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Near-edge x-ray-absorption study of transition-metal-implanted $YBa_2Cu_3O_{7-\delta}$

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We present near-edge measurements for *K*-absorption edges of Ni-, Fe-, and Co-implanted ultrahigh quality single-crystal and polycrystalline $YBa_2Cu_3O_{7-\delta}$ (YBCO). The samples were implanted using a metallized vapor vacuum arc high current ion source with a dose of approximately 1×10^{17} ions/cm^2, and subsequently annealed in an oxygen atmosphere for approximately 100 h. The results show that upon annealing the Fe-implanted sample has a valence structure that is consistent with doped powder studies. This suggests the substitution within the lattice in the Cu(1) and Cu(2) sites for the implanted ions, while the nickel implant case showed a valence structure closer to NiO with no shift in edge energy being observed during the anneal process. This was similar to the Co-implanted result that also showed very little change in valence structure after annealing, with a valence closer to Co^{3+}. We also performed Cu *K*-edge absorption measurements of the implanted materials in comparison with YBCO and found no change in edge energy or structure. The results are consistent with previous susceptibility studies.

I. INTRODUCTION

In the study of high-T_c superconductors the effect of transition-metal substitution has been used as an important probe in understanding the properties of these materials.[1–8] Moreover, the transition metals of Fe, Ni, and Co have been seen to decrease the transition temperature T_c with relatively small concentrations (<10%).[6–13] It is this suppression of T_c and the substitution of the dopant ion that has received much study during the last several years. Many studies of doped $YBa_2Cu_3O_{7-\delta}$ (YBCO) have concluded that Fe substitutes primarily in the Cu(1) site with some occupancy in the Cu(2) site, while for Co-doped materials it has been found that the Cu(1) site is occupied by Co.[14–16] Whereas absorption studies of Ni-doped YBCO are divided where some authors have reported the uniform occupation of both Cu sites[17] by Ni, while others report defect site location with a NiO precipitate[18] due to the insolubility of Ni in YBCO.

The use of ion-implantation and the subsequent post-annealing effects is a method by which a small quantity of a material can be altered in a controlled fashion. The implant can create dislocations, damage cascades and multiple vacancies, that when annealed, can change the structure of the implanted region. Its use in the field of high-T_c superconductors has been present since their discovery, and it is employed here to modify the surface and near-surface region of ultrahigh quality single-crystal and polycrystalline YBCO samples. We have reported previously on the magnetic and superconducting properties of transition-metal-implanted YBCO (Refs. 19–21) and have seen relative changes in T_c after annealing, but have never been able to definitively answer whether the implanted ion has substituted into the lattice, as is strongly suggested by our previous results, or the change in T_c is due to the annealing process. This paper reports on the near-edge x-ray-absorption study of Fe-, Ni-, and Co-implanted YBCO materials, and attempts to ascertain the valence structure and possible site occupation of the implant ion, if any, associated with the implantation and annealing processes in comparison to the more conventional methods of powder preparation and doping.

II. SAMPLE PROCESSING

The YBCO material used in this study consisted of both single-crystal and polycrystalline samples. The single crystals were prepared by the well-known flux-growth method using a $BaCuO_2$/CuO flux. Previously we have fired the presintered YBCO in dense Al_2O_3 crucibles,[22] but for this study we used specially prepared Y_2O_3 crucibles that produce ultrahigh-purity YBCO crystals. This eliminates any possible contamination from the previously used Al_2O_3 crucible,[23] that may alter the valance structure of the surrounding lattice. The resulting crystals had an average size of $3.0\times4.0\times0.5$ mm^3. These crystals were then oxygenated for several months to ensure complete oxygenation and sharp superconducting transitions. The polycrystalline samples were pressed from presintered YBCO into discs of diameter 25 mm, sintered for a further 24 h at 930°, and then oxygenated for 24 h in 1 atm of pure oxygen at 500 °C followed by a very slow cooling. Figure 1 shows the magnetic susceptibility for a single-crystal sample before implantation, and the associated sharp superconducting transition just above 90 K.

The implantation was achieved using a metallized vapor vacuum arc high current ion source. Each implant of Ni, Fe,

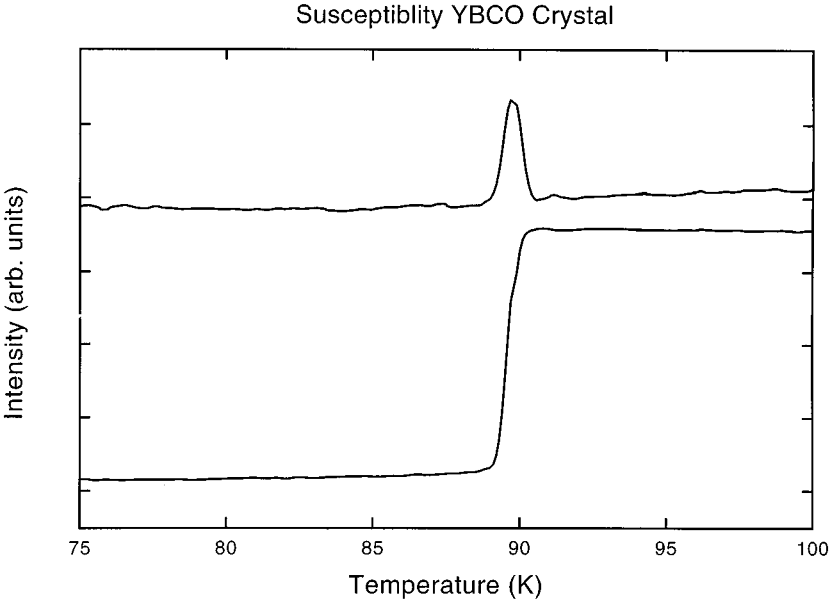

FIG. 1. Magnetic-susceptibility measurements (χ',χ'') of an Y_2O_3 crucible-grown single-crystal YBCO sample before implantation.

and Co was separately carried out at room temperature, with a cathode voltage of 30 kV. The implant ions exist in $+1$, $+2$, and $+3$ charge states, with the average implant ion energy being $\sim$55 keV. The source was pulsed at 15 Hz with a pulse duration of 250 μs to accumulate a total dose of $(1\pm0.2)\times10^{17}$ ions/cm^2. From Rutherford backscattering spectrometry (RBS) measurements performed on different samples after implantation the average implant depth was 250–300 Å. Half the resulting samples were then annealed in a flowing oxygen atmosphere for 100 h at 550 °C. Both magnetic-susceptibility and x-ray-diffraction measurements were taken at all intermediate stages. These results have been reported in previous studies.[19–21]

III. EXPERIMENTAL

The near-edge x-ray absorption measurements were carried out on the Australian National Beamline Facility (ANBF) on beamline 20B at the Photon Factory in Tsukuba, Japan. The experimental setup consisted of a Lytle detector at 90° to the synchrotron radiation.[24] The detector was flooded with He to minimize background from extra absorption. As the implanted region always consisted of less than the first 2000 Å of the surface of the material, the measurements were carried out in fluorescence mode with the sample positioned at 45° to the incoming radiation. This experimental setup also gave us a better signal-to-noise ratio.

The *K* edge of each implant ion (Fe,Ni,Co) was measured for each sample as well as the Cu *K* edge. The procedure for data collection involved high-resolution scans (0.25 eV steps) of the pre-edge, edge, and post-edge region. As the implanted ion is only located in the surface and near-surface region of the sample, these scans were repeated several times and added together to increase the signal-to-noise ratio. This also enabled us to monitor the monochromator energy during the spectrum acquisition time of 4 h. Spectra were also obtained for a series of standards that included Fe, Ni, Co, and Cu foils, and their associated oxides to assist in the energy calibration and subsequent analysis.

IV. PREVIOUS SUSCEPTIBILITY AND RBS MEASUREMENTS

A brief overview of our previous studies of transition-metal-implanted YBCO (Refs. 19–21) follows as the results are pertinent to the discussion of the current results. Table I shows a summary of the results obtained in these studies, giving the measured implant ion depth before and after annealing using Rutherford backscattering spectrometry (RBS). Also shown is the change in superconducting transition temperature ΔT_c, measured before the implantation and after the annealing process, using magnetic susceptibility.

The two most significant results are the diffusion of the implant ion during the anneal process and the corresponding change in T_c. For two ions, Ni and Co, there was significant diffusion during annealing and a corresponding positive change in the transition temperature. Whereas for Fe, the diffusion was not as great, and the corresponding change in T_c was negative. The conclusion arrived at for the Fe case was inferred by the possible substitution of Fe into the YBCO lattice, therefore explaining the small diffusion rate and change in T_c. An alternative process was also suggested that involved Fe oxidation, and in the process "scavenging" interstitial oxygen from the damaged YBCO lattice as well as from the oxygenation/anneal process. This process also accounts for a change in T_c arising from the decrease of oxygen in the YBCO matrix, and a smaller diffusion rate of the larger FeO interstitial, though it was thought that this would be the less likely process. For the Ni and Co cases, the more prolific diffusion rates were accounted for by a "nil-

TABLE I. Results obtained for previous studies of transition-metal-implanted YBCO (Refs. 19–21).

Implant ion	Implant depth	Depth after annealing	ΔT_c (after annealing)
Fe	280 Å	600 Å	-13 K
Co	280 Å	1200 Å	$+3$ K
Ni	300 Å	2000 Å	$+10$ K

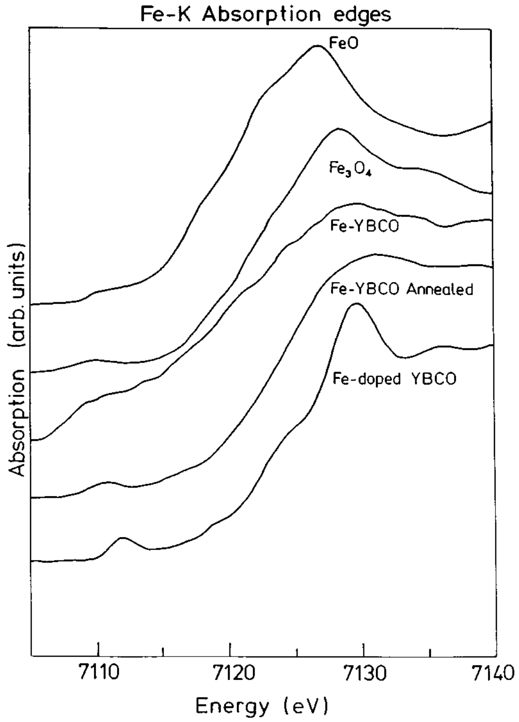

FIG. 2. The Fe near-edge spectra of Fe_3O_4, and Fe-implanted YBCO preanneal, and Fe-implanted YBCO post anneal, with a comparison of YBCO($Fe_{0.17}$) and FeO taken from Ref. 25.

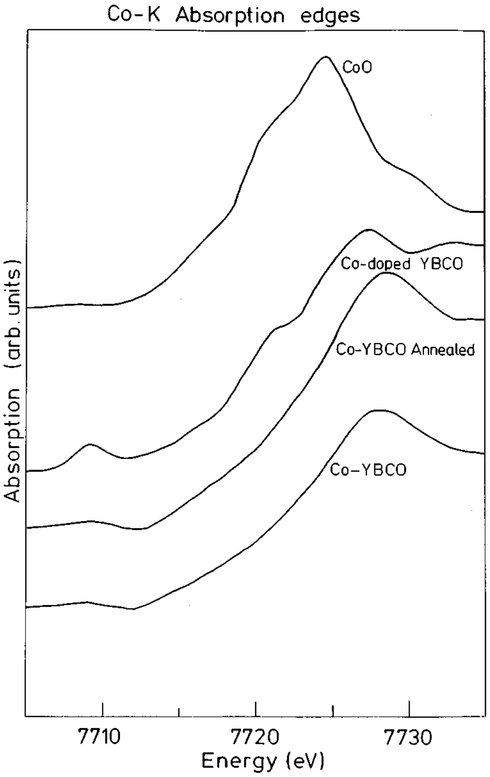

FIG. 3. The Co near-edge spectra of Co-implanted YBCO preanneal, and Co-implanted YBCO post anneal, with a comparison of YBCO($Co_{0.17}$) and CoO taken from Ref. 25.

reaction" with the surrounding lattice and just interstitial diffusion. Whereas the change in T_c was due to the natural rate of oxygenation, though the difference in ΔT_c between Co and Ni could not be explained by these results alone.

V. RESULTS AND DISCUSSION

We show here the results for the near-edge study of Ni-, Fe-, and Co-implanted YBCO. We include both the implant ion *K* edges and Cu *K*edges. Those results, Figs. 2–5, are for the polycrystalline material as the results for the single crystals were essentially the same, with the polycrystals having a better signal-to-noise ratio. All discussion is based on both the results from polycrystalline and single-crystal treated YBCO.

A. Iron implant

The near-edge spectra for Fe-implanted polycrystalline YBCO before and after annealing, along with Fe-oxide standards and a comparison with an Fe-doped YBCO material taken from Bridges *et al.*[25] are shown in Fig. 2. The most striking feature of the annealed Fe-implanted YBCO is the direct similarities to the Fe-doped YBCO of Bridges *et al.* Both edges are centered around 7124 eV, and they also have the characteristic pre-edge peak at 7111 eV. This, in comparison with the oxide standards, corresponds more closely with an Fe^{3+} valence structure, though the existence of the pre-edge peak also suggests some Fe^{2+} is present. Our results do not show any significant high-energy structure that Bridges *et al.* have reported previously to be associated with the presence of Fe^{4+}. This difference may arise from the sensitivity of the technique to the small volume of the implant region when compared to the larger volume of a doped sample. Bridges *et al.* also relate the observed structure, both near-edge and post-edge oscillations, to the substitution of the Fe in the Cu(1) and Cu(2) sites. We believe some form of lattice substitution is also the case here as previous RBS results, Table I, show very little movement of the Fe implant after the anneal cycle, that would be the case if the Fe was bonding with the YBCO lattice. Further, we observe a change in the Fe-edge energy of 5 eV from implantation to annealing. This represents a change in valence structure of the implanted Fe ions, and corresponds to a change from Fe^{2+} to Fe^{3+}. Moreover, the decrease in the relative height of the pre-edge peak centered at 7111 eV, after the anneal treatment, results from a lower proportion of Fe^{2+} present in this state. We believe this result, along with the similarities with the Fe-doped YBCO results, to be a product of the reforming YBCO lattice with the addition of Fe thus changing its valence structure. This is also supported by previously published susceptibility results, Table I, where no effect on the transition temperature is seen after implantation of Fe, but a decrease of 13 K is observed following the annealing process. This can be explained by the substitution of Fe into the YBCO lattice after annealing, as the addition of Fe has a deleterious effect on the superconducting transition temperature, as has been reported by many others.[6–13]

We have shown for the Fe-implant case that there is a change in edge energy of 5 eV from the implanted sample to the annealed sample, corresponding to a change in valence from Fe^{2+} to Fe^{3+}. In comparison with the results of Bridges *et al.*, as well as from our previous studies,[19–21] we conclude that the Fe is substituting in the YBCO lattice after anneal-

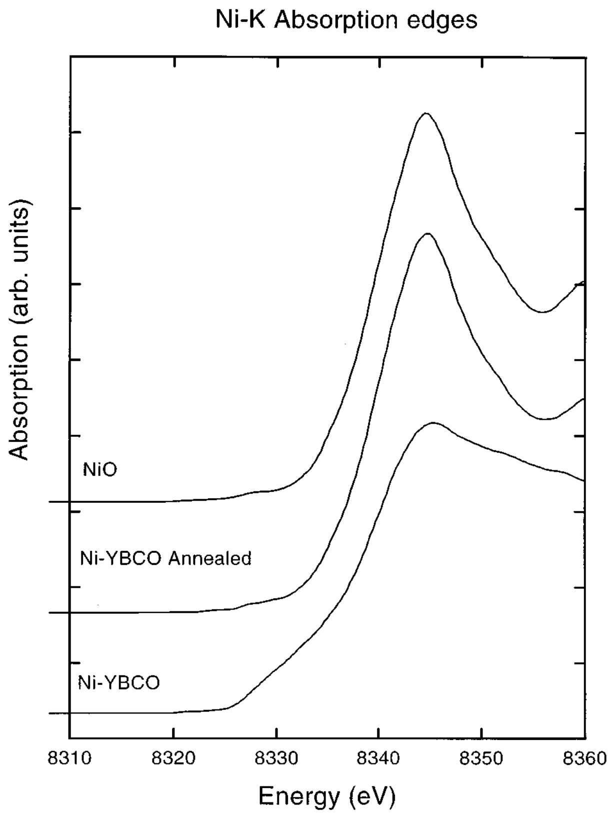

FIG. 4. The Ni near-edge spectra of NiO, Ni-implanted YBCO preanneal, and Ni-implanted YBCO post anneal.

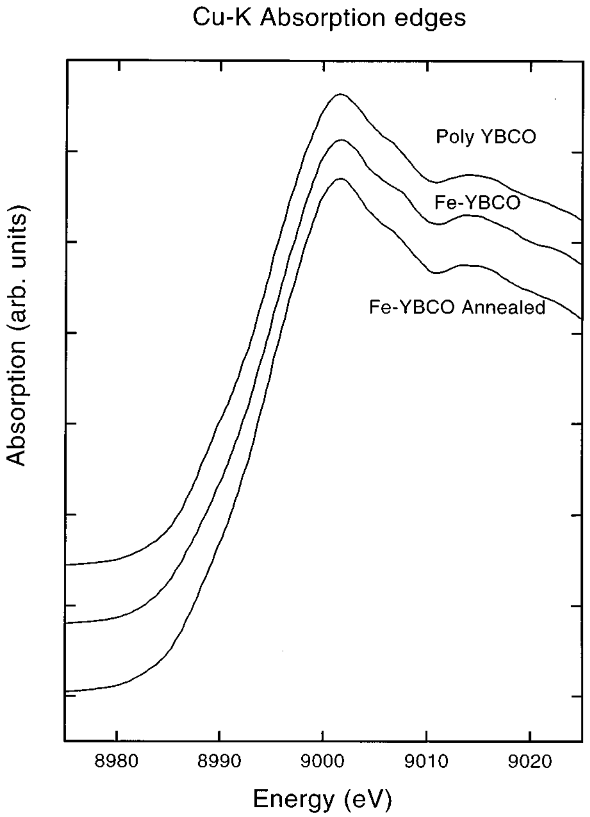

FIG. 5. The Cu near-edge spectra of as-prepared YBCO polycrystalline material, Fe-implanted YBCO preanneal, Fe-implanted YBCO post anneal.

ing, and most likely in the Cu(1) and Cu(2) sites due to the similarity in edge structures. The change in T_c and smaller diffusion rate is then a direct result of the Fe substituting in the YBCO lattice.

B. Cobalt implant

The results for the near-edge study of Co-implanted YBCO are shown in Fig. 3, with the implanted polycrystalline material before and after annealing, along with a Co-doped YBCO material taken from Bridges *et al.*[25] There is no change in the edge positions of the Co implanted to the Co-implanted annealed YBCO, for our samples. In comparison with studies of the doped material, the edge position both before and after the anneal treatment is the same as Bridges *et al.* Apart from the edge positioning of the Co-implanted cases, the implanted samples also do not show the considerable edge features that are present in the doped case of Bridges *et al.*, though, a pre-edge peak centered at 7710 eV is present in both methods of sample preparation. This suggests a small admixture of valence states in the case for Co-implanted YBCO.

In addition, there is no change in the pre-edge peak from implantation to annealing as reported for the Fe case. Our results suggest a valence structure closer to Co^{3+}, though the small presence of Co^{2+} is substantiated with the presence of a pre-edge peak. The absence of a change of the edge structure after annealing means the valence of the implanted ion does not change. This suggests that there is no, or very little, substitution within the YBCO lattice.

These results can also be related to previous work where susceptibility and RBS measurements showed a slight increase in the transition temperature upon annealing of Co-implanted YBCO, as well as a larger diffusion rate than for the Fe ions, respectively. The larger diffusion rate had been related to a "nil-reaction" with the surrounding lattice and is confirmed by the lack of change in the edge structure after the annealing process, shown in Fig. 3. The slight increase in T_c now seems to be due to the oxygenation of the YBCO samples, and not a result of the Co substituting into the lattice.

C. Nickel implant

The results for the Ni-implanted polycrystalline YBCO before and after annealing and Ni-oxide standard are shown in Fig. 4. There is no change in the edge positions after implantation or more surprisingly, after the annealing process, with the positioning of the Ni edge for the oxide standard and implanted sample centered around 8340 eV. The only discernible change is the sharpening of the edge after annealing, though the half-height position does not change. Even post-edge features are the same for the annealed sample and oxide sample. This indicates that there is no change in the valence structure of the Ni throughout the implantation and annealing, and more closely represents that of an oxide material.

This result is similar to that reported by Quain *et al.*[18] who described a NiO precipitate for Ni-doped YBCO, and a defect site location of Ni, not within the lattice. This can occur when the solubility limit has been surpassed for Ni in

YBCO, and is possibly the case when implanting into the near-surface region. Further, this result is in accordance with the RBS measurements that exhibit rapid diffusion of Ni throughout the YBCO lattice, and is more likely to be an equilibrating process to return the material to an equilibrium phase, after the implantation. The susceptibility data also showed the nondeleterious nature of the Ni implant,[19] and in fact the conclusion of an increase rate of oxygenation resulting from the dislocations created by the implant is also supported by these results.

D. Copper *K*-absorption edges

Finally, the near-edge structure of the Cu ions was measured with the results shown in Fig. 5 for the Fe-implanted material before and after the anneal treatment, along with an as processed YBCO polycrystalline sample. The results here show no significant changes in the edge positions after any ion-beam modification or subsequent treatments. This indicates the formal valence of Cu in YBCO. This result could be due to the true absence of a change in edge structure or to the majority of Cu ions sampled being from a region of the YBCO that has not been effected by the ion-beam modification and subsequent treatment due to the natural penetration depth of the incident radiation. Though, it is important to note that even in the reported cases of largely doped bulk materials, shifts and changes in the observed Cu edge structure have been minimal.[25,26] The results for the Ni- and Co-implant cases also showed no measurable shift in the Cu edge before or after annealing. These results clearly show that the Cu ions present are completely bonded in the YBCO lattice which dominates their valence structure even in the presence of dopants.

VI. CONCLUSION

We have used near-edge x-ray absorption in a study of transition-metal-implanted single-crystal and polycrystalline YBCO. Ion doses of 1×10^{17} ions/cm^2 were accumulated at room temperature using a metallized vapor vacuum arc high current ion source. The resulting samples were then annealed in an oxygen atmosphere at 550 °C for 100 h. The results reported here are for Fe, Ni, and Co implants with the valence structure of Fe changing from Fe^{2+} to Fe^{3+} after the anneal process and has a structure that is similar to Fe-doped YBCO. The Ni and Co implants do not change valence structure after the anneal treatment, with the Ni having a valence essentially the same as NiO and Co having a valence closer to Co^{3+}. Finally Cu *K*-edge absorption measurements showed no change after implantation and annealing. These results are consistent with previous susceptibility studies of these implanted materials.

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