Nuclear Quadrupole Resonance Study of Copper in Electron-Irradiated $YBa_2Cu_3O_{6.95}$ *

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NQR of Cu in $YBa_2Cu_3O_{6.95}$ was investigated before and after low-temperature electron irradiation as well as after annealing at several distinct temperatures up to 440 K. Irradiation with 2.76 MeV electrons (fluence $\phi t = 2.2 \cdot 10^{23}$ e^-/m^2) decreased the critical temperature T_c from 91.8 K to 89.5 K. The NQR spectra indicate that the e^- irradiation displaces so-called O(4) atoms in the Cu–O chains. It is argued that this results in a modification of the average valence of the Cu(2) atoms in the planes, which explains the reduction of T_c. Recovery of the radiation damage sets in (presumably due to the onset of mobility of displaced oxygen atoms) during annealing at 300 K but was still incomplete at 440 K.

Key words: NQR spectra, Superconductivity, $YBa_2Cu_3O_{7-\delta}$, Electron irradiation, Annealing experiments

1. Introduction

The present paper reports on the first NQR investigation on Cu nuclei in an electron-irradiated copper-oxide high-T_c superconductor. The motivation for this work was, on the one hand, that electron irradiation was known to reduce the transition temperature T_c of high-T_c superconductors [1, 2, 3] and, on the other hand, that NQR is capable of giving us fairly direct information on local atomic configurations, e.g. those arising from the displacement of nuclei from their lattice sites. In the specific case of $YBa_2Cu_3O_{7-\delta}$, the material investigated in the present work, NQR measurements on Cu allow us to investigate separately the surroundings of the so-called Cu(1) ions in the Cu–O chains and of the Cu(2) ions in the Cu_2O planes.

The Cu NQR spectra of polycrystalline powder samples of $YBa_2Cu_3O_{6.95}$ were studied at 3.9 K in the frequency range between 19.7 MHz and 32.4 MHz. Measurements of the spin–lattice relaxation rates, Γ_1, on the same samples have already been reported [4, 5].

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2. Experimental Details and Sample Characterization

Polycrystalline $YBa_2Cu_3O_{7-\delta}$ was prepared by solid-state reactions of the appropriate amounts of Y_2O_3, CuO, and $BaCO_3$. For the NQR studies the pressed ceramic pellets were crushed into powder of about 10 μm grain size. The oxygen content determined from the shift in the Fe^{2+}/Fe^{3+} redox potential and by iodometric analysis [6] are found to correspond to an oxygen deficiency of $\delta = 0.050 \pm 0.003$. X-ray diffraction confirmed the single-phase orthorhombic structure of the material. The transition temperature $T_c = (91.8 \pm 0.2)$ K was determined by means of AC-susceptibility and SQUID measurements.

The 2.76 MeV electron irradiation with $2.2 \cdot 10^{23}$ electrons/m^2 was carried out at the Van de Graaff accelerator of Forschungszentrum Jülich. In order to achieve a homogeneous irradiation, the powder samples were sealed under N_2 atmosphere in 18 small quartz tubes. These were arranged between two Al foils oriented perpendicular to the beam direction. After the first half of the irradiation period, the sample assembly was inverted with respect to the beam direction. During the irradiation the sample was cooled with liquid He. The irradiation reduced the transition temperature T_c by $\Delta T_c = 2.3$ K to $T_c = (89.5 \pm 0.2)$ K. In

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order to prevent recovery of radiation damage, the sample tubes were stored under liquid N_2 and transferred to the NQR sample holder without warming up. The annealing of the irradiated samples was carried out in N_2 atmosphere without removing them from the NQR sample holder. In each annealing step the samples were kept at the desired temperature for 30 minutes. Annealing at 440 K caused a T_c recovery of $\Delta T_c = 0.9$ K, leading to a critical temperature of $T_c = 90.4$ K.

The NQR measurements were performed in zero magnetic field using a home-built pulsed spectrometer with quadrature detection. The NQR spectra were obtained by recording the intensity of the Fourier-transformed spin echo as a function of frequency in steps of typically 70 kHz.

3. Results and Discussion

3.1 NQR spectra before and after e^- irradiation

Figure 1 shows the Cu NQR spectra measured at 3.9 K on the same sample before and after low-temperature e^- irradiation. The spectrum obtained before e^- irradiation is typical of the single-phase orthorhombic structure of $YBa_2Cu_3O_{7-\delta}$. It shows NQR line pairs characteristic of the two copper isotopes ^{63}Cu and ^{65}Cu. The pair with the NQR frequencies $\nu_0[^{63}Cu(1)_4] = 22.08$ MHz and $\nu_0[^{65}Cu(1)_4] = 20.40$ MHz is assigned to Cu on chain sites, that with $\nu_0[^{63}Cu(2)] = 31.61$ MHz and $\nu_0[^{65}Cu(2)] = 29.22$ MHz to Cu on plane sites [7, 8, 9, 10].

It is evident from Fig. 1 that the e^- irradiation affects the Cu NQR spectrum strongly. The lines attributed to Cu on plane sites are significantly reduced and shifted to lower frequencies by $\Delta\nu_0\,[^{65}Cu] = 160$ kHz and $\Delta\nu_0\,[^{63}Cu] = 190$ kHz, respectively. The $^{63}Cu(1)_4$ signal coming from Cu on chain sites surrounded by four oxygen atoms ($\nu_0\,[^{63}Cu(1)_4] = 22.08$ MHz), almost vanished. (The corresponding ^{65}Cu signal could not be observed since it fell outside of the frequency range accessible with the r.f.-circuit used for measurements on the irradiated sample.) The most striking feature is the occurrence of a pair of strong irradiation-induced NQR lines at frequencies (viz. $\nu_0\,[^{63}Cu] = 30.1$ MHz, $\nu_0\,[^{65}Cu] = 27.9$ MHz) previously observed in the semiconducting tetragonal phase $YBa_2Cu_3O_{7-\delta}$ $(0.5 \leq \delta \leq 1.0)$ [11], which differs from the superconducting phase in that the Cu atoms in the chains are surrounded by two oxygen atoms rather than by four. This suggests that these two lines belong to copper on $Cu(1)_2$ sites. Cu atoms in the chains surrounded by two oxygen atoms can be obtained by an irradiation-induced displacement of oxygen atoms on O(4) positions from their lattice sites. Displaced oxygen atoms modify the electric field gra-

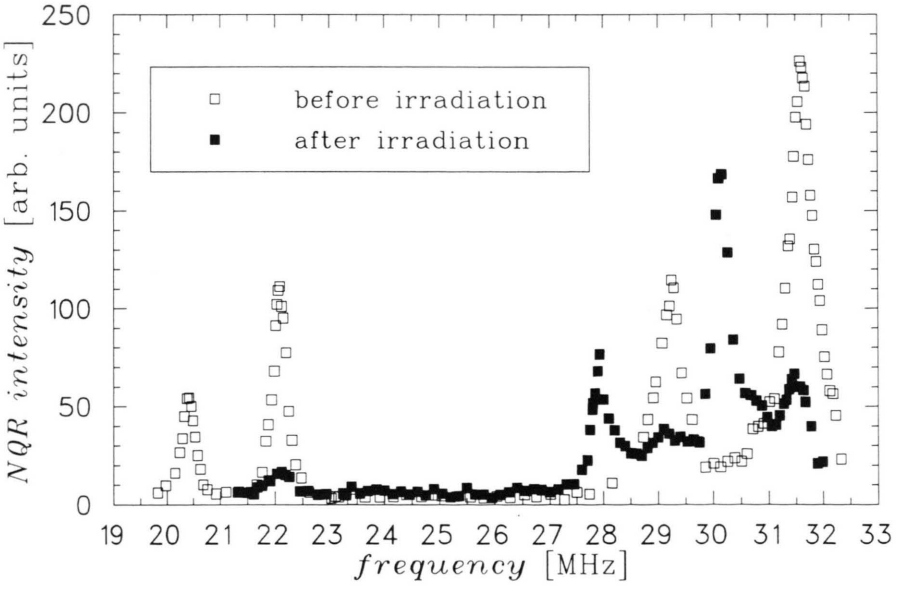

Fig. 1. NQR spectra of Cu in $YBa_2Cu_3O_{6.95}$ measured at 3.9 K before and after low-temperature electron irradiation

dients on the lattice sites and thus the NQR frequencies of the Cu nuclei. The observed broadening and slight shift in frequency of the Cu(2) signals may be attributed to a distribution of displaced oxygen atoms at nearby interstitial sites.

A striking result is that in the measurements immediately after the e^- irradiation no signal was observed at the NQR frequency of Cu on chain sites surrounded by three oxygen atoms ($\nu_0[^{63}Cu(1)_3] = 24.0$ MHz [12]). The NQR spectrum of the e^--irradiated sample can be interpreted entirely by a superposition of signals from regions with either full chains or empty chains.

The overall NQR intensity indicates that not all Cu nuclei contribute to the observed signals. Cu nuclei in strongly damaged regions, in which the $YBa_2Cu_3O_{7-\delta}$ structure was destroyed, may be invisible for NQR either because of very short relaxation times or because of significant changes of the electric field gradients.

3.2 Annealing experiments

After isochronal annealing at 205 K, 250 K, and 275 K, no change in the NQR spectra was observed. Neither the NQR frequencies nor the widths and intensities of the NQR signals differed from the NQR spectrum obtained immediately after electron irradiation. However, as shown in Fig. 2, a NQR line at 24.0 MHz appeared after annealing at 300 K, indicating that at this temperature displaced oxygen atoms become mobile and move to O(4) positions. According to the ratio of the quadrupolar moments of ^{63}Cu and ^{65}Cu, $^{63}Q/^{65}Q = 1.082$, the corresponding ^{65}Cu signal is expected at $\nu_0[^{65}Cu(1)_3] = 22.2$ MHz; hence it cannot be separated from the $^{63}Cu(1)_4$ peak at $\nu_0 = 22.08$ MHz. The two subsequent annealing steps at 325 K and at 350 K caused again no significant change in the NQR spectrum. After annealing at 375 K a pair of NQR signals appeared at $\nu_0 = 26.9$ MHz and $\nu_0 = 24.9$ MHz, respectively. The frequency ratio of these two sharp peaks, $^{63}\nu_0/^{65}\nu_0 = 1.081$, indicates that this pair is to be attributed to the two copper isotopes on identical lattice sites. Both frequencies deviate only by about $\Delta\nu \approx 70$ kHz from the NQR frequencies that we measured on solid Cu_2O. This suggests that these lines may be assigned to Cu_2O precipitates. Since X-ray diffraction did not show indications of the Cu_2O structures we assume that the 375 K annealing caused the formation of small precipitates of Cu_2O randomly distributed over the sample. Further annealing at 400 K and at 440 K left the NQR spectrum unchanged. After the annealing experiments the transition temperature was $T_c = 90.4$ K, which means that at the irradiation dose used in the present experiment the recovery was still incomplete at 440 K.

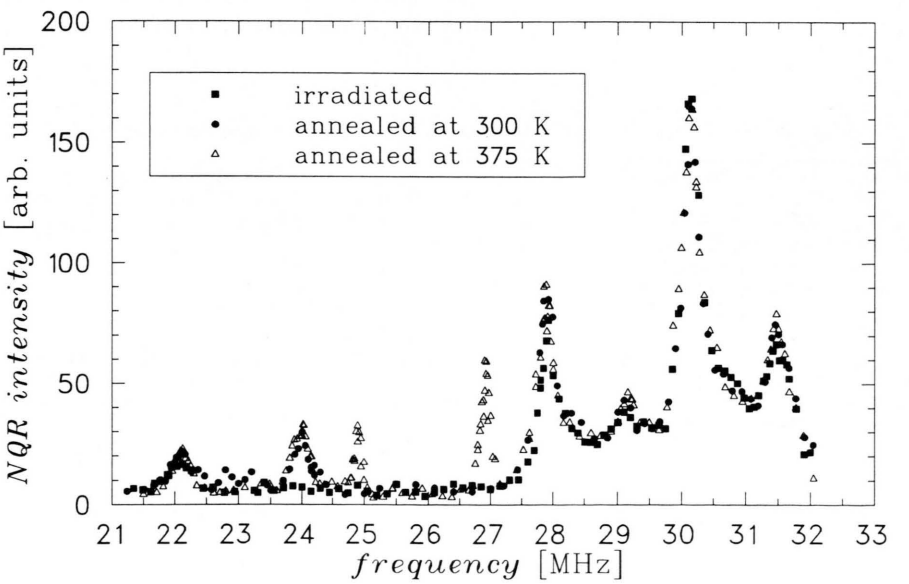

Fig. 2. Comparison of NQR spectra of Cu in $YBa_2Cu_3O_{6.95}$ measured at 3.9 K immediately after irradiation and after annealing at 300 K and 375 K, respectively.

3.3 Analysis of the NQR spectra

In order to compare the intensities of different peaks, the NQR spectra have to be normalized by dividing the echo intensities by the square of the resonance frequency. Since the electron irradiation removed oxygen atoms from O(4) positions, the $Cu(1)_4$ signal was reduced and a $Cu(1)_2$ signal appeared. In those parts of the sample where all O(4) positions are unoccupied, i.e., where the tetragonal structure $YBa_2Cu_3O_{6.0}$ exists, the CuO_2 planes are supposed to show anti-ferromagnetic ordering and therefore not to contribute to the Cu(2) NQR spectrum in the frequency range investigated [13]. This may explain the reduction of the Cu(2) lines by electron irradiation. The fact that the reduction of the signal intensity is more pronounced for $Cu(1)_4$ than for Cu(2) suggests that there are regions in the sample where the tetragonal structure exists but which are too small for anti-ferromagnetic ordering to develop.

The appearance of the $Cu(1)_3$ signal after annealing at 300 K has almost no influence on the intensities of the $Cu(1)_2$ and $Cu(1)_4$ lines, in accordance with the picture that it is the displaced oxygen atoms that become mobile at this temperature. At 375 K, where the Cu_2O signal appeared, no significant change in the signal intensities of the other NQR lines could be observed either. Thus, Cu_2O is presumably formed in those regions of the sample where, due to strong irradiation damage, the Cu nuclei did not contribute to the NQR spectrum before.

4. Summary and Conclusions

NQR investigations on electron-irradiated powder of $YBa_2Cu_3O_{6.95}$ indicate clearly that e^- irradiation displaces oxygen atoms out of the chains. The modification of the electron density in the planes and hence the average valence of Cu(2) atoms may account for the decrease in T_c.

At present it is not clear why immediately after e^- irradiation the Cu–O chains appear to be either full or empty and why the $Cu(1)_3$ configuration can be observed only after annealing at 300 K.

The irradiation-induced change in the signal-intensity ratio of Cu on chain sites and Cu on plane sites indicates that in parts of the irradiated sample the tetragonal structure exists, even though no anti-ferromagnetic ordering is observed. This can be explained by the assumption that a minimum extension of the tetragonal phase is required in order for the anti-ferromagnetic order to be established. The NQR spectrum obtained after annealing at 375 K suggests that randomly distributed Cu_2O precipitates form during this annealing treatment.

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