NQR Studies of Halogen Treated 1-2-3 System*

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NQR spectra of copper in polycrystalline samples of iodine treated $RBa_2Cu_3O_y$ (R = Y, Gd) were studied. The results of all the experiments show evidence for the modifications occurring in the oxygen sublattice in treated compounds.

Key words: NQR-spectra; Superconductors; Treatment; Halogens; Diffusion.

1. Introduction

Halogen doping at modest temperatures has been shown to provide an interesting method for restoring superconductivity in partially deoxygenated nonsuperconducting YBCO crystals [1 - 3]. In view of this, a number of important questions arise, the answers of which are important to elucidate the mechanism for the restoration of superconductivity. Nuclear quadrupole resonance (NQR) is a powerful tool which provides information on the electronic state at different atomic sites. We present here results of Cu NQR investigations of $RBa_2Cu_3O_y$+I_2 (R = Y, Gd) compounds.

2. Samples and Measurement Technique

The samples investigated were single-phase polycrystalline powders with a mean particle size less than 50 μm fixed in paraffin. Orthorhombic samples of 1-2-3, synthesized by a standard ceramic technology, were used as starting material. The oxygen content was determined by iodometric titration and controlled using data of crystal lattice parameters. The superconducting transition temperature was determined to be T_c = 90 K by measuring the magnetic a. c. susceptibility, $\chi_{a.c.}(T)$ (effect of magnetic screening). The samples were then treated in argon at various temperatures. This way we obtained tetragonal dielectric samples of $RBa_2Cu_3O_{6.1}$ (R = Y, Gd) and superconducting orthorhombic ones of $RBa_2Cu_3O_{6.5}$ (R = Y, Gd) with T_c = 55 - 60 K. The samples were then halogenated by the technique described in [1 - 3]. The beginning of the superconducting transition of the iodinated Y-Ba-Cu-O samples was $T_{c0} \approx 55$ - 60 K; for Gd-Ba-Cu-O samples it was $T_{c0} \approx 90$ K. All the crystals investigated were single-phase (as observed by X-rays), and they did not exhibit any impurities of other crystalline phases.

The NQR spectra were studied on a pulsed NQR spectrometer IS-3, using spin-echo signals accumulation. The NQR spectra were obtained by recording echo signal amplitudes and continuously retuning of the frequency of the exciting rf pulses.

3. Results and Discussion

The NQR spectra of the samples measured from 21 to 33 MHz at 4.2 K are shown in Figures 1 - 3. Natural Cu contains two isotopes, ^{63}Cu and ^{65}Cu, both with nuclear spin $I = {}^3/_2$. The frequency lines of the less abundant ^{65}Cu (31%) are shifted downward by about 10%. The signal amplitude is given in arbitrary units. The relative amplitudes shown in the figures are only approximate. The Cu NQR spectra of the starting orthorhombic $RBa_2Cu_3O_{6.9}$ (R = Y, Gd) samples correspond to the well-known spectra, i. e., the 31.5 MHz resonance line is attributed to copper

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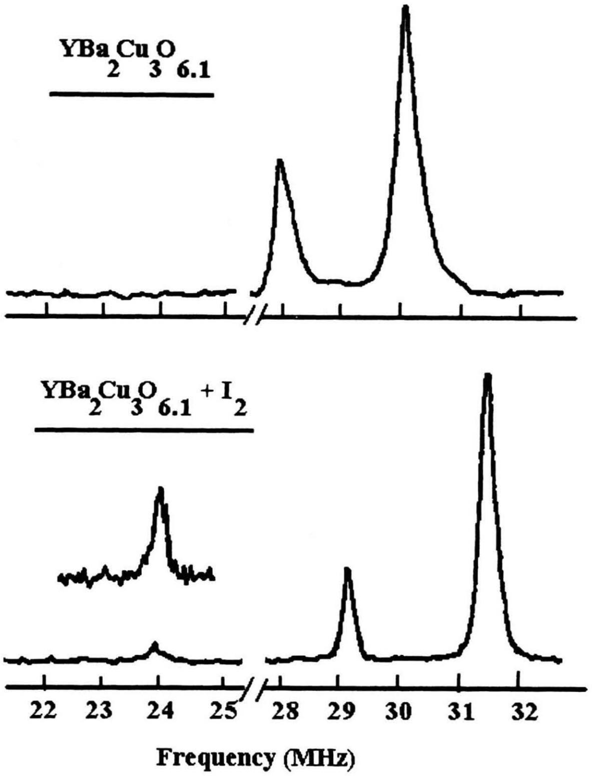

Fig. 1. ^{63,65}Cu NQR spectra of the compounds investigated, $T = 4.2$ K.

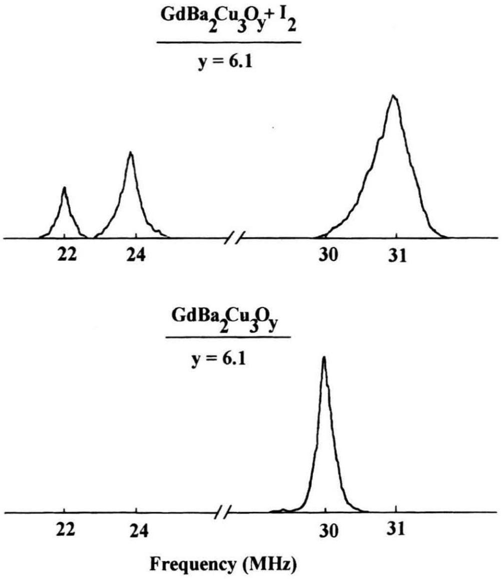

Fig. 2. ^{63}Cu NQR spectra of the Cu(1) sites ($y = 6.1$), measured at 4.2 K.

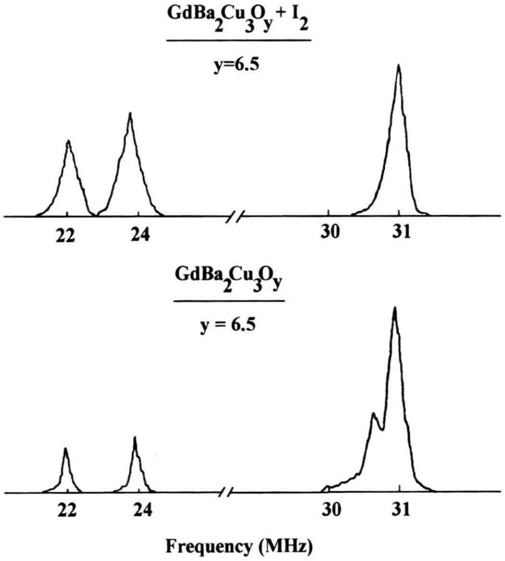

Fig. 3. ^{63}Cu NQR spectra of the Cu(1) sites ($y = 6.5$), measured at 4.2 K:

nuclei in Cu (2) atom positions, the 22.0 MHz line to Cu(1) positions [4, 5]. The spectra of tetragonal $RBa_2Cu_3O_{6.1}$ (R = Y, Gd) samples also agree with the known spectra. There is now general agreement about the assignment of the lines in the compounds with full chains ($RBa_2Cu_3O_7$) and with empty chains ($RBa_2Cu_3O_6$). Figures 1 - 3 show that the treatment affects the Cu NQR spectra strongly.

In the signal position the NQR spectrum of an iodinated sample (Fig. 1) is very much like that of an oxygen-deficient sample. The quadrupole spin-echo signals are observed at 31.4 MHz (^{63}Cu) and 29.1 MHz (^{65}Cu). However, the intensity of the NQR resonance lines (31.4 MHz) is almost one order of magnitude higher than the ones of $YBa_2Cu_3O_{6.56}$ (31.5 MHz). It should also be emphasized that the forms of the observed resonance lines are different: the iodinated sample exhibits a symmetric line, while $YBa_2Cu_3O_{6.56}$ exhibits an asymmetric resonance line with a weaker slope in the low frequency region, which indicates the superposition of lines with nearby frequencies. In an iodinated sample the resonance line width is $\Delta(_{Q} = 200$ kHz. The resonance line width is comparable with the published one for highest-quality samples of $YBa_2Cu_3O_7$ and may indicate a high degree of ordering of the samples after iodination.

One more feature of the NQR spectrum of an iodinated sample (Fig. 1) is the appearance of a weak signal 23.9 MHz. In the brominated sample the NQR signal was not observed at this frequency. At the same time we did not succeed in observing in these samples the NQR signals in the 22 MHz region, characteristic for crystallographic positions Cu (1) in the orthorhombic phase.

The Cu (2) and Cu (1) lines can be easily separated in the $GdBa_2Cu_3O_y$ compounds using the idea of the fluctuations of the rare earth moments [4, 5]. The fluctuation of the nearly paramagnetic Gd moments above the Neel temperature $T_n = 2.2$ K induce significant relaxation effects at the nearby nuclei in the Cu(2) layer. Therefore the spin-echo amplitude of the nuclei in the Cu(2) sites at 4.2 K (31 MHz) can be completely suppressed. Thus, only the lines corresponding to Cu(1) in these compounds appear at 4.2 K.

For our $GdBa_2Cu_3O_{6.1}$ sample, iodination has a noticeable effect on the Cu NQR spectrum. The treatment of the tetragonal sample results in additional peaks. We shall see that the treatment with iodine gives results very similar to the increase of the basal oxygen (Figure 2). The ^{63}Cu NQR spectrum of $GdBa_2Cu_3O_{6,1}$ consists of one line at 30.1 MHz. It is well known that in the antiferromagnetic compounds with $y < 6.4$ only the Cu(1) sites contribute to the NQR spectrum. The Cu(2) sites carry a magnetic moment and lead to an antiferromagnetic NMR spectrum at 90 MHz with a quadrupole splitting which proves that the hyperfine field is perpendicular to the symmetry axis of the EFG. The characteristic NQR spectra of $GdBa_2C_3O_y$ at different oxygen concentrations are reported for 4.2 K [4, 5]. In the high frequency region of the spectra of samples with y below about 6.55 two more lines appear, and the spectra exhibit three lines at the frequencies 31.2, 30.9 and 30.2 MHz. In an iodinated sample $GdBa_2Cu_3O_{6,5}+I_2$ the fine structure of the Cu NQR disappears (Figure 3).

It was shown that the Cu NQR spectra of the $RBa_2Cu_3O_y$ can be explained within the model of the ortho-II structure where in the samples with oxygen concentration $y > 6.59$ every "empty" chain is situated between two intact chains, and in the samples with $y < 6.59$ two or more neighbouring chains appear to be empty [4, 5]. The comparatively narrow lines of Cu(1) show that the EFG values are determined only by the nearest coordination sphere and that the different lengths of the neighbouring intact chain fragments do not influence the resonance frequency.

At present there are at least two models describing the interaction of halogens with ceramics. The first involves oxygen-halogen substitution and incorporation of the latter into well-defined positions in the crystal lattice. In the second, oxygen atoms occur in their usual position of Cu(1)-O type due to the chemical interaction of R-Ba-Cu-O ceramics with the halogen and, possibly, to its partial decomposition. The occurrence of the orthorhombic phase of a normal oxygen type is responsible for the observed superconductivity [6]. Unfortunately, experimental data yield different, often contradictory results.

We think the radius of the I ion is too large for permiting these ions to enter into the lattice of R-Ba-Cu-O ceramics. For this reason the second model [6] seems more suitable for discribing the iodination process. It is suggested that the vapours of iodine interact with ions of Cu and iodide forms. As a result, part of the crystal lattice is destroyed. Then the released nonmolecular oxygen diffuses in the lattice of the ceramics, and therefore the amount of oxygen is increased with the transformation of the lattice from tetragonal to orthorombic. To estimate the intensity of the process of oxygen diffusion, the corresponding Cu NQR experiments were performed [7]. In particular, interesting results were found from Cu NQR measurements of mixture of a $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$, and it was settled that the interparticle diffusion of oxygen is important too [7].

4. Conclusions

The analysis of the results obtained in the present study allows to conclude that halogenation of 1-2-3 ceramics results in a significant modification of the oxygen sublattice. The obtained Cu NQR spectra of the treated compounds indicate that halogenation results in disturbance of the oxygen vacancies ordering.

In our opinion the ions of I_2 do not penetrate in the lattice of these compounds. As a result of iodination, only destruction of part of the ceramic lattice takes place and a corresponding amount of oxygen released. The modification of the oxygen sublattice takes place through diffusion of the released oxygen. In this process both internal and interparticle diffusion of oxygen are important.

We think that this model is not common to all halogens. In particular for compounds treated by Cl this model is probably not correct, and it is necessary to perform the corresponding measurements in order to clarify the process of interaction of vapours of halogens with the ceramic lattice.

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