Nuclear magnetic resonance of copper in the $YBa_2Cu_3O_{7-\delta}$ single crystal

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The NMR spectra of the central transition ($1/2 \to -1/2$) of the quadrupole ^{63}Cu nucleus in a single crystal of a high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ have been measured. The tensors of the electric field gradient and of the Knight shift have been determined from the angular dependence of the line positions for copper nuclei in the chains (Cu1) and in the planes (Cu2).

Valuable information on the properties of high-T_c superconductors in the normal and superconducting states can be obtained from NMR and NQR studies based on copper nuclei. So far only $YBa_2Cu_3O_{7-\delta}$ polycrystal samples have been studied in this manner.[1–7] The NMR signals obtained in these studies are broad lines (several megahertz wide) which are broadened because of the quadrupole effects, because of overlapping of the contributions from copper nuclei of various crystallographic positions, and because of anisotropy of the Knight shift. All these factors greatly complicate or make it impossible to determine the parameters of the quadrupole interaction and Knight shift from the spectra of polycrystal samples. They also make it difficult to obtain reliable information on the superconducting state from the measurements of the nuclear relaxation times. These difficulties can be overcome by NMR studies of single crystals. We have measured the NMR spectra of ^{63}Cu in a $YBa_2Cu_3O_{7-\delta}$ single crystal and we have determined the tensors of the electric field gradient (EFG) and of the Knight shift from the angular dependence of the line position.

The experiments were carried out using a single crystal with dimensions

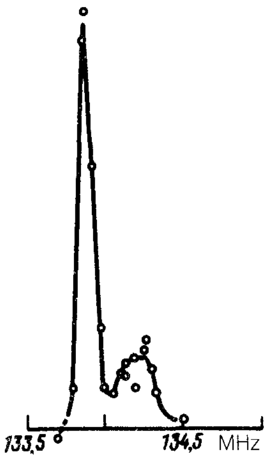

FIG. 1. NMR spectrum of the central transition of ^{63}Cu in a $YBa_2Cu_3O_{7-\delta}$ single crystal. The angle between the magnetic field and the c axis is $\alpha = 10.2°$.

$2.2 \times 2.0 \times 0.4$ mm and mass 8 mg. The superconducting transition temperature of this single crystal is 91 K and the superconducting width is 1.8 K. Both these values were measured from the screening signal. The NMR signal was measured at room temperature by means of a Fourier transform of the free-induction signal of the spin echo, using a Bruker spectrometer in a field $H_0 = 11.7$ T. The NMR coil had a diameter large enough to install a sample. The time of the 90° pulse of 5 μs was determined from the copper line in Cu1, whose position was used as a resonance frequency reference. The spectrum was measured from the points at intervals of 100 and 200 kHz. The angular dependence of the NMR spectrum was studied by rotating the crystal around the (100) axis. The angle θ between the c axis and the field H_0 was measured by reflecting the laser beam from the ab plane.

The NMR spectrum of the central transition ($1/2 \rightarrow -1/2$) of the quadrupole ^{63}Cu nucleus ($S = 3/2$, $Q = 1.6 \times 10^{-25}$ cm^2) exhibited for all orientations two lines with a width at half-maximum of 80 and 250 kHz and with a ratio of the areas of nearly 2:1 (Fig. 1). These lines refer respectively to two crystallographically nonequivalent positions of copper: Cu2 (in the CuO_2 planes) and Cu1 (in the CuO chains) in the $YBa_2Cu_3O_{7-\delta}$ lattice. The spin-spin relaxation times T_2 of these lines, measured by the spin-echo method in a 8.5-T field at $\theta = 0$, are respectively 80 and 150 μs. The uniform width, defined as $1/\pi T_2$, therefore does not exceed 4 kHz, so that both lines are broadened nonuniformly.

The lattice symmetry implies that the major axes of the electric-field-gradient tensor $\nu_{ij} = (eQ/2h)\partial v/\partial x_i \partial x_j$ and of the Knight shift tensor K_{ij} for Cu1 and Cu2 must coincide with the a, b, and c axes. The NMR frequency of the central transition $1/2 \rightarrow -1/2$ for spin 3/2, with allowance for the Knight shift and the second-order quadrupole effects (see, e.g., Ref. 8), in this case is

$$\nu = \nu_0[(1+K_{xx})\sin^2\theta\sin^2\varphi + (1+K_{yy})\sin^2\theta\cos^2\varphi + (1+K_{zz})\cos^2\theta] - (\nu_{zz}^2/2\nu_0)(A\cos^4\theta + B\cos^2\theta + c), \quad (1)$$

TABLE I.

i	Cu1 (ν_Q = 22.2 MHz)		Cu 2 (ν_Q = 31.2 MHz)	
	K_{ii}, %	ν_{ii}, MHz	K_{ii}, %	ν_{ii}, MHz
a	0.57	19.2	0.57	– 15.6
b	0.57	– 19.2	0.57	– 15.6
c	0.57	0	1.27	31.2

where ν_0 is the Larmor frequency, and θ and φ are the angles between the direction of H_0 and the lattice axes. The cumbersome equations for A, B, and C, which are functions of $\cos 2\varphi$ and of the principal values of the EFG tensor, are given in Ref. 8.

Using the principal values of the EFG tensor and the Knight shift tensor (see Table I), we have obtained a good description of the experimental angular dependences (Fig. 2). The values of the NQR frequencies ν_Q deduced from these values for Cu1 and Cu2 nuclei agree within the measurement error with the values measured in Refs. 3 and 5.

It can be seen from Table I that the c axis is, within acceptable error margin, the axial symmetry axis of both tensors for Cu2, which is not surprising because of the small orthorhombic distortions in the CuO_2 planes. The components of the EFG tensor are approximately six times larger than those that could be obtained at the site

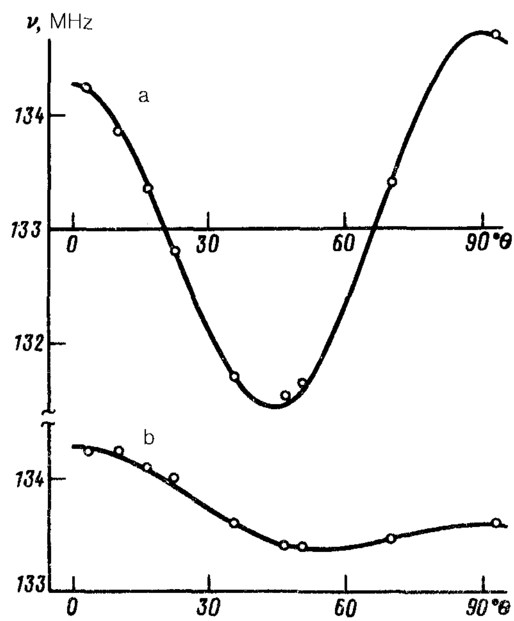

FIG. 2. NMR frequency vs the angle between the magnetic field and the c axis. a—Narrow Cu_2 line; b—broad Cu1 line. O—Experimental points; solid line—theoretical.

of the Cu2 nucleus from five $+2e$ point charges situated in the 01, 02, and 03 oxygen positions.

For Cu1 copper surprising results are the isotropy of the Knight shift and the extremely strong asymmetry of the EFG tensor which is characterized by $\nu_{zz} = 0$. The last result, which cannot be deduced even qualitatively from the point-charge model, is evidence that the Sternheimer shielding is strongly anisotropic.

We note in conclusion that the symmetry of the EFG tensor and the Knight shift tensor is such that regardless of the angular position, there is no splitting of the Cu1 and Cu2 lines into doublets due to twinning of the crystal.

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