Annealing of Irradiation Induced Defects In A LaSrCuO Crystal

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***Abstract*—Annealing experiments were performed on a LSCO single crystal irradiated with fast neutrons to a fluence of 2.52 x 10^{18} n/cm^2. This fluence increased the critical current density by a factor of 2-3. The sample was annealed for a total of 4.5 hours at 200°C and 8 hours at 300°C. It was found that annealing of LSCO has a much lesser effect on its critical current density, particularly along the c axis, compared to YBCO. It is hypothesized that the reduced annealing effect is due to the formation of either a more stable interstitial cluster (compared to the Cu-O cluster in YBCO), or clusters which do not act as pinning sites.**

I. INTRODUCTION

The discovery of high temperature superconductors (HTSCs) by Bednorz and Müller in 1986 [1] gave rise to great enthusiasm in the scientific community. It was soon discovered, however, that there were many materials problems that needed to be overcome before the HTSCs could be used in many applications. Some had been encountered earlier in the A15 superconductors, but were more severe in these new materials. These included the difficulty in pinning flux vortices and deterring thermally activated flux motion.

The introduction of pinning sites in the high temperature materials is complicated by the very small coherence lengths along the c axis (4 Å in LSCO, 6 Å in YBCO and 1 Å in BSCCO-2212). For a pinning site to be effective in hindering flux vortex motion, it must be of a similar size to the normal core of the flux vortices. Previous work by other researchers [2-3, for example] has indicated that neutron irradiation provides suitable pinning sites in most high temperature superconductors. Little is known, however, as to what defect is responsible for pinning the flux vortices, particularly in the more anisotropic of the HTSC. In this work, an attempt was made to enhance the understanding of these defects in the LaSrCuO superconductors. This was done through annealing experiments on a fast-neutron irradiated single crystal.

II. EXPERIMENTAL PROCEDURE

The superconducting samples examined were $La_{1.86}Sr_{0.14}CuO_4$ (LSCO) single crystals, cut from a larger crystal provided by H. Kojima at Yamanashi University, Japan, with the crystal surfaces approximately perpendicular to the crystal axes. The large crystal was prepared using a float zone technique [5]. The samples examined were two of a series which had been irradiated at various fluences and were approximately 1 x 1 x 0.75 mm^3 and 5 mg in weight.

The LSCO crystals were irradiated at the Omega West Reactor at Los Alamos National Laboratory using the EpiCd Rabbitt. This allowed for the shielding of low energy thermal neutrons. Two samples were irradiated to a fluence of 2.52 x 10^{18} n/cm^2 with the flux penetrating along two different crystal directions.

The crystal examined was annealed in a tube furnace in air. Due to the small number (2) of samples available, it was decided to sequentially anneal one sample at one temperature until no further change was observed in the magnetic properties. The sample was annealed first at 200°C and then at 300°C. Magnetic measurements were taken at various time intervals in the annealing process. When no further change was observed in the flux pinning behavior, the annealing temperature was raised and the process repeated.

Magnetic hysteresis loops and superconducting transition temperatures were determined using a commercial Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. A 3-cm scan was used for all measurements to minimize the effects of any field inhomogeneity.

Magnetization vs. temperature and hysteresis loops at several temperatures were determined for different orientations of the field with respect to the crystal surfaces. Using the width of the magnetic hysteresis loop, the critical currents, J_c^c and J_c^{ab}, were calculated using the modified critical state model [6]. Critical currents were calculated for various annealing times and temperatures.

The alignment of the LSCO samples was determined using a θ/2θ Rigaku X-ray diffractometer. Cu K_α radiation was used with a nickel foil filter. The samples were mounted on small amounts of glass and rotated in the x-ray diffractometer (in two directions) until peaks were observed. The orientation of the crystal surfaces was then determined with respect to the crystal axes. A secondary evaluation was made using a Laue camera and back-reflection.

III. RESULTS AND DISCUSSION

A. Induced Anisotropy

From the crystal structure, it would be expected that the superconducting properties in the a and b directions would be the same, but different in the c-direction. This has been seen to be true in unirradiated crystals. However, a measurement of the magnetic hysteresis loops for an irradiated LSCO crystal, measured with the field, H, parallel to each of the three crystallographic directions, indicates that not

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only is H || c different from the other two, but H || a and H || b are slightly different as well (see Fig. 1).

X-ray diffraction and Laue back-reflection were used to determine the orientation of the crystal. It was found, using a goniometer on the x-ray diffractometer, that the c planes of the crystal were rotated by an angle of 10.5° to the top crystal surface. A Laue back-reflection image confirms that the angle between the surface normal and the c axis is about 9°. A simulated image indicates that this is equivalent to a rotation of the c axis in approximately a {100} plane.

This misorientation of the crystal axes with respect to the crystal surfaces greatly affects the critical current measured, particularly for fields rotated away from the ab plane [7]. Thus the splitting of the two smaller loops may simply be due to the misorientation of the field with respect to the crystal axes, with the smallest loop being most representative of the true H || ab loop. However, due to the large changes in the critical current with even small changes in angle, it is difficult to quantify this effect.

For simplicity, the field orientations will be referred to in the next section as being parallel to c and ab, with the understanding that the surfaces of the crystal are actually not parallel to the crystal axes.

B. Effect of Annealing

The crystal to be annealed had been irradiated to a fluence of 2.52 x 10^{18} n/cm^2 and was overirradiated i.e. the fluence was greater than that to give the optimum critical current density [8]. The change in magnetic hysteresis for the annealing at 200°C is shown in Fig. 2, with the loop width increasing initially and then decreasing again.

The critical current density was calculated from each measurement for two orientations for a range of fields, taking into account the misorientation of the crystal. A typical example is shown in Fig. 3, with similar trends being observed at all fields. The critical current density along the c axis was calculated using the smaller of the two H || ab

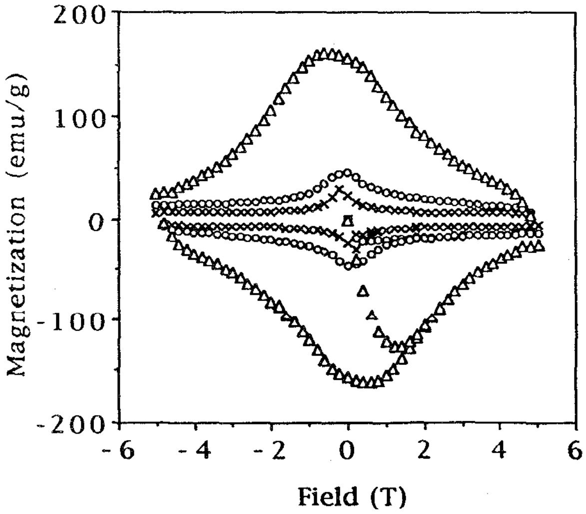

Fig. 1: Hysteresis loops for single crystal LSCO at 7 K, irradiated to a fluence of 2.52 x 10^{18} n/cm^2 and subsequently annealed at 200°C for 10 minutes. Field is applied parallel to a (X), b (O), and c (Δ) axes.

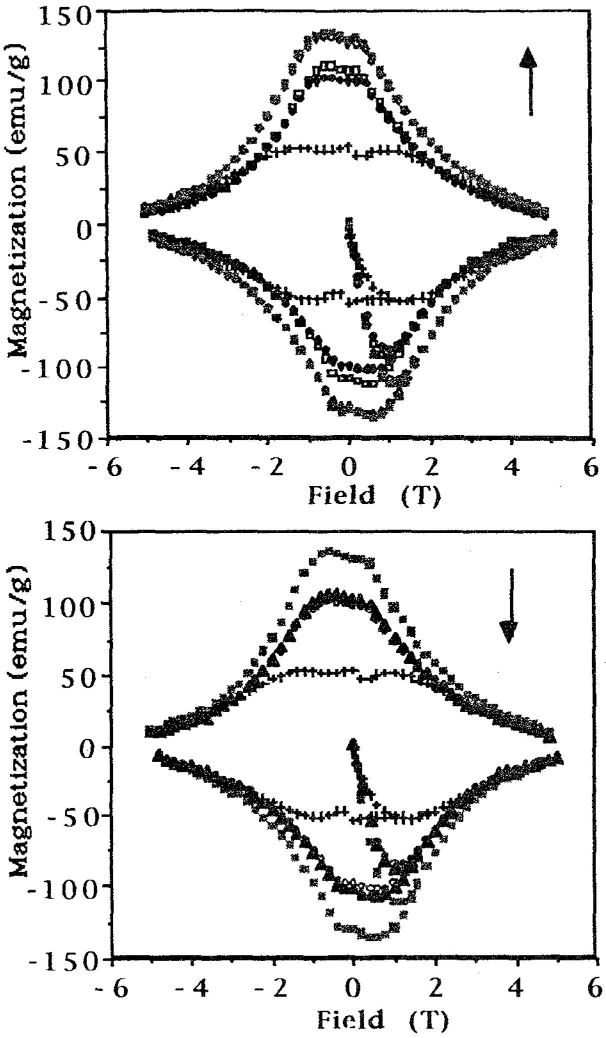

Fig. 2: Hysteresis loops for H || c at 10 K after annealing at 200°C. Loop width first increases (top) and then decreases (bottom) with increasing annealing time. Unirradiated (+), irradiated (◆) and annealed for 10 (▣), 40 (◇), 90 (▩), 150 (▲) and 270 (○) minutes. The magnetic hysteresis loop first expands and then contracts with annealing.

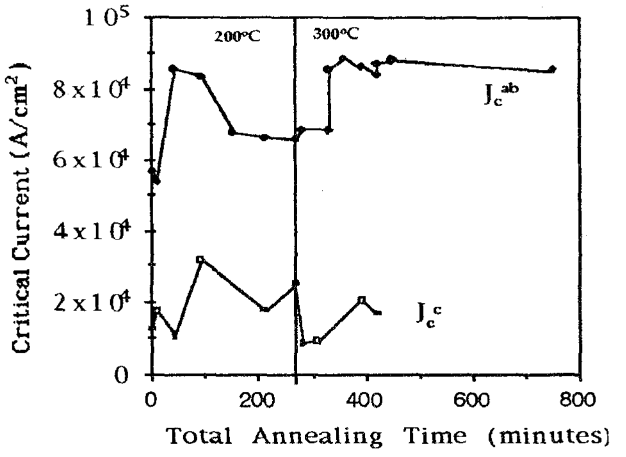

Fig. 3: Critical current density at 10 K as a function of annealing time (H= 4T). Unirradiated critical current in ab plane was approximately 2 x 10^4A/cm^2.

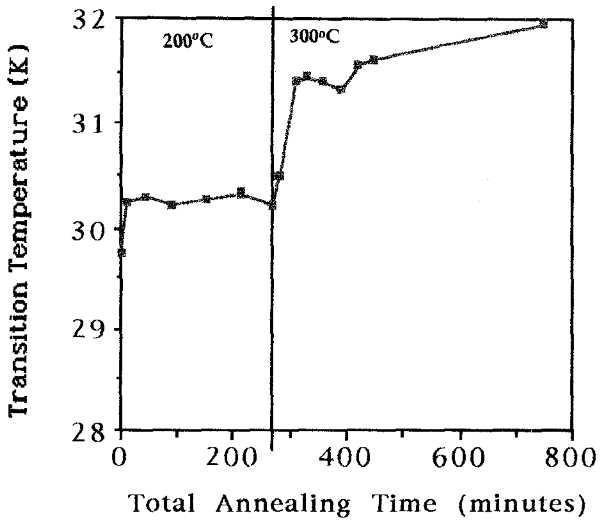

Fig. 4: Transition temperature as a function of annealing time (H || c). Unirradiated transition temperature was 36 K.

hysteresis loops. It can be seen that J_c^{ab} first increases and then decreases with increasing annealing time at 200°C. This shows that annealing is resulting in a pinning situation equivalent to a lower fluence irradiation, even to the extent of increasing the critical current density if the sample was originally overirradiated. With further annealing at 300°C, the critical current increases once again and then stabilizes.

The transition temperature, T_c, was determined from a plot of magnetization versus temperature for a small fixed field of 20 Oe (see Fig. 4).

T_c is reduced by the introduction of defects, and hence its increase, even though small, indicates a decrease in defect density, as would be expected through annealing. The critical current density increase at short annealing times can be explained as being due to this increase in T_c. However, the critical current density decreases at longer annealing times, despite the increase in T_c, indicating a decrease in pinning. Thus the annealing must remove defects which act as pinning sites.

It can be seen in Fig. 3 that there is little change in the critical current after an annealing time of 150 minutes at 200°C. At this temperature, the majority diffusing defects are oxygen vacancies. Thus it can be implied that the pinning in these materials, as determined from the magnetic properties, seems to be affected in a small part by the oxygen point defects. These may be in the form of some clusters. Since the pre-irradiation condition of the crystal was not recovered through this annealing, however, some other defect must also be involved in the pinning.

Compared to the irradiated sample, the final critical current of the sample in the ab plane (after annealing for 270 minutes at 200°C and 480 minutes at 300°C) was increased by nearly 87%, as calculated from [9]:

Amount of Increase (%)

$$= \frac{J_c(\text{after annealing}) - J_c(\text{after irr.})}{J_c(\text{after irr.}) - J_c(\text{before irr.})} x100. \quad (2)$$

This increase was calculated for currents at 10 K and fields of 1 T. This is in comparison to the work by Vlcek et al. [9] who found that the critical current was reduced by 33% after an neutron-irradiated YBCO sample was annealed for a final anneal of 8 hours at 300°C. In addition, the LSCO sample here experienced a slight increase (~3.5%) in the critical current in the c-direction while the YBCO sample of Vlcek completely recovered after its final anneal.

It should be noted again that the LSCO sample annealed here was over-irradiated, i.e., the optimum fluence for critical current enhancement had been exceeded. The YBCO sample examined by Vlcek et al. [9], on the other hand, was optimally irradiated. In addition, the YBCO sample after annealing had a T_c greater than or equal to the unirradiated sample. For the LSCO sample studied here, the transition temperature, while increasing significantly with annealing, is still some 4 K below its unirradiated value of 36 K. The LSCO crystal thus appears to be still highly defected.

It has been reported [10] that neutron irradiation produces two basic types of defects. For high energy primary knock-on atoms, localized melting occurs (as is the case for heavy-ion irradiation [11]), producing small amorphous regions in the material. These cascade defects are large enough to be TEM-visible. It has been observed by Vlcek et al. [12] that these defects in YBCO are stable to annealing at 300°C.

The second type of defect are interstitial (probably Cu and O) clusters, which are generally not visible in conventional TEM. Vlcek argued that these clusters provide the predominant pinning for H || ab, since their experiments indicated total recovery of the critical current for this field orientation after annealing.

Thus one would expect that, in LSCO too, two predominant types of defects are present with the amorphous cascade defects probably being stable to annealing at 300°C. These defects could provide the bulk of the pinning for H || c, as is the case for YBCO [9]. The lack of the decrease in J_c seen in this sample could simply be due to the original over-irradiation. With the competition between critical current and transition temperature, an increase in J_c could result from a increase in the transition temperature, even with decreasing amounts of pinning. If, hypothetically, there were no competition, for the fluence used, the critical current after irradiation may have been considerably higher than the critical current after annealing.

Alternatively, the amorphous cascade defects could be less stable with respect to annealing in this material or at these defect levels. The change in critical current density would then be explained by a gradual recrystallization of the amorphous regions, with the size of the defects diminishing. One could then hypothesize that the critical current may remain approximately constant for a period of time and then increase as the size of the defect becomes optimum for flux pinning. In this case, however, one would expect that the critical current would not stabilize after certain annealing times, but rather decrease as the cascade defects become too small or less numerous to efficiently pin the flux vortices.

The case of H || ab is also interesting. The data of Lessure [8] indicates that no optimum fluence was reached. Rather, the critical current density merely increased with increasing fluence. Thus, the argument above cannot be applied to this field orientation to explain the small increase actually due to misalignment, but even if the critical current density does not change with annealing, this contradicts the results in YBCO. A different mechanism for pinning in this material must therefore be proposed.

One possibility is that some of the interstitial clusters in this material are more stable to annealing than those existing in irradiated YBCO. If these more stable clusters are largely responsible for the pinning, a large change in T_c as the other (non-pinning) clusters anneal out could accompany little or no change in the critical current density.

A second possibility is that,in these materials, interstitial clusters provide little or no pinning for flux vortices in the ab plane. Due to the small coherence length along the c axis in LSCO, the superconducting order parameter drops to essentially zero between the Cu-O planes and hence the flux vortices are pinned between these planes (intrinsic pinning). If the interstitial clusters lie in the Cu-O planes, they may have little effect on the pinning behavior. Pinning in this material for H || ab would then be due to the amorphous cascade defects, and hence should be insensitive to annealing at 300°C. In YBCO, on the other hand, Cu and O atoms exist both in the Cu-O planes and in the chains, and thus Cu-O interstitial clusters can provide pinning between the planes.

IV. CONCLUSIONS

The annealing of an irradiated LSCO crystal provided some indication of pinning defects in this material, although misalignment of the crystal during cutting made the determination of any introduced anisotropy difficult, if not impossible. Simple diffusion modeling indicates that oxygen point defects or point defect clusters play a small role in the pinning of vortices in this material. Critical current densities after the full annealing cycle display behavior that is different from that observed in YBCO, with little or no change in critical current density along the c axis. It is hypothesized that this is due to either more stable interstitial clusters providing pinning sites, or no pinning by interstitial clusters in the ab plane. The importance of interstitial clusters in the pinning of vortices in the more anisotropic BSCCO superconductors is also different.

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