Ti and Zr doped MgB$_2$ bulk superconductors

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Abstract. We report on a thorough characterisation of MgB$_2$ bulk superconductors doped with 10 at% Ti (T$_c$ = 36.54 K) or 10 at% Zr (T$_c$ = 37.10 K). The upper critical field was determined resistively. It extrapolates to 28 T at 0 K in both cases and is, therefore, considerably larger than for pure MgB$_2$ (~20 T at 0 K). The irreversibility lines were also determined resistively (offset of the resistive transition). The irreversibility fields are much higher than in pure MgB$_2$ and reach, e.g., 15 T at 7.5 K in MgB$_2$ (10 at% Ti). The critical current densities were determined from ac measurements employing the flux profile technique. They are enhanced by a factor of 2 and more at 20 K compared to pure MgB$_2$. Finally, we report on results obtained after neutron irradiation of the samples, which show further significant improvements of their transport properties, especially at low temperatures and high magnetic fields.

1. Introduction

Since the discovery of superconductivity in MgB$_2$ [1], a lot of efforts have been made to improve the irreversibility fields and the critical current density. One method to improve J$_c$ in bulk samples is based on doping MgB$_2$. Powder of the doping material is used as a sintering assistant. This method does not change the crystal structure of MgB$_2$, but has a large influence on the growth rate of the grains and the connectivity between them. Another method to improve the high field characteristics of MgB$_2$ is neutron irradiation. The defects are mainly produced by the $^{10}$B(n,$\alpha$)$^{7}$Li reaction. Fast neutrons colliding with the lattice atoms induce less damage. The primary aim of this paper is to demonstrate the improvement of Ti- or Zr-doped MgB$_2$ compared to undoped MgB$_2$ for high magnetic field applications. Secondly, we will compare the upper critical field, the irreversibility field and the critical currents before and after neutron irradiation.

2. Experimental

The undoped MgB$_2$ sample was produced by the hot isostatic pressing method [2] (200 MPa, 1000 °C for 2 h). Bulk samples with a density reaching the theoretical density can be produced in this way [3]. The Ti- and Zr-doped MgB$_2$ samples were produced by a high pressure synthesis method [4] (2 GPa, 800 °C for 1 h with an addition of 10 wt. % Ti or Zr).

T$_c$ was obtained from ac susceptibility measurements (30 $\mu$T amplitude) in a commercial 1 T SQUID. T$_c$ is defined by the point of intersection of the zero line and the tangent through 90% and
10% of the magnetic moment in the superconducting state. $T_c$ is the temperature difference between 90% and 10% of the magnetic moment.

The resistive transitions of the samples were measured in a 17 T superconducting solenoid at fixed magnetic fields (0 – 15 T). The temperature was swept at a rate of 10 K/h. The current through the sample was set to 100 mA. The magnetic field was parallel to the longest side of the sample. The onset ($B_{c2}$) is defined as 90% of the normal state resistivity at each given magnetic field. For the offset ("irreversibility line") a 10% criterion was used.

A standard lock-in technique was used to measure the ac susceptibility. An ac field of 0.1-10 mT was superimposed parallel to the dc field (up to 15 T). The frequency of the ac field was set to 9.0 Hz. The critical current densities $J_c$ at different temperatures were calculated numerically based on the Bean model and the actual sample geometry.

The neutron irradiation of the samples was performed in the central irradiation facility of the TRIGA-MARK II research reactor in Vienna (fast/thermal neutron flux density: $7.6/6.1 \times 10^{16} \text{m}^{-2}\text{s}^{-1}$ [5]) to a fast neutron fluence of $10^{22} \text{m}^{-2}$ (E > 0.1 MeV). A cadmium shield was used to reduce the inhomogeneity of the resulting defect structure [6].

3. Results and Discussion

The transition temperature $T_c$ of the doped samples is lower than that of undoped MgB$_2$, by 2.36 K (Ti) and by 1.80 K (Zr), respectively. After irradiation, $T_c$ decreased further, by 2.45 K (Ti) and by 2.09 K (Zr), respectively. The transition widths are nearly the same for all samples, but clearly enhanced after irradiation. The results generally agree with previous work.

| Sample | Before neutron irradiation | After neutron irradiation |
|--------|-----------------------------|---------------------------|
|        | $x_1$ (mm) | $x_2$ (mm) | $x_3$ (mm) | $T_c$ (K) | $T_{irr}$ (K) | $T_c$ (K) | $T_{irr}$ (K) |
| MgB$_2$ +10 wt% Ti | 2.90 | 2.80 | 1.45 | 36.54 | 0.30 | 34.09 | 0.76 |
| MgB$_2$ +10 wt% Zr | 2.95 | 2.85 | 1.65 | 37.10 | 0.26 | 35.01 | 0.82 |
| Undoped MgB$_2$ | 11.40 | 2.50 | 1.50 | 38.90 | 0.25 | 36.35 | 0.75 |

In the irradiated states the upper critical field ($B_{c2}$) increases at temperatures below 19 K (figures 1 & 2). The $B_{c2}(T)$-curves become steeper indicating an increase of $B_{c2}$ at 0 K. Linear extrapolation of the resistive data to 0 K confirm the significant doping effect on $B_{c2}$ (0 K), i.e. ~28 T versus ~20 T in the undoped material. After the irradiation, we find 32, 33, and 34 T for the undoped, Ti- doped and Zr- doped material, respectively.

Neutron irradiation also results in an increase of the irreversibility field ($B_{irr}$) at temperatures below 19.6 K and 21.8 K for the Ti- and Zr- doped materials, respectively.

Table 1. Sample sizes, tranistion temperature $T_c$ and tranistion width $T_{irr}$ before and after neutron irradiation.
A comparison of the $B_{c2}$ and IL data for all samples is shown in figures 3 and 4. Whereas $B_{c2}$ and IL are clearly lower in the undoped material, the results are very similar for both dopants. However, after the neutron irradiation (figure 4) all data nearly collapse on a single curve within the investigated field and temperature range. This clearly indicates that the enhancement of $B_{c2}$, resulting from the reduction of the mean free path of the charge carriers and the corresponding reduction of the coherence length, is the dominating effect in MgB$_2$.

A comparison of the critical current densities $J_c$ in undoped and Ti- or Zr- doped MgB$_2$ confirms the beneficial effect of doping at all fields up to 11 T (figure 5). Below 1 T the critical current density in the doped samples is twice as high as in undoped MgB$_2$. The difference in $J_c$ between undoped and doped MgB$_2$ increases at higher magnetic fields, up to a factor of 10. After neutron irradiation, $J_c$ increases further in all samples at high magnetic fields (figure 6). Hence, neutron irradiation effects also dominate $J_c$, bringing the $J_c$-curves closer together and leading to nearly the same field dependence.
The influence of neutron irradiation on $J_c$ in the doped samples is emphasized in figures 7 and 8. We find very significant $J_c$ enhancements at 5 K at all fields above ~1 T. At 20 K, these effects are less pronounced and occur at higher fields ($2 - 3$ T). The results are in general agreement with the percolation model for current transport in polycrystalline MgB$_2$ [7] and provide further evidence for the interplay between anisotropy, mean free path effects and flux pinning, as outlined recently [8].

4. Summary
Doping MgB$_2$ with Ti or Zr enhances the upper critical field, the irreversibility fields and the critical current densities, whereas the transition temperature is only slightly reduced. It represents a promising method for producing a superconductor for high magnetic field applications in the temperature range of liquid hydrogen.

We demonstrate in this paper that the radiation-induced defect structures are even more effective and lead to almost identical results on the irreversible properties of MgB$_2$, whether or not the material is doped by suitable dopants, such as Ti or Zr.
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