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DEFECT STRUCTURES IN  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  PRODUCED BY ELECTRON IRRADIATION\*

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## DEFECT STRUCTURES IN $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ PRODUCED BY ELECTRON IRRADIATION\*

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### ABSTRACT

Defect structures in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  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 ( $\pm 7$  keV) in directions near the a and b ( $b > a$ ) axes (both perpendicular to c, the long axis in the orthorhombic structure), respectively. During above threshold irradiations in an electron flux of  $3 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ , extended defects were observed to form and grow to sizes of 10-50 nm over 1000 s in material thicknesses 20-200 nm. Such low electron threshold energies suggest oxygen atom displacements with recoil energies near 20 eV. The observation of movement of twin boundaries during irradiation just above threshold suggests movement of the basal plane oxygen atoms by direct displacement or defect migration processes. Crystals irradiated above threshold were observed after about 24 hours to have transformed to a structure heavily faulted on planes perpendicular to the c axis.

### INTRODUCTION

A traditional area of research on defects in solids has been that concerned with the simplest point defects, those that can be formed by electron irradiation. In metals the threshold energy for the production by electron irradiation of stable Frenkel pairs, self-interstitial atoms and vacant atom sites, has been considered of some fundamental importance. Knowledge of the structure and properties of these defects is central to understanding many macroscopic properties of materials and solid state reaction processes. Electron microscopy can be used to investigate certain aspects of point defects in materials, usually through the image produced by extended defects formed by the clustering of mobile point defects. A convenience in employing an electron microscope is in the use of the electron beam to both produce the point defects and image their clusters or reaction products.

In addition to the fundamental interest in determining a threshold voltage for producing defects in this new superconductor, and investigating the structure of resulting extended defects, the determination of a threshold voltage is important from a practical viewpoint. The use of high resolution techniques in medium voltage electron microscopes results in the exposure of the material to electrons with voltages ranging usually between 200 and 400 keV. It is thus quite necessary to know above what voltage electron beam damage can result, so that sufficient caution can be exercised in technique and interpretation of data.

### EXPERIMENTAL METHODS

Electron microscopy samples were produced by crushing tiny crystals, predominantly of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , produced during the growing of larger crystals [1]. The crushed crystalline material was deposited on carbon films supported on standard copper grids. When not in the microscope vacuum ( $10^{-6}$  torr), samples were stored in desiccated air. The identi-

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fication of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and selection of irradiation directions was determined by electron diffraction pole patterns.

Electron irradiations and much of the microscopy were performed with the AEI EM7 High Voltage Electron Microscope (HVEM) at Argonne National Laboratory, operating at voltages between 100 and 160 kV. To avoid anomalous transmission or electron channeling effects, irradiations were performed  $5-10^\circ$  off major crystallographic axes and with no excitations of strong Bragg reflections. Electron dosimetry was performed by in situ Faraday cup measurements. The irradiating electron flux was  $3 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$ . Sample temperatures are estimated to not exceed 50 C during irradiations which usually lasted 10-15 minutes. Microscopic investigations usually utilized subthreshold electron voltages and smaller beam currents. After an initial investigation of various imaging conditions on defects formed during the above threshold irradiations, 200 type diffraction vectors, in two beam and kinematic diffraction conditions, were found to yield the best defect images.

Electron microscopic investigations proceeded immediately following the electron irradiation at a particular voltage, and upon waiting about 24 hours following that irradiation, before the next higher voltage irradiation was performed. This 24 hour wait became necessary when it was first discovered that a defect reaction over this period of time did occur when the threshold energy was exceeded. Samples were again stored in desiccated air during this time period.

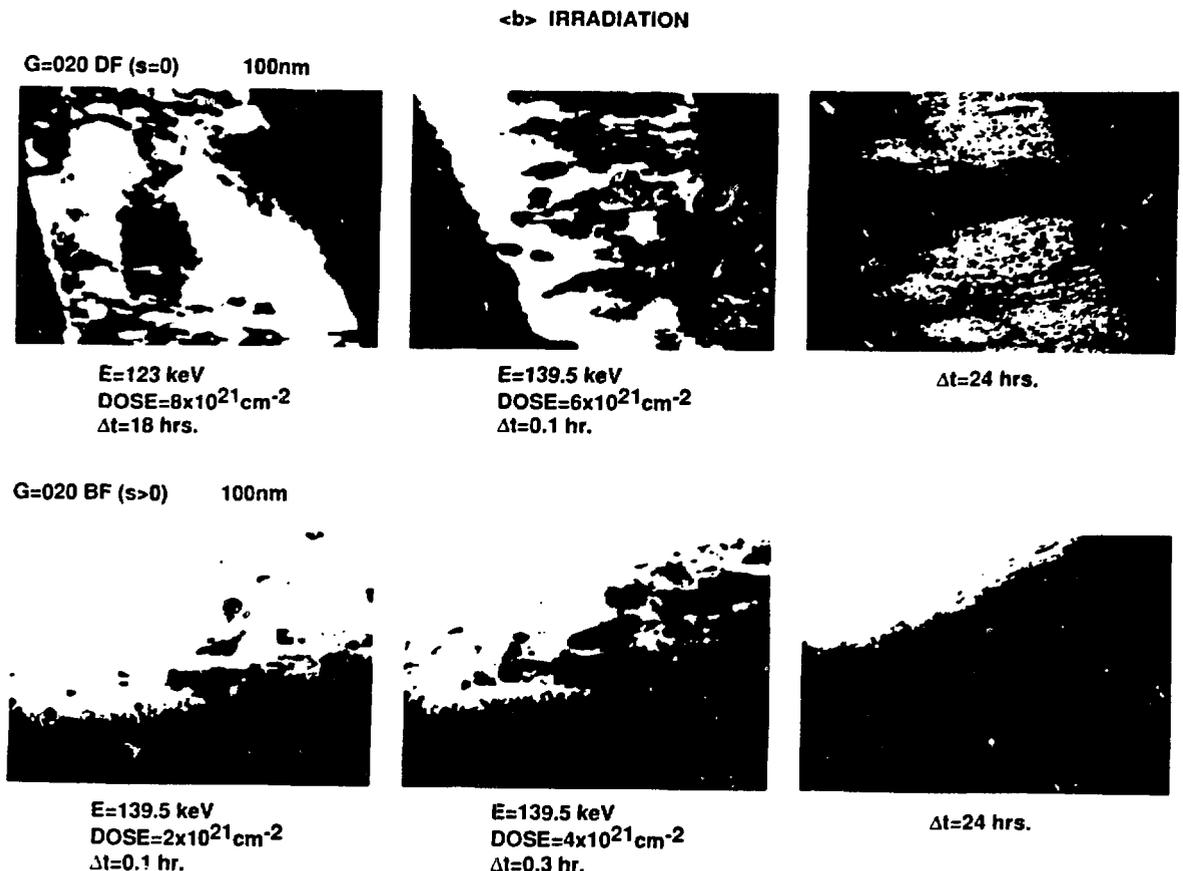


Fig. 1. TEM micrographs of electron irradiations in the <b> direction. Time following irradiation is given by  $\Delta t$ .

## RESULTS

The results of electron irradiations near the  $\langle b \rangle$  direction in this crystal structure, where the  $\langle b \rangle$  direction contains the oxygen atom in the basal plane, are illustrated in Fig. 1. The top series of micrographs demonstrates a threshold for defect production occurred between 123 and 139.5 keV. Extended defects formed and grew during the time of the irradiation, and a dramatic defect reaction (and cracking in the center of the area) took place within 24 hours of the irradiation at 139.5 keV. The lower series of micrographs in Fig. 1 illustrates the growth of defects during irradiation at 139.5 keV and again this defect reaction within 24 hours. Further data to determine the nature of the extended defects formed during irradiation is yet to be obtained, in part due to the occurrence of the second defect reaction.

The results of electron irradiations near the  $\langle a \rangle$  direction can be drawn from the micrographic evidence in Fig. 2. The  $\langle a \rangle$  direction results are taken from the grey areas between the darker (dynamic contrast from the twin boundaries) twinned material. The lower two micrographs demonstrate a threshold for the defect reaction at 24 hours to lie between 146.5 and

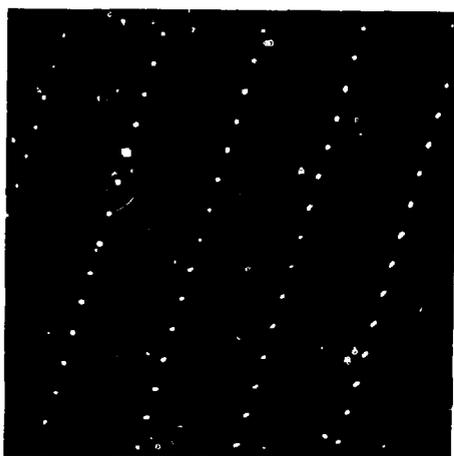


Fig. 2. TEM micrographs of electron irradiations in the  $\langle a \rangle$  direction.

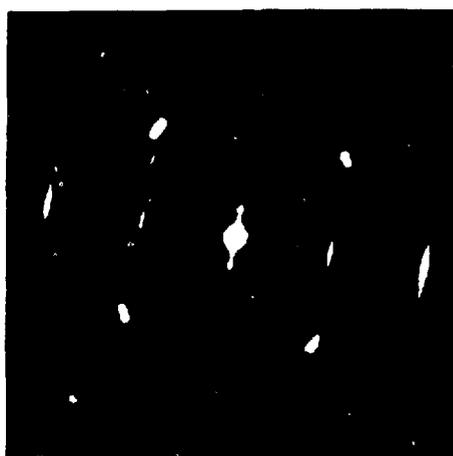
159.8 keV electron energy. Immediately following the irradiation at 159.8 keV, no extended defects were observed in the grey area, (Micrographs are not available due to a camera failure.) nor could any defect structure be observed within the twinned material. An interesting effect regarding the twinned material was observed at 146.5 keV, and is illustrated in the upper two micrographs in Fig. 2. Comparing the twin structure at 131.5 and 146.5 keV ( $\Delta t=0.2$  hr.), a shrinkage of the twinned material is observed under irradiation at 146.5 keV. Assuming that the twinned material is the same structure rotated  $90^\circ$  about the  $\langle c \rangle$  axis, this corresponds to  $\langle b \rangle$  direction irradiation within this material, and the observation of a shrinkage of the twinned material at this electron voltage is consistent with the threshold energy determined in the other  $\langle b \rangle$  direction irradiation of Fig. 1.

A summary of the electron diffraction evidence for the highly defective structure formed by above threshold irradiations in the two directions and within 24 hours is displayed in Fig. 3. This defective state is seen to be rather similar for the two irradiation directions, consisting of

### $\langle b \rangle$ IRRADIATION

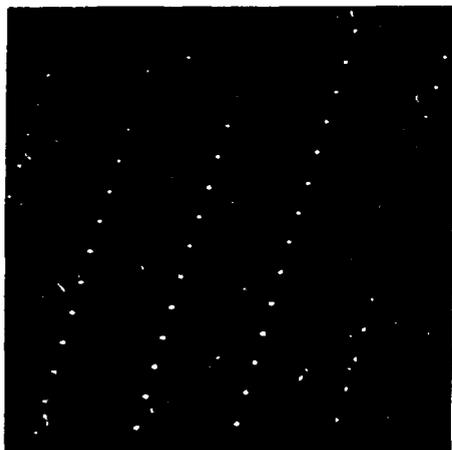


UNIRRADIATED



IRRADIATED (139.5 keV) + 24 hrs.

### $\langle a \rangle$ IRRADIATION



UNIRRADIATED



IRRADIATED (159.8 keV) + 24 hrs.

Fig. 3. Electron diffraction patterns of defect reaction into planar faulted state.

almost total loss of long range order in the  $\langle c \rangle$  direction, replaced by strong short range order peaks at real space distances of 13.9 Å in the  $\langle c \rangle$  direction under  $\langle b \rangle$  irradiation and 12.4 Å in the  $\langle c \rangle$  direction under  $\langle a \rangle$  irradiation. Within an accuracy of about 1%, the a and b lattice parameters remain unchanged by this irradiation and defect reaction. This evidence, along with the strong diffuse streaking in the  $\langle c \rangle$  direction, is consistent with heavy planar faulting perpendicular to the  $\langle c \rangle$  direction. The presence of rather strong 103 type reflections in this defective state is not understood.

Incomplete data to determine the threshold energy to produce extended defects by electron irradiation in the  $\langle c \rangle$  direction suggests that this threshold exceeds 124 keV.

## DISCUSSION

It seems quite likely that, based on these results, atoms are displaced by electron irradiations at energies exceeding the thresholds determined above. The most convincing evidence is the defect reaction that takes place at room temperature between 2 and 24 hours following irradiation, and throughout the observable range of thickness in the material. This thickness range is estimated to be from 20 nm to 200 nm.

The maximum recoil energies for the oxygen and copper atoms under electron irradiation can be calculated by relativistic kinematics [2]. For the electron threshold energies of 152 and 131 keV, the maximum recoil energies of oxygen atoms are 23.9 and 20.3 eV, respectively, and the maximum recoil energies of copper atoms are 6.0 and 5.1 eV, respectively. This suggests that the direct displacement of oxygen atoms is much more likely at these electron energies than that of the copper atoms. An indirect displacement of copper atoms by the recoil oxygen atoms is perhaps possible with maximum recoil energies of 15 and 13 eV by this mechanism, respectively to the above threshold energies. The observation of the motion of twin boundaries during irradiation argues for the displacement of oxygen atoms and the subsequent rapid diffusion at room temperature of an oxygen atom defect. Which of the four unequal oxygen atom sites in this structure is involved in this near threshold displacement process can not be determined from the data. However, effective twin boundary motion certainly requires movement of the oxygen atoms in the basal plane, and this is more likely accomplished by defect motion, rather than direct displacement.

A crude estimate of the concentration of point defects needed to produce the observed extended defects and defect reactions gives a cross section for oxygen atom displacement around 10 barns. For the typical electron doses employed in this study, this gives about 0.04 displacements per oxygen atom. Assuming two oxygen atoms per unit cell of the type that might be displaced at these threshold energies (for example, the basal plane or Ba plane oxygen atoms; one or two per unit cell, respectively), about one defect per ten unit cells is produced in these irradiations.

The observation of extended defects produced during above-threshold irradiations in the  $\langle b \rangle$  direction, but not in the  $\langle a \rangle$  direction, can have one of several possible explanations. Extended defects formed by the clustering of the rapidly moving defect during irradiation might be planar and thus be invisible in the projection in the  $\langle a \rangle$  direction. A different oxygen atom, which does not migrate rapidly or form extended clusters, might be displaced in the  $\langle a \rangle$  irradiation. Obviously, additional data will be needed to understand this observation.

The structure of the highly defective state, possibly formed by a slower moving defect requiring only one or two jumps into a planar configuration in the time period of 2 to 24 hours, is also unknown. This jump rate is consistent with a preliminary analysis of thermal diffusion data on oxygen [3]. How this planar defective state results in 7% and 20%

expansions of the c axis following <a> and <b> irradiations, respectively, is unknown. These expansions are seen in strong and relatively sharp short range ordered peaks, and with a total loss of long range order in the <c> direction. That there is a significant difference in the size of the expansions following irradiations in the two orthogonal directions again suggests that two different oxygen atom sites may be involved.

Finally, these results indicate that a moderate amount of exposure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  to an electron beam at voltages < 120 kV should produce no observable damage in the electron microscope at room temperature. However, if the cross section for displacement is a slowly rising function of electron voltage, higher doses at voltages below those determined as thresholds in this study might produce visible effects. This could also be true at slightly different temperatures or sample thicknesses than those employed here. A more sensitive technique than electron microscopy also might reveal lower threshold energies than those found here. In the use of higher voltages (200 to 400 kV) in high resolution microscopy, the exceedingly thin sample size (< 100 Å) may mask the presence of defects produced by the electron beam through the loss of the more mobile defects to the nearby surface. In the short term, the less mobile defects will remain dispersed through the sample.

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