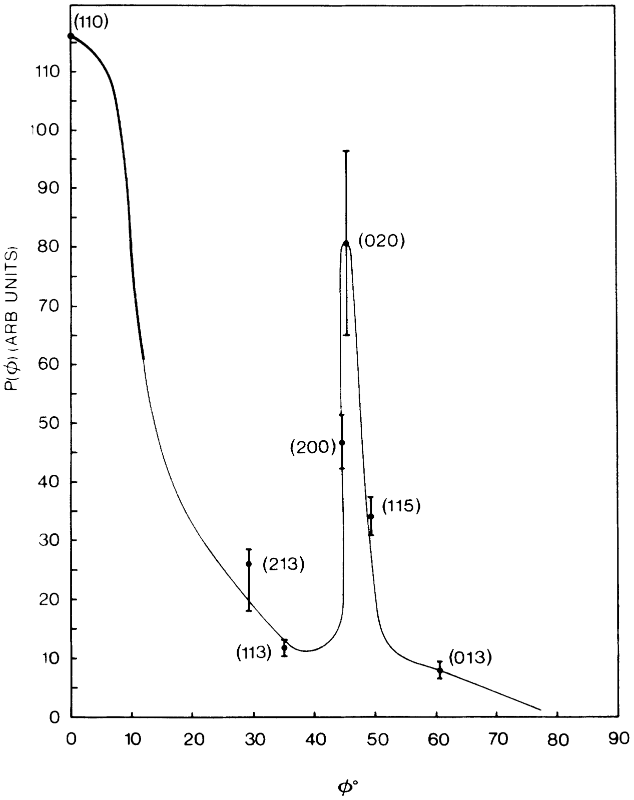

FIG. 3. Orientation distribution of the (110) planes of nonlevitating $YBa_2Cu_3O_{7-x}$ powder which has been exposed to a field of 0.5 T at 65 K. The heavy line was deduced from the rocking curve of the (110) reflection. The light line is a guide to the eye. The data points were obtained from the labeled reflections (see text).

be deduced from the intensity of each diffraction line in the oriented sample relative to that in the random sample as follows: Let $P_{hkl}(\phi)$ be the probability that the (hkl) planes of the grains in the specimen are aligned parallel to the specimen surface. Here (hkl) is one *particular* plane in an equivalent set and ϕ is the angle between the normal to that plane and the specimen normal. If we use a contracted index j to represent each plane in an equivalent set, the total diffracted intensity resulting from the entire set of $\{hkl\}$ planes will be

$$I_{hkl} = |F_{hkl}|^2 \left\{ \sum_{j=1}^{M} P_j(\phi) \right\} G(\theta_{hkl}), \tag{1}$$

where M is the multiplicity, F_{hkl} is the structure factor including temperature effects, and $G(\theta_{hkl})$ is a function that includes the usual Lorentz factor, etc., but only depends on the Bragg angle θ_{hkl}.[11]

For a specimen of randomly oriented grains, $P_j(\theta) = 1/4\pi$ and the intensity of a given $\{hkl\}$ set is proportional to its multiplicity. If we define I_i^{or} and I_{hkl}^{ran} as the intensities resulting respectively from a distribution in which the ith plane of the $\{hkl\}$ set is partially oriented parallel to the specimen surface and from the $\{hkl\}$ set of a randomly oriented specimen, then

$$I_i^{\mathrm{or}}/I_{hkl}^{\mathrm{ran}} = \left\{ \sum_{j=1}^{M} P_j(\phi_{ji}) \right\} (4\pi c'/M), \tag{2}$$

where ϕ_{ji} is the angle between the ith and jth planes in the set and c' is a normalization constant. If a pair of distinct reflections is unresolved in the x-ray diffraction pattern their individual contributions to the scattering intensity of the random sample can be deduced from their structure factors.[10]

Electron micrographs of $D < 5$ μm grains of $\mathrm{YBa_2Cu_3O_{7-x}}$ show that they contain unidirectional antiphase twin boundary domain walls parallel to *one* of the four equivalent $\{110\}$ planes.[12] Let the unique planes be $(1\bar{1}0)$. If they align perpendicular to the specimen surface (see below), the (110) planes which are essentially orthogonal ($\phi_{(1\bar{1}0)(110)} = 89.02°$) will align parallel to the surface. We have used Eq. (2) and the data of Figs. 2(a) and 2(c) to augment the rocking-curve portion (solid line) of the OD $P_{i=(110)}(\phi)$ shown in Fig. 3. The data points in that figure are labeled according to the reflections from which they were derived with use of the cutoff value $P_j(\phi_{ji}) = 0$ for $\phi_{ji} \gtrsim 60°$. The error bars reflect, in part, uncertainty introduced by this cutoff as well as the inherent error of the intensity measurements. This procedure did not yield an unambiguous result in the case of the (123)+(116) reflections and so they were omitted from Fig. 3. The OD shown in Fig. 3 indicates that $\simeq$ 60% of the HTSC particles align with their twin boundary planes along the field (HWHM = 12°) and $\simeq$ 13% align with their b axes along the field. Note that if the peak at $\simeq 45°$ were due to a subsidiary alignment of the (110) planes the (020) and (200) contributions would be of equal amplitude which is clearly not the case.

It can be shown[13,14] that a type-II magnetically anisotropic SC particle in the vortex state will align with one of its magnetic axes along an inhomogeneous applied field and that in this configuration, the levitation force is minimal. The preferred axis will be the one with minimum H_{c1} or equivalently maximum H_{c2} provided the applied field is sufficiently greater than H_{c1} that shape induced demagnetizing effects are negligible.[13] Bulk superconducting $\mathrm{YBa_2Cu_3O_{7-x}}$ particles should thus align with their a-b planes parallel to $\mathbf{H}$. If supercurrents are maximal along the b axis (parallel to the Cu-O chains),[10] then this axis would be preferred within the a-b plane for untwinned or lightly twinned single-crystal grains. To our knowledge the data of Fig. 3 constitute the first direct evidence indicative of this anisotropy. Note that heavily twinned grains which possess no unique b axis should show no preferred alignment in the a-b plane even if they exhibit a unidirectional domain structure.

An aligned small grain of $\mathrm{YBa_2Cu_3O_{7-x}}$ will levitate when dropped into a region of transverse field only if its gravitational mass density ρ is less than the magnetic mass density $\rho_{\max}^{\parallel}$ ($\parallel \rightarrow$ a-b plane $\parallel\mathbf{H}$) where for our experimental configuration $\rho_{\max}^{\parallel}$ is the maximum value of

$$\rho^{\parallel}(z) = [1/8\pi g][H(z)\nabla H(z)]\chi^{\parallel}(H(z),T). \tag{3}$$

Here g is the acceleration due to gravity and z is the height of the particle. Since for $\mathrm{YBa_2Cu_3O_{7-x}}$, $H_{c2}^{j} \gg H_{c1}^{j}$, $j = \parallel, \perp$,[15] the magnetization is approximately linear with applied field in the vortex state and

$$\chi^{\parallel}(H(z),T) \simeq (-1/4\pi) H_{c1}^{\parallel}(T)/H(z).$$

Then $\rho_{\max}^{\parallel} \propto H_{c1}^{\parallel}[\partial H(z)/\partial z]_{\max}$. From the reported value[16] $H_{c1}^{\parallel}(11\ \mathrm{K}) = 120 \pm 10$ G we find[17] that $H_{c1}^{\parallel}(77\ \mathrm{K}) = 37 \pm 3$ G. In our experiments $[\partial H(z)/\partial z]_{\max} = 8 \pm 1.3$ kG/cm in which case

$$\rho_{\max}^{\parallel} = 12.0 \pm 2.6\ \mathrm{g/cm^3} > \rho = 6.38\ \mathrm{g/cm^3}$$

and so the NL particles should levitate.

In the above described calculation, we have assumed reversible magnetization so that flux pinning effects[17] which would enhance $\rho_{\max}^{\parallel}$ are not included. The buoyancy correction is small, $\simeq$10%, since the density of liquid nitrogen is only 0.6 $\mathrm{g/cm^3}$. Note that incomplete flux expulsion for the NL particles does not derive from London-type flux penetration which can be appreciable in the SC state, but rather is a manifestation of the vortex state which under our experimental conditions obtains for both the NL and L particles alike.

Garcia *et al.*[18] have suggested that SC in $\mathrm{YBa_2Cu_3O_{7-x}}$ is not a bulk phenomenon but rather is confined to anisotropic slabs $\simeq$80 Å thick that extend along the antiphase twin boundary planes, the separation of which is 500–1000 Å. In their model the slab thickness is determined by the oxygen concentration profile and thus can be considerably larger than the domain wall itself. Isotropic conduction in the planes of the slabs would align them without selective orientation of any intraplane axis. However, anisotropic conduction with the c axis suppressed would result in the observed alignment of the (110) planes. Moreover, this model naturally accommodates the nonlevitation of small particles with a unidirectional domain structure since only a small volume fraction of each grain would contribute to flux expulsion even in the SC state. Large particles ($D > 20$ μm) which are multigrained and/or contain multidirectional domains possess no unique alignment direction and could thus levitate because the average magnetic mass density of a grain with randomly oriented twin domains can be much larger than $\rho_{\max}^{\parallel}$ and therefore greater than ρ. The alignment of some small number of particles along the crystalline b axes does not naturally follow from the model of Garcia *et al.*

It is generally recognized that twin boundary planes significantly influence the superconducting properties of $YBa_2Cu_3O_{7-x}$. These planes have been the central element in competing models which characterize the superconductivity as either a surface/interface effect[18] or a bulk effect.[19] But bulk superconductivity may be incompatible with the levitation and orientation results discussed here. Perhaps there is more than one superconducting mechanism functioning simultaneously in $YBa_2Cu_3O_{7-x}$, as suggested by the dual alignment peaks shown in Fig. 3, and the highly variable domain-wall densities in different samples, e.g., small crystallites, thin films, large single crystals, etc., determine which, if any, mechanism is dominant.

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