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Defect Cascades Produced by Neutron Irradiation in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ *

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ABSTRACT

The defect cascades produced by fast neutron irradiation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were studied by transmission electron microscopy. The visible defects were found to have sizes between 1 and 5 nm. Defect densities were obtained as a function of neutron fluence between 2 and $8 \times 10^{21} \text{ m}^{-2}$ ($E > 0.1 \text{ MeV}$) and compared to damage calculations. The measured defect density was found to scale linearly with fluence and to be $1 \times 10^{22} \text{ m}^{-3}$ at $2 \times 10^{21} \text{ m}^{-2}$. The defect stability was studied at room temperature and through annealing to 400°C . The high fluence regime ($\sim 10^{22} \text{ m}^{-2}$) was investigated as well.

§1. INTRODUCTION

Irradiation experiments in high temperature superconductors have been a very active field in the last years. They can help in the investigation of flux pinning mechanisms but they are also interesting from an application point of view because of the possibility of enhancements of the critical current density, J_c , which is too low in the bulk materials for applications. There is already an extreme wealth of literature on the response of the various

high T_c materials to different irradiation conditions, for reviews see, e.g., [Weber 1992, Weber and Crabtree 1992; Chu, Liu and Zhang 1991].

Transmission electron microscopy (TEM) is a very powerful tool to investigate defects in materials and has been used for this purpose for many years. The knowledge of defect concentration, sizes and their structure in combination with measurements of superconducting parameters, such as T_c and J_c , is necessary in order to understand the pinning mechanism in these materials. When this will be understood, it may be possible to tailor the properties of the high T_c materials for specific applications.

There have been some reports on TEM of irradiation induced defects in high T_c materials, for a review see [Kirk and Weber 1992]. However, these reports have been few and inconclusive. Therefore we performed an extensive program to study the defects produced by neutron irradiation.

To model the defects produced by the primary knock-ons (PKOs) with high energy, initial experiments with ions [Frischherz, Kirk, Zhang and Weber 1992] were performed. The first neutron irradiation experiments performed by us revealed a novel "cellular" structure [Kirk, Frischherz, Liu, Greenwood and Weber 1990] at a rather high fluence of $2 \times 10^{22} \text{ m}^{-2}$. In this paper we mainly report on individual defect cascades produced at lower fluences, but we also performed experiments at higher fluences and found some disagreement with our earlier results.

§2. EXPERIMENTAL PROCEDURES

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals were grown by the flux method in gold crucibles [Kaiser, Holtzberg, Chisholm and Worthington 1987], with typical sizes of $1 \times 0.5 \times 0.1 \text{ mm}^3$. After a suitable oxygen treatment the onset of the superconducting transition temperature was between 90 and 92 K, with a transition width of 0.5 - 1 K, measured in a low field SQUID [Vandervoort, Griffith, Claus and Crabtree 1991]. Thinning for TEM was done by crushing the crystals in methanol and transferring them to a 1000 mesh grid without the use of a carbon film. The grid material was copper for those samples, which were thinned prior to irradiation, and gold for those crushed after irradiation, since gold should be avoided in a reactor due to its high activation cross section. This mounting technique resulted in several thin areas most of the time, which were surprisingly stable mechanically. Even an occasional dropping of the sample usually did not result in a loss of areas, nor did the whole process of neutron irradiation, including removal of the quartz vial with a manipulator in a hot cell and transportation from the reactor. Samples were stored in a bell jar which was evacuated and backfilled with dry nitrogen. They were very stable, in one case a sample was looked at one year after preparation and irradiation and had not degraded.

The samples, either thinned and deposited on grids or whole crystals, were sealed in quartz tubes, which were backfilled with helium. The quartz tubes were sometimes wrapped loosely in 0.5 mm cadmium sheets in order to shield thermal neutrons. This was done for two reasons: Firstly, it cuts down the activity of the sample by approximately a factor two, and secondly, we wanted to investigate whether thermal neutrons produced any damage visible in TEM or magnetization measurements. Then the quartz tubes were put into flooded aluminium cans and irradiated in the H1 position (outside the core but within the graphite reflector) of the Missouri University Research Reactor (MURR), or in the core of the TRIGA reactor Vienna, and in one case in the low temperature irradiation facility (TTB) of the FRM reactor in Munich at 5 K. All three reactors have a mixed neutron spectrum with a degraded fission peak, a 1/E epithermal regime and a thermal peak. The water temperature reaches 43 °C at full power at MURR, 30 °C at the TRIGA, the sample temperature is known to not exceed 50 °C during irradiation at TRIGA. Samples were irradiated to 2, 4, 8 and $30 \times 10^{21} \text{ m}^{-2}$ ($E > 0.1 \text{ MeV}$).

Electron microscopy was performed at a voltage of 100 kV, which is below the threshold for knock-on damage in $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ [Kirk, Baker, Liu, Lam and Weber 1988], on a JEOL 100CX and a Philips CM 30 microscope. Dark field (DF) images with $g = 200$, 020 and 006 were taken near the [001] or [100] pole under two-beam diffraction conditions.

The *in situ* annealing in the microscope was performed in a Gatan double-tilt heating stage which is equipped with a thermo-couple for temperature measurement. Annealing was done with the electron-beam off by heating quickly to 200 °C or 400 °C and keeping the temperature constant for 10 minutes, turning off the heater and waiting for thermal equilibration. These annealing times and temperatures were chosen such that they amount to approximately the same diffusion lengths for oxygen in the basal plane as the conditions under which the bulk crystals of [Vlcek, Frischherz, Fleshler, Welp, Liu, Downey, Vandervoort, Crabtree, Kirk, Giapintzakis and Farmer 1992] were annealed. The diffusion lengths were calculated using the diffusion constants from [Rothman, Routbort and Baker 1991].

Counting and sizing of the defects has been described elsewhere [Frischherz, Kirk, Zhang and Weber 1992]. For calculating the defect densities, the projected thickness had to be determined. This was usually done by tilting a twin boundary by a known angle along [110] and measuring its apparent width. If a twin boundary was encountered in a [100] oriented piece, it is, of course, already tilted by 45°. Comparing the measured thicknesses with DF images at the exact Bragg angle ($s = 0$), showed a rough agreement with the value of the extinction distance ξ , as calculated by the computer code EMS [Stadelmann 1987], i.e. 40 nm for $g = 200$, although in most cases, where the comparison was made, it was between 40 and 50 nm. In pieces where no twin boundary was found, the thickness fringes in $s = 0$ DF images were used for a rough estimate of the thickness.

§3. RESULTS

§3.1 INDIVIDUAL DEFECT CASCADES: STRAIN FIELD, SIZES AND DENSITIES

Fig. 1 shows an area prior to and after irradiation to $2 \times 10^{21} \text{ m}^{-2}$. The area, which was photographed on one negative after irradiation is divided between two negatives before irradiation (left panel), but the two negatives overlapped perfectly (the white horizontal line shows the border between the negatives). This area does not show any visible defects prior to irradiation, but after irradiation several defects, some of them circled, can clearly be identified. Under $g = 200$ (middle panel) all of them appear as black/white lobe features with $\mathbf{l}$, the vector from the centre of the black to the centre of the white lobe, parallel or anti-parallel to g . The viewing direction in this piece is $[010]$ (a and b axes arbitrarily assigned), hence, the second most intense reflection is 006. The right panel shows a DF image taken with the 006 diffracted beam. Some of the defects shown in the middle panel also appear with a black/white contrast (these are labelled "1"), some show up only with a black dot contrast (labelled "2"), and some are not visible in 006 (labelled "3"). The defects, which exhibit black/white contrast, have again $\mathbf{l}$ parallel to g .

It was found that the defect contrast was critically dependent on the exact diffraction conditions, with a normalized excitation error $w = |s| \xi_g$ of 1.3 being best, i.e., in a diffraction pattern (DP) the bright (300) Kikuchi line is outside the (300) and the (400) Kikuchi line inside the (400) spot, similar to our observations in ion-irradiated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [Frischherz et al. 1992]. There, we showed that ion irradiation produced defects with hydrostatic strain fields of the vacancy type. Because $\mathbf{l}$ oscillates with depth [Chik, Wilkens and Rühle 1967] and because neutron irradiation produces defects, which are homogeneously distributed throughout the foil, we expect parallel and anti-parallel to be randomly distributed, which is the case. We therefore suggest, that most of the visible defects produced here are of the same kind as the ones produced by low energy medium to heavy ions.

One of the best pictures at a dose of $2 \times 10^{21} \text{ m}^{-2}$ is shown in Fig. 2. Again a number of black/white features can be seen, some of them arrowed. From this and several other pieces, both crushed and electropolished, Cd-wrapped and unwrapped, close to both major poles, $[001]$ and $[100]$, always the same density of visible defects was measured within the experimental error: $1 \pm 0.5 \times 10^{22} \text{ m}^{-3}$. For six areas this yields a standard deviation of 30%.

Similar to earlier observations in ion-irradiated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [Frischherz et al. 1992] an asymmetry between $g = 200$ and 020 has been observed. This is demonstrated in Fig. 3 which compares the same area in 200, 020 and 110 DF images. The defects labelled a, b, d, g and i are visible in all three micrographs, defects c, e and f only in 200 and 020, defects h and j only in 200 and 110 and defect k only in 200. This is in contrast to the ion results, where it

was found that all defects visible in 200 are visible in 110 and $1\bar{1}0$, but only about 60 % of them are visible in 020. Generally, it is difficult to image these defects in any other condition than 200. Visibility seems to be more sensitive to s , and therefore a slight bending of the foil can bring the defects up in one part of an area, but make them invisible in another one. Particularly, in the electropolished sample, it was impossible to find defects in 020. Since it was thinned after irradiation, it is possible that some interaction between the polish, which contains lithium [Wheeler 1991], and the defects occurred. Li could intercalate into $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and relieve the strain in the 020 direction, which is already weaker than the strain in the 200 direction due to the presence of the oxygen atoms along the chains. This could explain the invisibility. The invisibility cannot be due to a $\mathbf{g} \cdot \mathbf{b} = 0$ criterion, because dislocation loops have $\mathbf{l}$ parallel to $\mathbf{b}$, whereas we find $\mathbf{l}$ almost always parallel (or anti-parallel) to $\mathbf{g}$. Another observation to be made here is that surface artefacts show up more prominently in 020 images than in 200 images (most of the little black dots in 020 cannot be found in the two other images and are therefore believed to not be irradiation defects). Also the curved line (a dislocation) in the middle of the 020 image shows up only partly in 110 and not at all in 200.

The fluence dependence of the defect density is qualitatively demonstrated in Fig. 4. Three different samples are shown, irradiated to 2, 4 and $8 \times 10^{21} \text{ m}^{-2}$ ($E > 0.1 \text{ MeV}$). The samples at the two lower fluences were irradiated at MURR, the sample with 8×10^{21} was irradiated at 5 K in the low temperature irradiation facility of the research reactor Munich (FRM-TTB). The defect densities are $1 (\pm 0.3)$, $2 (\pm 1)$ and $4 (\pm 2) \times 10^{22} \text{ m}^{-3}$. Thus, the defect density is seen to increase linearly with fluence up to $8 \times 10^{21} \text{ m}^{-2}$ within the experimental error.

Fig. 5 shows a sample that was irradiated to $8 \times 10^{21} \text{ m}^{-2}$ at MURR. It, too, has a defect density of $4 \times 10^{22} \text{ m}^{-3}$, demonstrating that the visible defect density does not depend on the irradiation temperature, and is also insensitive to some neutron-spectrum differences (unless the two effects are compensating each other, which is unlikely). MURR has a softer spectrum than FRM, in particular more thermal neutrons. 31 % of the neutrons at FRM have an energy $> 0.1 \text{ MeV}$ but only 9 % at MURR. The visible defect density in the twin to the left of the twin boundary is much lower. This is due to two effects: Firstly, the operating reflection is 020, and secondly, the excitation error is smaller in this twin when it is optimized for the other twin, as can be seen from the different spacings of the thickness fringes.

The defects were also characterized in their sizes. Fig. 6 shows a distribution of sizes, defined as the length of the interface between the black and the white lobe, from a sample irradiated to $4 \times 10^{21} \text{ m}^{-2}$. [Saldin, Stathopoulos and Whelan 1979] found that this interface length corresponds closely to the defect size. The mean diameter is 2.5 nm. The strain field

measured perpendicular to the black-white interface is about 2.5 times the length of the interface for each defect. Thus, the mean strain field diameter amounts to 6 nm.

§3.2 DAMAGE CALCULATIONS

Calculations of the recoil spectrum and damage [Frischherz, Kirk, Weber and Greenwood 1992] were also performed in order to compare the measured defect densities with the calculated density of events above some energy. The computer code SPECTER [Greenwood 1989] was used. Fig. 7 shows the cross sections (normalized for neutron fluences with $E > 0.1$ MeV) for events above a certain energy, for all four sublattices for irradiation at MURR and for Cu additionally for the TRIGA reactor. Then the density of events > 30 keV was calculated, which was chosen as an approximate threshold energy for production of TEM visible defects. This threshold was observed for neutron - [Rühle 1967] and self ion - irradiation [Merkle 1966] of Cu. Earlier experiments of ion - irradiated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [Frischherz et al., 1992] have shown that 50 % of the defects produced by 50 keV Kr or 50 keV Xe ions are visible, which makes 30 keV a reasonable threshold energy for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The calculated density is $1.9 \times 10^{22} \text{ m}^{-3}$ for $2 \times 10^{21} \text{ m}^{-2}$ at MURR. Considering that only 50 % of the ion produced defects were visible, the measured defect density of $1 \times 10^{22} \text{ m}^{-3}$ agrees nicely with this calculation.

§3.3 STABILITY OF THE DEFECTS AT ROOM TEMPERATURE AND AT ELEVATED TEMPERATURES

Because there was some evidence for annealing at room temperature in magnetization measurements [Vlcek et al. 1992], the stability of the defects was investigated. [Vlcek et al. 1992] found a considerable decrease of the radiation induced J_c enhancements for measurements with $\mathbf{H} \parallel \mathbf{ab}$ after 10 weeks of storage at room temperature, but very small changes for $\mathbf{H} \parallel \mathbf{c}$. Fig. 8 shows the same area 3 weeks and 3 months after irradiation. Some of the defects are arrowed. Clearly, almost all defects that were visible shortly after irradiation, are still visible, the few missing ones ($< 10\%$) can be attributed to surface degradation due to the long electron beam time spent on this sample, or to not exactly reproducing the earlier diffraction conditions. Clearly, no substantial, if any, annealing of the defect cascades takes place.

In order to investigate the stability at elevated temperatures, one sample was annealed *in situ*. The result is shown in Fig. 9, where the same area of a sample is shown prior to annealing, after annealing for 10 minutes at 200°C and after annealing to 400°C . Three strong defects are labelled in (a) and are clearly visible in (b), too. Of these, two are still visible in (c), albeit with somewhat weaker contrast, the third cannot be found. However, another change, namely the appearance of two perpendicular sets of lines parallel to $[110]$ and $[1\bar{1}0]$,

the tweed structure, makes it difficult to decide whether this defect has in fact disappeared or is just obscured due to the background. The tweed structure can be linked to the loss of O₂ in the microscope vacuum, when the sample was heated, and was observed in O-deficient samples before [van Tendeloo and Amelinkx 1988].

In order to ensure that the stability of the defects might not just be due to the vicinity of the surface in a necessarily thin TEM specimen, one of the crystals used by [Vlcek et al. 1992] was crushed and thinned after it had been irradiated and then annealed in air for 8 hours each at 100, 200 and 300 °C. An area is shown in Fig. 10. Several defects are arrowed, the density is $\sim 1 \times 10^{22} \text{ m}^{-3}$, the same as for the samples that were not annealed. Thus, the defects are not just stabilized by the vicinity of the surface, but are also stable in the bulk.

§3.4 IRRADIATION TO HIGH FLUENCES

It was also tried to repeat the results on high fluence irradiation published earlier [Kirk et al. 1990], where a cellular structure was found to precede amorphization. Fig. 11 shows two different areas irradiated to $3 \times 10^{22} \text{ m}^{-2}$. We find two different microstructures in these samples, one (a) with individual black/white defects as observed at lower fluences with a density of $\sim 1 \times 10^{23} \text{ m}^{-3}$, the other one (b) hardly shows any individual defects, rather just a messy picture with no clearly distinguishable features. A high resolution diffraction pattern (HRDP) across a twin boundary is shown in Fig. 11 (d). The spot splitting due to twinning is visible, but the higher order spots are not clean, rather there is some streaking along the 110 direction along which the spots are split, and some of the spots are split multiply. In contrast, a HRDP (Fig. 11c) taken in the area of Fig. 11 (a), does not show any streaking, rather all spots (even up to the highest order) are clean, except for the usual splitting due to twinning. The latter results in $b/a = 1.017$. The difference to the theoretical value of 1.014 is probably due to an inaccuracy in the sample tilt. This implies that within experimental accuracy the sample has the theoretical orthorhombicity. The same is true for (d). Also shown in (e) is the actual diffraction condition used to take (b). The same kind of two beam condition could be achieved for this sample as for unirradiated samples, the 300 and 400 excess and deficient Kikuchi lines are also visible. This is in contrast to our earlier observation [Kirk et al. 1990] that true two beam conditions could not be achieved, rather the whole systematic row of spots was excited equally, and Kikuchi lines were not observed at $1.7 \times 10^{22} \text{ m}^{-2}$. It should be pointed out here that although Fig. 11 (a) and (b) were prepared from two different crystals, the two crystals were irradiated in the same quartz tube together. They were prepared for TEM in the same way as that of the earlier study.

An explanation of these different results based on different crystals will be suggested in the discussion section.

§4. DISCUSSION

One of the main results of this investigation is the characterization of the strain field of the defects produced by neutron irradiation. It is a hydrostatic pressure centre like the defects produced by, e.g., 50 keV Xe [Frischherz et al.]. By analogy it is assumed that the defects produced by neutron irradiation have their strain field also inwardly directed. The sizes are somewhat smaller here (2 - 5 nm) as opposed to 3-7 nm for ion produced cascades, reflecting the difference in the recoil spectrum.

Individual defect cascades as reported in the present paper have been associated with flux pinning already in the conventional superconductors, for a review of irradiation effects in conventional superconductors see [Weber 1986]. Therefore, when enhancements of the critical current density, J_c , after neutron irradiation were reported for the first time [Umezawa, Crabtree, Liu, Weber, Kwok, Nunez, Moran, Sowers and Claus 1987] in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals, they were attributed to defect cascades. The sizes we report here (2-5 nm) are very close to the coherence length in the ab-plane (at ~ 77 K), and therefore of ideal size for pinning the core of a vortex line.

A good correlation between magnetization measurements and TEM can be seen in the fluence dependence. [Sauerzopf, Wiesinger, Kritscha, Weber, Frischherz and Gerstenberg 1992] report an almost exactly linear dependence of J_c (with a flattening tendency in the higher fluence range) on the neutron fluence in the range of $0.5 - 8 \times 10^{21} \text{ m}^{-2}$. This corresponds well with the linear increase of TEM visible defects in the same fluence range. Nicely corresponding with the findings of strongly overlapping defects, and a cellular structure in some cases, is the saturation and eventual degradation of J_c at fluences above $1.2 \times 10^{22} \text{ m}^{-2}$ [Sauerzopf, Wiesinger, Weber and Crabtree 1992]. The high fluence range will be discussed in more detail later on.

Defect cascades certainly provide most of the pinning enhancement observed after neutron irradiation, as can be seen from simple energy arguments [Sauerzopf et al. 1992]. However, point defects or small clusters thereof play some role, too. This was shown by electron irradiation experiments [Giapintzakis, Lee, Rice, Ginsberg, Robertson, Wheeler, Kirk and Ruault 1992]. Irradiation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with 1 MeV electrons enhanced J_c ($\mathbf{H} \parallel \mathbf{c}$) at 10 K and 1 T by factors of up to two, while TEM could not reveal defects, implying a defect size < 2 nm. Small clusters of copper point defects were proposed as pinning centres. Annealing at 200 °C reduced the enhancement completely [Giapintzakis 1992].

The role of point defects and their clusters for pinning was also investigated in neutron and proton irradiation and annealing experiments in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [Vlcek, Viswanathan, Frischherz, Fleshler, Vandervoort, Downey, Welp, Kirk and Crabtree 1992b]. In spite of different recoil spectra (point defects dominate over cascades in proton irradiations), comparable enhancements of J_c were found for both field directions. A bigger (68 %) annealing effect (at 300 °C) is observed in proton irradiated samples than in neutron irradiated samples (33 %) for $\mathbf{H} \parallel \mathbf{c}$. However, for $\mathbf{H} \parallel \mathbf{ab}$ annealing leads to a reduction of the critical currents by almost 100 %, for both types of irradiation. The data presented in this paper show that the defect cascades are stable with time at room temperature and for up to eight hours at 300 °C, in the bulk and in the thin foil. The results for $\mathbf{H} \parallel \mathbf{c}$ can be explained if we assume the pinning to be the sum of the pinning by defect cascades and some other, smaller and TEM invisible, defects, which anneal. The different amount of J_c reduction in neutron and proton irradiated samples is explained by the different relative amounts of small defect clusters and defect cascades caused by the different recoil spectra.

More puzzling is the result for $\mathbf{H} \parallel \mathbf{ab}$. Why is there no pinning in some cases when there are defect cascades? One possible explanation is the following: Because of the small coherence length ξ_c along the c-axis, the superconducting order parameter $|\psi|^2$ is almost zero in-between the CuO_2 planes, and therefore the flux lines are confined between these planes (intrinsic pinning [Tachiki and Takahashi 1989]). In this case the presence of cascades does not make a difference. However, if there are also small defects, their effect would be to smear out $|\psi|^2$ and $|\psi|^2$ would not reach zero between the planes, and defect cascades would be seen.

Another possible explanation is that defect cascades never pin for $\mathbf{H} \parallel \mathbf{ab}$. In this case the question arises what does produce the enhancement after irradiation? The answer might be provided by the results obtained on ion irradiated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [Frischherz et al. 1992]. It was shown there that low energy ion irradiation produces a melted core in the cascade which can recrystallize incoherently. The observation that only 50 % of the ions produce a TEM visible defect led to the conclusion that the remaining defects recrystallized coherently as far as the cation lattice is concerned. However, some evidence for a lower oxygen content in the incoherently recrystallized regions was found. Thus, an area of about the same size as a visible defect, ~ 3 nm, with a perfect cation lattice but depleted of oxygen, would be produced. This could be the pinning site for $\mathbf{H} \parallel \mathbf{ab}$. This could explain the annealing results, since the elevated temperatures would homogenize the O, thus annihilate this defect, but no change would be observable in the TEM.

The discrepancy between earlier results and the ones presented here for high fluences is difficult to explain. The cellular structure was observed not only in the neutron irradiated

samples but also repeatedly in ion irradiated samples [Kirk et al., 1990; Kirk, Frischherz, Liu, Funk, Thompson, Ryan, Ockers and Weber 1989], and is therefore believed not to be an artefact. There are two differences, however, between the earlier experiment at MURR and the present one: the samples were Cd shielded in the first experiment and not in this one, and the samples were thinned before irradiation then, but after irradiation now. The sample that was irradiated at the TRIGA reactor, on the other hand, had also been thinned after irradiation. The spectrum at the TRIGA reactor is considerably harder than the spectrum at MURR. Fig. 7 compares the PKA spectrum on the copper lattice for the two reactors. The cross section for recoil events > 30 keV is about 50 % higher in the TRIGA reactor than at MURR. Taking all four sublattices into account, the density of PKAs > 30 keV is $2.9 \times 10^{21} \text{ m}^{-3}$ for $3 \times 10^{22} \text{ m}^{-2}$ at MURR and $2.5 \times 10^{21} \text{ m}^{-3}$ for $2 \times 10^{22} \text{ m}^{-2}$ in the TRIGA reactor. Thus, the difference in spectrum is not enough to explain this difference. Another possibility is, that the crystal that was irradiated in the TRIGA reactor, which was grown much earlier than all the other samples, albeit by the same crystal-grower, was of lower quality than later crystals.

The different response of crystals to higher fluences of neutron irradiation can also be seen in magnetization measurements. While [Sauerzopf, Wiesinger, Kritscha, Weber, Crabtree and Liu 1991] report initial enhancements for a neutron fluence of $2 \times 10^{21} \text{ m}^{-2}$, no further enhancements in J_c were found for higher fluences up to $1.2 \times 10^{22} \text{ m}^{-2}$. This experiment was performed on a crystal from the same batch as the one in which we observed the cellular structure described in [Kirk et al. 1990]. However, later magnetization experiments, performed on a crystal grown two years later, found increasing values J_c up to $8 \times 10^{21} \text{ m}^{-2}$, as described above [Sauerzopf et al. 1992].

It is likely though that the cellular structure would be observed at higher fluences. It was already assumed in [Kirk et al. 1990] that the appearance of the cellular structure is related to the high energy events rather than to dpa values. Further calculations [Frischherz 1992] showed that the cellular structure was reached at a density of events > 30 keV of $1.2 \times 10^{24} \text{ m}^{-3}$ for irradiation with 1.5 MeV Ne, and $2.7 \times 10^{24} \text{ m}^{-3}$ for 1.7 MeV Kr. This density would be reached only after neutron fluences 5 - 10 times higher than the ones used here.

Finally we wish to comment on electron microscopy work on irradiated samples reported on by other groups. There has been a report on TEM of neutron irradiation induced defects in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. [Lee, Lessure, Laughlin, McHenry, Sankar, Willis, Cost and Maley 1990] observed dark, strain-induced contrast of circular defects with a mean size of 4.5 nm at a fluence of $3 \times 10^{22} \text{ m}^{-2}$ ($E > 0.1$ MeV), and a density of $3 \times 10^{21} \text{ m}^{-3}$. Their lack of well established diffraction conditions would explain the black dot contrast rather than the black/white contrast which is observed in this paper. While our earlier work [Kirk et al. 1990] would have suggested to expect the cellular structure at this fluence, this work suggests that

this is not necessarily the case. It is interesting to note that the irradiation by [Lee et al. 1990] was performed at 80 °C rather than at 43 °C as in our work.

Another group [Zandbergen, Kulik and Nieuwendijk 1991] reported on limitations on the monitoring with TEM of neutron irradiation induced defects. Their samples were either ion milled or crushed and deposited on holey carbon films. The latter has two disadvantages: the holey carbon film disintegrated during the irradiation leading to a loss of many areas, and secondly, the carbon can intercalate under irradiation into $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, as seen by one of us earlier under the electron beam of a TEM (Kirk: unpublished). Indeed, the most prominent defect this group observes is intercalation of extra Cu and O along the *ab*-plane. Another shortcoming of their experimental setup is the failure to backfill the radiation capsule with an exchange gas, to ensure proper cooling of the sample. They conclude that the observation of neutron induced defects is impossible in the same area before and after irradiation. While this might be true for high resolution TEM, this work shows unequivocal proof that it is possible at least in conventional TEM, provided the experiment is performed carefully.

[Zandbergen et al. 1991] also report on a cellular structure produced by neutron irradiation which was easily removed by ion milling, revealing it as a surface layer, and suggest that the cellular structure found by [Kirk et al. 1990] is also merely an artefact. This cannot be the case, since the image information was accompanied by diffraction information, showing that the damage was throughout the foil thickness, and this structure was also observed after *in situ* ion irradiations, where intercalation due to the presence of air clearly could not have happened.

[Janam, Ramakrishna, Srivastava, Dasannacharya and Vijayaraghavan 1991] report a high density of "defect stripes" after irradiation to a fluence of $1 \times 10^{20} \text{ m}^{-2}$ (no energy range is stated), and attribute it to irradiation damage. These defects appeared much like planar faults perpendicular to the *c*-axis. [Janam et al. 1991] suggest that rather than a stacking fault, these defects are long (1 μm) tubes of disorder formed by a "thermal spike" or a long cascade defect produced by the passage of a neutron. This description cannot be right because the defects must be planar to produce a sharp lattice image. Also, this description of a defect formation process by a fast neutron is unprecedented both experimentally and theoretically. However, we have observed similar planar defects in unirradiated samples.

[Xin, Jirong, Yitong, Guosheng, Xixian, Xiaoning, Meisheng and Kemin 1990] show very extensive defect structures ("dislocation loops") after fluences of $2 - 5 \times 10^{14} \text{ m}^{-2}$, fluences 7 orders of magnitude lower than the ones used in this investigation. It seems likely that this experiment suffered of problems in TEM sample preparation and handling.

§5. CONCLUSION

Neutron irradiation to low fluences was found to produce the same kind of defect cascades as ion - irradiation, hydrostatic pressure centres inwardly directed. The defects are found to be stable at room temperature and at temperatures up to 400 °C. The mean size is 2.5 nm. The visible defect density is proportional to neutron fluence up to $8 \times 10^{21} \text{ m}^{-2}$ and found to be $0.5 \times 10^{22} \text{ m}^{-3} / 10^{21} \text{ m}^{-2}$. This agrees nicely with a calculated density of PKA events above 30 keV of $0.9 \times 10^{22} \text{ m}^{-3} / 10^{21} \text{ m}^{-2}$. Irradiation to higher fluences produced in some cases a cellular structure. The fluence at which this happens seems to depend on the sample quality. Comparisons with magnetization measurements emphasize the importance of these defects as pinning centres.

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FIGURE CAPTIONS

Fig. 1 DF images of the exact same area before (left panel) and after (middle and right panels) neutron irradiation to $2 \times 10^{21} \text{ m}^{-2}$. (left and middle): $g = 200$, (right): $g = 006$.

Fig. 2 $g = 200$ DF image of an area irradiated to $2 \times 10^{21} \text{ m}^{-2}$. Several defects are arrowed.

Fig. 3 DF images of the same area after irradiation with $2 \times 10^{21} \text{ m}^{-2}$. (left) $g = 200$, (middle) $g = 020$, (right) $g = 110$.

Fig. 4 DF images of three different areas, irradiated to 2 and $4 \times 10^{21} \text{ m}^{-2}$ at MURR and to $8 \times 10^{21} \text{ m}^{-2}$ at FRM.

Fig. 5 DF image of an area irradiated to $8 \times 10^{21} \text{ m}^{-2}$ at MURR. Several defects are arrowed.

Fig. 6 Size distribution of defect cascades produced by neutron irradiation.

Fig. 7 Cross section for recoil events above some energy, for all four atomic species of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at MURR, and for Cu at TRIGA. ($\square$) Cu (TRIGA), ($\times$) Ba (MURR), ($\circ$) Cu (MURR); ($\triangle$) O (MURR), (+) Y (MURR).

Fig. 8 DF images of the same area 3 weeks and 3 months after irradiation with $2 \times 10^{21} \text{ m}^{-2}$. Several defects, which are visible in both images, are arrowed.

Fig. 9 DF images of the same area irradiated to $4 \times 10^{21} \text{ m}^{-2}$ before annealing and after annealing *in situ* for 10 minutes at 200 and 400 °C.

Fig. 10 DF image of an area from a crystal, which was irradiated to $2 \times 10^{21} \text{ m}^{-2}$ and then annealed in air for 8 hours each at 100, 200 and 300 °C before thinning for TEM.

Fig. 11 (a,b) DF images from two different crystals, irradiated to $3 \times 10^{22} \text{ m}^{-2}$. (c) High resolution diffraction pattern (HRDP) of (a), (d) HRDP of (b), (e) overexposed DP of (b).

100 nm

$g = 200$

$g = 020$

$g = 110$

100 nm

pre irr.
g = 200

irr.
g = 200

irr.
g - 006

$2 \times 10^{17} \text{ n cm}^{-2}$
 $B = [010], g = 200$

100 nm
 $4 \times 10^{17} \text{ n cm}^{-2}$
 $B = [010], g = 200$

$8 \times 10^{17} \text{ n cm}^{-2}$
 $B = [001], g = 200$

100 nm

3 weeks
after irr.

3 months
after irr.

$n (4 \times 10^{17} \text{ cm}^{-2}, 330\text{K}) \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{7-x}$
 100 nm

before annealing

10 min @ 473K

10 min @ 673K

100 nm

100 nm