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Observation of the Wohlleben effect in $YBa_2Cu_3O_{7-\delta}$ single crystals

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During systematic low-field magnetization measurements on high-quality single crystals of $YBa_2Cu_3O_{7-\delta}$ we discovered several crystals with a paramagnetic contribution to the field-cooled magnetization. This magnetization saturates at very low fields. It is attributed to spontaneous current loops caused by π junctions which are aligned in small external fields (Wohlleben effect). The effect is only seen with the field parallel to the c axis, demonstrating that the spontaneous currents are confined to the CuO_2 planes.

Recently it was reported by Wohlleben and co-workers[1] that the magnetic susceptibility of certain high-T_c ceramics increased to positive values when cooling in a small field through the superconducting transition temperature. This "paramagnetic Meissner effect" is just the opposite of the normally observed flux expulsion. While the effect was observed before by others,[2] Wohlleben and co-workers were the first to systematically investigate this effect. They also proposed an interesting physical model in terms of π junctions between weakly coupled superconducting grains, giving rise to spontaneous orbital currents in arbitrary directions. An external field will align those spontaneous current loops and can produce a net positive magnetization. This paramagnetic Meissner effect has been described as the "Wohlleben effect."[3]

It is the purpose of this paper to report that the Wohlleben effect is also observed in high-quality, twinned, single crystals of $YBa_2Cu_3O_{7-\delta}$. Thus grain boundaries as origin of the π junction can be ruled out. The effect is seen only with the magnetic field parallel to the c axis, i.e., the spontaneous currents are confined to the ab plane. We also demonstrate why the Wohlleben effect is seen so seldom.

The single crystals investigated were grown in Y_2O_3-stabilized ZrO_2 crucibles as described earlier.[4] Crystals used in the present study had typical dimensions of 2×2 mm^2 in the ab plane and 0.2–0.5 mm in c direction. All crystals had oxygen concentrations near 6.95 and displayed the usual twinning.[4] As we have previously demonstrated by neutron scattering,[5] resistivity,[6] magnetization,[7] and specific-heat[7] measurements our crystals are of excellent quality.

The magnetization of all crystals were determined with a superconducting quantum interference device magnetometer as described in Ref. 8. The measuring fields B_a between 0.01 and 1.0 mT were supplied by a Cu coil (1850 turns, length 182 mm, inner diameter 36 mm). The axial field profile was constant to within 1% over a length of 10 mm. The Nb-Ti pickup coil was in the form of a double gradiometer (4 coils of 6 turns each, 5 mm apart). The Dewar system was surrounded by a μ-metal shield reducing the Earth's magnetic field to about 0.01 mT. Further reduction of the vertical component of the remanent field was accomplished by an offset current through the field coil. The magnetometer was calibrated with small spheres of a superconductor (Pb) and a ferromagnet (EuS).

The samples were mounted on the sample rod, inserted into the cryostat and cooled in zero applied magnetic field (ZFC) to temperatures well below the superconducting transition temperature. A field between 0.02 and 1.0 mT was then applied and the vertical position of the crystal optimized for maximum signal. Afterwards, the sample was never moved. The ZFC magnetization was then determined on warming. The crystal was then cooled in the same field to well below T_c and the field cooled (FC) magnetization was determined on warming. The whole procedure, except for the position optimization, was then repeated in a different field. For a given field, the whole cycle gave identical results when repeated later after the initial position optimization, thus ruling out possible measuring artifacts which could mimic a paramagnetic magnetization.[9]

We have started a systematic study to investigate the low-field behavior of $YBa_2Cu_3O_{7-\delta}$ single crystals. Of the 30 or so crystals investigated about 20% showed anomalous behavior but only one of those exhibited a fully developed Wohlleben effect.

Magnetization measurements of this one crystal (sample 1) for the applied field $B_a \parallel c$ are displayed in Fig. 1. The upper part (a) shows the ZFC magnetization and the lower part (b) the FC magnetization. Within our accuracy which is mainly due to the uncertainty in determining the demagnetization factor (±10%), all our crystals show complete shielding, i.e., the ZFC magnetization sufficiently below T_c is given by

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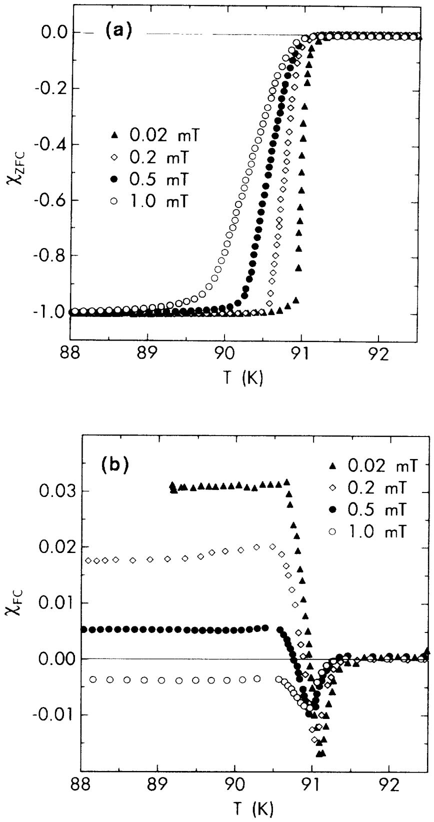

FIG. 1. Susceptibility $\chi = \mu_0 M/B_a$ of the crystal sample 1 in various applied fields B_a vs temperature T. (a) χ_{ZFC} after zero field cooling; (b) χ_{FC} after field cooling. B_a is parallel to the c axis. For complete flux expulsion $\chi = -1$.

$$M_{ZFC} = -\frac{1}{\mu_0}\frac{1}{1-n}B_a \equiv \frac{1}{\mu_0}\chi_{ZFC}B_a$$

where n is the demagnetization factor. In all cases we normalize the susceptibility $\chi = \mu_0 M/B_a$ to the complete shielding value $|\chi_{ZFC}|$.

The shielding (ZFC) behavior [Fig. 1(a)] is typical of high-T_c materials.[10] However, the Meissner (FC) data are rather unusual [Fig. 1(b)]. With decreasing temperature the susceptibility first becomes negative just below T_c reaching a sharp minimum and then increases again reaching a constant value several degrees below T_c. At fields below 0.7 mT this constant value is positive. This effect has been observed before for ceramic high-T_c materials and was referred to as paramagnetic Meissner effect or PME.[1,2,11] The magnitude of the observed positive signal here is considerably smaller than that observed in the ceramic samples (less than 3% of the full shielding value as compared to up to 50%).[1,2,11] The field, however, below which a paramagnetic Meissner effect is observed in the sample of Fig. 1 is considerably larger than that in the ceramic samples (0.7 mT compared to about 0.05 mT).[1,2,11] The susceptibility curves of Fig. 1 are completely reproducible and do not change with time. They have been measured a period of 1 year apart and were exactly the same. The observed sharp features suggest two transition temperatures, one associated with the onset of bulk superconductivity producing a diamagnetic magnetization and a second one a few tenths of a degree lower, associated with the sudden appearance of a positive magnetization, counteracting the diamagnetic Meissner effect. According to Wohlleben and co-workers,[1,2] this positive magnetization is due to small regions of the crystal coupled by π junctions. These π junctions produce spontaneous current loops which can be aligned in an external field. These current loops, however, can only form when the critical current through the junction is high enough, which in this crystal is a few tenths of a degree below T_c. The mutual independence of the positive and negative contribution to the magnetization can be immediately checked by measuring the FC magnetization directly during the cooling cycle. Because the flux expulsion below T_c is an activated process the flux is expelled slowly on cooling giving rise to a very broad transition region.[12] This is demonstrated for a "normal" crystal in Fig. 2. On cooling, the flux leaves the crystal only reluctantly, extending the flux expulsion process down to 85 K. During the warming cycle some more flux is expelled before suddenly the flux can enter the crystal when superconductivity disappears, i.e., at T_c. The observed hysteresis (Fig. 2) is very common in high-T_c materials (when indeed the dc magnetization is measured upon warming *and* cooling) and has been recently theoretically confirmed in model calculations.[12]

For the anomalous crystal, sample 1, we expect a similar behavior for the diamagnetic contribution to the magnetization. This should permit a test whether the alignment of the spontaneous current loops is indeed the same on cooling or warming. This is demonstrated in Fig. 3 in a field of 0.8 mT. On warming the positive magnetization has essentially decayed before the flux enters the crystal. However, during the cooling cycle the flux leaves the crystal over an extended temperature range and the alignment of the spontaneous current loops which occurs in exactly the same temperature interval as on warming, now sits on top of the decreasing normal Meissner effect. This directly shows that the paramagnetic signal is completely reversible as has been suggested before by ac susceptibility measurements of higher harmonics.[11]

Figure 4 displays FC susceptibilities of the same crys-

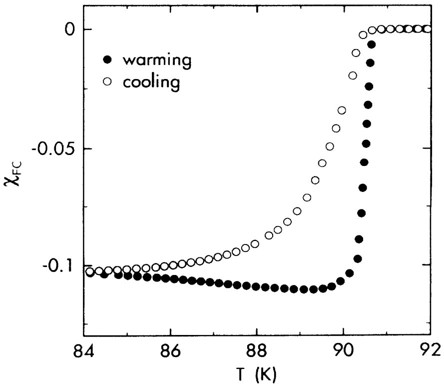

FIG. 2. FC susceptibility χ_{FC} of a "normal" crystal sample 4 in $B_a = 0.1$ mT measured during cooling (○) and warming (●).

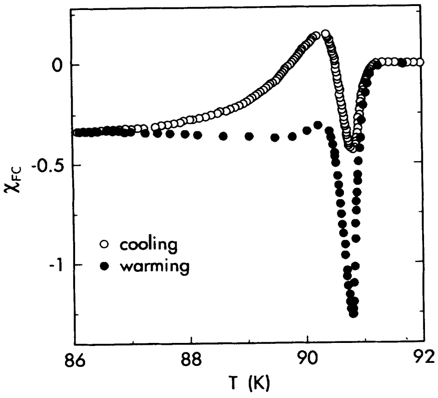

FIG. 3. FC susceptibility $\chi_{\rm FC}$ of crystal sample 1 in $B_a = 0.8$ mT measured during cooling (○) and warming (●).

tal but with the field aligned parallel to the *ab* plane. In this orientation, the normal behavior typical of high-T_c superconductors[10] is observed with the diamagnetic susceptibility decreasing in magnitude with increasing field. Thus it seems that the spontaneous current loops can only occur in the *ab* planes, yielding a potentially strong hint at the origin of those junctions in single crystals.

Several other crystals also displayed anomalous behavior of $\chi_{\rm FC}$ just below T_c, two of which are displayed in Fig. 5. For crystal sample 2 the paramagnetic signal again sets in a few tenths of a degree below the onset of the normal Meissner effect and leads to the pronounced maximum in $\chi_{\rm FC}$. However, unlike crystal sample 1 (Fig. 1), the normal Meissner effect still further increases in magnitude after the paramagnetic signal saturates, and the net magnetization levels off at a negative value. For crystal sample 3 the paramagnetic signal sets in very close to the diamagnetic onset, causing the net magnetization to become positive before the normal Meissner effect takes over and causes the net magnetization to become negative again. At lower temperature the paramagnetic effect again takes over for a small temperature interval yielding a second maximum in $\chi_{\rm FC}$. For both crystals, the ZFC susceptibility behaves normally with a transition width of less than 0.5 K. Also, for both crystals the FC susceptibility with B_a parallel to the *ab* plane behaves normally.

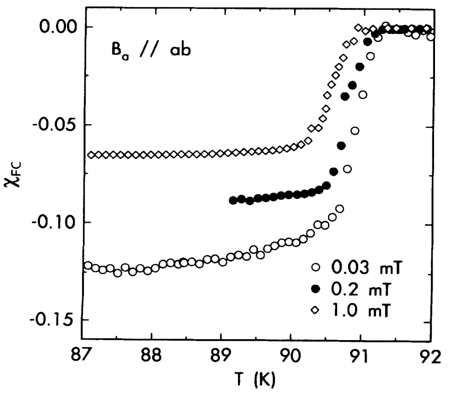

FIG. 4. FC susceptibility $\chi_{\rm FC}$ of the crystal sample 1 in various applied fields B_a vs temperature T with the field parallel the *ab* plane.

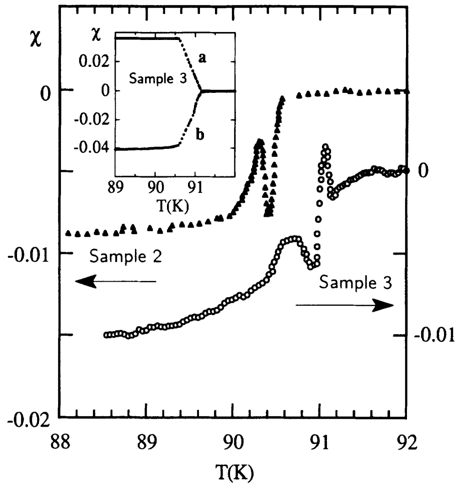

FIG. 5. FC susceptibility $\chi_{\rm FC}$ in $B_a = 0.1$ mT parallel to the *c* axis for crystal samples 2 (left ordinate) and 3 (right ordinate) vs temperature. The inset demonstrates how the small measured susceptibility is the difference of two large contributions: the paramagnetic signal due to the spontaneous current loops (*a*) and the normal, incomplete Meissner effect (*b*) (see text).

The inset of Fig. 5 demonstrates, for crystal sample 3, this interplay between the positive and negative contributions to the magnetization. The curve labeled *a* is an estimate of the paramagnetic magnetization due to the spontaneous current loops. If we subtract this curve from the measured magnetization for this crystal, we obtain curve *b* which is typical for the normal Meissner effect. This clearly demonstrates why the Wohlleben effect is seen so seldom. If the superconducting and the PME transitions are broadened by inhomogeneities in similar fashion the anomalous behavior as shown in Fig. 5 will not be seen.

Because of the strong field dependence of the susceptibility $\chi = \mu_0 M/B_a$ even in very small fields (see Figs. 1 and 4) it is more meaningful to analyze the magnetization curves, $M_{\rm FC}$ vs B_a. Examples are shown in Fig. 6 for crystal samples 1 and 3 with the field parallel to the *c* axis. Displayed are magnetization values taken at about 88 K (in this range $M_{\rm FC}$ is independent of the temperature). For sample 1 at low fields $M_{\rm FC}$ (solid circles in Fig. 6) rises to positive values before becoming negative at higher fields. It is tempting to assume that the linear behavior of $M_{\rm FC}$ vs B_a at fields above 0.5 mT, where $dM_{\rm FC}/dB_a$ is constant, reflects the regular Meissner effect. We can then determine the paramagnetic contribution to the magnetization, attributed to the spontaneous current loops, by subtracting from the actual data a straight line going through the origin with a slope equal to the high-field slope. This difference is shown in Fig. 6 as open circles. Thus the positive magnetization of the spontaneous current loops is observed to saturate near $B_a = 0.5$ mT, i.e., above this field all spontaneous current loops are aligned. The same procedure for sample 3 yields the open squares as the paramagnetic contribution for this crystal. In reality, the positive contribution

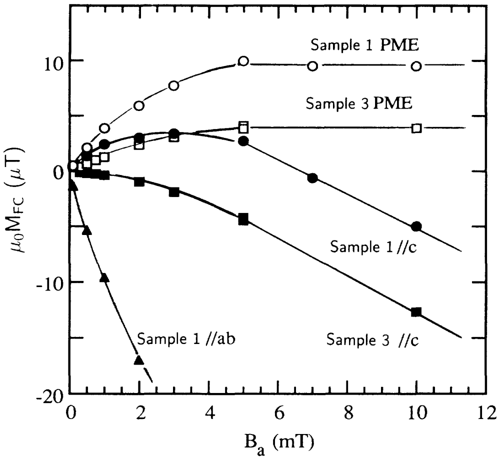

FIG. 6. FC magnetization M_{FC} (at about 88 K) with B_a parallel to the c axis for crystal samples 1 (●) and 3 (■) vs B_a; (▲) B_a parallel ab plane. The open circles and squares are the difference between the actual data points ($B_a \parallel c$) and a straight line through the origin with the same slope as the line through the high-field data points (solid symbols). They represent the paramagnetic contribution of the spontaneous current loops (see text).

is probably larger than that obtained by this construction because the normal, incomplete Meissner effect is usually not linear in field, as can be seen in Fig. 6 for crystal sample 1 with the field parallel to the *ab* planes (triangles). It is quite possible that a paramagnetic contribution to the FC magnetization is present in all crystals. However, it can be seen easily only when the superconducting transition is sharp or the contribution due to the spontaneous current loops is larger in magnitude as the normal Meissner effect and the net magnetization below T_c is positive.

In order to investigate the possibility that the spontaneous current loops are associated with twin boundaries we measured several untwinned crystals as well as looked carefully at the arrangement of the twin boundaries in the twinned crystals. The results are inconclusive. All untwinned crystal, indeed, displayed a normal Meissner effect. However, we did not observe any difference in the twin boundary pattern between the normal and anomalous twinned crystals.

Several microscopic models have been invoked to explain spontaneous orbital currents. One mechanism is a Josephson coupling in the presence of paramagnetic impurities[13] or inelastic scattering centers in dirty junctions.[14] The other mechanism explicitly invokes d wave pairing of $d_{x^2-y^2}$ symmetry.[3] Clearly, our observation of the Wohlleben effect is compatible with all these scenarios. A recent paper explains the Wohlleben effect in terms of an orbital glass made of spontaneous vortex-antivortex pairs.[15] The observation of the Wohlleben effect in single crystals rules out grain-boundary junctions as the only mechanism. The directional dependence shows that the spontaneous orbital currents flow within the CuO_2 planes which would be consistent with the recent suggestion of d-wave superconductivity with a $d_{x^2-y^2}$ symmetry.[16] The confinement of the paramagnetic Meissner effect to the CuO_2 planes established in the present work puts important constrains on its origin. For example, a loop through a system of well-ordered twin boundaries, intersecting at right angles, cannot produce a spontaneous current. On the other hand, topological defects within the twin boundary system such as disclination lines, might support the effect.

In summary, we have found a paramagnetic Meissner effect (Wohlleben effect) in several $YBa_2Cu_3O_{7-\delta}$ single crystals. This paramagnetic magnetization is thought to be due to spontaneous current loops in the *ab* planes associated with π junction. These loops can be aligned in relatively small fields. It is the relative magnitude of this paramagnetic term compared to the normal Meissner effect which will determine if the net magnetization will actually become positive. Further work will have to establish the characteristic difference of the various crystals which lead to the different low-field behavior.

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[1] W. Braunisch *et al.*, Phys. Rev. Lett. **68**, 1908 (1992).

[2] For a review of the paramagnetic Meissner effect including earlier observations see W. Braunisch *et al.*, Phys. Rev. B **48**, 4030 (1993).

[3] M. Sigrist and T. M. Rice, J. Phys. Soc. Jpn. **61**, 4283 (1992).

[4] A. Erb *et al.*, J. Cryst. Growth **132**, 389 (1993).

[5] P. Schweiss *et al.*, Phys. Rev. B **49**, 1387 (1994).

[6] H. Claus *et al.*, Physica C **200**, 271 (1992).

[7] H. Claus *et al.*, Physica C **198**, 42 (1992).

[8] K. Vandervoort *et al.*, Rev. Sci. Instrum. **62**, 2271 (1991).

[9] F. J. Blunt *et al.*, Physica C **175**, 539 (1991).

[10] L. Krusin-Elbaum *et al.*, Physica C **153-155**, 1469 (1988).

[11] Ch. Heinzel *et al.*, Phys. Rev. B **48**, 3445 (1993).

[12] J. R. Clem and Z. Hao, Phys. Rev. B **48**, 13 774 (1993).

[13] L. N. Bulaevski *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 314 (1977) [JETP Lett. **25**, 290 (1977)].

[14] B. T. Spivak and S. A. Kivelsen, Phys. Rev. B **43**, 3740 (1991).

[15] F. V. Kusmartsev, Phys. Rev. Lett. **69**, 2268 (1993).

[16] D. A. Wollman *et al.*, Phys. Rev. Lett. **71**, 2134 (1993), and references therein.