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Fast-neutron irradiation of $YBa_2Cu_3O_x$

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We have studied the effects of fast neutron ($E > 0.1$ MeV) irradiation on the superconducting properties of polycrystalline $YBa_2Cu_3O_x$ with $x = 7 \pm 0.1$. For fluences less than 1×10^{18} n/cm^2, the superconducting transition temperature T_c decreases at a linear rate of about 3.0 K/(10^{18} n/cm^2). Measurements of the critical magnetization current density J_c at 7 K and zero field show an increase by a factor of 3 to 4.4×10^4 A/cm^2 at 1×10^{18} n/cm^2 fluence and larger relative increases at high fields. At 75 K, J_c is also enhanced with neutron irradiation, although the absolute values of J_c are nearly two orders of magnitude smaller than at 7 K.

I. INTRODUCTION

The discovery of superconductivity[1] near 35 K in the Cu–O based $La_{1-x}Sr_xCuO_4$ perovskitelike compound had only recently been reported when transition temperatures above 90 K were reported in multiphase samples of Y-Ba-Cu-O.[2,3] The superconducting phase was soon discovered[4] to be $YBa_2Cu_3O_x$, with x near 7. Neutron-diffraction measurements revealed the ordering of O vacancies on certain sites, resulting in one-dimensional Cu–O chains parallel to the orthorhombic b axis.[5] These chains are absent[6] in the related tetragonal compound $YBa_2Cu_3O_6$, which lacks any Cu^{+3} ions and which shows no superconductivity.[7] Thus discordering or breaking the Cu–O chains might be very destructive to the superconductivity. One way to test this thesis is to vary the oxygen stoichiometry, although this can bring on the complication of a structural phase change. Fast neutron irradiation of the orthorhombic superconducting compound offers another technique, the one chosen here, for probing the effect of disorder on the Cu–O chains.

Many of the technological uses of superconductors, such as conductors in magnets for fusion reactors or accelerators and in power transmission lines, require the material to have a high critical-current density. It is well known that the $A15$ superconducting compound Nb_3Sn can attain current densities at 4 K in excess of 10^6 A/cm^2 in fields of 40 kOe. However, it is sensitive to radiation damage, a fluence of 6×10^{19} n/cm^2 ($E > 0.1$ MeV) reducing the critical current to zero at 4 K.[8] There has to date been only one published study of the effects of neutron radiation damage on the high transition temperature, Cu–O based superconductors. That study[9] on $La_{1.85}Sr_{0.15}CuO_4$ showed a decrease in T_c of 2.7 K and an increase in the critical-current density at a fluence of 1.3×10^{18} n/cm^2. In this work we have concentrated on the 90 K superconductor $YBa_2Cu_3O_x$ and have investigated the effects of neutron irradiation on the current-carrying properties of polycrystalline material. The findings are compared to those observed in $A15$ superconductors.

II. EXPERIMENT

A mixture of reagent-grade Y_2O_3, $BaCO_3$, and CuO powders in the proportion 1:4:6 was ball-milled for 10 h using an alumina jar and grinding media. From these powders a cylindrical pellet 0.95 cm in diameter and weighing 5 g was pressed with no lubricant at 270 bars. This pellet was then heated for 10 h at 800 °C in flowing oxygen to drive off the CO_2. Next, the pellet was broken up, ball-milled to < 20 μm-size powder, and again compacted into cylinders at 270 bars. Final heating at 950 °C for 24 h with oxygen flowing at 50 cc/h was followed by constant-rate cooling to room temperature over a 24 h period.

The x-ray pattern of the pellet was that of the orthorhombic $YBa_2Cu_3O_x$ phase with a barely distinguishable amount (~ 2 vol %) of CuO. The microstructure was uniform with the CuO distributed randomly within grains of average size 10 μm. The density was 72% of theoretical and the porosity was equiaxed with average size 15 μm. Chemical analysis for oxygen gave $x = 7.0 \pm 0.1$ on a similarly prepared sample.

Sequential neutron irradiations were performed on a single sample at the Omega West Reactor at Los Alamos. The port was shielded with cadmium to attenuate the thermal-neutron flux by 10^4. The neutron energy spectrum at this port has recently been determined from measurements of count rates on activation foils.[10] Based upon this spectrum the fast neutron flux ($E > 0.1$ MeV) is estimated to be 4×10^{12} $n/\mathrm{cm}^2\,\mathrm{s}$. The sample was held in the reactor for desired irradiation times and then removed for measurements. A polyethelene (or aluminum) "rabbit" was used to insert and retrieve the sample from the reactor. Helium flowed into and over the "rabbit" during irradiation. Previous investigations[11,12] have shown that with a helium atmosphere and samples of less than 1 g, gamma heating does not increase the sample temperature significantly above reactor ambient, roughly 80 °C.

All the magnetic measurements were performed in a Quantum Design superconducting quantum interference device (SQUID) magnetometer with range capabilities of

2 to 380 K and 0 to 55 kOe. The sample, of mass 0.0993 g and dimensions 0.147×0.191×0.818 cm, was oriented with the long axis parallel to the direction of the applied magnetic field. The sample shape was approximated by an ellipsoid of revolution and demagnetization factor of $0.08\times4\pi$ was determined.[13] The superconducting transitions were determined while warming the sample in an applied field of 85 Oe after previously cooling to 7 K in zero field. The Meissner effect was determined by cooling in an 85 Oe field. Magnetization curves were determined at 7 and 75 K by tracing the loop beginning at the maximum positive field.

III. RESULTS AND DISCUSSION

A. Effect of irradiation on T_c

Figure 1 shows the superconducting transition of $YBa_2Cu_3O_x$ for several fluences. The inset shows the full curve for the sample in the initial and the most highly irradiated state. The magnetic moment m at 7 K corresponds to essentially 100% of perfect diamagnetism when corrected for the sample demagnetizing factor and porosity, i.e., the x-ray density was used to calculate the volume from the sample mass. This moment value at 7 K varied nonsystematically by about 5% from run to run, a variation probably related to small changes in the amount of trapped flux in the magnet and in the sample orientation with respect to the applied field. Thus, our results indicate that the superconducting volume fraction is unchanged at the fluence levels attained in this study.

We do observe a continuous change in the shape of the superconducting transition that can best be described as a monotonic sharpening of the transition with neutron irradiation. That is, T_c for the onset of the transition decreases with fluence; however, this shift of the curve to lower temperatures decreases and then vanishes for the lower-temperature portions of the curve. Thus, the maximum slope dm/dT increases monotonically with fluence up to a fluence of 5.1×10^{17} n/cm^2; above this fluence it shows a small drop. The resultant increase from the unirradiated to the most highly irradiated state is 40% as shown in the Fig. 1 inset. The increase in slope is believed to be due to a larger radiation-induced decrease in T_c for those portions of the sample with the highest-T_c values. It is widely believed[6] that the high T_c's in the Y-Ba-Cu-O compounds are due to chains of Cu and O atoms along the crystallographic b axis giving rise to anisotropies of 10 or more in several superconducting properties.[14] Breaking these chains, or disorder in general, should be detrimental for superconductivity as has been discussed by Sweedler, Cox, and Moehlecke[15] for *A*15 compounds, which also have chains. If we assume that T_c correlates inversely with the number of defects present in a sample volume, i.e., perfectly ordered, stoichiometric $YBa_2Cu_3O_7$ has the highest T_c, then the high-T_c regions in which these chains are relatively defect-free will be the most sensitive to a decrease in T_c during the early stages of radiation damage. This would tend to sharpen a superconducting transition as determined by a bulk measurement such as dc susceptibility. At higher fluence levels when radiation-induced defects dominate, one expects the T_c of every region to decrease more uniformly.

For analysis purposes we define T_c by the intersection of the lines formed by the slope at the steepest part of the m vs T curve and by the normal-state m value, essentially

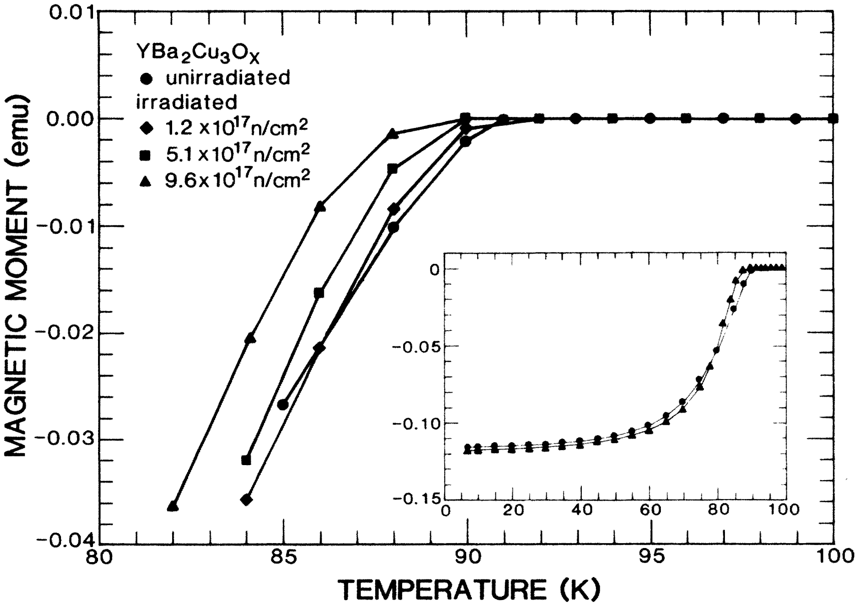

FIG. 1. Superconducting transition as determined by warming the sample in an applied magnetic field of 85 Oe. The magnetic moment is plotted vs temperature for the neutron fluences indicated. The inset shows the full temperature curve.

zero on the scale shown in Fig. 1. For our data this intersection point was calculated by a least-squares fit of a third-order polynomial to the data near the inflection point. We find that this intersect temperature agrees well with T_c measured resistively on samples from the same and similarly prepared batches of $YBa_2Cu_3O_x$. A typical resistive T_c is 90 K with a 10% to 90% width of 0.6 K.[16] As shown in Fig. 2, we find that T_c for our magnetic-moment data decreases roughly linearly with fluence from the unirradiated value of 89.8 ± 0.25 K at a rate of 3.0 K/(10^{18} n/cm^2). The total decrease in T_c was 3 K after the final fluence. Our rate of decrease may be compared to neutron irradiation of $La_{1.85}Sr_{0.15}CuO_4$, in which T_c decreased at a rate of roughly 2 K/(10^{18} n/cm^2).[9]

It is of interest to compare this rate of decrease of T_c with that for neutron irradiation of the superconducting A15 compounds. Sweedler *et al.*[15] showed that the fractional decreases in the transition temperature of six different *A*15's fit the same master curve when plotted versus fluence. Furthermore, the decreases were nearly linear up to a fluence of 2×10^{19} n/cm^2 ($E > 0.1$ MeV). We find this same linear behavior for $YBa_2Cu_3O_x$; however, the fractional rate of decrease is roughly three times faster [3.3%/(10^{18} n/cm^2) vs 1.2%/(10^{18} n/cm^2) for Nb_3Sn]. The important finding is that our results are not greatly different than the master curve for six different *A*15 compounds. Further comparisons with the *A*15's require irradiation to higher fluences. Preliminary results indicate that a factor of twenty more fluence than in this study is enough to destroy superconductivity above 4.2 K.[17]

Meissner-effect curves, which are a measure of flux expulsion on cooling through T_c in an applied field, were measured after some of the irradiations. The size of the Meissner-effect diamagnetism corresponds to about 33% of the volume of an unirradiated companion sample of $YBa_2Cu_3O_x$. This is typical of the values observed on several other samples of this same compound. Flux pinning on voids, inhomogeneities, and other defects are known to reduce the size of the Meissner effect in all but the most perfect superconductors. In addition, we find that the Meissner effect decreases monotonically with neutron irradiation, presumably because of flux pinning at the additional defects that are generated, to a value of 18% of the volume after the final irradiation.

B. Critical current measurements

Figure 3 shows the magnetic moment m at 7 K plotted versus applied magnetic field H_a for the sample in the unirradiated and the most highly irradiated state. The deviation of the magnetic moment from the equilibrium value is caused by flux pinning which manifests itself as a magnetization current. The curve is nearly reversible above 35 kOe for the unirradiated sample but is very hysteretic after a fluence of 9.6×10^{17} n/cm^2, indicating much larger magnetization currents for the latter condition. Relaxation of the sample magnetization has been reported on similar compounds[9,14] and has been attributed to flux creep. We did not investigate time-dependent behavior here, but rather used the magnetization value determined several minutes after the magnetic field had been changed.

Figure 4 shows the development of the hysteresis at maximum H_a values of 10 and 20 kOe for several intermediate irradiations. The increase in the critical currents with fluence can be seen by observing the increase in the irreversibility for the three loops with a maximum of 10 kOe. In addition, we observe that for a fluence of 1.2×10^{17} n/cm^2 the critical magnetization current is saturated for $H_a < 10$ kOe because the ± 10 and ± 20 kOe loops give the same m values for $H_a < 10$ kOe. However, for the data at 5.1×10^{17} n/cm^2, the ± 20 kOe loop yields larger m values, i.e., more trapped flux, than does the ± 10 kOe loop, implying that in the latter case the critical current has not been reached throughout the entire sample volume. The data for 9.6×10^{17} n/cm^2 are almost identi-

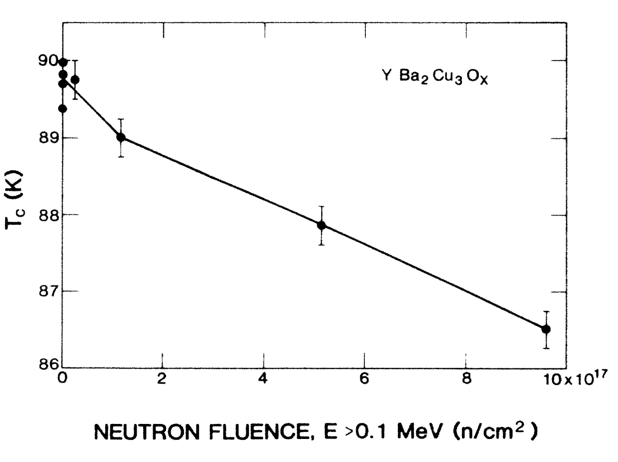

FIG. 2. The superconducting critical temperature of the sample plotted vs neutron fluence. The error bars indicate the estimated scatter in the data obtained from the low fluence measurements.

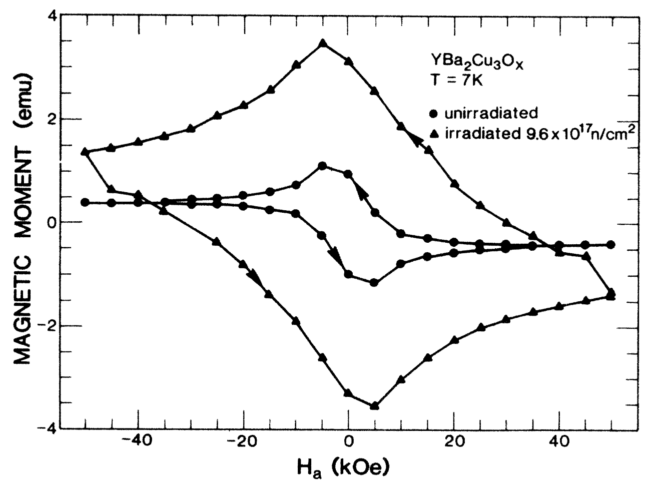

FIG. 3. Magnetic moment vs applied magnetic field at 7 K for the sample in the unirradiated and the most highly irradiated state. The arrows indicate the direction of the field changes.

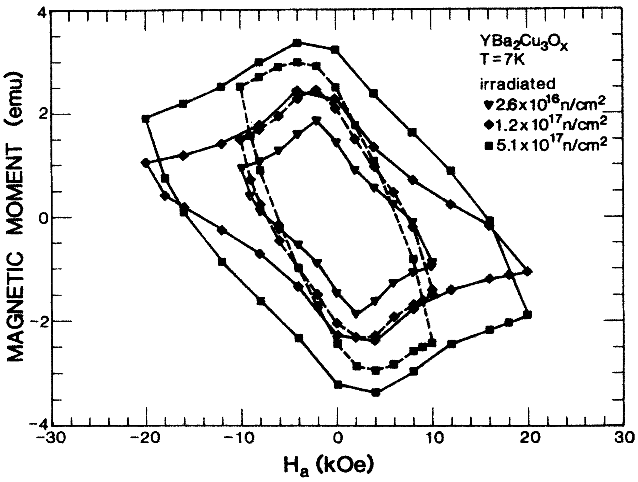

FIG. 4. Magnetic moment of the sample vs applied magnetic field at 7 K for the neutron fluences indicated. The dashed lines for the loops to maximum applied fields of 10 kOe at the two higher irradiations are to facilitate comparison with the corresponding loops to applied fields of 20 kOe.

cal to those at 5.1×10^{17} n/cm^2 and have not been shown for clarity.

Figure 5 shows two hysteresis loops for 75 K; note the much smaller H_a and (especially) magnetic-moment scales. The critical magnetization currents of the sample are much smaller than at 7 K and approach zero above 1 kOe for the unirradiated state and above about 6 kOe for the most highly irradiated state. The additional flux pinning from the neutron irradiation increased the critical currents by about a factor of 2.7 at $H_a=0$.

We have analyzed our data in terms of the critical state model of Bean[18] as further developed by Fietz and Webb.[19] In this model a critical current $J_c(H,T)$ will flow in a superconductor in response to an applied field. For a long, thin cylinder oriented parallel to the field direction, J_c can be calculated from $J_c=(15/R)\times(M_+-M_-)$, where R is the mean sample radius in cm, M_+ and M_- are the sample magnetization in emu/cm^3 in increasing and decreasing fields respectively, and J_c is in A/cm^2. We have used the measured sample dimensions to reduce the magnetic moment to a magnetization per unit volume and have thus neglected the effect of the 28% porosity on this calculation. The results are shown in Fig. 6 plotted as J_c vs H_a for five fluences. The critical current shows a fairly strong field dependence at all fluences, dropping by a factor of 8 between 0 and 40 kOe even at the highest fluence studied. What is also striking is the large enhancement of J_c, amounting to a factor of 3.3 increase at $H_a=0$ for the most highly irradiated relative to the unirradiated state. At higher fields the enhancement becomes much larger. For the 5.1×10^{17} n/cm^2 irradiation, based upon comparison with other data not shown on this plot, we believe that the entire sample was not in the critical state. Thus, J_c for this fluence is probably underestimated with the error increasing with H_a, and is of the order of 10%. Note that the critical current at zero field shows negligible increase between the last two irradiations. This same behavior has also been reported for neutron irradiation of superconducting $\mathrm{Nb_3Sn}$, which shows a peak in the critical current at a fluence of roughly 2×10^{18} n/cm^2 ($E>0.1$ MeV).[20]

Several types of damage and disorder are known to result from fast neutron irradiation of compound superconductors; we discuss two of these mechanisms below. We assume an average elastic-scattering cross section of 2 barns and calculate that for the most highly irradiated condition the atom fraction of primary collision events is $\sim10^{-6}$. Thus, the centers of the collision cascades are only 100 atoms apart. Depending on the size of the cascades, this is the fluence regime in which overlap can be

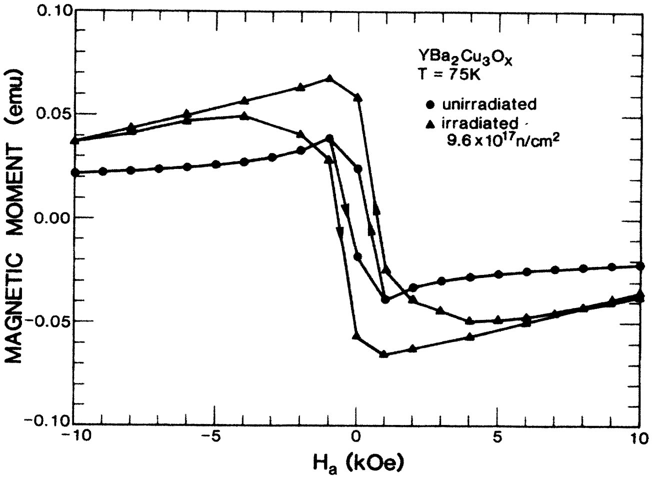

FIG. 5. Magnetic moment of the sample vs applied magnetic field at 75 K for the neutron fluences indicated. Note the large increase in the hysteresis for the irradiated sample for $H_a>1$ kOe.

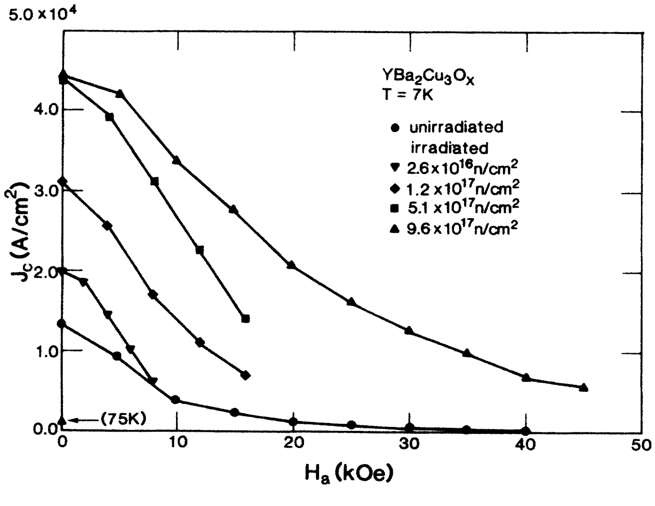

FIG. 6. Critical current vs applied magnetic field at 7 K for the neutron fluences indicated. The arrow indicates the much reduced value of J_c at 75 K for irradiation to 9.6×10^{17} n/cm^2.

expected to become important. Also, in this range the number of displacements per atom is roughly 10^{-3}, so that the amount of site-exchange disorder (or other defect types), as discussed by Sweedler *et al.*,[15] has increased to a level at which local relaxation and different electronic structures due to displaced atoms become important.

Also shown in Fig. 6 is the critical current at 75 K, zero field, and a fluence of 9.6×10^{17} n/cm^2. The value is less than 3% of the value at 7 K for the same magnetic field and fluence. Not shown is the rapid decrease at 75 K of J_c with applied field (vanishing above 6 kOe).

The critical-current density is on the order of 10^4 $\mathrm{A/cm}^2$ for the unirradiated sample at 7 K. This is the same order of magnitude as that reported by others for polycrystalline $YBa_2Cu_3O_x$ (Ref. 21) and $La_{1.85}Sr_{0.15}CuO_4$.[9] The data on single-crystal $YBa_2Cu_3O_x$ reveal large anisotropies in the lower critical-field H_{c1} by a factor of 10 (Ref. 14) and in the critical-current density by factors of 10 or more.[14,21] For the applied magnetic field oriented parallel to the orthorhombic c axis (perpendicular to the Cu—O planes) J_c attains its highest values, in excess of 10^6 $\mathrm{A/cm}^2$, near 4 K. The field dependence of J_c is much smaller in this orientation than for H_a in the a-b (the Cu—O) plane. For random orientations in a polycrystalline sample, the critical current will be limited by those grains with H_a in the a-b plane. Indeed, we observe the relatively rapid decrease of J_c with H_a and obtain values somewhat smaller than seen in single-crystal data for H_a in the a-b plane. Presumably, poor intergranular contact and porosity may lead to further degradation of J_c relative to single-crystal values.

IV. CONCLUSIONS

We find two main conclusions concerning the behavior of $YBa_2Cu_3O_x$ irradiated with fast neutrons to a fluence of 1×10^{18} n/cm^2. First, T_c decreases nearly linearly at a rate of 3.0 $\mathrm{K}/(10^{18}$ $n/\mathrm{cm}^2)$. Second, the critical-current density at 7 K and for fields up to 45 kOe increases monotonically with fluence but appears to approach a limiting value at zero field for the most highly irradiated states. Both of these findings closely parallel the behavior reported for *A*15 compounds suggesting that similar mechanisms of radiation damage are involved.

Although the critical current densities at liquid-nitrogen temperatures are still quite small, our findings are encouraging for use of $YBa_2Cu_3O_x$ in radiation environments at these temperatures since the critical current is increased by irradiation (by a factor of about 3 for zero field). But more important for technical applications is our finding that the irradiation-induced fractional decrease in T_c occurs at a rate which is only three times faster than for the *A*15's, thus $YBa_2Cu_3O_x$ should still be useful under conditions of low to moderate radiation fluence ($< 1 \times 10^{18}$ n/cm^2).

Note added in proof. We have recently become aware of another radiation damage study on $YBa_2Cu_3O_x$ by A. Umezawa, G. W. Crabtree, J. Z. Liu, H. W. Weber, W. K. Kwok, L. H. Nunez, T. J. Moran, C. H. Sowers, and H. Claus, Phys. Rev. B **36**, 7157 (1987). Except for the much larger J_c values of their (single crystal) sample, those results are in good agreement with the present study.

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