CONF-880207--5

ELECTRON IRRADIATION EFFECTS IN $YBa_2Cu_3O_{7-\delta}$ SINGLE CRYSTALS*

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DE88 010050

April 1988

Submitted to the International Discussion Meeting on High-T_c Superconductors, February 7-11, 1988, Schloss Mauterndorf, Austria.
*Work supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

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Defect structures in $YBa_2Cu_3O_{7-\delta}$ produced by electron irradiation at 300 K, were investigated by transmission electron microscopy. Threshold energies for the production of visible defects were determined to be 152 keV and 131 keV (± 7 keV) in directions near the a- and b-axes, respectively (b > a, both perpendicular to c, the long axis in the orthorhombic structure). During above - threshold irradiations in an electron flux of 3×10^{18} $cm^{-2}s^{-1}$, extended defects were observed to form and grow to sizes of 10 - 50 nm over 15 minutes, in material thicknesses varying between 20 and 200 nm. Upon irradiation between the a- and b-thresholds, movement of twin plane boundaries and shrinkage of twinned volume were observed. All these findings suggest oxygen atom displacements in the basal plane with recoil energies near 20 eV. Above - threshold irradiations also show the collapse of c-axis long range order into a planar faulted defect structure with short range order peaks at 1.2 c and 1.07 c, depending on the irradiation direction.

INTRODUCTION

Several neutron and ion irradiation experiments (cf., e.g., references 1-3) on single- and polycrystalline samples of $YBa_2Cu_3O_{7-\delta}$ have been performed. They have shown that both the primary superconductive properties, such as the transition temperature T_c, as well as the intrinsic defect states responsible for flux pinning are affected by radiation. Whereas the transition temperature T_c immediately starts to decrease with radiation dose, thus indicating adverse effects on the pairing mechanism in these superconductors, the critical current densities j_c were observed to increase significantly at lower fluences (thus indicating the formation of new defects capable of flux pinning) and to decrease only at higher radiation doses. Of course, an investigation of the mechanisms responsible for these property changes is of fundamental interest.

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The simplest defects that can be produced in a metal, are those formed by electron irradiation. The threshold energy for the production of stable Frenkel pairs, self-interstitial atoms and vacancies, as well as the structure and properties of these defects, are essential for the understanding of many macroscopic properties. In the present paper, we report on experiments with single crystalline pieces of $YBa_2Cu_3O_{7-\delta}$ aimed at this task and made in an electron microscope with variable electron energy.

EXPERIMENTAL PROCEDURES

Samples suitable for electron microscopy were prepared from the same stock as those subjected to neutron irradiation[2,4]. Tiny single crystals formed during the growing procedure described in ref. 3 were crushed, deposited onto carbon films and then placed onto standard copper grids. The samples were either kept in the vacuum of the electron microscope ($\sim 10^{-6}$ mbar) or in desiccated air.

Samples having the correct orthorhombic phase were selected by pole diffraction patterns, either in a Philips 420 or in the AEI EM7 High Voltage Electron Microscope (HVEM). The imaging conditions were chosen to be G = 200 or 020, bright field and dark field. For the electron irradiation experiments, the beam energy was varied between 100 and 160 keV, the electron flux density was 3.10^{18} $cm^{-2}s^{-1}$. Electron dosimetry was made by in-situ Faraday cup measurements. The samples were kept at a temperature of 15 ^oC; the influence of beam heating is not known accurately, but estimated to result in sample temperatures below 50 ^oC.

Experimental investigations usually proceeded immediately following electron irradiation at a particular energy. However, when defect reactions after above-threshold irradiation were noted for the first time, waiting times of up to 24 hours had to be included.

RESULTS

The results of ambient temperature electron irradiation experiments are summarized in Figs. 1 - 4. Specific directions for the incident beam were selected from pole diffraction patterns. However, in order to avoid anomalous transmission and electron channeling effects, the beam was directed 5 - 10^o off major crystallographic axes.

Fig. 1 illustrates the results of irradiation near the b-direction, which contains the oxygen atom in the basal plane. The upper series of 3 micrographs demonstrates the existence of a threshold energy between 123 and 139.5 keV, the formation of extended defects during irradiation with an electron energy of 139.5 keV, and a highly defective structure formed within 24 hours after irradiation. The lower series shows bright field micrographs of the defect production during above-threshold irradiation. The defects are found to grow to appreciable sizes (10 - 50 nm); their nature could not yet be determined, partly because of the heavy second defect reaction already occuring within a period of 24 hours.

From the results shown in Fig. 2 we will firstly discuss the threshold effect in the a-direction. In these micrographs, images along the a-direction are represented by the gray areas, whereas the darker areas inbetween results from dynamical contrast caused by twin boundaries. The data show clearly, that upon irradiating near the a-direction no extended defects are formed during irradiation, whereas a highly defective state is produced following irradiation at 159.8 keV and a waiting time of 24 hours. Hence, the threshold for damage production in the a-direction is determined to be (152 ± 8) keV. Secondly, important information on the behavior of the twin structure can be deduced from Fig. 2. Irradiation at 146.5 keV clearly demonstrates that the volume of twinned material (dark areas) shrinks considerably. If we assume, that the twinned material has exactly the same crystal structure, but is rotated by 90° about the c-axis with (110) boundary planes, then an irradiation along the a-direction corresponds to an irradiation along the b-direction in the twinned volume and is, therefore, *above* the threshold energy for defect production as determined from Fig. 1. Hence, the contrast features of these micrographs confirm the differences in threshold energies for the two crystal directions in the basal plane and are consistent with current ideas on the nature of twinning.

Some details of the highly defective state formed by above-threshold irradiation along the a-direction and after a waiting time of 24 hours are illustrated in Fig. 3. Amorphous appearing and planar faulted regions can be seen. The lattice fringes, corresponding to local planar configurations perpendicular to the c axis, are seen to include segmented sections and some very local bending. A relatively undamaged area in the very thinnest part of the material is also noted, which may perhaps be due to a loss of defects to very near surfaces.

Electron diffraction patterns taken from the highly defective structures formed following above-threshold irradiation and after a

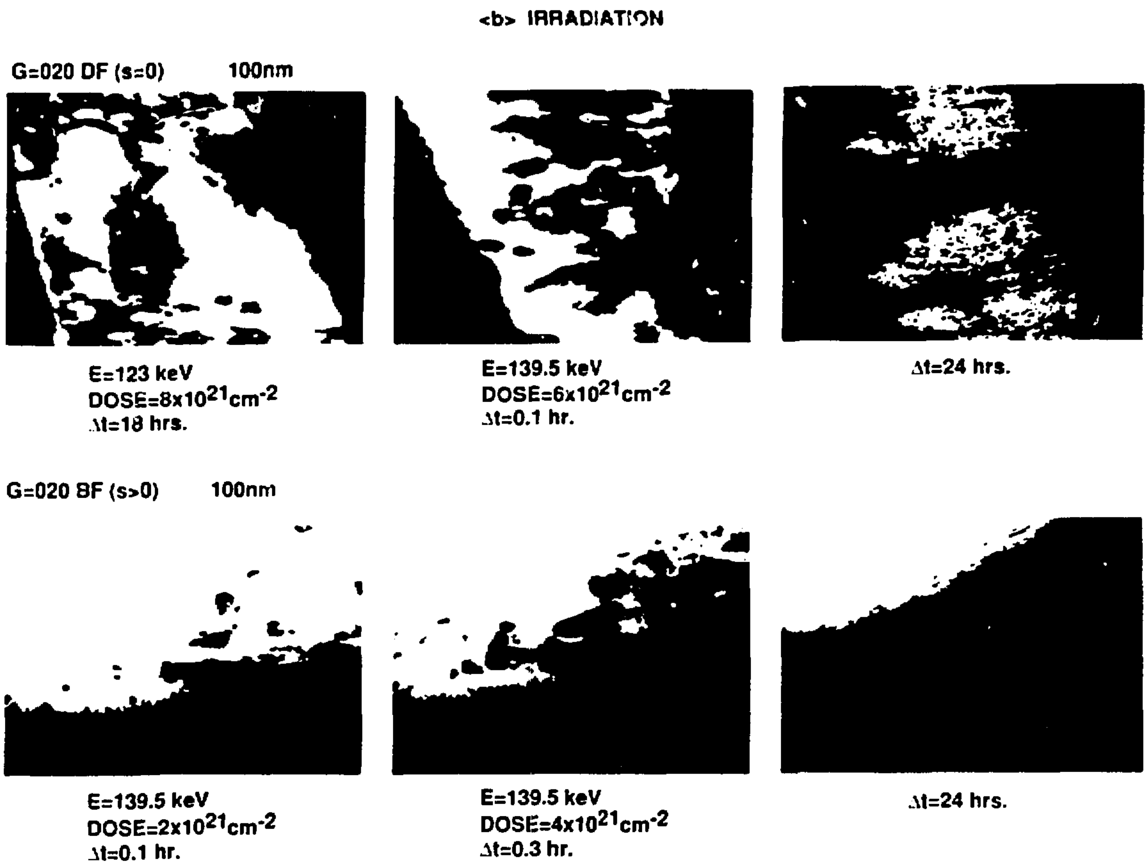

Fig. 1. Transmission electron micrographs of electron irradiation effects in the b-direction.

waiting time of 24 hours are displayed in Fig. 4. The data for both irradiation directions indicate an almost complete collapse of long range order in the c-direction and the formation of short-range order peaks with extended lattice spacings. These short-range order peaks occur at real lattice spacings of 1.39 nm for irradiation near the b-direction, and at 1.24 nm for irradiation near the a-direction. Within an accuracy of about 1 %, the a and b lattice parameters remain unchanged. Also the (103) type reflections are preserved (although broadened), and are especially strong following irradiation in the b-direction.

The diffraction patterns in Fig. 4 are consistent with recent observations of defect structures in this material obtained using high resolution techniques in electron microscopes at 200-400 kV. One observation[6], where electron beam damage was produced and followed, showed the expansion in the c-direction to take place, at least some of the time,

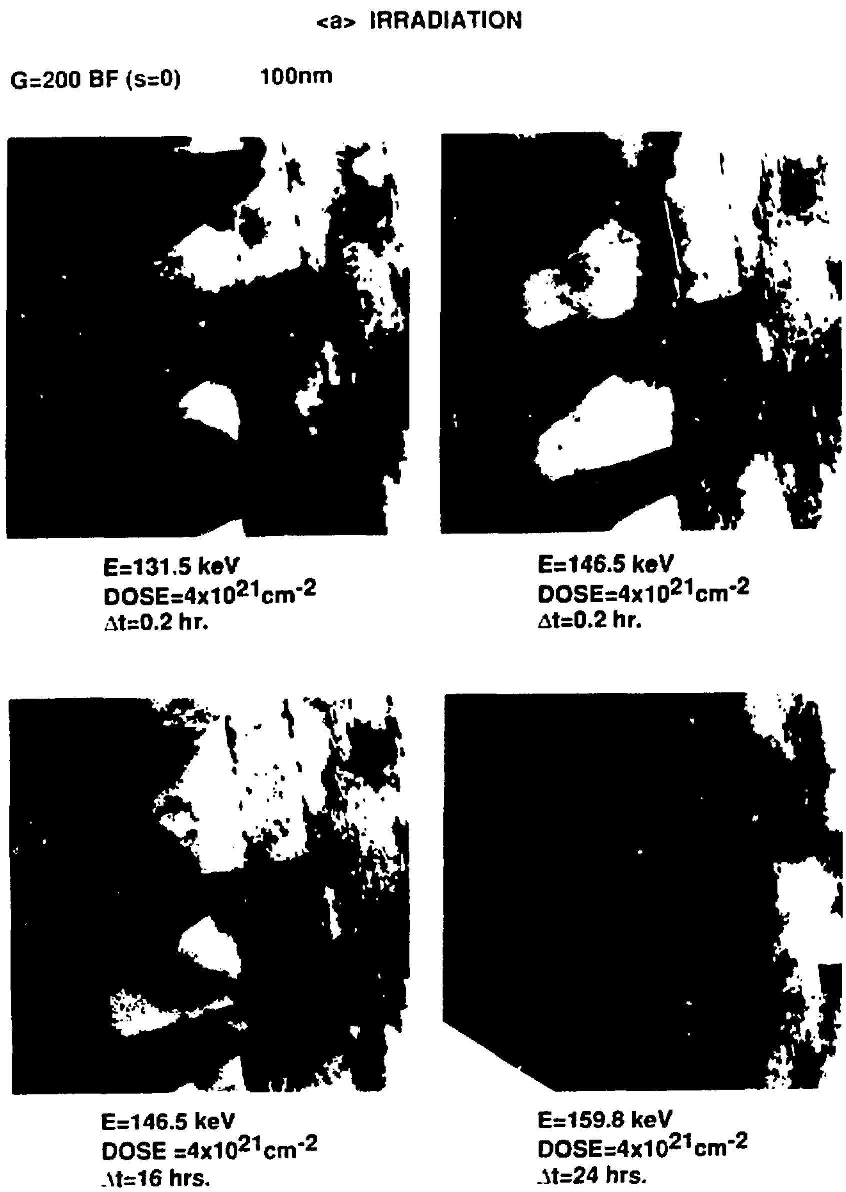

Fig. 2. Transmission electron micrographs of electron irradiation effects in the a-direction.

in the basal plane of the original structure at the interface of a growing amorphous-appearing region. A defect structure in this same plane was observed by Zandbergen, et al.[7]. They proposed a model for the defective structure that includes an extra Cu-O "basal" plane adjacent to the original basal plane and displaced by a/2 or b/2. These $(CuO)_2$ double layers, as they call them, inserted randomly throughout a volume would produce a diffraction pattern exactly the same as for the b-irradiation in Fig. 4, including the approximate preservation of the (103) reflections and short-range order peaks at 1.39 nm.

From all these results, it seems highly probable that atoms are displaced by electron irradiations, at energies exceeding the respective thresholds. Applying relativistic kinematics[8], the maximum recoil energies for oxygen and copper atoms can be calculated. The results for the a- and b-directions (thresholds: 152 and 131 keV) are 23.9 and 20.3 eV for oxygen, 6.0 and 5.1 eV for copper, and 15 and 13 eV for copper displaced by recoil oxygen atoms. The observed motion of twin boundaries is consistent with the displacement of oxygen atoms and probable motion of an oxygen atom defect. The formation of an extra CuO layer over 24 hours suggests the additional displacement of Cu atoms, most likely by recoil oxygen atoms displaced near threshold, expecially in the b-direction irradiation. This resulting highly defective state would necessarily include high concentrations of oxygen and copper atom vacancies to produce the extra planes. The long time following irradiation needed to form this structure could be related to the long diffusion times of oxygen at room temperature[9].

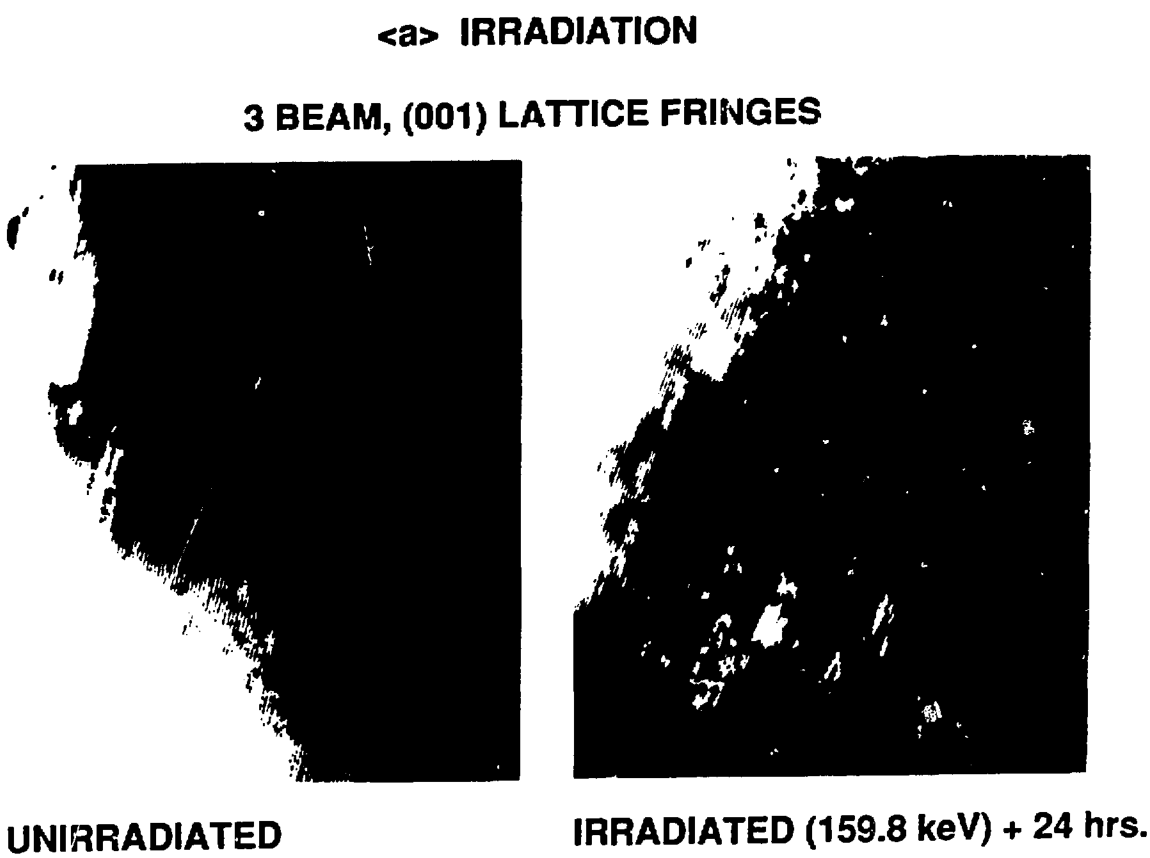

Fig. 3. Defect production by above-threshold irradiation and after a reaction period of 24 hours, a-direction.

CONCLUSIONS

Electron microscopy of single crystalline pieces of $YBa_2Cu_3O_{7-\delta}$ at various electron beam energies and as a function of electron fluence, has provided the following information on microstructural effects in this high-T_c superconductor:

- The threshold for defect production is anisotropic and depends on the crystal direction aligned parallel to the incident beam. The threshold energies were determined to be 152 and 131 keV (± 7 keV) for a- and b-axis irradiation, respectively. Preliminary data suggest, that the c-axis threshold exceeds 124 keV.
- Extended defects are observed to form and grow during b-axis irradiation above the threshold energy. Above-threshold irradiation in the a-direction does not lead to visible defect production *during*

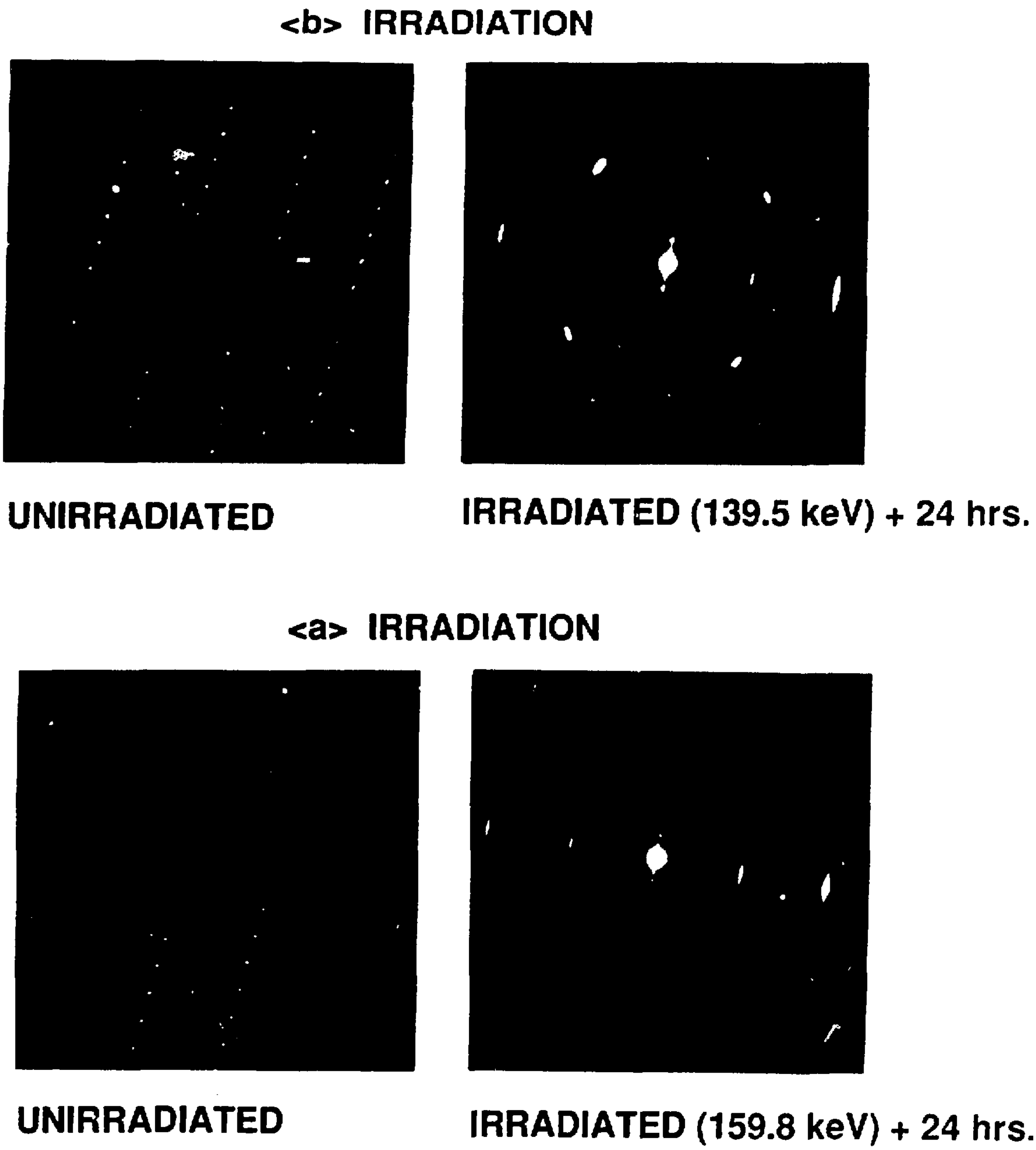

Fig. 4. Electron diffraction patterns of the planar faulted state formed by above-threshold electron irradiation and defect reaction within 24 hours.

irradiation.

- In both cases, slower defect motions occur over periods of 2 to 24 hours leading to highly defective states characterized by loss of long-range order in the c-direction and the appearance of short-range order peaks.
- These highly defective state is consistent with the formation of another CuO plane adjacent to the original basal plane and displaced by a/2 or b/2. The formation of this extra plane implies the displacement of Cu atoms by above-threshold electron irradiation.
- Twin boundary motion and shrinkage of twinned volume occurs during irradiation with electron energies between the two thresholds for the a- and b-directions. This effect implies a net movement of oxygen in the basal plane, in agreement with calculated recoil energies and structural considerations on the nature of twinning.
- As a practical conclusion, we wish to point out, that conventional transmission electron microscopy and high resolution electron microscopy *free* of electron beam effects, can only be carried out at beam energies $\leq$120 keV.

ACKNOWLEDGEMENT

One of us (H.W.Weber) wishes to express his gratitude for the hospitality, support and stimulating atmosphere experienced during an extended stay in the Materials Science Division, Argonne National Laboratory.

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