

New Type of Vortex Pinning Structure Effective at Very High Magnetic Fields

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We report on a new type of correlated nanometer-scale pinning structure observed in a melt-processed $(\text{Nd}_{0.33}\text{Eu}_{0.38}\text{Gd}_{0.28})\text{Ba}_2\text{Cu}_3\text{O}_y$ (NEG-123). It consists of NEG/Ba-rich clusters in the stoichiometric NEG-123 matrix forming a lamellar array with a period of a few nanometers. These lamellas appear within regular twins, thus representing their fine substructure—sometimes straight, sometimes wavy. This new material structure correlates well with the significant enhancement of pinning at high fields, represented by irreversibility field above 14 T at 77 K ($B \parallel c$). We believe that the new pinning medium enables one to significantly broaden the limits for high-field applications.

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Irreversibility field, B_{irr} , beyond which the superconducting currents are zero, limits the field range where electromagnetic properties of high temperature superconductors can be practically exploited. In $\text{YBa}_2\text{Cu}_3\text{O}_y$ (Y-123), the typical irreversibility field values at 77 K with $B \parallel c$ range between 3 and 5 T [1]. The flux pinning in Y-123 can be dramatically improved by neutron and heavy ion irradiation, but this improvement has been usually limited to low and intermediate fields and could not allow for a reasonable improvement in B_{irr} . Nd-123 [2] has been found to possess exceptionally good material parameters within the family of R -123 compounds, namely, T_c around 95 K and B_{irr} in the range of 9 T. The physical reason for that was found in formation of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ (Nd123ss) clusters of 20–50 nm size dispersed in the Nd-123 matrix [3]. The size of these clusters is comparable to the vortex core size and, thus, these clusters can serve as pointlike pins, effectively enhancing J_c , especially at intermediate and high fields and increasing thus B_{irr} value. Concentration of this type of pin is controlled by a different mechanism than oxygen deficiency [4]. Therefore, Nd-123 samples could be optimally oxygenated to achieve maximum T_c , without any loss of pinning efficiency. Later on, it has been found that also light rare-earth elements Sm, Eu, and Gd can form $R_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ solid solution clusters [5].

The experiment with a high-oxygen-pressure treatment of an Nd-123 single crystal, resulting in B_{irr} of 13 T [6], showed that B_{irr} could be, in principle, improved in bulk materials.

In melt-textured materials there is always some amount of a normal secondary phase present in the form of micrometer-sized particles. These particles have been found as effective pinning sites especially at low fields [7] and can thus affect remanent current or trapped magnetic fields but not directly B_{irr} .

In ternary compounds, combination of different light rare-earth elements on the rare-earth site enables variation of the Nd:Eu:Gd chemical ratio [8,9]. Surprisingly

strong pinning at high fields was observed for a narrow range of chemical ratio around Nd:Eu:Gd = 33:28:38 [10]. Both irreversibility field and secondary peak position systematically possessed particularly high values.

In this work we focus on the composition $(\text{Nd}_{0.33}\text{Eu}_{0.28}\text{Gd}_{0.38})\text{Ba}_2\text{Cu}_3\text{O}_y$ doped with (3–40) mol % of NEG-211 (Nd:Eu:Gd = 1:1:1). 0.5 mol % of Pt was added to refine the secondary phase particles and 10 wt % of Ag_2O to improve mechanical properties. All samples were fabricated by the oxygen-controlled-melt-growth process under oxygen partial pressure of 0.1% O_2 and gas flow rate of 300 ml/min [8]. For magnetic measurements, small specimens with dimensions of about $a \times b \times c = 2 \times 2 \times 0.5 \text{ mm}^3$ were cut from the as-grown pellets and annealed in flowing oxygen in the temperature range (300–600) °C [8]. The microstructure was studied by means of transmission electron microscopy (TEM) and scanning tunneling microscopy (STM). Chemical composition was locally analyzed by energy dispersive x-ray spectroscopy (EDX). Superconducting properties were investigated by means of a vibrating sample magnetometer with maximum field of 14 T. J_c was estimated on the basis of the extended Bean critical state model [11]. In this work external field was applied always parallel to the c axis.

Field dependence of the critical current density at 77 K in the sample with 5 mol % NEG-211 measured with field sweep rate of 0.6 T/min is shown in Fig. 1. The most striking feature of this experiment was that the $J_c(H_a)$ curve remained open up to the maximum field, $B_a = 14 \text{ T}$ (see the top inset of Fig. 1 for detail). The secondary peak was observed at 4.5 T. These are the highest secondary peak position and irreversibility field reported so far for high- T_c superconductors at 77 K. The critical current density reached 70 kA/cm² at the top of the secondary peak and at 10 T it was still 22 kA/cm², a reasonable engineering value. Extrapolation of $B_{\text{irr}}(T)$ dependence from high temperatures (94–79 K) to 77 K indicated B_{irr} value even 15 T (see bottom inset of Fig. 1).

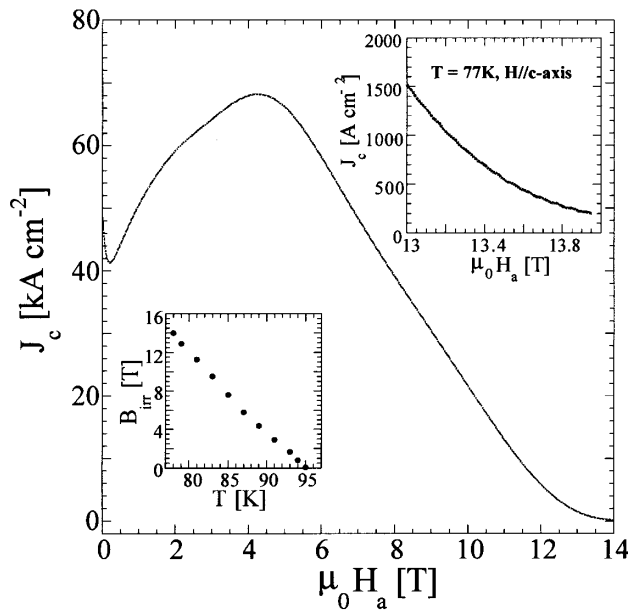


FIG. 1. Field dependence of the critical current density, $J_c(H_a)$, for sample $(\text{Nd}_{0.33}\text{Eu}_{0.38}\text{Gd}_{0.28})\text{Ba}_2\text{Cu}_3\text{O}_y$ with 5 mol % NEG-211, 10 wt % silver oxide, and 0.5 mol % Pt, at 77 K and $B_a \parallel c$ axis. Note the relatively high critical current density of 70 kA/cm² at the secondary peak around 4.5 T at 77 K ($B_a \parallel c$). The top inset shows a still nonzero value of J_c at 14 T. The bottom inset shows the extrapolation of $B_{\text{irr}}(T)$ dependence from high temperatures to $B_{\text{irr}} \approx 15$ T at 77 K, $H \parallel c$ axis.

Similar J_c - B properties were obtained for the samples cut from various locations of the as-grown pellet, showing its good homogeneity. Irreversibility field values of the samples with 3 and 7 mol % of NEG-211 were close to that in the previous sample. However, in materials with NEG-211 content above 10 mol %, the irreversibility field gradually dropped.

Seeking for the reason of excellent magnetic properties in the present material, we examined its microstructure by different techniques. Figure 2 shows the dark-field TEM image of the sample with 5 mol % NEG-211 viewed from the [001] direction. One can see regular twins (the broad dark and light strips) and a fine substructure with nanometer-scale periodicity, mostly aligned with the twins. Periodicity of this nanostructure was a few nanometers. Further, we denote this structure as nanolamellas.

The nanoscale lamellar structure systematically appeared in samples with 3–7 mol % NEG-211. All these compounds also exhibited very high irreversibility fields. On the other hand, the lamellas were not found in samples with NEG-211 content higher than 10 mol %. These materials exhibited significantly lower irreversibility field at 77 K. These results were also confirmed by independent dynamic force microscopy experiments. All these facts lead us to the conclusion that the observed pinning enhancement at high fields is due to the nanolamella array.

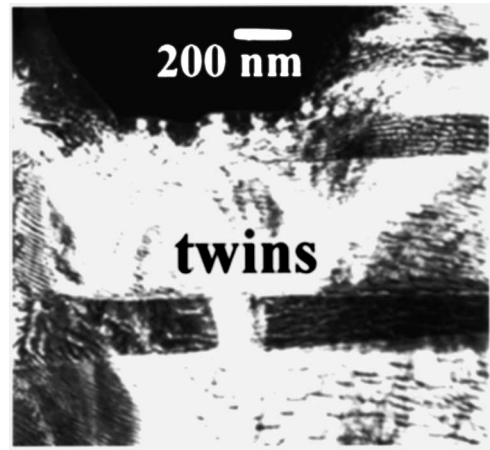


FIG. 2. Transmission electron micrograph of the material from Fig. 1. One can see a fine structure modulation within twins (dark and light broad strips).

More detailed information on the character of the material microstructure was obtained by scanning chemical analysis made by TEM-EDX. The analysis was made in discrete steps of 5 nm across the nanolamella system. The diameter of the analyzed spot was about 2–3 nm. The NEG/Ba ratio regularly oscillating between 0.48 and 0.53 was observed (see Fig. 3). The finite size of the analyzed areas might slightly influence the results so that in reality even higher chemical ratio differences between lamellas and the matrix could be expected. In the TEM-EDX experiment the lamella array period was evidently close to the scanning step, i.e., about 5 nm.

Figures 4(a) and 4(b) show STM topographs of the sample with 5 mol % NEG-211 in different magnifications. A system of straight nanolamellas can be seen in Fig. 4(a), some of them being marked by arrows. The

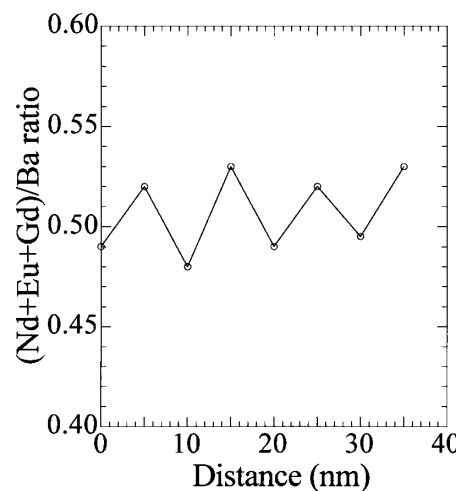


FIG. 3. TEM with EDX analysis of the material from Fig. 1. Higher and lower values of the (NEG)/Ba ratio regularly vary with the step of 5 nm between extremes 0.485 and 0.515. Diameter of the analyzed spot was about 3 nm.

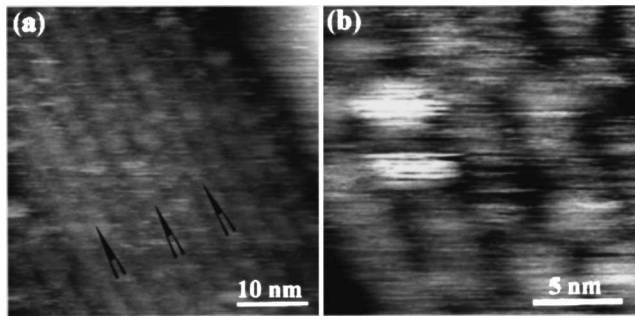


FIG. 4. STM images of the sample with 5 mol % NEG-211 [(a)–(b)]. The image was recorded with bias voltage $V_s = 1$ V and tunneling current $I_t = 0.3$ nA. The black arrows in (a) mark some nanolamellas. Note the presence of arrays of clusters around 3 to 4 nm in diameter dispersed in an organized manner in the NEG-123 matrix.

average period was around 3.5 nm. Here we note that different samples cut from the same pellet were examined in different experiments, which can explain slightly different periods of the lamellar array. Even in one sample the scale slightly varied as seen in Fig. 2 but always stood in nanometer range.

A higher magnification [Fig. 4(b)] showed that the nanolamellas in fact consist of chains (or planes) of aligned clusters of 3 to 4 nm in size. Evidently, these clusters were identified by EDX analysis as $(\text{NEG})_{1.015}\text{Ba}_{1.985}\text{Cu}_3\text{O}_y$. In the sample with 40 mol % NEG-211, only individual noncorrelated clusters of the 3–5 nm size were found.

Tunneling current spectra taken on the rare-earth-rich clusters, and the regular matrix (white and dark spots in Fig. 4, respectively) showed a similar conductivity of both parts. This was not very surprising as the composition of the rare-earth-rich clusters was not much different from the NEG-123 matrix around.

The above structural analysis seems to present a quite reliable picture of the new pinning medium. Now we can speculate on the pinning mechanism associated with this new structure. First, we have to bear in mind that this nanostructure coexists with regular twins. This raises the question if the observed enhancement of B_{irr} cannot be attributed to the effect of twins. Twins are strong pinning objects that might be effective at high fields and high temperatures. It has been, however, many times reported in literature that though the twin structure really shifts the magnetization hysteresis loop to higher fields, this shift is only slight.

The width and spacing of the nanolamellas are comparable to coherence length [in YBCO $\xi_{ab}(77\text{ K}) \approx 4.5$ nm]. Individual randomly distributed pointlike pins of such a size arising from oxygen deficiency [12], Barich clusters [13], *R*-Ba solid solution [14,15], and other defects are usually considered to be responsible for the secondary peak effect. This peak lies in intermediate fields, at 77 K usually not exceeding 3.5 T. What is then

the difference in the pinning mechanism of the new structure and individual pointlike pins of a similar size?

The $(\text{NEG})\text{Ba}_2\text{Cu}_3\text{O}_y$ samples studied in this work were optimally oxygenated; hence, the effect of oxygen deficiency was strongly suppressed. Further, it seems that the nature of the individual nanoscale pins in the present material does not differ from that in other light-rare-earth 123 compounds. The only difference seems to be in the rare-earth-rich cluster organization and probably also the alignment with regular twins.

The question if the twins themselves cannot cause the observed irreversibility field increase can be negatively answered. First, even such strong pinning centers as twin boundaries do not necessarily result in an overall enhancement of critical currents: channeling effect leads to a redistribution of the current flow and appearance of additional in-plane anisotropy in the sample [16], which usually results in a suppression of J_c in the region of the secondary peak. Though an enhancement of irreversibility field due to a twin structure has been often observed, it was usually on a few tenths of tesla.

We suggest that the dense lamellar structure between regular twin planes slows down the channeling effect of twins or even prevents it and at the same time shifts the high-field vortex lattice transformation to even higher fields. We note that a nanolamellar array was also observed in Y-123 single crystals [17] and another nanometer-scale platelike structure was obtained in a heavily Pb-doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ single crystal [18]. They also significantly enhanced J_c and B_{irr} , in accord with the present work.

In summary, an irreversibility field of about 15 T and a critical current density of 70 kA/cm² at 4.5 T were achieved at 77 K ($H \parallel c$ axis) in the ternary melt-processed material NEG-123 with the initial Nd:Eu:Gd ratio of 33:38:28 added with 5 mol % of NEG-211. TEM analysis revealed formation of a nanoscale lamellar array in the NEG-123 matrix. In accord with that, TEM with EDX showed a slight but clear chemical ratio fluctuation in the matrix on a nanometer scale. STM maps of different parts of the NEG-123 sample with 5 mol % NEG-211 always showed rare-earth-rich clusters of 3 to 5 nm in size. These clusters were organized into highly ordered tracks with period of a few nanometers. The appearance of such a structure was always accompanied by a significant increase of B_{irr} and vice versa. Our results suggest that the improved flux pinning at high fields is due to formation of a nanoscale lamellar array of rare-earth-rich clusters mostly aligned with regular twin planes. From a technological point of view, a proper small concentration of a secondary phase seems to be important for the formation of the desired pinning nanostructure, but the exact role of the secondary phase in this process is not yet clear.

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