AN ION-CHANNELING STUDY OF IRRADIATION-INDUCED AMORPHIZATION OF YBa$_2$Cu$_3$O$_{7-x}$

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We previously employed Brillouin scattering to demonstrate that the irradiation-induced crystalline-to-amorphous (c-a) transformation in several intermetallic compounds was preceded by a large (>50%) decrease in shear elastic constant, indicative of an elastic instability. In situ electron diffraction revealed that the elastic softening was caused by static atom displacements. Here we report the results of an ion-channeling study designed to examine whether parallel changes occur during ion irradiation of single crystals of YBa$_2$Cu$_3$O$_{7-x}$. The (static plus thermal) atomic displacements introduced during 1.5-MeV $^4$He irradiation at a temperature of 100K were determined from [001] axial channeling scans taken after several irradiation increments between 0 and 0.04 dpa. It was possible to obtain reliable channeling information at quite low doses, as low as 0.0004 dpa, because of the excellent minimum yields ($X_{min} < 3\%$) obtained from the high-quality single crystals. In agreement with the previous observations in intermetallic compounds, large atomic displacements, implying a drop in elastic modulus of >90%, were found prior to the onset of amorphization. However, $X_{min}$ was found to be directly proportional to dose over a very broad range. The observed linear dependence on dose indicates that the irradiation-induced disorder develops continuously, and at the same rate, from the very onset of the irradiation to nearly complete amorphization.

1. INTRODUCTION

Similar to what occurs in many traditional superconductors, irradiation of YBa$_2$Cu$_3$O$_{7-x}$ with ions or neutrons has been shown to generate large (x10) enhancements in its critical current density [1-3]. Simultaneous with these enhancements, this high-$T_c$ material undergoes a metal to semiconductor phase transition as a function of increasing irradiation dose. It becomes amorphous, and insulating, at doses between 0.1 and 0.2 dpa [4,5]. The large effort now focussed on understanding these irradiation-induced phase changes is driven by the strong technological incentive for increasing the critical current capacity of high-$T_c$ materials.

Kirk et al. [5] have used *in situ* electron microscopy to identify the formation of a cellular microstructure, in which 10-30 nm regions of apparently good superconductor are surrounded by walls of an amorphous phase, during both ion and neutron irradiation of YBa$_2$Cu$_3$O$_{7-x}$. This cellular microstructure forms near dose levels where the peak in critical current enhancement is found, and offers a simple explanation for the metal-semiconductor-insulator phase development. We have previously shown that irradiation-induced amorphization of ordered intermetallic compounds is preceded by a first-order phase transformation triggered by an elastic instability [6]. Such a transformation, which in many ways parallels the melting of a solid at its absolute limit of superheating [7], would provide a natural explanation for the observed cellular microstructure in YBa$_2$Cu$_3$O$_{7-x}$. Additionally, the identification of a similar phase transformation in YBa$_2$Cu$_3$O$_{7-x}$ could provide a convenient and accurate marker for optimizing the critical current capacity.

Although not directly addressed by the original authors, there is in fact previous evidence to suggest that an elastically driven phase transformation does occur in YBa$_2$Cu$_3$O$_{7-x}$ during irradiation. Meyer et al. [8] used ion channeling along the [001] axis of a thin-film specimen to measure the apparent change in Debye temperature, $\Delta \theta_D$, after irradiation at room temperature to several doses with 2-MeV He. In the Debye approximation, $\theta_D$ is directly proportional to the velocity of sound. Since the elastic constant equals the product of the density times the sound velocity squared, and the density change is small, the relative change in elastic modulus, $\Delta C/C$, can be written:

$$\frac{\Delta C}{C} = \left(\frac{\Delta \theta_D}{\theta_D}\right)^2$$

Meyer et al. [8] found that $\theta_D$ dropped from 230 to 170K by a calculated dose of ~0.02 dpa. According to Eq. 1, this 60 oK decrease corresponds to an ~50% decrease in
elastic modulus, which agrees very well with our previous studies of irradiation-induced amorphization in intermetallic compounds [6].

Unfortunately there are problems in interpreting the previous ion-channeling results in such a simple fashion. First, the results were obtained using a nonsuperconducting (tetragonal phase) sample. Furthermore, the minimum RBS channeling yield, $X_{\text{min}}$, of the thin-film specimens measured prior to irradiation was relatively high, 5-30%, precluding accurate measurements at very low doses. Finally, a sharp drop in $\theta_D$, which is indicative of a phase transformation triggered by an elastic instability, was actually seen over only one of the selected irradiation intervals. For these reasons, we have performed an ion-channeling study along the [001] direction (c-axis) in high-quality (minimum RBS yield of ≤3% and a $T_c$ ≥ 92K), orthorhombic single-crystals of YBa$_2$Cu$_3$O$_{7-x}$ after irradiation to several doses with 1.5-MeV $^4$He. The results, which yield a drop in $\theta_D$ of almost 75%, and therefore imply a decrease of ≥ 90% in elastic modulus, are discussed below.

2. EXPERIMENT AND RESULTS

Experimental details related to the present measurements can be found elsewhere [10]. Briefly, single crystals of YBa$_2$Cu$_3$O$_{7-x}$ were grown by a self-flux method. Magnetic shielding measurements on samples annealed in flowing O for 10 days at 450 °C exhibited sharp (~1.5K width) superconducting transitions centered at 92.8K. Samples were mounted with a metal-containing epoxy on a precision double-axis goniometer (angular resolution of 0.01°). The 0.5-mm-diameter analysis beam of 1.5-MeV $^4$He was collimated to a divergence ≤0.05°. A solid-state RBS detector (FWHM = 16 keV; 30 mm$^2$ area) was positioned approximately 4 cm from the specimen at a scattering angle of 165°. The vacuum in the chamber was <5 x 10$^{-9}$ torr during analysis. The specimen temperature was monitored with a platinum resistance thermometer attached
to the specimen stage, and could be stabilized to within ± 3° between 30 and 300K.

Irradiations were performed at 100K with a 3-mm diameter beam of 1.5-MeV ⁴He at a nominal flux of 1 x 10¹³ ions/cm². The angle between the specimen normal and the beam was ~7°. This temperature was chosen because it is low enough to obtain good minimum yields, but still high enough to prevent potential complications from the previously observed anomalies in channeling scans at Tc [10]. The channeling data were taken with a 0.5 mm diameter beam, sequentially from the same specimen area, without intermediate warming (one exception is discussed below). A TRIM89 calculation [11] using an average threshold displacement energy of 20 eV yields 1 dpa for a dose of 1.28 x 10¹⁸ cm⁻², and an average projected range of 2.9 μm. A dose of ~1 x 10¹⁵ cm⁻² is required to obtain one axial scan to the desired statistical accuracy. However, the damage rate is reduced greatly along a channeling direction, so the effect of the analysis beam is essentially insignificant. The energy discriminator was set to accept RBS counts from immediately below the Cu leading edge to just above that of O. The RBS yield therefore contains information from Y, Ba and Cu weighted by the square of their respective atomic numbers. The analysis depth is ~700 nm, i.e., much less than the projected ion range.

[001] axial RBS-channeling scans obtained after irradiation doses of 0, 0.0015, 0.015, and 0.04 dpa are shown in Fig. 1. The low minimum yield, ≤3%, found for Y, Ba, and Cu in the initial scan over the relatively large depth of 700 nm demonstrates the excellent quality of the single-crystal specimens. The absence of prominent "shoulders" on the scans is due to the large depth of analysis. The FWHM decreases and X_min increases monotonically with increasing irradiation dose in Fig. 1.
The $X_{\text{min}}$ values extracted from the raw data shown in Fig. 1 are displayed in Fig. 2. $X_{\text{min}}$ is seen to increase linearly with increasing dose. The slight drop evident at a dose of 0.0155 dpa is a result of annealing during an inadvertent overnight warm-up to near room temperature. It is clear that the total amount of recovery was small. Some annealing of irradiation-induced defects is known to occur in YBa$_2$Cu$_3$O$_{7-x}$ between 150 and 300K, and is believed to result from a rearrangement of displaced O atoms [8].

3. DISCUSSION

Previous studies have also yielded a linear dependence of $X_{\text{min}}$ on dose. The slope of the present results, $< 10$ dpa$^{-1}$, is somewhat less than the 12 dpa$^{-1}$ reported for the highest-quality thin-film studied by Meyer et al. [8]. The lower slope found here is consistent with the generally held view that the higher the initial crystal quality in YBa$_2$Cu$_3$O$_{7-x}$, the more resistant the structure is to irradiation. An extrapolation of the disordered atom fraction, which is essentially equal to $X_{\text{min}}$ [12], indicates complete amorphization ($X_{\text{min}} = 1$) at a dose $\geq 0.1$ dpa, which is also in good agreement with determinations made using x-rays [8] and TEM [5]. By a dose of 0.05 dpa, the disordered fraction equals 50%, i.e., the disordered fraction is ten times larger than the calculated dpa. This high ratio indicates that the atomic displacements are converted into structural order extremely efficiently.

The steady decrease in the width of the axial scans in Fig. 1 indicates a corresponding increase in the Debye-Waller factor (static plus dynamic contributions). As discussed in detail elsewhere [10,12], the FWHM or $X_{\text{min}}$ of the individual scans can be used to estimate the lattice Debye temperature, $\theta_D$. Values of $\theta_D$ obtained according to this prescription are also shown as a function of dose in Fig. 2. The general shape of the curve, an initial strong
decrease followed by a gradual leveling off above about 0.02 dpa is very similar to the behavior reported [8] in tetragonal YBa$_2$Cu$_3$O$_{7-x}$. Previous work [4] has also shown that the T$_c$ drops to below 4.2K after irradiation with O atoms to a dose of 0.035 dpa. The observed drop in T$_c$ therefore correlates well with the strong decrease seen in $\theta_D$.

We turn next to a discussion of the evidence regarding the possible triggering of the observed structural disorder, and eventual amorphization, by an elastic instability. We have previously reported [6,13] large (≥50%) decreases in the elastic constants of three intermetallic compounds (Zr$_3$Al, Nb$_3$Ir, and FeTi) prior to their becoming amorphous during irradiation; only relatively small (≤10%) changes were measured in two compounds (FeAl and NiAl) that did not amorphize. This correlation was one of two strong indications that the irradiation-induced amorphization of intermetallic compounds was induced by an elastic instability. The large decrease (Fig. 2) in $\theta_D$ found in YBa$_2$Cu$_3$O$_{7-x}$, and the correspondingly large change in elastic properties indicated by Eq. 1, are clearly consistent with such an interpretation.

The second indication that an elastic instability was responsible for amorphization of the intermetallic compounds was the discovery of discontinuous changes in the lattice parameter, in the long-range chemical order, and in the measured elastic constant, over a very narrow dose range prior to amorphization [6]. In this respect, the information shown in Fig 2 is quite different. Only a smooth monotonic decrease is evident for $\theta_D$, although the measurement statistics certainly allow room for small fluctuations to have occurred. Nevertheless, the X$_{\text{min}}$ data, which can be determined with quite high accuracy, exhibit a very clear linear dependence on irradiation dose. Hence there is no indication that the accumulation of disorder during irradiation of YBa$_2$Cu$_3$O$_{7-x}$ is anything but linear, and no evidence of an abrupt structural collapse is found.
The strikingly linear dependence of $X_{\text{min}}$ on irradiation dose, in particular over the broad range from 0.0004 to 0.04 dpa, is actually quite remarkable in itself. This direct proportionality indicates that the lattice is disordering at the same rate when less than one out of every two-thousand atoms has been displaced as it does when one out of 25 atoms are displaced. The simple picture we have taken above, and which has often been assumed by others [12], is that $X_{\text{min}}$ represents the fraction of atoms that has been displaced from regular lattice sites. The extrapolation pointed out above, that yields $X_{\text{min}} \approx 1$ for a dose of 0.1 dpa in agreement with x-ray and TEM results showing complete amorphization at the same dose, is consistent with this simple picture. However, the value 0.1 dpa means that only one-tenth of the atoms have actually been displaced, not the nearly 100% that complete amorphization implies.

Furthermore, because of radiation annealing effects, in which previously generated Frenkel defects spontaneously recombine due to nearby subsequent displacements, the production of lattice defects as a function of irradiation dose is known to exhibit negative curvature even at very low doses, $\leq 10^{-5}$ dpa [14]. Hence it is clear that $X_{\text{min}}$ is in reality measuring a more complex lattice rearrangement than the simple Frenkel-pair picture usually adopted [15]. In this regard, the conclusion by Meyer et al. [8] that the same number of atoms were displaced on each sublattice in YBa$_2$Cu$_3$O$_{7-x}$ seems worthy of further examination.

In summary, the present channeling results clearly show that irradiation at 100K induces large average atom displacements in orthorhombic single-crystals of YBa$_2$Cu$_3$O$_{7-x}$. The change in Debye temperature extracted from these measurements implies a very strong decrease in the elastic properties of YBa$_2$Cu$_3$O$_{7-x}$ prior to amorphization. However, the simultaneous measurements of $X_{\text{min}}$ indicate that the structural disorder characteristic of an amorphous structure accumulates in a linear fashion with ion dose, beginning from the very onset of irradiation. This latter
observation, with the caveat that the interpretation of $X_{\text{min}}$ on the atomistic level remains unclear, appears inconsistent with the triggering of amorphization by an elastic instability.

REFERENCES


FIGURE CAPTIONS

Fig. 1. [001] axial channeling scans measured at 100K in YBa$_2$Cu$_3$O$_{7-x}$ after doses of (0, 2, 20 and 50) x $10^{15}$ cm$^{-2}$ of 1.5 MeV He.

Fig. 2. The relative change in Debye temperature ($\Delta \theta_D/\theta_D$), and the minimum yield ($X_{\text{min}}$) plotted as a function of irradiation dose (dpa).