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Characteristic microstructure in small Bi-2212 grains showing the Wohlleben effect as revealed by High-Resolution Electron Microscopy

B. Freitag[1], B. Büchner[2], N. Knauf[2], B. Roden[2], H. Micklitz[2]
A. Freimuth[3] and V. Kataev[4]

[1] *Institut für Anorganische Chemie, Universität Bonn*
Römer Str. 164, D-53113 Bonn, Germany
[2] *II. Physikalisches Institut, Universität zu Köln*
Zülpicher Str. 77, 50937 Köln, Germany
[3] *Physikalisches Institut, Universität Karlsruhe - 76128 Karlsruhe, Germany*
[4] *Kazan Institute for Technical Physics, Russian Academy of Sciences*
420029 Kazan, Russia

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Abstract. – By means of high-resolution transmission electron microscopy and electron diffraction we show that samples of Bi-2212 high-temperature superconductors which exhibit the Wohlleben effect have an extremely polydomain microstructure on a μm length scale. In directions perpendicular to the *c*-axis small crystallites are separated by well-defined atomically sharp ($\lesssim$ 1 nm) interfaces which provide good contacts between the domains in the *ab*-planes. The observed microstructure strongly favors the explanation of the Wohlleben effect due to spontaneous currents flowing in the closed paths between differently oriented unconventional (*d*-wave) superconductors.

The Wohlleben effect (WE) is characterized by an anomalous *paramagnetic* behavior in the superconducting state in small magnetic fields of certain samples of Bi-based high-temperature superconductors (HTSC) as well as other accompanying anomalies, *e.g.*, of the microwave absorption [1]. It has attracted much interest due to its possible explanation as an intrinsic property of a network of unconventional (*d*-wave) superconductors [2]. In such a network the Cooper pairs may acquire intrinsically a phase shift of order π in the contacts between superconducting crystallites with different orientations of their respective crystallographic *a*- and *b*-axes (π-contacts). As a result, in the loops incorporating π-contacts (π-loops) superconducting currents and corresponding orbital magnetic moments may arise *spontaneously* leading to a paramagnetic behavior of the system in the superconducting state. In fact, the observation and interpretation of the WE have triggered several sophisticated "phase-sensitive" experiments, which have recently been performed on artificial structures with a π-loop geometry [2-4]. Spontaneous magnetic flux in the superconducting state has been detected in these structures in favor of unconventional pairing symmetry in the cuprates. Regarding the WE it is up to now unclear whether the necessary morphology for the creation of π-loops is actually provided in samples showing the WE.

We have shown recently [5, 6] that the WE is an *intragrain* property, *i.e.* it is present in isolated grains of Bi-2212 samples with dimensions of order $\lesssim 1$ μm. This finding has rather strong implications for the nature of the WE. We conclude from the data that the WE cannot be explained by flux pinning (see comments in ref. [5, 6] and ref. [7]). In particular the idea of flux compression suggested by Koshelev and Larkin [8] to explain the paramagnetic magnetization observed in some thin plates of niobium [9, 10] is not consistent with the results on the Bi-2212 HTSCs. The data give strong evidence that the WE is indeed due to intrinsic spontaneous currents. Thus, the superconducting loops with π-contacts should be present *within* the small grains. Furthermore, to be responsible for the observed effect, the π-contacts in the μm size powders should be able to sustain high critical current densities of order 10^5–10^6A/cm^2 [5, 6]. Remarkably, in line with the results of our experiments Kirtley *et al.* have very recently reported on visualization of spontaneous flux in a superconducting grain of a Bi-2212 sample showing the WE [11]. Hence indeed, for an arrangement of π-loops with the required properties in the samples with WE there should exist a certain particular microstructure on a μm length scale.

In this letter we present the results of a comparative High-Resolution Transmission Electron Microscopy (HRTEM) study of samples which do exhibit the WE and of those which do not. Our main finding is the observation of a well-developed domain structure on the μm size scale in all examined samples with WE. The single crystalline domains are preferably c-axis oriented. However in the basal ab-plane they are oriented differently. The interfaces which separate them are extremely sharp (width $\lesssim 1$ nm). Hence there exist obviously good contacts between the neighboring crystallites in the ab-planes. A respective electron diffraction study reveals a rather broad scatter of the orientations of the different domains in the ab-plane. The typical mutual orientation of the crystallites suggests that they are in the regime of a strong Josephson coupling. Altogether this gives the necessary prerequisites for creation of π-loops with strong spontaneous supercurrents. Therefore, the observation of such specific microstructure in the Bi-2212 samples showing WE gives strong evidence that the WE is a macroscopic manifestation of unconventional pairing in HTSC.

The HRTEM experiments were carried out on a Philips CM30 electron microscope. The electron diffraction patterns were obtained using the same equipment. Nine different Bi-2212 samples have been investigated. Measurements of the magnetic susceptibility and of the microwave absorption revealed the presence of the WE in some of these samples.

All specimens for the HRTEM study were prepared as cross-sections to preserve the microstructure of the bulk material and to avoid problems with the sample handling of the brittle material after the HRTEM preparation steps [12]. At least two different specimens of each Bi-2212 sample were examined. Since for all samples no variations between the different cross-sections of the same sample are found, the observed microstructure can be considered as being representative for the whole sample.

At low magnifications, *i.e.* on a scale $\gtrsim 100$ μm, we find *no* correlation of the morphology of the samples with the presence of the WE. For instance, there are samples with loose microstructure which do show the WE and samples with compact microstructure which do not.

A clear qualitative distinction between the morphology of the samples with and without the WE is apparent from our results when approaching a length scale of several microns. We illustrate this in fig. 1 where HRTEM photos of two respective samples are shown. The samples

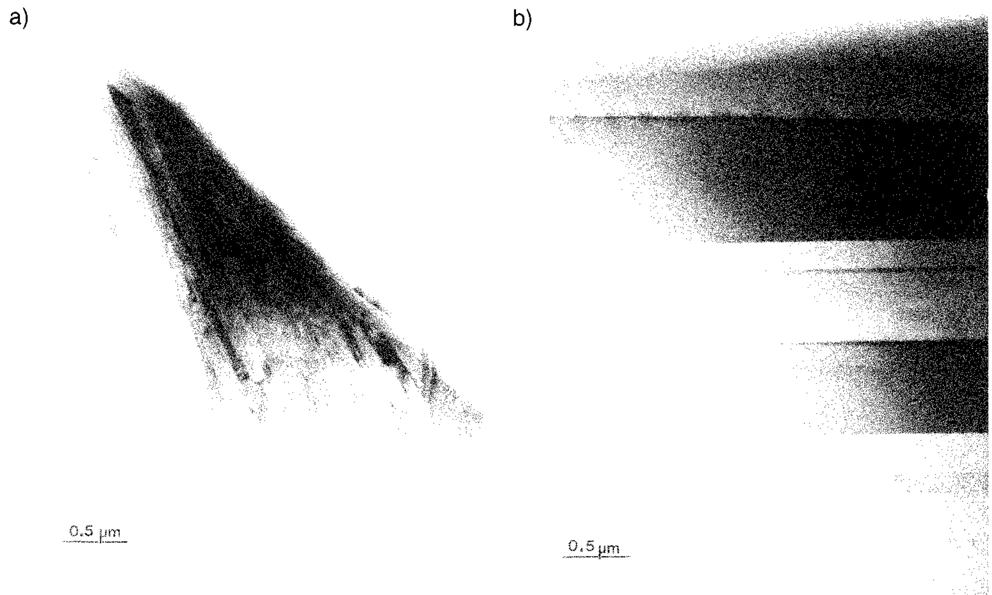

Fig. 1. – HRTEM photos of samples with WE (a) and without WE (b) on the scale of several μm.

with WE are characterized by an extremely polycrystalline "chaotic" structure with typical sizes of the single crystalline domains $\lesssim 1$ μm (see fig. 1(a)). In contrast, samples without the WE show a pattern of large well-ordered single crystalline domains (see fig. 1(b)). Obviously, the density of the domain boundaries is much larger for the former samples than for the latter.

A more attentive look at finer scales reveals further important features. In fig. 2 HRTEM images of two representative samples, one with (left column) and another without WE (right column), can be seen for different magnifications. This figure is exemplary for all samples examined. It clearly shows that on the μm length scale not only the density of the domain boundaries in the samples with and without WE is quite different (see first row in fig. 2, left and right panels, respectively) but, moreover, the *type* of the boundaries is also quite different. This can be seen by comparing the left and right panels of the second row in fig. 2. They represent the bright field images of the samples viewing in the $a(b)$, c-planes of the regions marked with the rectangles in the respective first rows of fig. 2. The crystallographic axes indicated by the arrows are verified by electron diffraction.

In both types of samples there are boundaries which occur perpendicular to the c-axis. These boundaries are the so-called 90°-twist boundaries or small-angle twist boundaries between two crystallites whose respective crystallographic axes are not exactly parallel to each other. However, what represents the important characteristic of the samples showing the WE is the presence of interfaces preferably *parallel* to the c-axis. The interface plane can freely rotate around the c-axis and is not fixed as in twin boundaries. It separates crystallites with differently oriented a- and b-axes. As is evident from fig. 2 the density of such type of interfaces in the samples with WE is very high. In contrast to this, only few of them can be found in the samples without WE.

The two types of boundaries observed in the samples are shown in the largest magnification in the right and left panels of the third row in fig. 2, respectively. The 90°-twist boundary shown in the right panel is atomically sharp and terminated by the Bi-O layers of the normal

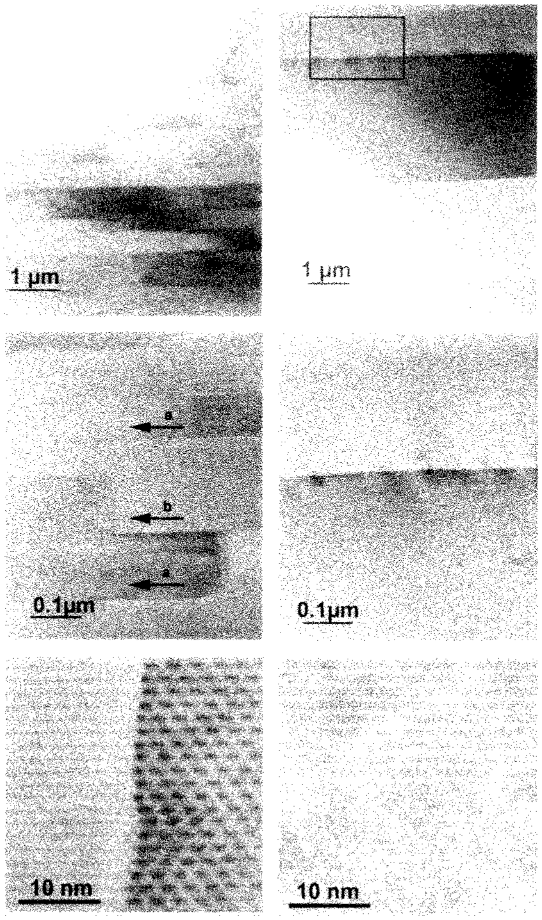

Fig. 2

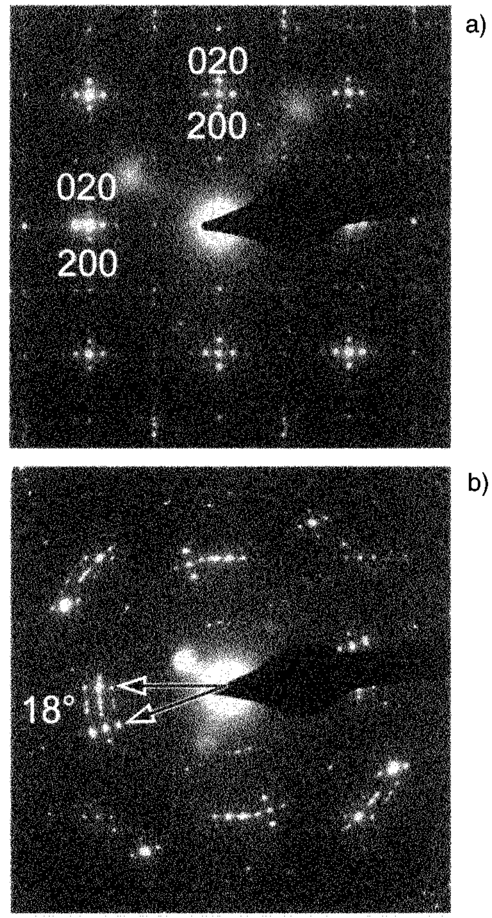

Fig. 3

Fig. 2. – HRTEM photos of samples with (left column) and without WE (right column). For both columns the magnification increases successively from the first to the third row as indicated in the figures. The crystallographic axes of the single crystalline domains are indicated by the arrows.

Fig. 3. – Electron diffraction patterns taken along the [001] zone axis of a submicron area of the sample without WE (a) and with WE (b). Arrows in (b) indicate the misorientation of the b-axes of two single crystalline domains in the ab-plane with the parallel c-axes. For further details see text.

Bi-2212 structure, visible as the periodical two darkest rows of spots in the HRTEM image. The lower part of this image shows the incommensurate superstructure along the b-axis [13]. In the upper part this superstructure is not visible, since it runs in the direction perpendicular to the image plane. Obviously boundaries of such a type which consist of insulating Bi-O layers are strong barriers for supercurrents.

The interfaces which are characteristic for the samples with WE, *i.e.* those which are mainly parallel to the c-axis, are extremely sharp too. In the corresponding image (third row of fig. 2, left column) the crystallite on the right side is oriented in the [100]-zone axis and the interface to the other crystallite on the left side of the image is exactly in the electron beam direction. In this way the sharpness of the interface can be visualized. The left crystal is not oriented exactly in the [010]-zone axis, but is tilted along the c-axis with respect to the right crystal. Consequently the a- and b-axes in the neighboring domains are not parallel. The dark horizontal lines represent the Bi-O layers in this projection. In this image the perturbed region at the interface has an extremely small width (< 1 nm) and no amorphous layer is visible. In fact, the boundary between crystallites is coherent, *i.e.* the crystal structures on both sides are correlated apart from a few stacking faults due to intergrowth of the Bi-2201 phase. This means that there should be a good contact between the ab-planes of the neighboring crystallites across the interface. Therefore, from all the above we may conclude that due to its sharpness and crystallographic orientation this kind of coherent boundary is a highly transparent barrier with respect to supercurrents.

Further insight into the arrangement of the crystallographic boundaries in the samples with and without WE can be obtained by analyzing the electron diffraction patterns taken from a submicron area along the c-direction of the grains (see fig. 3). The 90°-twist boundaries lead to appearance of periodical crossed rows of spots of superstructure reflections which correspond to the mutually perpendicular b-directions of the crystalline domains stacked along the c-axis. Such an array is most clearly seen in fig. 3(a) for the sample without WE. However, a specific arrangement of the crystallites in the samples with WE leads to new important features. Weak textured ring structures are visible in fig. 3(b) showing the disorder between the grains in the ab-plane. Respectively, the interfaces which separate the crystallites in the ab-plane have a rather broad distribution of orientations. In particular, a representative angle of about 18° between the b-axes of two larger crystalline domains can be obtained from the diffraction pattern as indicated by the arrows in fig. 3(b).

As was discussed by Hilgenkamp *et al.* [14], the angle between superconducting grains, *i.e.* the angle α of a grain boundary, determines the properties of the boundary with respect to superconductivity. For small α the boundary does not form a barrier for supercurrents. With increasing angle an interface between the grains with weakened superconductivity develops. The crossover to strong Josephson coupling is found to occur for $\alpha \gtrsim 8°$. The increase of α leads to strong reduction of the supercurrent across the interface. Thus our electron diffraction data suggest that in the samples with WE there is a significant portion of the interfaces in the ab-plane which on the one hand have the angle sufficient for tunneling to occur and, on the other hand, can still sustain rather strong spontaneous supercurrents.

The conclusions derived from our HRTEM and electron diffraction studies are in perfect agreement with our observation of the WE in isolated μm size grains of Bi-2212 HTSC [5, 6] and magnetic imaging experiments reported by Kirtley *et al.* [11]. The data in ref. [5, 6, 11] strongly suggest that the WE arises due to a specific morphology of individual grains of a *d-wave* superconductor. In particular, we have argued that π-loops of the μm size able to sustain supercurrents of the order 10^5–10^6A/cm^2 may be arranged across highly transparent interfaces (π-contacts) between the crystallites differently oriented in the ab-plane. Therefore, for the typical values of the spontaneous paramagnetic magnetization $M_0 \simeq 0.1$ Oe observed for the samples with WE [1, 5] and for the estimated value of the spontaneous orbital magnetic moments $m_{\rm s} \simeq 10^7$–$10^8 \mu_{\rm B}$ [5], the concentration of the π-loops N/V should be $N/V = M_0/m_{\rm s} = 10^{11}$–$10^{12}\,{\rm cm}^{-3}$. Hence, the average distance between the loops with spontaneous supercurrents, which is roughly $(N/V)^{-1/3}$, is of the order of several μm. Indeed, the required length scale for the occurrence of π-loops in the network of small single crystalline domains in the Bi-2212 samples showing the WE is found in the present study. This gives an additional confidence that the analyzed HRTEM images and electron diffraction patterns are representative for the whole sample.

In summary, we have studied by means of high-resolution transmission electron microscopy and electron diffraction the morphology of several representative samples with and without the Wohlleben effect. We have found a particular microstructure on the μm scale which is characteristic only for the samples which show the WE. On such a small length scale these samples are extremely polycrystalline. Single crystalline domains with sizes $\lesssim 1$ μm are preferably c-axis oriented. In the ab-plane they are disordered. The domains are separated by atomically sharp (< 1 nm) boundaries (parallel to the c-direction) which may serve as highly transparent interfaces for tunneling currents. This specific arrangement is obviously favorable for the creation of π-loops with spontaneous supercurrents in unconventional superconductors. The presence of such π-loops in the samples allows to explain consistently all observations regarding the WE. Hence the results of the present study give strong evidence that the WE is a macroscopic manifestation of the unconventional (d-wave) pairing symmetry in high-temperature superconductors.

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