Cu-NQR Frequencies and Linewidths in High-T_c Superconductors *

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Z. Naturforsch. **47a**, 27–29 (1992); received August 3, 1991

The Cu-NQR lines of various high-T_c superconductors at the Cu(2) site appear between 15 and 40 MHz. There exists an experimental correlation showing that the NQR frequency increases with decreasing T_c. By comparison, it can be concluded from these results that a formal valence state of the Cu ion around 2+ is favourable for superconductivity. All lines exhibit a strong broadening compared to CuO_2 crystals, which is attributed to lattice modulations within the CuO_2 layers. This effect also influences the temperature dependence of the linewidth in $YBa_2Cu_3O_{7-\delta}$.

Key words: NQR, Superconductivity, High-T_c compounds, Resonance frequency, Linewidth.

Introduction

Nuclear Quadrupole Resonance (NQR) is a useful tool in studying high-T_c superconductors [1]. The non-cubic environment of the copper nuclei, which are present in nearly all of these compounds, gives rise to Cu-NQR lines appearing in the range between 15 MHz and 40 MHz.

As the observable resonance frequency ν_{NQR} is proportional to the total electric field gradient q at the site of the nucleus, this method generally allows to obtain valuable information about the structural and electronic properties involved. However, for complex systems like the cuprate superconductors, it is fairly difficult to perform a quantitative analysis of the NQR results which reflect the ionic charge distribution within the material. Furthermore, with the exception of $YBa_2Cu_3O_{7-\delta}$ all resonance lines exhibit a strong broadening up to a few MHz, which makes the interpretation of the experimental data even more difficult.

In order to achieve at least a qualitative understanding, we have tried to combine observations obtained from NQR measurements on various high-T_c compounds, particularly on the Cu nuclei in the CuO_2 planes, as this structural element can be investigated through NQR and is believed to be responsible for superconductivity.

Experimental

A conventional NMR pulse spectrometer was used to investigate the NQR lines at room temperature, at 4.2 K or – as in the case of $YBa_2Cu_3O_{7-\delta}$ – in the temperature range in between. An echo pulse sequence $\pi/2-\tau-\pi$ with varying but short pulse lengths and separation times was used. The spectra were obtained by determining separately the amplitude of the Fourier transform of the echo at a number of frequencies. The powder samples had been prepared by the usual solid state reactions.

Frequencies

Figure 1 shows a number of Cu-NQR spectra of the Cu(2) site taken at 4.2 K on various high-T_c superconductors which are given in the figure caption. By determining the Cu-NQR frequency ν_{NQR} through the maximum of the resonance line and by comparison with the transition temperature T_c into the superconducting state it can be seen that both quantities are correlated in such a way that *T_c decreases with increasing ν_{NQR}*.

The main contribution to the electric field gradient q at the site of the Cu nucleus arises from the binding between the copper and oxygen ions within the CuO_2 plane. Since charge has been transferred from copper

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* Presented at the XIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, London, United Kingdom, July 15–19, 1991.

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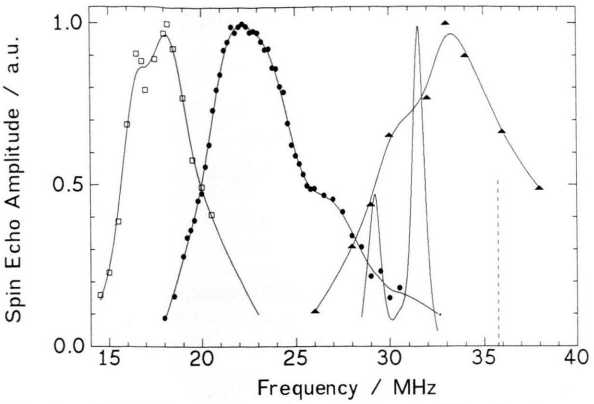

Fig. 1. Cu-NQR spectra at 4.2 K of $YBa_2Cu_3O_{7-\delta}$ (line only), $Bi_2Ca_2Sr_2Cu_3O_y$ (●), $Tl_2Ca_2Ba_2Cu_3O_y$ (□), $Bi_2Ca_1Sr_1Cu_1O_y$ (▲), and $La_{1.85}Sr_{0.15}CuO_4$ (only position marked by dashed line).

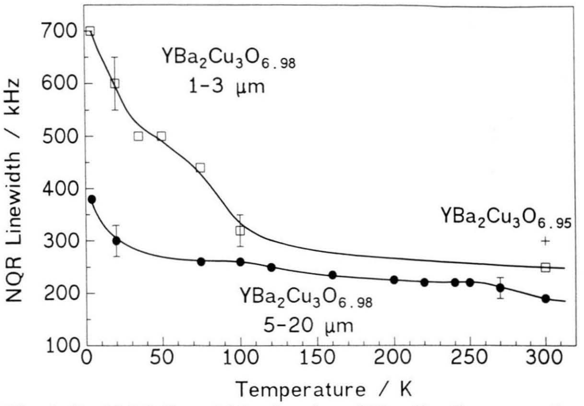

Fig. 2. Cu-NQR linewidth of various $YBa_2Cu_3O_{7-\delta}$ samples as a function of temperature. The oxygen content as well as the average grain size are given.

to oxygen, this Cu–O bond means a partially emptied Cu-$3d_{x^2-y^2}$ orbital which leads to a non-spherical charge distribution in the surroundings of the Cu nucleus. The Cu-NQR frequency will be strongly affected because the d-electrons are closer to the Cu nucleus than any other charges. It turns out that with decreasing Cu–O distance the number of holes in the $3d_{x^2-y^2}$ orbital increases, which is equivalent to the statement that the formal charge of the copper ion draws nearer to 3+. Also, according to Garcia and Bennemann [2], ν_{NQR} increases with the number of holes in the Cu-$3d_{x^2-y^2}$ orbital. Comparison of these arguments with the experimental results in Fig. 1 shows that a large value of ν_{NQR} corresponds to a formal valence state of copper near to Cu^{3+} and to a lower observable T_c at the same time, and vice versa. Thus it can be concluded that a formal valence of the copper ion around 2+ is rather favourable for superconductivity. This result is supported additionally by comparison with NQR investigations on non-superconducting copper salts with a known formal Cu valence [3].

Linewidths

The Cu-NQR lines of the cuprate superconductors in ground ceramic samples exhibit a strong broadening compared to Cu_2O crystals. As shown in Fig. 1, in the Bi- and Tl-based high-T_c compounds it is even not possible to separate the NQR lines arising from the two copper isotopes ^{63}Cu and ^{65}Cu, whose frequencies are separated by a factor of 1.08. Even in the 1-2-3-compounds, the Cu-NQR line is more than twenty times larger than in CuO_2 crystals, so that a distribution of resonances must be assumed to explain this behaviour. In addition, the 2-2-2-3-compounds contain three CuO_2 layers with two distinct kinds of surroundings, two with a pyramidal and one with a planar oxygen environment [4, 5]. This structural difference should broaden the NQR lines, too.

The main contribution to the large observed linewidths in these compounds arises from incommensurable lattice modulations within the CuO_2 planes. Such a modulation keeps every copper ion in a slightly different environment, thus leading to a spatially varying electric field gradient and hence to a distribution of resonance frequencies. The resulting Cu-NQR line does not possess any pronounced shape and its width strongly depends on the amplitude of the modulation. This observation is consistent with structural results indicating incommensurate modulations in the Bi- and Tl-containing high-T_c superconductors with a high amplitude [4, 5]. In $YBa_2Cu_3O_{7-\delta}$ commensurate superstructures due to ordered oxygen vacancies have been reported [6, 7]. This effect also gives rise to a distribution of resonances, which are able to appear as a line broadening.

As presented in Fig. 2, the linewidth in $YBa_2Cu_3O_{7-\delta}$ strongly depends on the oxygen content of the sample, which agrees well with previous observations [8]. The smallest line arising from the Cu nuclei in the CuO_2 planes which we have been able to detect so far, shows a width of 190 kHz at room temperature in a powder sample with $\delta \approx 0.02$. This value increases up to about 450 kHz for samples with $\delta \simeq 0.1$. This behaviour can be understood in terms of vacancies at the oxygen crystal sites in conjunction with O ions on the free sites in the ideal perovskite structure (1-2-3-O_9) [9].

For all $YBa_2Cu_3O_{7-\delta}$ samples the Cu-NQR linewidth increases with decreasing temperature. We think that this increase is not caused by possible internal magnetic fields arising from antiferromagnetic ordering but rather by changes in the crystal structure. There are a number of possible mechanisms leading to a broadening of the Cu-NQR lines. Microtwinning occurring particularly below 100 K [10] is such a candidate. Also, freezing out of vibrational modes of oxygen ions is able to distort the symmetry of the crystal so that slightly different electric field gradients give rise to a distribution of resonance T_c frequencies. Finally, the superstructures which modulate the lattice may vary with temperature, which might be able to explain the observed broadening of the Cu-NQR lines in $YBa_2Cu_3O_{7-\delta}$.

Acknowledgement

This work was supported by the Bundesministerium für Forschung und Technologie (13N 5479A).

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