Cu NQR Study in a High-T_c Superconductor $YBa_2Cu_3O_{6.1}I_x$*

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NQR-spectra and nuclear relaxation of ^{63}Cu in ceramic samples of the Y–Ba–Cu–O system with various oxygen content have been compared with those in iodinated $YBa_2Cu_3O_{6.1}$.

Key words: NQR-spectra, Relaxation, Superconductivity, $YBa_2Cu_3O_y$, Iodination.

1. Introduction

Earlier [1–4] we showed that thermal treatment in halogen vapours (Cl, Br, I) of initially dielectric tetragonal samples of $YBa_2Cu_3O_{6.1}$ gives rise to orthorhombic superconducting phases with different T_c values. Further studies by other authors [5–8] confirmed the observed phenomenon. The central questions seem to be concerned with the connection of CuO_2 planes with other elements of the crystalline structure, determining both the appearance of charge on planes (holes in a 2p oxygen shell) and stability of the crystal structure as a whole.

A study of nuclear relaxation is known to be a most informative approach for elucidating the electronic structure of high-T_c superconductors. The experiments yield valuable information about elementary excitations in the electronic spin system both in the normal and superconducting states [9]. In turn, NQR spectral parameters are very sensitive to a change of the symmetry of the closest environment to the resonance atoms.

Earlier, $^{63,65}Cu$ NQR was employed to obtain the preliminary results on $YBa_2Cu_3O_{6.1}$ ceramic samples thermally treated in bromine and iodine gases [10]. Within the thermal treatment regimes used, the brominated samples consisted, usually, of two-phases, comprising the initial tetragonal phase. Iodination gave rise to single-phase samples (as observed by X-ray diffraction) with orthorhombic structures [2, 3]. The present work reports a further systematic study of quadrupole interactions and nuclear relaxation of ^{63}Cu in Y–Ba–Cu–O ceramics exposed to iodine vapours. Since the detailed magnetic properties depend on the sample preparation and the precise value and homogeneity of the oxygen content, it is important to make NQR measurements on a series of samples. Therefore a comparative NQR-study using starting samples with different oxygen content is presented.

2. Samples and Measurements Technique

The samples were single-phase polycrystalline powders with a mean particle size of <50 μm fixed in paraffin. Orthorhombic samples of $YBa_2Cu_3O_{6.9}$, synthesized by a standard ceramic technology, were used as starting ones. The oxygen content O_y was determined by an iodometric titration method and controlled via the crystal lattice parameters a, b, c vs.y [11, 12]. The superconducting transition temperature was determined by measuring the magnetic susceptibility at a.c., $\chi_{a.c.}(T)$ (effect of magnetic screening). In the said sample it amounted to $T_c = 90$ K. The samples were then treated in argon at various temperatures. This made it possible to obtain tetragonal dielectric samples of $YBa_2Cu_3O_{6.1}$ and superconducting orthorhombic ones of $YBa_2Cu_3O_{6.56}$ with $T_c = 55$–60 K. The choice of the latter ones is not occasional since it seems interesting to compare the iodinated and $YBa_2Cu_3O_{6.56}$ samples, having close T_c. The samples were iodinated by the technique described in

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Table 1. Values of the crystal lattice parameters.

	Sample	a (Å)	b (Å)	c (Å)
1	$YBa_2Cu_3O_{6.1}$	3.855	3.855	11.822
2	$YBa_2Cu_3O_{6.9}$	3.825	3.880	11.670
3	$YBa_2Cu_3O_{6.1}I_x$	3.840	3.877	11.722
4	$YBa_2Cu_3O_{6.56}$	3.832	3.861	11.730

[2, 3]. The starting samples to be iodinated were the mentioned tetragonal samples of $YBa_2Cu_3O_{6.1}$. The beginning of the superconducting transition of the iodinated samples T_c was at 55–60 K, the width $\Delta T_c = 10-15$ K. The values of the crystal lattice parameters of the samples are listed in Table 1. All crystals were single-phase (as observed by X-ray diffraction), and they did not exhibit any foreign crystalline phases.

The NQR spectra were studied on a pulsed NQR-spectrum IS-3, using spin echo signals accumulation. The NQR spectra were registered by recording echo signal amplitudes at a continuous retuning of the input frequency of the exciting rf pulses. We have measured the spin-lattice relaxation time T_1 in an unoriented powder sample using NQR technique. The relaxation time T_1 was determined from the recovery of the echo amplitude after a saturation sequence of radiofrequency pulses.

3. Results and Discussion

3.1 Quadrupole Interactions

An overall view of obtained ^{63,65}Cu NQR spectra is demonstrated in Figure 1. The ^{63,65}Cu NQR spectrum of the orthorhombic $YBa_2Cu_3O_{6.9}$ sample conforms with [14], i.e., the resonance lines of ^{63}Cu are at 22.0 and 31.5 MHz (4.2 K). They are related to the signals of the Cu atoms which occupy the Cu (1) and Cu (2) sites, respectively [14].

The signal position of the iodinated sample (Fig. 1) is very much like that of the oxygen-deficient sample with $y = 6.56$. The signals are observed at 31.4 MHz (^{63}Cu) and 29.1 MHz (^{65}Cu). However, the intensity of the NQR resonance line (31.4 MHz) is almost by one order higher than with $YBa_2Cu_3O_{6.56}$ (31.5 MHz). It should also be emphasized that the shape of the lines is different: The iodinated sample exhibits a symmetric line while the $YBa_2Cu_3O_{6.56}$ line shows a milder sloping on the low frequency side, which probably indicates a superposition of lines with

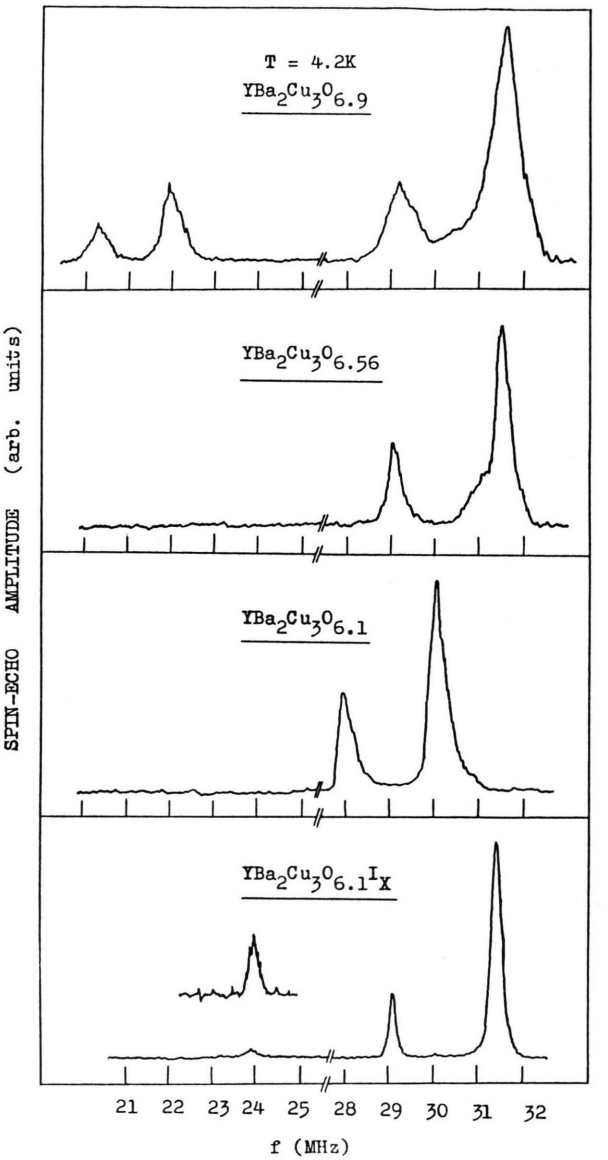

Fig. 1. ^{63}Cu, ^{65}Cu NQR spin-echo frequency spectra in $YBa_2Cu_3O_x$ ($x = 6.9$; 6.56; 6.1 and $YBa_2Cu_3O_{6.1}I_x$.

close frequencies. In the iodinated sample the resonance line width reaches $\Delta\nu_Q = 200$ kHz (for comparison, $\Delta\nu_Q = 700$ kHz in $YBa_2Cu_3O_{6.9}$). The resonance line width is comparable with the published data for the highest-quality samples of $YBa_2Cu_3O_7$.

One more feature of the NQR spectrum of the iodinated sample is the appearance of a weak signal at 23.9 MHz while we did not find signals in the region of 22 MHz, characteristic of the crystallographic positions Cu (1) in the orthorhombic phase.

The frequency ν_Q of the Cu NQR signal (with nuclear spin $I=3/2$) is given by

$$\nu_Q = \tfrac{1}{2} eQq_{zz}(1+\eta^2/3)^{1/2}, \quad (1)$$

where q_{zz} is the largest component (z component) of the total field gradient tensor in the set of principal axes, η is the asymmetry parameter defined as $\eta=(q_{xx}-q_{yy})/q_{zz}$ and eQ is the nuclear electric quadrupole moment of the respective Cu isotope. Thus the ratio of the NQR frequencies of the two Cu isotopes equals the ratio of their quadrupole moments (1,08), which was confirmed experimentally. This proves that no static internal magnetic field due to any type of magnetic ordering is present at the Cu sites in an iodinated Y–Ba–Cu–O–I sample. Such a magnetic field would split and/or shift the NQR lines.

So, a comparative analysis of the ^{63,65}Cu NQR spectra in the samples investigated suggests that intensive resonance lines, appearing after iodination, may be attributed to copper atoms in the crystallographic positions Cu(2). In this case the NQR spectrum obtained in iodinated ceramics confirms directly the presence of a nondistorted structure of CuO_2 planes, and the small width of the observed lines indicates a sufficiently high degree of the crystal lattice ordering. A small (0.1 MHz) shift of the resonance lines towards lower frequencies (as compared with $YBa_2Cu_3O_{6.9}$) may be associated with the large value of the parameter c, resulting in an increase of the Cu(2)–O(4) spacing, or with a partial substitution of oxygen in positions O(4) by iodine. The appearance of weak NQR signals in the region of 23.9 MHz can, probably, be attributed to chain atoms Cu(1).

Many NQR experiments have been performed for the various high-T_c compounds and particularly for both copper sites Cu(1) and Cu(2) in $YBa_2Cu_3O_x$. Now it is known that the two lines at 30.1 and 27.9 MHz of tetragonal $YBa_2Cu_3O_{6.1}$ correspond to NQR signals of ^{63}Cu and ^{65}Cu, respectively, in Cu(1) chain positions. The antiferromagnetic ordering of Cu^{2+}(2) ions in copper-oxygen planes gives rise to a strong magnetic field; in this case no NQR signal is observed in the 31.5 MHz region, but a quadrupole-perturbed NMR spectrum arises in the internal magnetic field at 70–110 MHz [13, 14]. However, in $YBa_2Cu_3O_{6.1}I_x$ the holes introduced by iodination induce a delocalization of the ordered electron spins, and the corresponding Cu(2) NQR signals appear in the 31.4 MHz region.

Our results may support the conclusion that iodine atoms are incorporated into the crystal lattice and arranged orderly in certain lattice sites. For a random incorporation of iodine atoms into the structure one should expect a considerable broadening of the spectral lines, since the local electric field gradient (EFG) is very sensitive to a change of the symmetry of the closest environment of the resonating copper atoms. However, it should be emphasized that at present we cannot directly prove that the effects observed are due to incorporation of iodine atoms into vacant oxygen positions in the Cu(1)–O plane. Possibly, a more complicated process takes place, associated with iodine atom assimilation by the Y–Ba–Cu–O lattice into other positions, or with the formation of Y, Ba, or Cu iodides, accompanied by a transfer of oxygen atoms to Cu(1)–O chains. Elucidation of this question necessitates X-ray studies.

Conventionally EFG's are calculated by simple point charge models, which require assumptions about the charge of the ions. However, due to the complicated structure of the high-T_c materials, it remains difficult to obtain from the values of the total EFG for Cu(1) and Cu(2) a complete understanding of the charge distribution. A calculation of the Cu EFG in Y–Ba–Cu–O from the self consistent charge density has recently been performed by using the full potential linearized augmented plane wave method [15, 16]. In this approach, the EFG V_{zz}^{tot} can have two contributions: one, V_{zz}^{MT}, from the anisotropic charge distribution inside a muffin-tin (MT) sphere and the other, V_{zz}^{latt}, from the lattice summation (other muffin-tin regions and interstitials).

$$V_{zz}^{tot} = V_{zz}^{MT} + V_{zz}^{latt}. \quad (2)$$

It is found that the main contribution to the EFG for both Cu(1) and Cu(2) arise from V_{zz}^{MT}. These results indicate that the most important part of the EFG at the Cu sites in $YBa_2Cu_3O_7$ comes from the anisotropic charge distribution inside the MT spheres (i.e., local charge anisotropy) rather than the external (lattice) charge distribution. The anisotropy of the charge distribution is due to the covalent nature of the Cu(d)–O(p) hybridization. Antiferromagnetic exchange is also stipulated by hybridization of $Cu(3d^9_{x^2-y^2})$–$O(2p_{x,y})$, and in the absence of holes leads to antiferromagnetism. A decrease of the negative charge on oxygen sites decreases hybridization appreciably, and, hence, the exchange [17]. This is exactly what happens upon doping of $YBa_2Cu_3O_{6.1}$

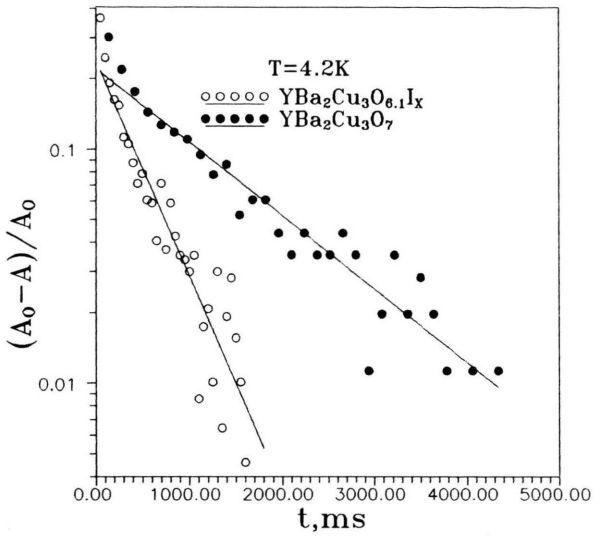

Fig. 2. Recovery of the nuclear magnetization for $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_{6.1}I_x$.

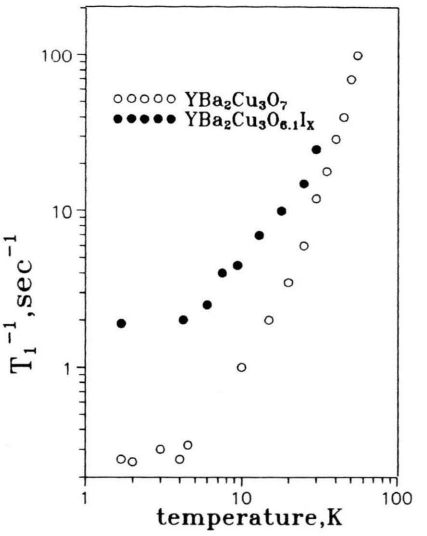

Fig. 3. The temperature dependence of the spin-lattice relaxation velocity for $YBa_2Cu_3O_7$ (from [19]) and $YBa_2Cu_3O_{6.1}I_x$.

ceramics by iodine. A decrease of the exchange in an iodinated sample leads to absence of the magnetic ordering, i.e. to independence of spins in the chains. An analysis of the specific features of the ^{63}Cu NQR spectral parameters of the investigated samples suggests that the treatment leads to significant changes in the distribution of the electronic density in the crystal.

3.2 Spin-Lattice Relaxation of ^{63}Cu

The temperature dependence of the ^{63}Cu nuclear spin-lattice relaxation rate $T_1^{-1}(T)$ in the iodinated sample was measured by ^{63}Cu NQR within 1.7–40 K at 31.4 MHz. In the vicinity of the superconducting phase transition a difficulty in the relaxation measurements arises from the fact that the line intensities and signal-to-noise ratios are considerably reduced. At low temperatures the recovery of the nuclear magnetization equilibrium in the sample is not described by a single exponential relation, as indicated in Fig. 2, where the results for the Cu(2) sites in starting sample $YBa_2Cu_3O_7$ are also shown. As seen in the figure an initial rapid decay is observed in both samples. The form of the longer relaxation function of ^{63}Cu can be fitted by a single exponential function. Thus, at 4.2 K we find for the longer relaxation constant $T_1 = 0.5$ and 2.1 s in the iodinated and orthorhombic superconducting phase $YBa_2Cu_3O_{6.9}$, respectively. It should be noted that such a behavior at lower temperatures was also observed in other recent measurements of the nuclear relaxation in the superconducting phase [18]. The anomalous dependence of the nuclear magnetization arises from the inhomogeneous distribution of $(T_1)^{-1}$. The small intensity of the NQR signals at 23.9 MHz in an iodinated sample impedes accurate measurement of the relaxation time; a rough estimation yields $T_1^{-1}(4.2\,\mathrm{K}) \approx 1\,\mathrm{s}^{-1}$.

The temperature dependence of the long component $(T_1)^{-1}$ at the Cu(2) sites in the iodinated sample is shown in Fig. 3, which shows T_1^{-1} of $^{63}Cu(2)$ in $YBa_2Cu_3O_7$ [19]. Evidently the nuclear relaxation for the iodinated sample is faster than that for $YBa_2Cu_3O_7$. It has already been reported that the same behaviour is observed for the 60-K phase, where the nuclear relaxation is stipulated by antiferromagnetic correlations [18]. This mechanism is expected to be predominant for the nuclei of magnetic atoms.

Quite generally, $1/T_1$ depends on the dynamical spin susceptibility [20]:

$$\frac{1}{T_1} = \frac{\gamma_n^2 k_B T}{2\mu_B^2} \sum_q A_q^2 \frac{\mathrm{Im}\,\chi(q,\omega)}{\omega_0}, \tag{3}$$

where

$$A_q = \sum_i A_i \exp\{i q r_i\}. \tag{4}$$

In (3), γ_n is the nuclear gyromagnetic ratio, A_i the hyperfine coupling between the nuclear spin and the electron spin at site r_i and ω_0 is the nuclear resonance

frequency, which is much smaller than the characteristic energy of the electronic spin system.

If the system has short-range antiferromagnetic correlations, $\chi(q)$ will have a peak at $q=Q=(\pi,\pi)$. This makes $\sum \mathrm{Im}\,\chi(q,\omega)/\omega_0$ much larger than $\pi\chi^2_{\mathrm{spin}}/\mu_B^2$ or equivalently this leads to a large enhancement of $1/(T_1TK^2_{\mathrm{spin}})$ over the Korringa value.

We apply the phenomenological model of Millis, Monien, and Pines (MMP) [21] to the case of $YBa_2Cu_3O_{6.1}I_x$. A one-component form for $\chi(q,\omega)$ is assumed, which for convenience is written as the sum of two parts:

$$\chi(q,\omega)=\chi_{\mathrm{FL}}(q,\omega)+\chi_{\mathrm{AF}}(q,\omega). \tag{5}$$

Here $\chi_{\mathrm{FL}}(q,\omega)$ is a normal Fermi-liquid-like contribution, which is spread broadly over the q space, and $\chi_{\mathrm{AF}}(q,\omega)$ characterizes the antiferromagnetic fluctuations and is taken to be Lorentzian centered at $q=Q$. The MMP theory gives

$$T_1^{-1}(^{63}\mathrm{Cu})=A_0\{0.294+(\beta/\pi^2) \cdot [0.49(\xi/\alpha)^2-0.62\ln(\xi/a)+0.0175]\}, \tag{6}$$

where $A_0=24\pi B^2 k_B T\chi_0/\mu_B^2 h^2 \Gamma$, B is the hyperfine coupling constant, χ_0 the static spin susceptibility, Γ the energy scale of the noninteracting electronic system, β measures the relative contribution of the antiferromagnetic enhancement, and α is the distance between the nearest-neighbour Cu(2) atoms. If we assume that this relation is valid also for $T<T_c$ (and it should be noted that in reality the situation is much more complicated), it is possible to express the low-temperature relaxation rate via the correlation length ξ. After fitting of (6) with our experimental data we obtain a reasonable value $\xi/a\approx 2.8$ at 4.2 K. We used typical values $B=41\,\mathrm{k0\,e}/\mu_B$, $\beta\approx 10$, and $\Gamma=0.4$–0.5 eV.

The obtained value of the correlation length ξ is of the same order of magnitude as the lattice parameter α, which is a reasonable value for a strongly hole-doped material. It should be noted that the full analysis of the relaxation data for $T<T_c$ would require a modification of the theory of MMP [22]. Thus the results of the investigation of the ^{63}Cu nuclear relaxation give rise to the indirect suggestion that antiferromagnetic correlations are present in the iodinated sample. This is reasonable, since the antiferromagnetic phase $YBa_2Cu_3O_{6.1}$ is the starting sample for the treatment in this case. The low temperature treatment of the initially insulating $YBa_2Cu_3O_{6.1}$ with I_2 gas leads to transfer of the negative charge to the chains and to the formation of holes in the CuO_2 plane. This treatment leads also to the disappearence of antiferromagnetic ordering, however, antiferromagnetic correlations remain.

5. Conclusion

An analysis of the ^{63}Cu NQR spectral parameters indicates a considerable restructuring and associated significant changes in the distribution of the electronic density in the crystal as a result of the treatment of nonconducting Y–Ba–Cu–O by iodine vapour. A deeper comprehension of the processes resultant from exposure of Y–Ba–Cu–O ceramics to halogen vapours needs further investigation and, in particular, a detailed study of the nuclear relaxation in the normal state and, also, a study of chlorinated and brominated samples of the system Y–Ba–Cu–O.

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