NQR Investigations of $La_{3-x}Ba_{3+x}Cu_6O_y$ ($x = 0, 0.75, 1$)*

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NQR spectra due to ^{63}Cu and ^{139}La have been recorded for $La_{3-x}Ba_{3+x}Cu_6O_y$ ($x=0$, 0.75, 1). Two groups of ^{63}Cu NQR lines were observed (around 20–23 MHz and 29–36 MHz). The former is assigned to the Cu atoms in the CuO_4 square planar groups, and the latter to that in the CuO_5 square pyramidal group. For the ^{63}Cu NQR lines in $La_3Ba_3Cu_6O_y$, the time dependent NQR spectra and the temperature dependence of NQR frequencies were observed.

Key words: $La_{3-x}Ba_{3+x}Cu_6O_y$ system, ^{63}Cu NQR, ^{139}La NQR, Temperature dependence, Site assignment.

Introduction

X-ray and neutron diffraction studies clarified that the crystal structure of the superconducting Cu-oxides is significantly influenced by the superconducting phase transition [1]. In particular, the local coordination of Cu is of great interest because of its influence on the superconducting transition temperature (T_c). In such a case, NQR spectroscopy plays an important role in investigating the electronic structure of the resonant atom because the electric field gradient (EFG) at the atom depends sensitively on the surrounding charge distribution. The NQR frequency is expected to be strongly affected by the phase transition and changes in the electronic structure, oxygen coordination, and oxygen vacancies.

The NQR investigation of the superconducting oxides $La_{2-x}Ba_xCuO_4$ and $YBa_2Cu_3O_7$ [2] has drawn the attention to a series of compounds with the general formula $La_{3-x}Ba_{3+x}Cu_6O_y$. In this system, the compounds except for $x=0$ exhibit superconductivity [3]. In the present study, we examined the compounds with $x=0$, 0.75, and 1 by means of ^{63}Cu and ^{139}La NQR in order to obtain information about the superconductivity, the Cu atoms being located in the conduction pathways.

Experimental

Polycrystalline samples were prepared by the standard solid state reaction [4, 5]: $LaBa_2Cu_3O_y$ was prepared from a mixture of La_2O_3, $BaCO_3$, and CuO by solid reaction at 950 °C for 50 h and then at 1050 °C for 10 h in O_2 atmosphere, and the others were treated at 950 °C for 12 h in air and at 950 °C for 12 h in O_2 atmosphere. NQR spectra were recorded by super-regenerative spectrometers. The NQR frequency was measured by use of a signal generator and frequency counter with an estimated accuracy of ± 0.005 MHz. The desired sample temperature was obtained by adding liquid nitrogen to light petroleum in a Dewar vessel. The temperature precision was not worse than ± 1 K.

Results and Discussion

Table 1 lists NQR frequencies due to ^{63}Cu and ^{139}La in $La_3Ba_3Cu_6O_y$ at 77 K. The assignment of the NQR lines to ^{63}Cu was based on the finding of corresponding ^{65}Cu signals whose frequencies were in agreement with those expected from the known quadrupole moment ratio $Q(^{63}Cu)/Q(^{65}Cu) = 1.0806$. The other signals were assigned to ^{139}La and grouped into three sets because ^{139}La with spin 7/2 yields three resonance lines corresponding to the $\pm 7/2 - \pm 5/2$, $\pm 5/2 - \pm 3/2$, and $\pm 3/2 - \pm 1/2$ transitions. The frequency of the $\pm 7/2 - \pm 5/2$ transition ($\nu_{7/2-5/2}$) was estimated from $\nu_{3/2-1/2}$ and $\nu_{5/2-3/2}$. The results show that two of the three $\nu_{7/2-5/2}$ lines overlapped by chance with frequencies due to ^{63}Cu as tabulated in Table 1. The quadrupole coupling constants and

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Table 1. Observed NQR frequencies of $La_3Ba_3Cu_6O_y$ at 77 K.

Resonance line	Frequency (MHz)	Assignment
ν_1	35.395	^{63}Cu
ν_2	32.393	^{63}Cu
ν_3	30.119	^{63}Cu
ν_4	21.416	^{63}Cu
ν_5	21.033	^{63}Cu, ^{139}La
ν_6	20.266	^{63}Cu, ^{139}La
ν_7	19.184	^{139}La
ν_8	13.949	^{139}La
ν_9	13.464	^{139}La
ν_{10}	12.712	^{139}La
ν_{11}	7.404	^{139}La
ν_{12}	7.044	^{139}La
ν_{13}	6.782	^{139}La

Table 2. ^{139}La quadrupole coupling constants and asymmetry parameters in $La_3Ba_3Cu_6O_y$ at 77 K.

Resonance frequency (MHz)			Quadrupole coupling constant (MHz)	Asymmetry parameter
$\nu_{1/2-3/2}$	$\nu_{3/2-5/2}$	$\nu_{5/2-7/2}$		
6.782	12.712	19.184	89.68	0.129
7.044	13.464	20.266	94.69	0.108
7.404	13.949	21.033	98.44	0.123

asymmetry parameters listed in Table 2 were calculated using the first-order perturbation theory. These values are close to those reported for other La-Ba-Cu-O compounds [2, 6, 7].

The crystal structure of this compound was studied by X-ray powder diffraction and neutron diffraction [8–10]. The structure reported is built up from triple oxygen deficient perovskite layers $[Cu_3O_{7+x/2}]_\infty$ perpendicular to the *c*-axis, each triple layer forming one $[CuO_{3-y}]_\infty$ layer of corner sharing oxygen deficient octahedra surrounded by two $[CuO_{2.5}]_\infty$ layers of CuO_5 pyramids. Oxygen vacancies are mainly located in the basal plane of the octahedra and statistically distributed at the level $z=0$ leading to CuO_4 square planar groups oriented at random along [100] or [010]. The localization of oxygen vacancies in the oxygen site at the apex of the square pyramid is uncertain [10]. The oxygen ordering leads to three coordination geometries for Cu: square planar, square pyramidal, and octahedral. Since Cu surrounded octahedrally by six oxygens has a very small quadrupole coupling constant, we can observe NQR signals of only four- or five-coordinated ones in the frequency range higher than 10 MHz. In this compound the NQR lines due to ^{63}Cu can be divided into two groups as listed in Table 1.

In Y-Ba-Cu-O systems, ^{63}Cu NQR lines were observed around 31.5 MHz and 22.0 MHz and assigned to two different Cu sites, Cu(1) and Cu(2): the former is related to Cu in the CuO_4 square planar group while the latter to Cu in the CuO_5 square pyramidal group [11, 12]. In $La_3Ba_3Cu_6O_y$, therefore, three ^{63}Cu lines are assigned to Cu(2) and the other to Cu(1). Our NQR results indicate the presence of three crystallographically different positions of each La, Cu(1), and Cu(2), in contrast to the results of X-ray and neutron diffraction [8–10]. These studies showed that the number of crystallographically nonequivalent atoms is 1, 1, and 2 for Cu(1), Cu(2), and La, respectively. One of the two La atoms is in the site occupied by La and Ba in the proportion 1:3, and its resonance line will not be observed because of weak intensity. Therefore, the crystal structure predicts one resonance line for each of La, Cu(1), and Cu(2). This discrepancy suggests the existence of three different phases which have the same crystal structure but different occupancy of oxygen sites because NQR is very sensitive to environmental change around a resonant nucleus.

Figure 1 shows stick diagrams of the NQR spectra observed at 77 K with the passage of time. The lengths of the sticks roughly indicate relative intensities of a resonance line in each multiplet spectrum. With respect to the relative intensity, there is no relationship between two spectra which were observed at different times and also in different frequency ranges. The spectra in Fig. 1 were recorded at different periods as follows: (1a)(2a) – March 1988, (1b)(2b) – April 1988, (1c–1f)(2c–2d) – June 1988, (1g)(2e–2g) – May 1989. Although the time passes from bottom to top in Fig. 1, no regularity can be seen in the observed spectra. The spectra (1c–1f) and (2c, 2d) were often observed from June 1988 to January 1989. The same spectrum as (1a) was also observed in September 1988, and the spectra (1b) and (1c) were obtained in January 1989. The reproducibility of the spectra indicates that the sample did not decompose by heating or cooling in our experiment. The change of intensity is pronounced while the change of frequency is not so remarkable. The frequencies at which resonance lines were detected remain almost constant though the observed spectra are different from each other; that is, most of the resonance lines are found near 21.3 MHz, 21.0 MHz, 20.7 MHz, 20.1 MHz, and 19.6 MHz in the

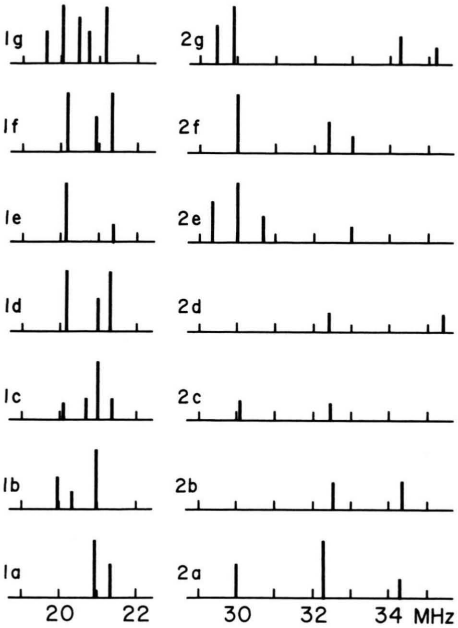

Fig. 1. Stick diagrams of the NQR spectra in $La_3Ba_3Cu_6O_y$ at 77 K. For 1a, 1b etc. confer text.

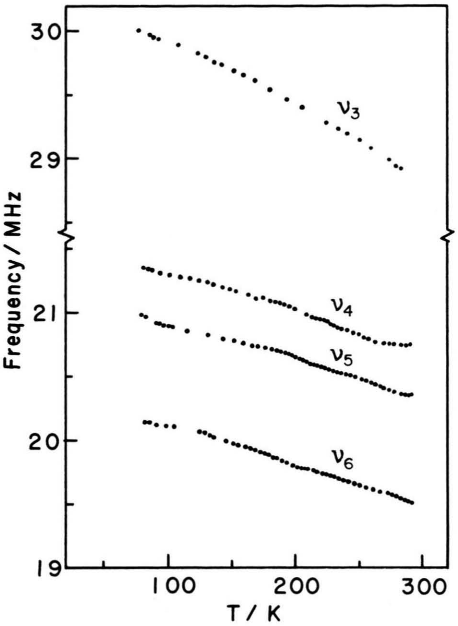

Fig. 2. Temperature dependence of NQR frequencies in $La_3Ba_3Cu_6O_y$.

Table 3. NQR frequencies in La-Ba-Cu-O system at 77 K.

Compound	Frequency (MHz)			
$LaBa_2Cu_3O_y$	36.294	35.744	33.423	32.045
	31.293	29.348	23.725	22.459
	20.648	19.807	19.483	17.722
$La_{2.25}Ba_{3.75}Cu_6O_y$	36.136	35.632	33.612	32.908
	31.143	29.026		

lower frequency range, and near 35.3 MHz, 34.3 MHz, 33.0 MHz, 32.4 MHz, 30.0 MHz, and 29.4 MHz in the higher frequency range. Serikov et al. have reported that $YBa_2Cu_3O_{6+x}$ yields fine structure in the ^{63}Cu NQR spectra and that the frequency and the intensity depend on the oxygen concentration [12]. In the present experiment, since the sample was sealed in a glass tube, the oxygen content did not change. Therefore, as mentioned above, the sample consists of different phases which have the same crystal structure but in which oxygen atoms do not occupy the same positions, and the proportion of different phases changes by repetition of heating and cooling. This inhomogeneous oxygen deficiency causes very broad resonance lines of multiplet lines, as shown in Figure 1.

During the experimental period, a change in the spectra was sometimes observed: for example, when the temperature of the sample was maintained at 77 K, two ^{35}Cl NQR lines (ν_b, ν_e) of five ν lines which were observed at 21.173 MHz (ν_a), 20.740 MHz (ν_b), 20.462 MHz (ν_c), 20.047 MHz (ν_d), 19.607 MHz (ν_e) as shown in Fig. 1 (1g) disappeared after 6 h and the ν_c line became very strong. This finding suggests the presence of a phase transition.

In $La_{3-x}Ba_{3+x}Cu_6O_y$ ($x=0.75$, 1) several NQR lines were observed as listed in Table 3. Their intensity was considerably weaker than that in $La_3Ba_3Cu_6O_y$ and, therefore, all resonance lines could not be observed. The observed lines are also divided into two groups. It is known that the structure of $LaBa_2Cu_3O_y$ is similar to that of $YBa_2Cu_3O_y$ [3]. Kato et al. have reported that the La-containing system ($La_{1+x}Ba_{2-x}Cu_3O_y$) has essentially the same structure as $YBa_2Cu_3O_y$ [13]. Therefore, in $La_{3-x}Ba_{3+x}Cu_6O$ ($x=0$, 0.75, 1) two inequivalent Cu sites exist as well as in $YBa_2Cu_3O_y$, in which there are Cu(1) and Cu(2) [9]. Taking into account the NQR results of $YBa_2Cu_3O_y$ [11, 12], the resonance lines higher than 29 MHz are assigned to Cu(2) and the others higher than 20 MHz, to Cu(1).

Figure 2 shows the temperature dependence of the ^{63}Cu NQR frequencies in $La_3Ba_3Cu_6O_y$. All resonance frequencies decreased monotonically with increasing temperature although ν_3 has the largest temperature coefficient $[(1/\nu)(\Delta\nu/\Delta T)]$. A phase transition was sometimes observed at 77 K as mentioned above, but abnormalities such as the disappearance of the signal and a pronounced slope change of the curve were not observed on heating from 77 K to room temperature. These findings indicate that the degree of oxygen deficiency did not vary between 77 K and room temperature.

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