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Nuclear quadrupole resonance and nuclear magnetic resonance of copper in the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$

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The ^{65}Cu and ^{63}Cu zero-field nuclear quadrupole resonance (NQR), nuclear magnetic resonance at 4.7 and 8.5 T, and the spin-lattice relaxation time T_1 at 8.5 T are measured in the superconducting oxide $YBa_2Cu_3O_{7-\delta}$ between 80 and 300 K. No sign of magnetic order or localized moments is found. The NQR linewidth is strongly dependent on the oxygen content. We assign the ^{63}Cu NQR line at 22 MHz to the Cu site with oxygen coordination 5; T_1 is dominated by the quadrupolar relaxation due to spin-phonon coupling.

In all the newly discovered[1] high-T_c superconducting ceramics Cu—O sheets or Cu—O chains seem to play a central role. This is demonstrated by the equally high transition temperatures of a number of compounds isostructural to $YBa_2Cu_3O_7$ (Refs. 2 and 3) in which yttrium is substituted by other rare-earth elements.[4] Nuclear magnetic resonance (NMR) or nuclear quadrupole resonance (NQR) on copper, thus, may prove to be crucial in understanding the microscopic origin of the anomalously high T_c. NMR and NQR are sensitive, among other factors, to possible magnetic order, localized moments,[5] perturbations of the crystal field due to disorder, nonstoichometry, or phonons. In this paper, a detailed nuclear resonance study of copper in $YBa_2Cu_3O_{7-\delta}$ is presented. No magnetic interaction between the Cu nuclei and ordered or localized magnetic moments is found, in agreement with a less comprehensive study of Lütgemeier and Pieper.[6] The resonance was found to be sensitive to the presence of oxygen vacancies and this feature opens the possibility of studying the disorder in the compound. The spin-lattice relaxation time T_1 is dominated by phonons and not electrons.

The samples were prepared by firing Y_2O_3, $BaCO_3$, and CuO in two steps. First the well-mixed powder was heated to 900 °C in air for 24 h. The product was reground, pressed into pellets, heated to 950 °C in oxygen atmosphere for 12 h, and cooled to room temperature in 5 h. According to thermogravimetric and neutron diffraction studies,[7] the specimen obtained this way (sample I) was not fully oxygenated, and an oxygen deficiency of $\delta \approx 0.02$ can be inferred from the data. Sample II was prepared by further annealing in oxygen atmosphere.

The superconducting transition midpoints determined from the resistivity curves (Fig. 1) were 89.5 and 91.3 K and the transition widths were $\Delta T = 5$ K and $\Delta T = 1.5$ K for samples I and II, respectively. From the resistivity data, sample II seems to be more homogeneous and the NQR results show that this sample indeed has a higher perfection on the microscopic scale.

The NQR spin-echo spectra were taken on a Bruker SXP-100 spectrometer in the frequency range between 19 and 35 MHz. The echo delay time was 100 μs. At each frequency the amplitude was calibrated to a reference ^{31}P NMR. The high-field NMR spectra were recorded at 4.7 and 8.5 T on a Bruker CXP-200 spectrometer with a homemade probe. The echo delay time was 20 μs and a Fourier transform of 64000 scans was taken at each frequency. The spin-lattice relaxation was measured from the recovery of the signal after saturation.

The NQR spectra of the two samples, taken at 170 K, are presented in Fig. 2. For sample I the full range between 19 and 35 MHz was investigated and two pairs of lines were found at 20.5 and 22.0 MHz, and 28.7 and 31.2 MHz, respectively. Similar frequencies were reported by Lütgemeier and Pieper.[6] Each pair corresponds to the ^{65}Cu and ^{63}Cu resonances of a particular site, as evidenced by the frequency and intensity ratios of magnetic moments and abundances of these isotopes, We refer to the site giving rise to the ^{63}Cu resonance at 22.0 MHz as site *A*, and at 31.2 MHz as site *B*. For sample II we investigated site *A* only.

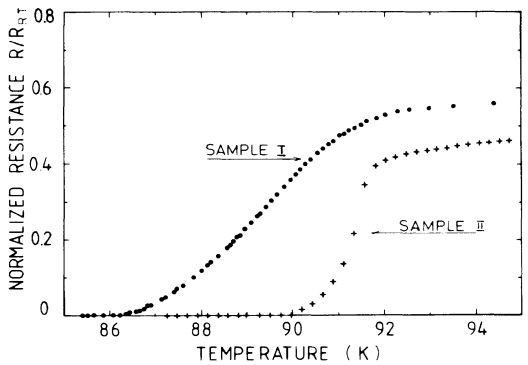

FIG. 1. Temperature dependence of the resistance around the transition temperature for the two samples. Sample II was obtained by oxygen annealing.

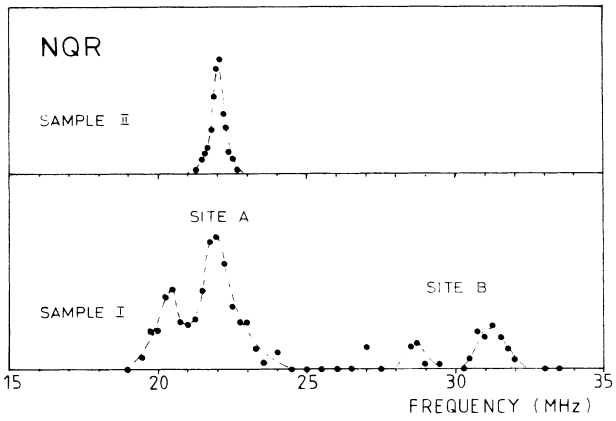

FIG. 2. Nuclear quadrupole resonance spectra at 170 K. For sample II only the resonance at 22 MHz was investigated.

The homogeneous spin-spin relaxation time T_2 of the 22.0-MHz line was found to vary from 40 μs at room temperature to 80 μs at 170 K. The linewidth of sample I is broad, 1.1 ± 0.2 MHz and 1.2 ± 0.2 MHz for sites A and B, respectively. The intensity of site B is three to four times less than that of site A. The linewidth strongly depends on sample quality; sample II, which has a higher oxygen content, has a full linewidth of 0.38 ± 0.05 MHz (including the instrumental resolution of 0.07 MHz). This width is much less than that of sample I.

The high-field NMR spectra of sample I are presented in Fig. 3. Measurements were performed at 300 K for magnetic fields of 4.7 and 8.5 T, and also at 80 K, 8.5 T. At 4.7 T, the spectrum is rather complex as it is composed of the overlapping lines of the ^{65}Cu and ^{63}Cu isotopes. Two peaks near the unperturbed Larmor frequencies and broad shoulders extending over more than 10 MHz, are observed. At 8.5 T the NMR spectrum is simpler as the lines of the two isotopes are separated. Only the ^{63}Cu resonance was investigated. This line has a half width at half maximum of 4.1 ± 0.2 MHz; it is situated asymmetrically around the unperturbed Larmor frequency $\nu_L = 95.4$ MHz and it has a rather flat top, sided by fast decreasing tails. Neither the 8.5-T spectrum, nor the relaxation time T_1 was much affected by cooling to 80 K, showing that at this magnetic field a large part of the sample remains normal. This is in agreement with the reported smearing of the resistivity transition in a magnetic field,[8] which may be due to the anisotropy of the critical field.[9] On the other hand, at 80 K the NQR line intensity of sample I was only a few percent of that observed above the transition temperature.

The spin-lattice relaxation rate T_1^{-1} measured as a function of temperature at 8.5 T is shown in Fig. 4. A small difference is found between the two isotopes: at 80 K the relaxation rate of ^{65}Cu is smaller than that of ^{63}Cu. The temperature dependence is close to quadratic.

In discussing the results, first we want to emphasize that our measurements do not show any evidence for magnetic interaction. A magnetic order would split both the NMR and NQR lines even if the magnetic moments are

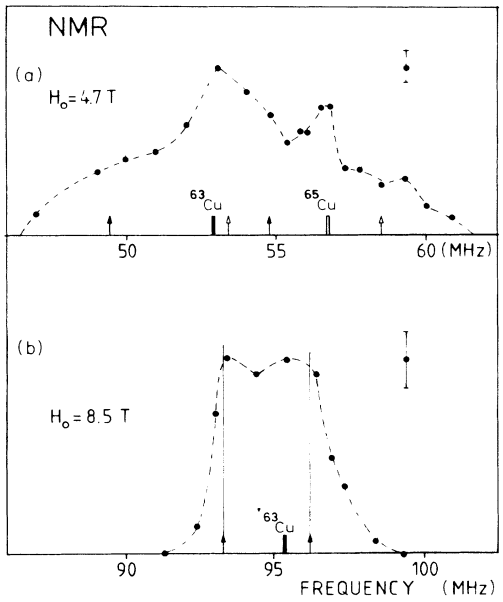

FIG. 3. NMR spectrum of sample I at two magnetic fields. The data shown were obtained at room temperature. The vertical bars indicate the Larmor frequencies; the arrows indicate the position of divergences calculated from the measured quadrupole frequency. Full and empty symbols are used for ^{63}Cu and ^{65}Cu, respectively.

on sites other than the observed ones.[10] Disordered localized magnetic moments on Cu sites (e.g., near oxygen deficiencies) would give rise to an NMR linewidth proportional to the applied magnetic field, and inversely proportional to the temperature. In fact, the NMR linewidth is approximately inversely proportional to the field and independent of the temperature, features characteristic of a quadrupole interaction. Our data show that the paramagnetic susceptibility as high as 0.3 μ_B per copper atom[3]

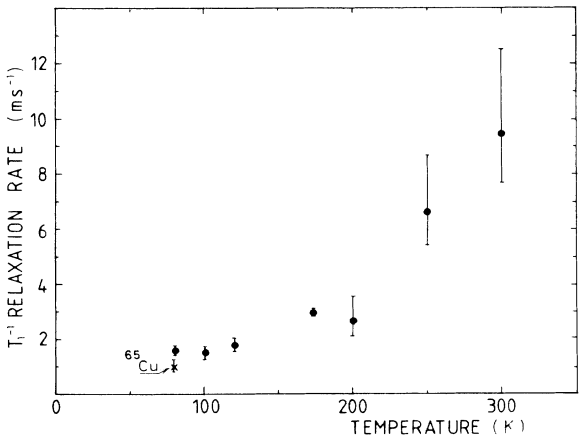

FIG. 4. Spin-lattice relaxation rate vs temperature for sample I. Most of the data were taken on ^{63}Cu. The isotope effect was investigated at 80 K.

does not arise from localized defects as these would certainly broaden the NMR line.

The relaxation rate T_1^{-1} is dominated by the quadrupolar spin-phonon mechanism and, therefore, no estimates can be made for the electronic density of states. Two-phonon Raman processes may explain the nearly quadratic temperature dependence. At low temperatures, the isotope effect clearly shows that the relaxation is due to the fluctuations of the electric field gradients and the electron-nuclear Korringa relaxation is negligible: The faster relaxation is observed for the ^{63}Cu isotope which has the larger quadrupole moment and the smaller magnetic moment. The relaxation rate at 80 K is an order of magnitude faster than the Korringa relaxation of copper metal.

In principle, the observed linewidth of the NMR spectra can be interpreted in terms of quadrupolar broadening, using the parameters estimated from the NQR measurements. At 8.5 T the NMR spectrum is well accounted for by the Zeeman $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition, perturbed in second order by the quadrupole interaction. At 4.7 T the perturbation theory may be only roughly correct, although the Zeeman energy is still larger than the quadrupole interaction.

The NQR spectrum is due to twofold degenerate $|\frac{3}{2}| \rightarrow |\frac{1}{2}|$ transitions. The position of the resonance is determined by two parameters: ν_Q, proportional to the largest component of the diagonalized EFG tensor, and the asymmetry parameter η.[11] For tetragonal symmetry $\eta=0$ and the observed NQR frequency determines ν_Q. The NMR powder spectrum of a site with $\eta=0$ consists of a broad line with diverging edges at $\nu_L - \nu_Q^2/3\nu_L$ and $\nu_L + 3\nu_Q^2/16\nu_L$. The expected divergences of the NMR spectra, calculated from the NQR spectrum of site A with $\eta=0$ and indicated in Fig. 3, are in good agreement with the shape of the resonance. On the other hand, the contribution of site B to the NMR spectra cannot be understood by assuming $\eta=0$. A component situated between the divergences is clearly present in the high-field NMR. This may correspond to site B with a particular choice of η, or a third site may also contribute to the spectrum.

The NQR linewidth is due to the imperfections of the lattice as dipolar interactions, dominating for a perfect crystal, may account for a width in the order of 10 kHz only. In metals charged impurities induce Friedel oscillations of amplitude decreasing with the distance as $1/r^3$ in the isotropic case. This slow decrease leads to an extreme sensitivity of the resonance to the impurities. The mere fact that NMR and NQR lines are observed supports the view[12] that oxygen atoms are mostly ordered. Figure 2 demonstrates that the NQR linewidth increases for the oxygen-deficient sample, in agreement with the decrease of the superconducting transition temperature and the increase of the transition width (Fig. 1).

A tentative assignment of sites A and B to crystallographic sites may be made as follows. In the unit cell of the perfect $YBa_2Cu_3O_7$ structure, there are two inequivalent Cu sites.[12] Copper oxide *planes* and *chains* are situated between the Y and BaO layers, and BaO and BaO layers, respectively. Site A most probably corresponds to the more abundant copper site situated in the CuO *planes*. This site has a fivefold oxygen coordination and a nearly tetragonal symmetry in agreement with our finding of $\eta=0$. Site B can be most likely associated to copper nuclei situated in the CuO *chains*. Oxygen vacancies appear preferentially in the CuO *chains*, giving rise to further copper coordinations. For $\delta=0.02$ approximately 8% of the Cu in the CuO *chains* has an oxygen neighbor missing. Since sites with first-neighbor vacancies will have a resonance at a different frequency, the intensity of the NQR line for site B should be very sensitive to the oxygen content. Further studies are in progress to test this hypothesis.

In conclusion, we have shown that nuclear quadrupole and magnetic resonance may be an effective tool for investigating the microscopic properties of $YBa_2Cu_3O_{7-\delta}$. No magnetic order or localized magnetic moment is observed. The spin-lattice relaxation is dominated by phonons. The NQR line at 22.0 MHz is assigned to the Cu site of fivefold oxygen coordination and the linewidth is sensitive to the variation of oxygen content.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3] R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. M. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[4] D. W. Murphy, S. Sunshine, R. B. van Dover, R. J. Cava, B. Batlogg, S. M. Zahurak, and L. F. Schneemeyer, Phys. Rev. Lett. **58**, 1888 (1987); P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, *ibid.* **58**, 1891 (1987); S. Shamoto, M. Onoda, M. Sato, and S. Hosoya, Jpn. J. Appl. Phys. **26**, L642 (1987); Z. Fisk, J. D. Thompson, E. Zirngiebl, J. L. Smith, and S.-W. Cheong (unpublished).

[5] J. Owen, M. Brown, W. D. Knight, and C. Kittel, Phys. Rev. **102**, 1501 (1956).

[6] H. Lütgemeier and M. W. Pieper, Solid State Commun. (to be published).

[7] L. Mihaly, L. Rosta, G. Coddens, F. Mezei, Gy. Hutiray, G. Kriza, and B. Keszei, Phys. Rev. B (to be published).

[8] K. Takita, T. Ipposhi, and K. Masuda, Jpn. J. Appl. Phys. **26**, L668 (1987).

[9] T. R. Dinger, T. K. Worthington, W. J. Gallagher, and R. L. Sandstrom, Phys. Rev. Lett. **58**, 2687 (1987); Y. Hidaka,

Y. Enomoto, M. Suzuki, M. Oda, A. Katsui, and T. Murakami, Jpn. J. Appl. Phys. **26**, L726 (1987).

[10]Antiferromagnetic order was observed in the related compound La_2CuO_4 by Y. Yamaguchi, H. Yamauchi, M. Ohashi, H. Yamamoto, N. Shinoda, M. Kikuchi, and Y. Syono, Jpn. J. Appl. Phys. **26**, L447 (1987). The NQR measurements of Y. Kitaoka, S. Hiramatsu, T. Kohara, K. Asayama, K. Ohishi, M. Kikuchi, and N. Kobayashi, *ibid.* **26**, L397 (1987) are interpreted in terms of antiferromagnetic order by I. Furo and A. Janossy, *ibid.* **26**, L1307 (1987).

[11]M. H. Cohen and F. Reif, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 322.

[12]W. I. David, W. T. A. Harrison, J. M. F. Gunn, O. Moze, A. K. Soper, P. Day, J. D. Jorgensen, D. G. Hinks, M. A. Beno, L. Soderholm, D. W. Capone II, I. K. Schuller, C. U. Segre, K. Zhang, and J. D. Grace, Nature (London) **327**, 310 (1987); P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, and D. W. Murphy, Mater. Res. Bull. (to be published); J. J. Capponi, C. Chaillot, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyroux, J. L. Tholence, and R. Tournier, Europhys. Lett. **3**, 1301 (1987).