NQR and Zeeman Split NQR Investigations on Oriented $YBa_2Cu_3O_{7-\delta}$ and Non-Oriented Bi–Ca–Sr–Cu–O Powder *

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Powder samples of $YBa_2Cu_3O_{7-\delta}$ were oriented by mechanically vibrating the powder at 2.4 K in a magnetic field of 1.2 T. Zeeman split NQR spectra of $^{63,65}Cu$ were obtained for the two different Cu sites. The data confirm the orientations of the principal axis system: $x \parallel c$ for the Cu (1) site and $z \parallel c$ for the Cu (2) site. Asymmetry parameters were determined for the two Cu sites yielding $\bar{\eta}_1 = 0.95 \pm 0.2$ and $\bar{\eta}_2 = 0.008 \pm 0.002$. At the Cu (1) site local variations of the symmetry of the EFG tensor were observed. For the Cu sites (CuO_2-layers) in the $Bi_2Ca_2Sr_2Cu_3O_y$ phase a nearly axially symmetric EFG tensor was found.

Introduction

In the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ two different orientations of the principal axes system of the electrical field gradient (EFG) with respect to the crystallographic axes were found according to the two Cu sites [1, 2]. At the Cu (2) site, where an NQR frequency of about 31 MHz is observed, the *z*-axis is parallel to the crystallographic *c*-axis, and the asymmetry parameter η is found to be close to zero [3–7]. At the Cu (1) site, where a 22 MHz NQR line is observed, the *x*-axis is parallel to the crystallographic *z*-axis and η is found to be close to 1 [3–6]. In the superconducting Bi–Ca–Sr–Cu–O system no chain site (equivalent to the Cu (1) site in Y–Ba–Cu–O) exists. For the copper atoms in this system two NQR line pairs were observed for the plane sites by Fujiwara et al. [8], both in the vicinity of 20 MHz. In this paper we present Zeeman split NQR measurements on oriented and non-oriented powder samples of $YBa_2Cu_3O_{7-\delta}$ and mixed phase Bi–Ca–Sr–Cu–O superconductors. An advantage of this low field technique is that the line broadening due to the distribution of the static EFG's is reduced considerably and therefore permits precise determinations of η.

Sample Preparation

The $YBa_2Cu_3O_{7-\delta}$ samples were prepared by the usual solid state reaction and characterized by resistivity, susceptibility and x-ray diffraction measurements. After powdering the pellets to average grain sizes of about 15 μm, an additional heat treatment in oxygen was performed. The highly anisotropic magnetic properties of these samples allow to orientate the powder grains by vibration in a dc-magnetic field. In the normal conducting state an alignment of the crystallographic *c*-axes with the orientation field is obtained. In the superconducting state, however, an alignment of the *c*-axes within a plane perpendicular to the applied magnetic field occurs [7, 9]. This latter orientation is caused by the magnetic flux lines which prefer to penetrate along the planes and therefore a higher magnetic moment in the (*a*, *b*)-planes results as compared to the *c*-direction. Since the magnetic anisotropy is considerably larger in the Shubnikov phase than in the normal conducting state, the orientation is easier to perform in the superconducting state and yields a nearly perfect alignment. The Zeeman split NQR measurements were carried out on samples which were oriented in this way.

The Bi–Ca–Sr–Cu–O samples were prepared by the solid state reaction method, too. The starting composition for preparation of the 2223-phase was 4:3:3:6 (Bi:Ca:Sr:Cu). The powder was ground several times after calcination at 770–850 °C. The final calcination was carried out at 875 °C for 48 h without pressing the powder into pellets before. From ac-susceptibility measurements three superconducting transitions were obtained which correspond to the three known structures [10]. An estimation of the fractional volume of the 110 K phase (2223-phase) from the relative ac-susceptibility values yields a content of about 50%. A transition width of $\delta T_c = 10$ K was observed.

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Apparatus and Measurements

The experiments were performed with a pulsed NMR spectrometer. The signals were obtained by scanning magnetic field or 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. The applied magnetic field was of the order of 0.3–0.5 ν_Q/γ_{Cu}.

In low magnetic fields the double degenerated $\pm 1/2$-quadrupole levels are split. For the most simple case, $\gamma B_0 \ll \nu_Q$ and $\eta = 0$, the Zeeman split spectrum exhibits a singularity when the spherical angle θ reaches 90°. θ is the angle between the applied field and the z-axis of the EFG tensor. The frequency corresponding to this singularity is $\nu_{\theta=90°} = 2\gamma B_0$. Segel and Barnes [11] showed that in Cu_2O-powder the 2γ-resonance is experimentally detectable, and they determined the quadrupole frequency from the field dependence of the Zeeman split resonance frequency.

In the general case with none zero η one has to diagonalize the Hamiltonian for discrete values of the spherical angles θ and ϕ. For the 31 MHz NQR line which is assigned to the Cu (2) sites and for $\theta = 90°$ the eigenvalues of the Hamiltonian matrix were calculated assuming a statistical distribution of the angle ϕ. In Fig. 1 the resulting frequency spectra are shown for different η-values and a fixed Larmor frequency of 8 MHz. As can be clearly seen the line shape depends sensitively on η.

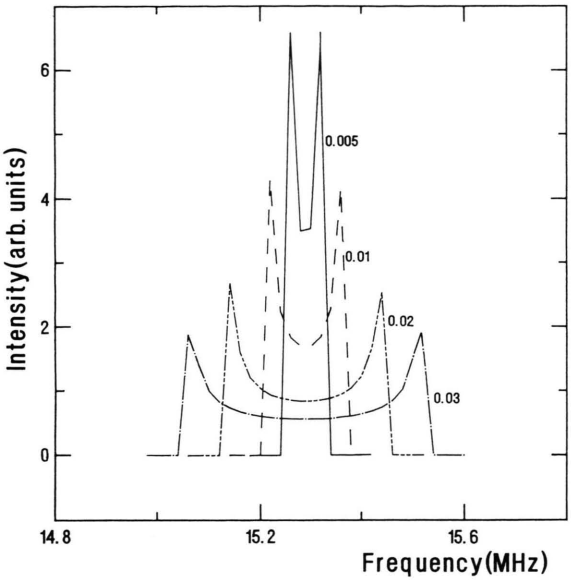

Fig. 1. Calculated Zeeman split spectra for $\theta = 90°$, different small η-values and a Larmor frequency of 8 MHz. A statistical distribution of the spherical angle ϕ is assumed.

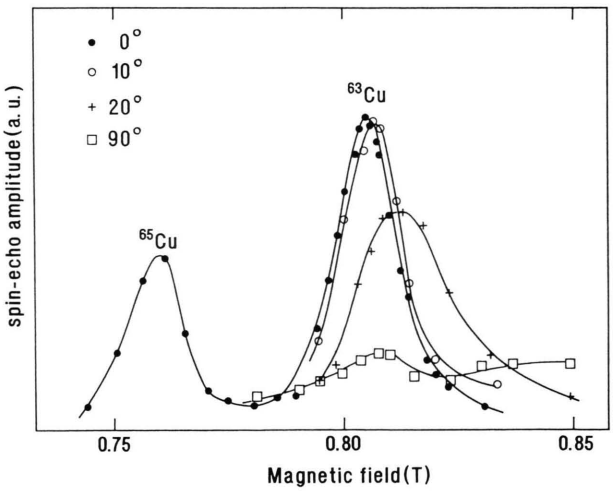

Fig. 2. $^{63,65}Cu$ Zeeman split spectra of oriented $YBa_2Cu_3O_{7-\delta}$ powder at 100 K for various values of α. The resonance frequency was $\nu = 17.2$ MHz. The crystallographic c-axes are statistically distributed within one plane. α is the angle between the magnetic field $\boldsymbol{B}_0$ and the normal $\boldsymbol{n}$ of this plane.

Results and Discussion

Figure 2 shows experimental data taken at a fixed frequency of 17.2 MHz by sweeping the magnetic field from 0.7 T to 0.9 T. A two pulse sequence with pulse lengths of 5 and 10 μs was used. The resonance lines were obtained by plotting the spin-echo amplitude against the magnetic field for discrete field values. As B_0 is perpendicular to the plane of c-axes the appearance of the Zeeman split line with an effective gyromagnetic ratio of 1.89 γ (^{63}Cu) confirms the results of other groups [1–3] who found the z-axis of the EFG to be parallel to the crystallographic c-axis in the case of the 31 MHz NQR line. From the angular dependence of the line intensity in Fig. 2 nearly complete alignment of the sample can be deduced.

Since the NQR line for $B_0 \perp c$ (solid line in Fig. 2) is not essentially broadened by the distribution of the NQR frequencies, a line shape analysis provides a method to determine η. A fit of the calculated lines to the experimental curves yields an average value of $\bar{\eta}_2 = 0.008$. The smearing out of the expected two-peak structure (Fig. 1) may be explained by a distribution of the η_2-values around the average value combined with a slight misalignment of the grains.

It should be mentioned that an other broadening mechanism may arise from weak internal magnetic fields caused by small magnetic moments of the Cu (2) atoms. Such an internal field would also broaden the zero-field NQR lines. Indeed it is found that for the 31 MHz NQR line the linewidth is considerably larger than the 22 MHz linewidth. This large difference in the Cu-NQR linewidths is observed even in samples with an oxygen content very close to 7 as obtained by Schiefer et al. [12].

In the magnetic field range of 0.6–1 T a second line pair was detected at 22.87 MHz. This line pair corresponds to the 22 and 20.4 MHz NQR lines which were assigned to the Cu (1) site. A resonance with an effective $\gamma_{eff} \approx 2.5\, \gamma\, (^{63}Cu)$ is expected if the applied field is perpendicular to the x-axis of the EFG. A statistical distribution of θ leads to a singularity when $\theta = 90°$. As this resonance depends sensitively on η, it is possible to determine high η-values from this Zeeman split NQR experiments. As can be seen in Fig. 3 the resonances for the two copper isotopes are not clearly separated in this case. Since this experiment was done in the superconducting state at 4.2 K, the lines are broadened by the inhomogeneity of the internal magnetic field. For the Cu (2) site, on the other hand, the resonances of the two Cu isotopes are well separated even in the superconducting state. Obviously the line broadening (Fig. 3) is mainly caused by local variations of the symmetry of the EFG at the Cu (1) site. Taking into account a distribution of the η-values of ± 0.02 around $\eta_1 = 0.96$, the smearing out of the observed spectrum can be explained. This result is consistent with the line shape of the zero field NQR line which may also be broadened by a distribution of η. The assumed variation of η_1 leads to the observed NQR linewidth of $\delta\nu \cong 200$ kHz.

For the superconducting Bi–Ca–Sr–Cu–O system we observed a very broad NQR spectrum between 18 and 30 MHz. In contrast to the results of Fujiwara et al. [8], on a partly Pb substituted sample no structure was found in this spectrum. On the other hand T_1-measurements, carried out at different frequencies in the region of 21–24 MHz at 4.2 K, yield a relaxation time $T_1 \cong 0.8$ s for all frequencies. Hence we conclude that the atoms contributing to the NQR signal have a similar electronic environment as expected for Cu in the CuO_2 layers in this system.

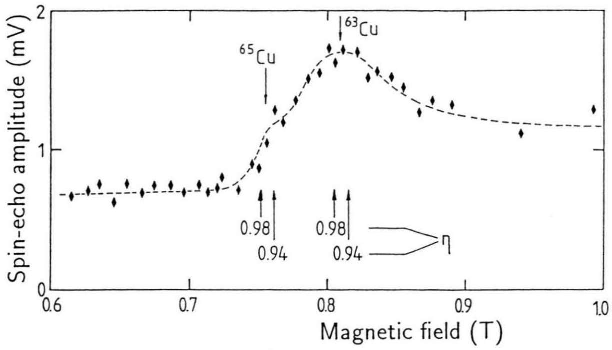

Fig. 3. ^{63,65}Cu Zeeman split spectrum of oriented $YBa_2Cu_3O_{7-\delta}$ powder at 4.2 K ($c \perp \boldsymbol{B}_0$). The resonance frequency was $\nu = 22.87$ MHz. The crystallographic c-axes are statistically distributed within one plane. The dashed line is calculated assuming an average $\bar{\eta}_1 = 0.96$ and a distribution of ± 0.02.

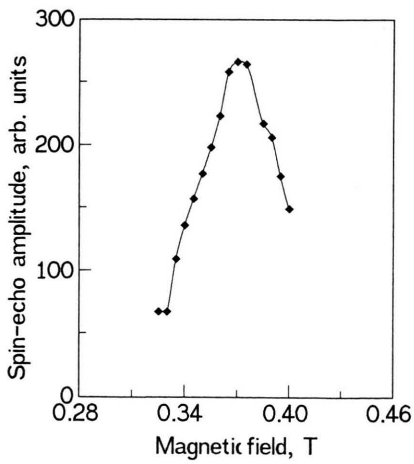

Fig. 4. ^{63,65}Cu Zeeman split spectrum of non-oriented Bi–Ca–Sr–Cu–O. The resonance frequency was $\nu =$ 8.2 MHz.

In a low magnetic field, a Zeeman split line was obtained at 8.2 MHz and 4.2 K (Figure 4). From the field strength where the maximum intensity is observed an effective gyromagnetic ratio of $\gamma_{eff} = 1.96\, \gamma\, (^{63}Cu)$ is determined. The expected two peak spectrum for the two Cu isotopes is smeared out due to a distribution of the NQR frequencies over a wide range. Taking the data at higher field strengths and higher frequencies, a strong line broadening and a lower effective γ is observed. The field dependence of γ_{eff} indicates an average NQR frequency of about 24 MHz. From the line shape we conclude that the EFG tensor is nearly axially symmetric at the sites of most of the nuclei which contribute to the Zeeman split spectrum.

It should be mentioned that NQR investigations on 85 K single phase Bi–Sr–Ca–Cu–O superconductors were also carried out, but only very weak NQR and Zeeman split signals were observed. Hence we conclude that in the mixed phase the Cu nuclei belonging to the 110 K phase (2223 phase) contribute predominantly to the NQR spectrum.

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