Grain boundaries as weak links: The case of MgB_2 with reference to YNi_2B_2C

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The grain boundaries (GB's) in the intermetallic superconductor MgB_2, interestingly, do not show suppression of supercurrent density. This unexpected behavior has been investigated by a scanning tunneling microscopy/spectroscopy technique at atomic resolution. The GB in MgB_2 is seen as an amorphous region extending from ~50 to 200 Å and has a metallic character. This observation supports proximity coupling between the grains, which explains why supercurrent density does not degrade in this material. The results for another intermetallic superconductor YNi_2B_2C having GB's (average width ~30 Å) that are quasi-insulating in nature have also been presented and compared with the former.

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Grain boundaries (GB's) play an important role in determining the dissipationless critical current density (J_c) in technologically important polycrystalline superconductors. Depending on the exact nature and width of the GB, the J_c may get enhanced or degraded. As is well known[1] in high-T_c cuprate superconductors, the GB cannot support large J_c. In contrast, one of the important features of intermetallic superconductor MgB_2 (magnesium diboride[2]) with an unexpected high superconducting critical temperature T_c of 39 K is that the natural GB's in its polycrystalline sample[3] do not, or only marginally, exhibit J_c supression. This is technologically extremely important. In this paper we present results on the nature and width of the GB's in MgB_2 using an ambient temperature scanning tunneling microscopy/spectroscopy (STM/STS) technique at atomic resolution. A comparison of similar results in the case of superconducting quaternary borocarbide YNi_2B_2C, which has a GB response similar to that of cuprates, is also given.

One reason for the different GB response between cuprates and MgB_2 may be that the latter possesses a relatively large coherence length[2] (around 40 to 50 Å) exceeding the supposedly narrow grain-boundary width. This contention, however, seems erroneous for at least two reasons: (i) recent high-resolution transmission electron microscopy (HRTEM) studies[4] of MgB_2 have revealed the amorphous region of the grain boundary to be considerably wider, extending up to 500 Å wide, which far exceeds the coherence length, and (ii) with YNi_2B_2C, another intermetallic superconductor[5] but with a lower T_c of 15.5 K and a larger coherence length of about 60 Å, the grain boundaries do indeed manifest the ''weak-link effects'' across the GB's just like cuprates.[6,7] Our results show the nature of the amorphous region of the grain boundaries in the two intermetallics to be widely different. In the case of MgB_2 the amorphous region, although quite broad, is still metallic, while in the latter it is quasi-insulating. The metallic nature of the grain boundary in MgB_2 gives rise to proximity-type junctions between the neighboring grains with negligible weak-link effects, while in YNi_2B_2C the quasi-insulating boundary forms

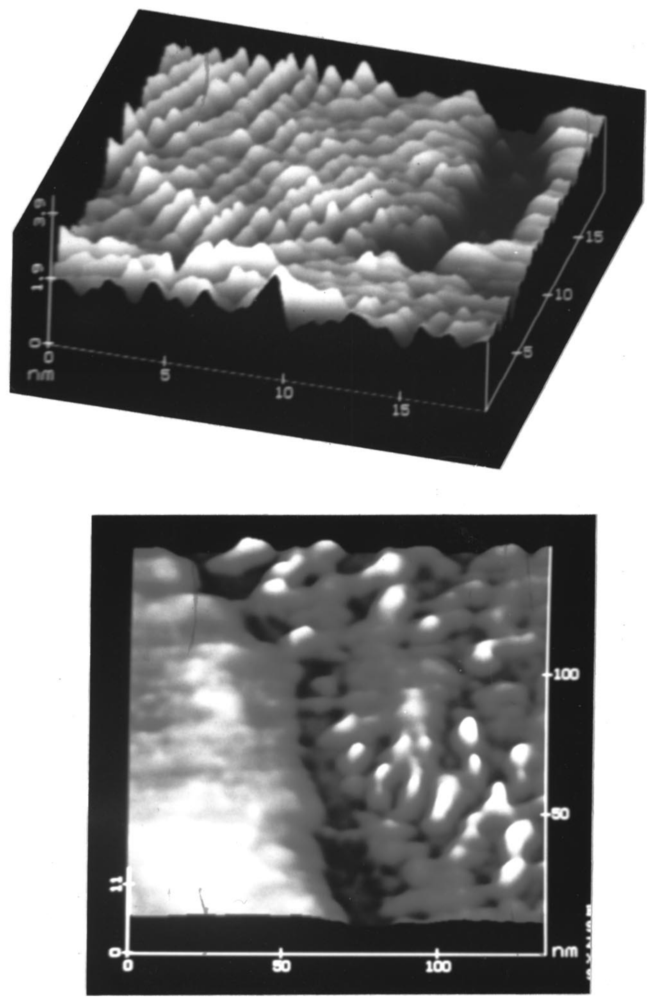

FIG. 1. (a) STM image of a grain boundary 30 Å wide in YNi_2B_2C (scan size 180×180 Å). Image in three-dimensional (3D) mode at 30° pitch. (b) STM image of a grain boundary 50 to 200 Å wide in MgB_2 (scan size 1750×1750 Å). Image in 3D mode at 60° pitch.

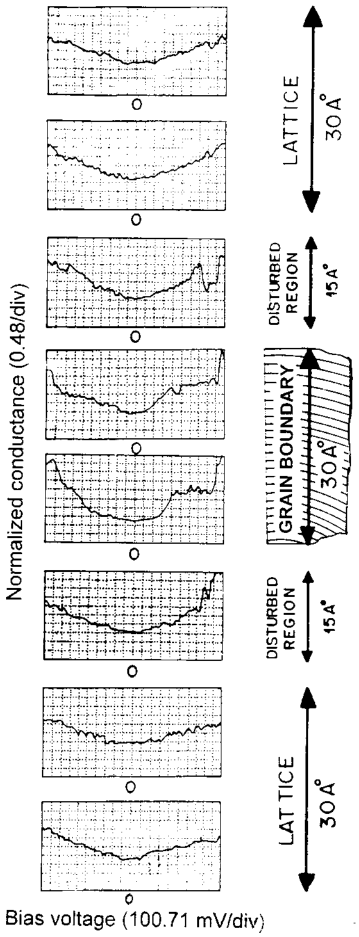

FIG. 2. Conductance spectra obtained within and at different distances away from the grain-boundary edges on both sides of the boundary in YNi_2B_2C. Overall boundary region over which the disorder is spread is seen to be 60 Å wide.

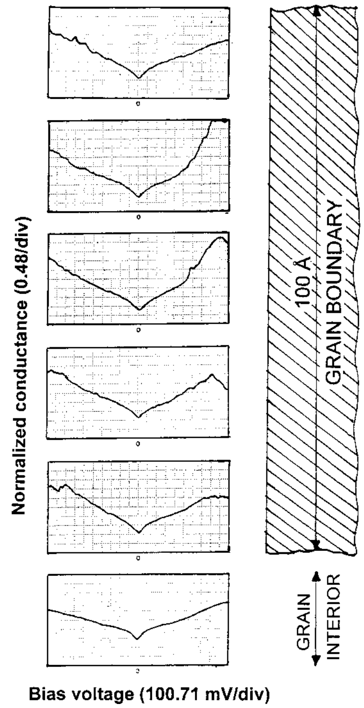

FIG. 3. Conductance spectra obtained within the amorphous region as one moves on a line along the width of the grain boundary and a representative single spectra obtained at the grain interior for the MgB_2 sample.

superconductor-intermetallic-superconductor (S-I-S) junctions, giving rise to a pronounced weak-link behavior.

The sample of MgB_2 for the present study was synthesized at Aoyama-Gakuin University, Tokyo, with preparation details that have been described elsewhere.[1] It had a sharp T_c of 39 K as measured by both resistive and inductive techniques. The polycrystalline YNi_2B_2C was synthesized by R. Nagarajan at Tata Institute of Fundamental Research, Mumbai, using the conventional arc-melting technique. The sample was phase pure, as confirmed by x-ray diffraction, and exhibited a sharp diamagnetic susceptibility at 15.5 K.

STM/STS studies on both intermetallic samples were carried out using a nanoscope system operating under ambient conditions. All the studies reported here were performed using a Pt-Ir tip scanning the surface in the constant current mode with a zero input filter and using a moderate feedback gain. Once stable and repetitive real time images of both grains and grain boundaries were obtained at the atomic level resolution, the instrument was switched into the STS mode and the normalized conductance spectra could be obtained within the boundary region as well as inside the grains. The normalized conductance spectra are a measure of local density of states and they change sensitively from the characteristic V-shaped metallic type to the quasi-insulating type if the scanned layer becomes significantly resistive. Thus by mapping the conductance spectra and the way they are changing as one moves away from the center of the amorphous grain-boundary region to the adjoining grains on either side, the relative change in the resistive nature of the scanned layer can be determined.

A number of GB's were investigated by STM/STS in both YNi_2B_2C and MgB_2. Figures 1(a) and 1(b), respectively, show the high-resolution images of typical grain boundaries in both the materials. The boundary region, which is amorphous, appears as a dark broad band separating the crystalline grains on either side, which are atomically resolved. In the case of the former the amorphous region is around 30 Å wide while in the case of the latter it varies from 50 to 200 Å. HRTEM studies[4] have shown an even larger width of grain boundaries in MgB_2. In order to estimate the range over which the disorder is spread on either side of the grain boundary, we have carried out a systematic study of the conductance spectra and the way their characteristics change as one moves away from the boundary into the adjoining grains. The results for YNi_2B_2C are shown in Fig. 2. As may be seen, within the grain-boundary region, the normalized conductance as a function of bias voltage is markedly distorted from the characteristic metallic type and is near U-shaped, indicating the quasi-insulating nature of the grain boundary. The disturbed region of the grain boundary seems to persist within the adjoining grains up to a distance of about 15 Å on either side of the two edges of the boundary region, where the spectra observed continue to be distorted. Beyond this distance the metallic type spectra, however, seem to get restored on either side of the boundary. These observations indicate that the effective overall width of the grain-boundary region in YNi_2B_2C, where the atomic lattice is noticeably disturbed, is around 60 Å. The overall boundary width of 60 Å observed for YNi_2B_2C compares well with the reported value of its range of coherence and thus it is not surprising that the boundary does serve as a weak link as manifested through the rf superconducting quantum interference device effect.[6,7]

The above studies, when repeated for MgB_2, however, yielded unexpected results. The spectra obtained at the center of the grain boundaries, where the amorphous disorder is expected to be maximum, were far from quasi-insulating and instead were metallic-type and indeed did not seem to change significantly from those obtained from the center of the metallic grains. Figure 3 depicts a number of normalized conductance spectra obtained on a line as one moves along the width of the grain boundary and typical spectra observed at the middle of one of the adjoining grains. The characteristic V-shaped spectra observed in the grain-boundary region do not seem to vary noticeably from each other and from the grain interior. Moreover, a small dip at lower bias voltages is also observed in all STS plots. The origin of this dip is at present not clear.

These results show that the amorphous region of the grain boundary in MgB_2 is quite different from YNi_2B_2C, and instead of being quasi-insulating it is metallic. Consequently, the grains in MgB_2 seem to be mutually coupled through strong proximity or superconductor-normal-superconductor-type junctions. Such junctions, unlike the S-I-S type, in general may have only marginal effect on J_c, except perhaps close to the upper critical field Hc_2. This might explain the negative curvature of $Hc_2(T)$ near $T=T_c$ observed[2] for MgB_2. Further, in the case of low-T_c superconductors it has been shown that the proximity junctions can serve as effective pinning centers[8] for realizing high J_c values and thus it may not be unlikely that the presence of such junctions might in fact be responsible for the observed high J_c potential of MgB_2.

To sum up, our STM/STS studies have revealed that grain boundaries in intermetallic superconductor YNi_2B_2C, which show weak-link effects, are quasi-insulating in nature. On the other hand, the metallic character of the grain boundaries in MgB_2, although the grain boundaries are wider, leads to strong proximity coupling between the grains, and hence the absence of weak-link behavior could be explained.

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