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Cu nuclear magnetic resonance of aligned single crystals of $YBa_2Cu_3O_{7-\delta}$

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There are two types of Cu sites in $YBa_2Cu_3O_{7-\delta}$, plane and chain. One gives a nuclear quadrupole resonance (NQR) at 22.0 MHz, the other at 31.5 MHz. Measurements of nuclear spin-lattice relaxation time in the superconducting state show that the 31.5-MHz site has a much larger energy gap (as though its T_c were 200 K), but different experimental workers have differed as to whether this is the chain or plane site. We report nuclear magnetic resonance (NMR) studies at 81.1 kG and 100 K on oriented single crystals, and conclude from symmetry arguments that the 31.5-MHz NQR arises from the plane site.

The nuclear spin-lattice relaxation time, T_1, of a metal is strongly affected if the metal makes a transition into the superconducting state.[1,2] Indeed, comparing the temperature dependence of $1/T_1$ with that of the ultrasonic absorption[3] provided one of the first confirmations of the pairing concept of the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity.[4] Recently several workers[5-7] have reported measurements of the T_1 of Cu in the 90 K superconductor $YBa_2Cu_3O_{7-\delta}$. Using powder samples, they studied the nuclear magnetic resonance (NMR) in the presence of a strong static magnetic field H_0 and in the absence of magnetic fields [nuclear quadrupole resonance (NQR)]. Since there are two types of Cu sites in the crystal, the so-called plane and chain sites [sometimes called Cu(2) and Cu(1), respectively], there are two resonance lines seen in NQR. One occurs at approximately 22.0 MHz, the other at 31.5 MHz. (We quote values corresponding to a temperature of 100 K.) Warren *et al.*[5] report dramatically different temperature dependences of the T_1's of the two lines in the superconducting state corresponding to very different superconducting energy gaps. They suggest that their data can be interpreted as implying that the 31.5 MHz site has an incipient T_c of 200 K and the 22.0 MHz site an incipient T_c of 60 K. The great importance of these NQR relaxation-time results arises from the possibility that they provide a powerful clue as to the mechanisms of the high transition temperatures. Walstedt *et al.*[5] used two means to conclude that the 31.5 MHz line arises from the chain sites. The first was a relative intensity measurement based on the fact that there are twice as many plane as chain sites. The second compared relaxation behavior with that of Y which is close to the planes but far from the chains. Mali *et al.*[6] get relaxation-time data which agree substantially with that of Warren *et al.*,[5] but use intensity to conclude that the 31.5 MHz NQR line arises from the plane sites.

The important implications of the relaxation measurements have stimulated us to study the assignment of the NQR lines by NMR studies of oriented single crystals. We conclude that the 31.5 MHz line arises from the plane sites.

Our sample is made up of about 30 single crystals of $YBa_2Cu_3O_{7-\delta}$ (total mass of 2 mg). The individual crystals have a smooth face $\sim 0.2\ \mathrm{mm} \times 0.2\ \mathrm{mm}$ whose normal is the crystal c axis,[8] and they are about 0.05 mm thick in the direction parallel to the c axis. They are set flat on a piece of Plexiglas whose face is perpendicular to the magnetic field, H_0, so that the c axis is parallel to H_0. We report measurements with $H_0 = 81.1$ kG at 100 K. The magnetic transition of the sample is shown in Fig. 1 and discussed in the figure caption.

From crystal structure studies[9] one knows that for both

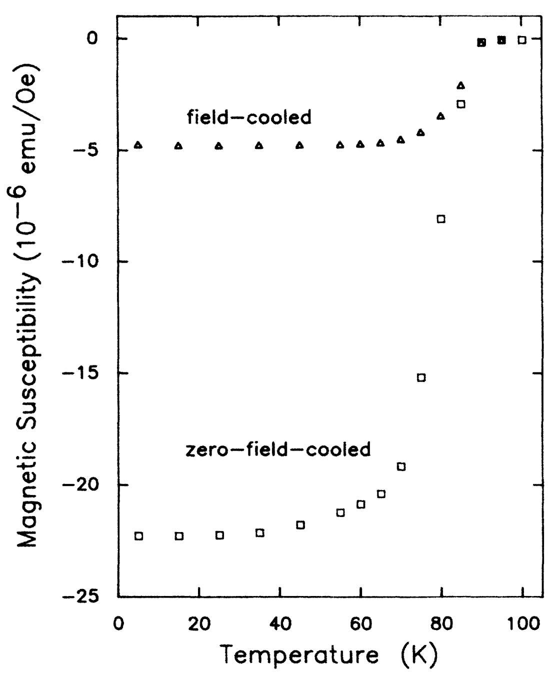

FIG. 1. The magnetic susceptibility (magnetic moment divided by the field) of the sample vs temperature, showing a good superconducting transition at about 90 K. The applied field was oriented in the *ab* plane, and was 78 Oe. (An even sharper transition would be seen at a lower applied field.) Within the accuracy of the known mass of the sample, the magnetic shielding shown by the zero-field-cooled curve is complete.

sites the crystalline a, b, and c axes are the principal axes of both the electric field gradient tensor $\partial^2 V/\partial\alpha^2$ ($\alpha = x,y,z$) and the Knight-shift tensor $K_{\alpha\alpha}$. At the plane site, both tensors should be nearly axial about the c axis since the distance to the four nearest oxygen atoms differs by less than 2%. The chain site should be at best only crudely axial about the a axis which is perpendicular to both the c axis and the chain (b) direction.[9]

We assign each of the two ^{63}Cu NQR lines (31.5 and 22.0 MHz) to its crystallographic site (plane and chain, respectively) in two steps. First, we assign each of the two NMR lines to its NQR frequency and second we assign each NMR line to its crystallographic site.

To explain the experiment, we give some facts about NMR and NQR of spin-$\frac{3}{2}$ nuclei such as ^{63}Cu and ^{65}Cu. In a strong field, H_0, oriented along the z axis, the eigenvalues of the z component of spin I_z ($m = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$) are good quantum numbers.

We define the frequencies $\nu_{\alpha\alpha} = (eQ/2h)(\partial^2 V/\partial\alpha^2)$ ($\alpha = x,y,z$) with eQ the nuclear quadrupole moment. Then $\nu_{xx} + \nu_{yy} + \nu_{zz} = 0$. For our experiments, H_0 lies along the direction of the crystal c axis. Then the x and y directions lie along the crystal a and b axes.

We define $\nu_{00} = \gamma H_0/2\pi$, $\Delta_H\nu = \gamma H_0 K_{zz}/2\pi$, $\nu_0 = \nu_{00} + \Delta_H\nu$, where γ is the nuclear gyromagnetic ratio. $\Delta_H\nu$ is thus the Knight shift (plus any extra chemical shift characteristic of the metal).

Then, using second-order perturbation theory one finds that there are three transition frequencies ν,

$$\nu_{1/2,-1/2} = \nu_{00} + \Delta_H\nu + \Delta_2\nu \ , \qquad (1a)$$

$$\nu_{\pm 1/2, \pm 3/2} = \nu_{00} + \Delta_H\nu \pm \nu_{zz} \ , \qquad (1b)$$

where

$$\Delta_2\nu = \frac{(\nu_{xx} - \nu_{yy})^2}{12\nu_0} \ . \qquad (1c)$$

The resonance frequency ν_Q in an NQR experiment occurs at

$$\nu_Q^2 = \nu_{zz}^2 + \frac{(\nu_{xx} - \nu_{yy})^2}{3} \ . \qquad (2)$$

From Eqs. (1) and (2) we see that knowledge of ν_{zz}, ν_0, and $\Delta_2\nu$ enables one to compute the NQR resonance frequency, since

$$\nu_Q^2 = \nu_{zz}^2 + 4(\Delta_2\nu)\nu_0 \ . \qquad (3)$$

Since $\Delta_H\nu$ is proportional to γ and $\Delta_2\nu$ is proportional to Q^2/γ, their values for the two isotopes are related:

$$(\Delta_H\nu)_{65} = 1.0713(\Delta_H\nu)_{63}$$

and

$$(\Delta_2\nu)_{65} = 0.7988(\Delta_2\nu)_{63} \ .$$

We first discuss the $(+\frac{1}{2}, -\frac{1}{2})$ transition. Our spectrum consists of two NMR lines for each isotope, one of which is narrow and intense [40 kHz full width at half maximum (FWHM)], the other broad and weak (150 kHz FWHM). Figure 2 shows the ^{63}Cu and ^{65}Cu

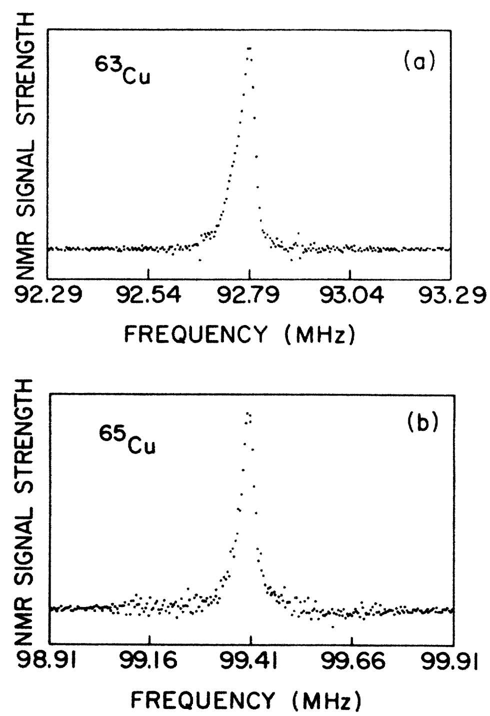

FIG. 2. (a) ^{63}Cu and (b) ^{65}Cu NMR line shapes of the $(+\frac{1}{2}, -\frac{1}{2})$ "narrow line" by Fourier transform of the spin echo. The FWHM was 40 kHz. 1 000 000 echoes have been averaged for each line shape.

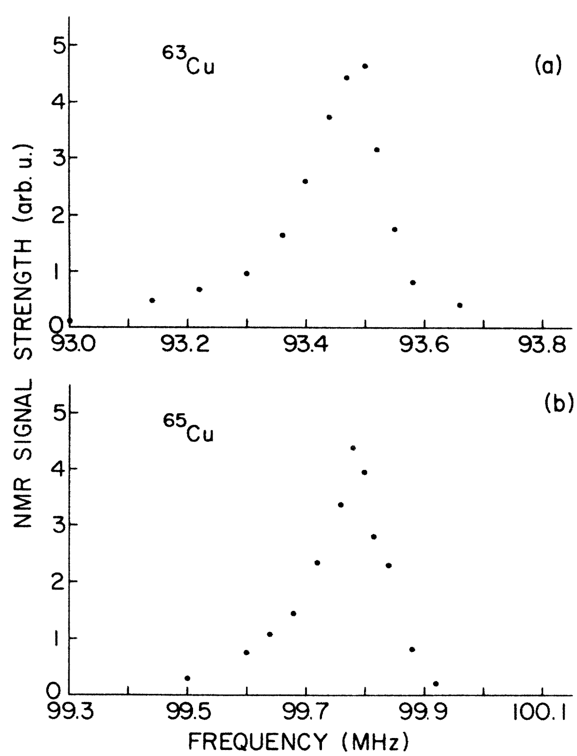

FIG. 3. (a) ^{63}Cu and (b) ^{65}Cu NMR line shapes of the $(+\frac{1}{2}, -\frac{1}{2})$ "broad line." Plotted is the integral of the spin echo vs oscillator frequency. The FWHM was 150 kHz. 500 000 echoes have been averaged for each point.

TABLE I. Results from the narrow- and broad-line $(+\frac{1}{2},-\frac{1}{2})$ spectra.

	$(\Delta_2\nu)_{63}$ (MHz)	$(\Delta_H\nu)_{63}$ (MHz)	Knight shift K_{zz} (%)	ν_0 (MHz)	Relative NMR signal area
Narrow-line spectrum	(0.00 ± 0.05)	1.17 ± 0.05	1.25 ± 0.05	92.79 ± 0.05	2.2 ± 0.7
Broad-line spectrum	(1.3 ± 0.2)	0.6 ± 0.2	0.6 ± 0.2	92.20 ± 0.2	1

narrow-line spectra obtained by Fourier transform of the spin echoes. Figure 3 shows the ^{63}Cu and ^{65}Cu broad-line spectra obtained by point-by-point measurements of spin-echo areas. From these data and the isotope relationships, we have deduced $\Delta_H\nu$ and $\Delta_2\nu$ and from them K_{zz} and ν_0 listed in Table I.

Consider first the narrow line, for which $\Delta_2\nu$ is zero. Equation (3) shows us that for it $\nu_{zz}\cong\nu_Q$. Combined with Eq. (1b) we must then have the ^{63}Cu $(\pm\frac{1}{2},\pm\frac{3}{2})$ transitions at $\nu_0\pm\nu_Q$ of either 31.5 MHz or 22.0 MHz above and below ν_0 (92.79 ± 0.05 MHz). Figure 4 shows these transitions approximately 31.5 MHz above and below the $(\frac{1}{2},-\frac{1}{2})$ transitions. There may be a modest spread in values of ν_Q as is shown by the linewidth of the NQR lines. To avoid errors from crystal misalignment, we take the transition frequencies to be defined by the upper (lower) edge of the higher (lower) frequency transition, obtaining $\nu_0=92.84\pm0.07$ MHz and $\nu_{zz}=31.46\pm0.07$ MHz. The ν_0 agrees with that of Table I (92.79 ± 0.05 MHz) deduced from the $(\frac{1}{2},-\frac{1}{2})$ transitions. Using ν_{zz} and $\Delta_2\nu$ in Eq. (3), we calculate $\nu_Q=31.46\pm0.07$ MHz for the narrow NMR line.

From the $\Delta_2\nu$ of the broad line (1.3 ± 0.2 MHz) one can place limits on where its $(\pm\frac{1}{2},\pm\frac{3}{2})$ lines may be. Using these limits we searched for and found these transitions (Fig. 5). The central dip at 92.20 ± 0.03 MHz agrees with ν_0 of Table I, indeed greatly increasing the precision with which we know ν_0 and thus K_{zz}. The two peaks above and below ν_0 (at 92.05 ± 0.03 MHz and 92.32 ± 0.03 MHz) give $|\nu_{zz}|$ as 0.15 ± 0.08 MHz, but the length of the tail clearly visible on the low-frequency side suggests a fairly broad distribution of values of $|\nu_{zz}|$, perhaps reflecting crystal imperfections. Using $\Delta_2\nu$ and ν_{zz}, we calculate ν_Q of the broad NMR line to be 22 ± 2 MHz. We find $K_{zz}=0.52\pm0.03$ MHz (0.56 ± 0.03%).

The site symmetry is given by the three components of the field gradient tensor. For the narrow line we calculate them from ν_{zz}, $\Delta_2\nu$, and the sum rule ($\sum\nu_{\alpha\alpha}=0$). For the broad line we use ν_{zz}, together with $\nu_Q=22.07\pm0.05$ MHz from our NQR measurements on powder samples, plus the sum rule. We find the components (ν_{xx}, ν_{yy}, ν_{zz}) to be

$$\text{narrow line } (\nu_Q=31.5\text{ MHz}):\ \pm(15.8\pm3.7,\ 15.8\mp3.7,\ -31.46\pm0.07)\text{ MHz},$$

$$\text{broad line } (\nu_Q=22.0\text{ MHz}):\ \pm(19.0\pm0.1,\ -19.2\mp0.1,\ 0.15\pm0.08)\text{ MHz}.$$

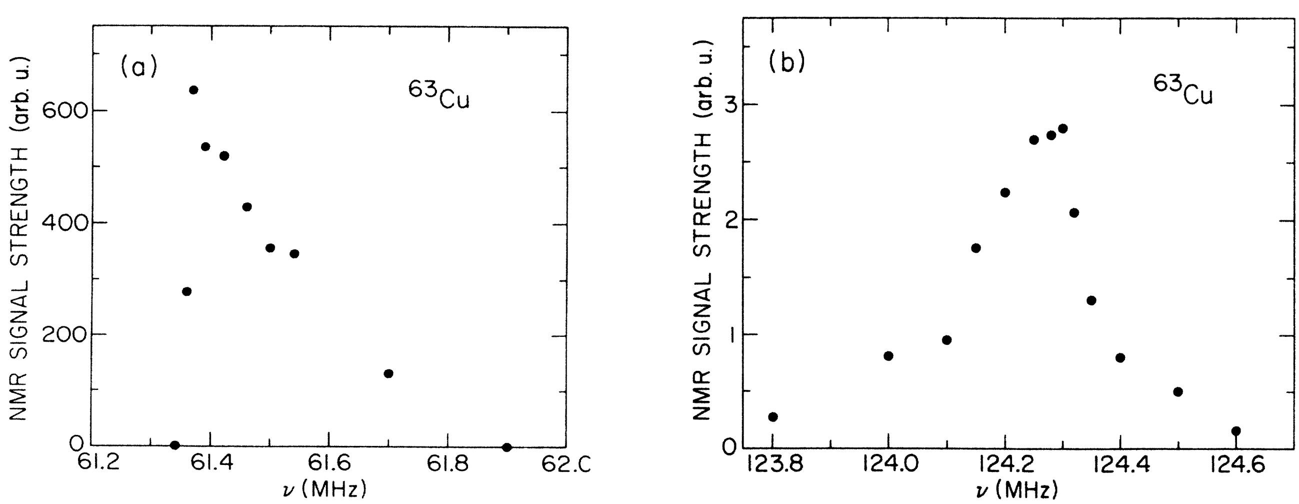

FIG. 4. ^{63}Cu NMR line shape of the (a) lower and (b) upper transitions corresponding to the "narrow line." Plotted is the integral of the spin echo vs oscillator frequency. 1 000 000 echoes have been averaged for each point.

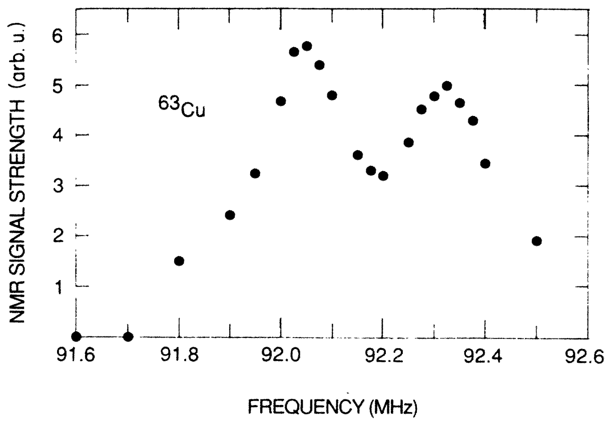

FIG. 5. ^{63}Cu NMR line shape of the $\frac{3}{2},\frac{1}{2}$ and $-\frac{3}{2},-\frac{1}{2}$ transitions corresponding to the "broad line." Plotted is the integral of the spin echo vs oscillator frequency. Approximately, 500000 echoes have been averaged for each point.

The narrow line ($\nu_Q = 31.5$ MHz) is essentially axially symmetric about the z axis (crystal c direction). Only the plane site could exhibit this symmetry. We thus identify the narrow NMR line with its ν_Q of 31.5 MHz as arising from the plane sites. The intensity ratio of 2.2 ± 0.7 of the narrow line to the broad line (Table I) is consistent with the assignment since there are twice as many plane as chain sites.

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