Temperature Dependence of the NQR Frequency and Linewidth of the High-T_c Superconductor $YBa_2Cu_3O_{7-\delta}$*

H. Riesemeier, J. Pattloch, E. W. Scheidt, M. Schaefer, and K. Lüders
Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33, FRG

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For $YBa_2Cu_3O_{7-\delta}$ powder samples of different average grain sizes the temperature dependences of ^{63}Cu NQR frequencies and signal intensities are reported for the Cu (1) site in a temperature range of 4–300 K. Both quantities show a non-monotonic behaviour in the vicinity of the superconduction transition temperature T_c. In the superconducting state the line shape of the NQR signal in zero-field depends on the strength of the dc magnetic field applied during the cooling-procedure. The resulting linewidth yields information about the internal trapped magnetic field.

Introduction

In the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ the ^{63}Cu isotope exhibits two nuclear quadrupole resonance (NQR) frequencies, ν_Q. For the Cu(1) sites (chain sites with a planar oxygen environment) ν_Q is about 22 MHz and for the Cu(2) sites (with a distorted pyramidal oxygen environment) ν_Q is about 31.5 MHz [1–3]. In the normal conducting state a linear temperature dependence of these two frequencies was found, but with opposite temperature coefficients [4, 5]: with decreasing temperature the Cu(1) frequency decreases and the Cu(2) frequency increases. Up to now it is not clear whether this different behaviour is predominantly due to lattice vibrations or changes in the lattice parameters. In the vicinity of T_c and in the superconducting state the situation is more complex, and different results have been published so far [4, 5]. A general difficulty arises from the fact that the line intensities and signal-to-noise ratios are reduced considerably in this region.

There are only very few NQR investigations on conventional superconductors, which may be known by referring to [6]. Both positive and negative shifts of ν_Q were found at the superconducting transition temperature T_c. Whereas the shift $\Delta\nu_Q=(\nu_Q)_s-(\nu_Q)_n$ (s, n refers to the superconducting and normal conducting state, respectively) is positive in orthorhombic Ga and hexagonal La metals, it is negative in tetragonal In metal and in $LaAl_2$. Although these findings are not well understood so far, there is no doubt that in the superconducting system $YBa_2Cu_3O_{7-\delta}$ the temperature dependence of ν_Q should provide valuable information about eventual phase transitions, changes in the electronic band structure and the oxygen coordination or oxygen vacancies.

In this paper we report on NQR measurements on $YBa_2Cu_3O_{7-\delta}$ powder samples of different grain sizes. In all samples the linewidth at the Cu(1) sites was found to be smaller by a factor of about 2 compared to that at the Cu(2) sites. Therefore, and for reasons of signal intensity, the NQR measurements were limited to the ^{63}Cu resonance at the Cu(1) site.

Experimental

Powder samples of $YBa_2Cu_3O_{7-\delta}$ were prepared by means of the usual solid state reaction yielding an average grain size of about 15 μm and by a purely chemical technique (citrate synthesis [7]) yielding an average grain size of about 60 nm. The samples were characterized by X-ray diffraction and by dc and ac susceptibility measurements. A conventional NMR-pulsed spectrometer was used to determine the quadrupole frequency ν_Q in the range 4–300 K and the NQR lineshapes at 4.2 K. The signals were obtained by scanning the frequency and measuring in quadrature the spin-echo amplitude. A $\pi/2-\tau-\pi$ pulse sequence with pulse width of 5 μs for the $\pi/2$ pulse and a separation time τ of 70 μs was used.

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Reprint requests to Prof. K. Lüders, Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33.

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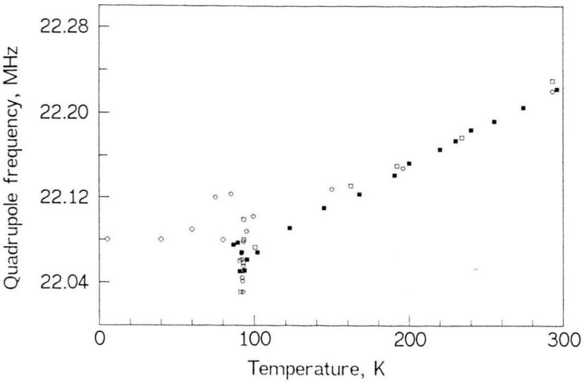

Fig. 1. Temperature dependence of the ^{63}Cu nuclear quadrupole frequency ν_Q for the Cu (1) site in $YBa_2Cu_3O_{7-\delta}$. The different open symbols mark different series of measurements. For comparison the results of the Zürich group of Brinkmann and coworkers are also plotted [8] (full squares).

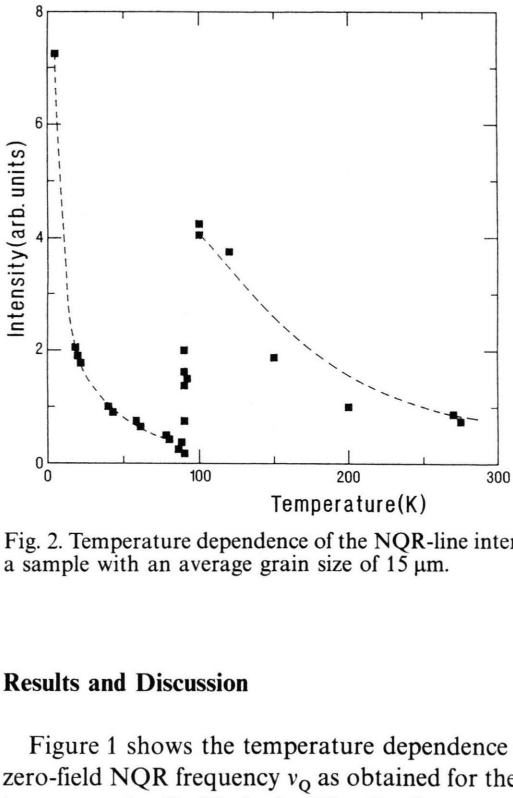

Fig. 2. Temperature dependence of the NQR-line intensity of a sample with an average grain size of 15 μm.

Results and Discussion

Figure 1 shows the temperature dependence of the zero-field NQR frequency ν_Q as obtained for the ^{63}Cu isotope as the Cu (1) site in $YBa_2Cu_3O_{7-\delta}$ powdered samples. Within experimental errors the temperature dependence of ν_Q agrees with that of earlier measurements [4]. Upon cooling, ν_Q decreases linearly down to T_c. In the vicinity of T_c, however, a discontinuous change of ν_Q is observed. Within a very small temperature range ν_Q steeply decreases at T_c but increases again in the superconducting state.

The discontinuity of ν_Q in the vicinity of T_c may be indicative for some kind of phase transition associated with changes in the lattice parameters. This is also supported by neutron diffraction experiments [9]. One possible explanation may be a freezing out of certain motional degrees of freedom of the oxygen system such as the hopping of the oxygens between the two possible sites of the zig-zag chains. If such an explanation is correct, one also would expect a broadening of the NQR lines for $T < T_c$. Near T_c, however, the lineshape may also be influenced by other factors originating from the superconducting state. One of these factors is connected with the distribution of the magnetic field inside the sample grains. The actual magnetic field distribution in the sample depends in a complex manner on the cooling procedure, the magnetic field strengths and the flux pinning properties. Using conventional NMR equipment, besides the earth magnetic field additional small residual fields may be applied to the samples. In order to learn more about these influences on the NQR lineshape we started systematic investigations of the lineshape under different experimental conditions.

At first the NQR line intensity is strongly influenced by the superconducting magnetic penetration depth. Figure 2 shows the temperature dependence of the line intensity of a sample with an average grain size of 15 μm. Within experimental errors a Curie-Weiss behaviour was observed above and below T_c. At T_c, however, a pronounced reduction of the intensity of about 90% was found upon cooling. This behaviour can be explained by the reduced volume penetrated by the rf-field. The estimated average magnetic penetration depth of $\lambda \approx 3500$ Å at 4.2 K agrees with the dc magnetization results of Scheidt et al. [10] yielding average λ-values of $\lambda^{\parallel} = 1400$ Å and $\lambda^{\perp} = 6100$ Å at this temperature.

Beside the magnetic penetration depth, the NQR lineshape yields information about the strengths of internal magnetic fields and the pinning properties. In order to investigate the influence of the dc magnetic field on the NQR lineshape, experiments were carried out under the following conditions:

(a) zero-field cooling and performing the NQR measurements in zero-field at 4.2 K,
(b) zero-field cooling down to 4.2 K, applying dc magnetic fields of different strengths and performing the NQR experiments in zero-field,

(c) field cooling at various field strengths down to 4.2 K and performing the NQR experiments again at zero-field.

The external field was applied perpendicular to the linear polarized rf-field.

The results for a powder sample with an average grain size of 15 µm are presented in Figure 3. The smallest line is observed for condition (a), showing a linewidth of about 200 kHz (curve a, Figure 3). To realize condition (b), the sample is then exposed to a dc magnetic field of 0.1 T. On detecting the data at zero-field, a slight broadening of the NQR line is obtained (curve b, Figure 3). Cooling in a field of 0.1 T, however, and taking the data at zero-field again (c), leads to considerable broadening of the NQR line (curve c, Figure 3). Further results according to (b) are given in Figure 4.

The total intensity (Fig. 3) is enhanced in both cases (b, c), indicating that a larger amount of nuclei contributes to the NQR signal as compared to curve a. This may be explained by a larger effective penetration depth of the rf-field as compared to λ which is caused by oscillating flux lines. The trapped flux also gives rise to the observed line broadening. The large linewidth of curve c corresponds to an average internal field of about 30 mT, which is comparable to results from dc magnetization measurements [11]. For such a magnetic field, a second peak due to Zeeman splitting is expected at about 21.4 MHz. This peak, however, is smeared out by the magnetic field gradient inside the grains and by the distribution of quadrupole frequencies, but an asymmetry of curve c can still be seen.

The slightly broadened line (curve b, Fig. 3) indicates a much lower internal field as compared to the field cooling experiment. This is in qualitative agreement with susceptibility measurements and the inner magnetic field distribution, which can be estimated from these measurements.

To investigate the grain size influence on the flux trapping, similar measurements were performed on powder samples with an average grain size of about 60 nm. In Fig. 5 the resulting NQR-lines detected in zero-field are shown for different fields applied during the cooling procedure. For these samples a line broadening with increasing field strength is observed, too. However, the linewidths and therefore the internal magnetic fields are considerably smaller than those obtained from the larger grains. Above magnetic field

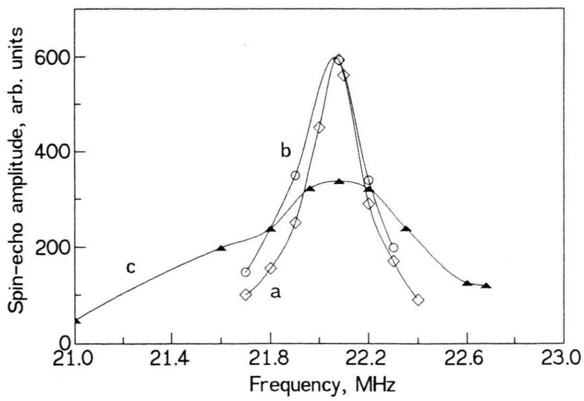

Fig. 3. NQR spectra of a $YBa_2Cu_3O_{7-\delta}$ powder sample with an average grain size of 15 µm detected in zero-field after different cooling procedures. The curves a–c refers to the conditions (a)–(c) described in the text.

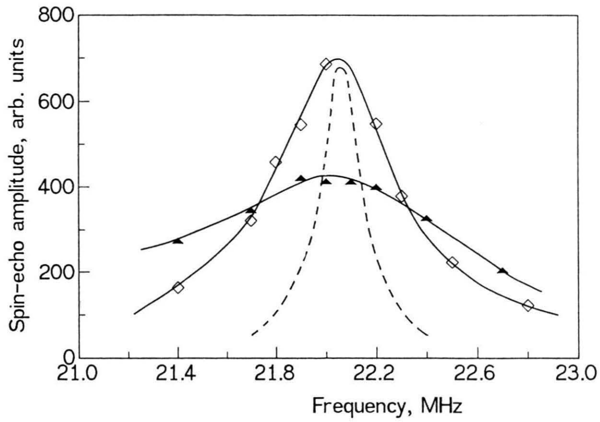

Fig. 4. Zero-field NQR spectra of a $YBa_2Cu_3O_{7-\delta}$ powder sample with an average grain size of 15 µm after zero-field cooling and subsequent application of magnetic fields (triangles: 0.2 T, rhombi: 1.8 T).

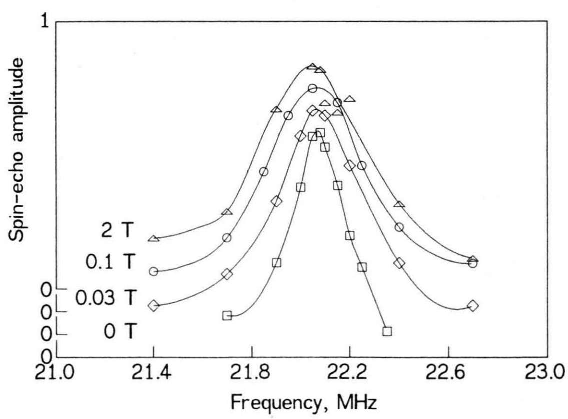

Fig. 5. NQR spectra of a $YBa_2Cu_3O_{7-\delta}$ powder sample with an average grain size of 60 nm detected in zero-field after field cooling in different external fields.

strengths of about 0.1 T the field dependence of the NQR linewidth does not vary significantly with increasing field strength. The corresponding internal trapped field is estimated to about 20 mT in zero external magnetic field for this grain size. This behaviour is understandable as the grain size is smaller than λ so that the usual field distribution due to the variation in the density of flux lines is not possible.

Acknowledgements

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