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Copper nuclear quadrupole resonance in $GdBa_2Cu_3O_7$: Determination of site assignment

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We have measured the copper nuclear relaxation rate in $GdBa_2Cu_3O_7$ in zero applied field using nuclear quadrupole resonance. Fluctuations in the $4f$ moment associated with the gadolinium contribute strongly to the copper relaxation rate, and this contribution will depend strongly on the copper-gadolinium separation. This separation differs considerably for the two copper sites. Comparison of the relaxation rates shows that the copper signal at the higher frequency (32 MHz) originates from the Cu(2) site, which is located closer to the gadolinium than is the Cu(1) site.

The discovery of superconductivity at temperatures above 90 K in the yttrium-based copper oxides[1] has stimulated much study of the properties of $YBa_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O). Copper nuclear quadrupole resonance (NQR) has been a very effective tool in exploring the electronic properties of Y-Ba-Cu-O both above and below the superconducting transition temperature T_c. Copper occupies two distinct sites in the Y-Ba-Cu-O crystal, the so-called chain or Cu(1) site and the plane or Cu(2) site (see Fig. 1). ^{63}Cu nuclear quadrupole resonances have been observed at two distinct frequencies, 22.0 and 31.5 MHz, corresponding to these two Cu sites. A major problem to be addressed is the identification of which NQR resonances correspond to the chain and plane copper sites, respectively. This will allow the study of the behavior at the two sites separately. The spin-lattice relaxation rates $1/T_1$ for the two resonances[2(a),3,4] show completely different temperature dependences both above and below the superconducting transition temperature T_c (see Fig.

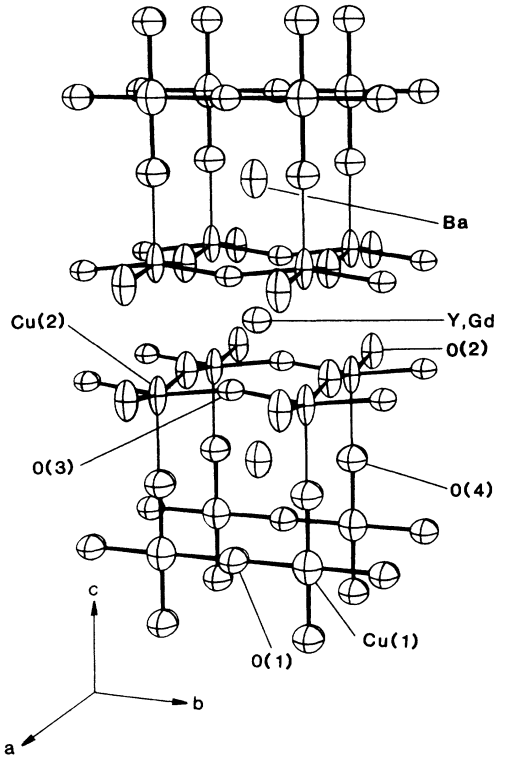

FIG. 1. The crystal structure of $RBa_2Cu_3O_{7-\delta}$ (R=Y, Gd). Note the large difference in the Cu(1)-Gd and the Cu(2)-Gd separation. The $YBa_2Cu_3O_{7-\delta}$ crystal structure shown is due to Ref. 17.

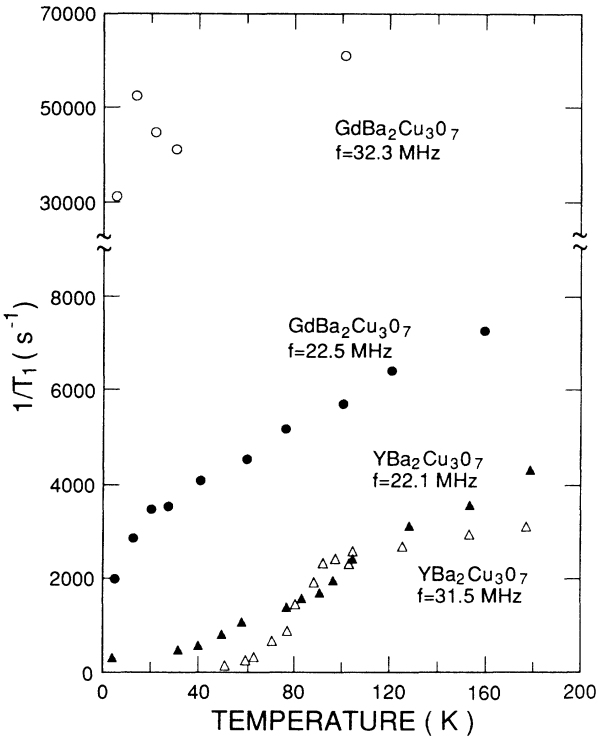

FIG. 2. Spin-lattice relaxation rates ($1/T_1$) for $GdBa_2Cu_3O_7$ (this work) and $YBa_2Cu_3O_{7-\delta}$ (Ref. 2) as a function of temperature. Note the break in the vertical axis. The temperature-independent contribution to the relaxation rate due to the gadolinium $4f$ electronic moment is evident. In $GdBa_2Cu_3O_{7-\delta}$, this contribution is 18 times larger for the 32 MHz signal than for the 22 MHz signal, demonstrating that the 32 MHz signal originates from the Cu(2) site which is much closer to the gadolinium. In Gd-Ba-Cu-O, $1/T_1$ at 32.3 MHz is shown by open circles and at 22.5 MHz by closed circles, in Y-Ba-Cu-O at 31.5 MHz by open triangles and at 21.5 MHz by closed triangles.

2). At 31.5 MHz $1/T_1$ shows a weak temperature dependence above T_c, while it decreases rapidly below T_c, indicating the presence of a large superconducting energy gap. In contrast, $1/T_1$ for the 22 MHz signal displays behavior above T_c close to that described by the Korringa[5] law. Furthermore, the rapid decrease in $1/T_1$ below T_c seen at 31.5 MHz is not observed at 22.0 MHz. Thus the assignment of the NQR signals to the correct copper sites is critical to the interpretation of any resonances data.

Several measurements which bear on this question have been reported, but conflicting conclusions have been drawn. Through analysis of the NMR spectrum of Y-Ba-Cu-O (in single crystals[6] and magnetically aligned powders[7]) in a large applied magnetic field, the electric field gradients at the two copper sites have been determined. Comparison of the experimentally determined values with the expected symmetry of the two sites[6] and calculated values[7] has led to the identification of the higher-frequency NQR line with the plane, or Cu(2) sites. Measurements of copper relaxation rates in $SmBa_2Cu_3O_{7-\delta}$ and $NdBa_2Cu_3O_{7-\delta}$ (Ref. 8) similar to those reported here also support this assignment.

Several arguments supporting the opposite assignment have also been presented. One is based on the relative intensities of the two NQR lines. Reported measurements have provided evidence in agreement with[3] and opposing[9-11] the assignment of the 31.5 MHz signal to the Cu(2) site. The ratio of the intensities of the two lines should, in principle, reflect the fact that the occupancy of the Cu(2) site is twice that of the Cu(1) site. However, the intensities and linewidths of the NQR signals are considerably affected by disorder and impurities. (There has been considerable variation in the NQR linewidths reported, presumably reflecting differences in the samples measured.) Because these effects can differ for the two copper sites they can complicate a comparison of the signal intensities.

A second argument[2(a)] opposing the assignment of the 31.5 MHz NQR line to the Cu(2) site is based on a comparison of the temperature dependence of $1/T_1$ for the 22 MHz line to that of ^{89}Y above T_c. $1/T_1$ of the 22 MHz line roughly obeys the Korringa law ($T_1T=0.05$ sec K), while for the 31.5 MHz signal $1/T_1$ is only weakly temperature dependent. The ^{89}Y relaxation rate[12] also obeys the Korringa law ($T_1T=4600$ sec K). Warren *et al.*[2(b)] argue that the same carriers must be responsible for relaxation of both the Cu(2) and the ^{89}Y nuclei, and, therefore, that they will have the same temperature dependences. While suggestive, this argument is not conclusive without a detailed understanding of the relaxation processes for the Cu(2) and the Y nuclei (particularly in view of the large differences in the magnitude of the Korringa constants). We also note that below T_c, the temperature dependence of the relaxation rate for the 31.5 MHz signal is much more similar to that of the ^{89}Y which would argue for the opposite site assignment.

In order to unambiguously identify the resonance frequency corresponding to the copper plane site, we have measured copper nuclear spin-lattice relaxation rates in $GdBa_2Cu_3O_{7-\delta}$ (Gd-Ba-Cu-O) by NQR in zero applied field. The substitution of gadolinium for yttrium leaves both the structure and the T_c virtually unchanged. However, unlike yttrium, gadolinium possesses a $4f$ electronic moment. Fluctuations in the orientation of the electronic moment contribute to the copper nuclear spin-lattice relaxation rate through a dipolar coupling between the copper nuclear moment and the $4f$ electronic moment. Well above the ordering temperature (the gadolinium moments order antiferromagnetically at 2.24 K),[13] the contribution to $1/T_1$ from the $4f$ moment is expected to be temperature independent and roughly proportional[14] to $\Sigma 1/r_j^6$, where r_j is the distance from the given copper site to the jth gadolinium site. Thus, the signal showing the larger temperature-independent contribution to the relaxation rate in Gd-Ba-Cu-O can be unambiguously identified with Cu(2) nuclei which are situated much closer to the gadolinium (see Fig. 1). We find that the higher-frequency line satisfies this criterion and thus identify the 31.5 MHz line in Y-Ba-Cu-O with the plane-Cu(2) site.

A polycrystalline sample of Gd-Ba-Cu-O was made by the standard solid-state reaction method in the form of a pressed pellet which was then ground into powder for the NQR measurement. The powder had a transition temperature of 94 K and showed nearly complete flux exclusion at 4 K. The nuclear relaxation rate was measured by recording the intensity of the spin echo signal after a single saturating pulse. In Fig. 3, we show spectra for the two ^{63}Cu resonances. Not surprisingly, the resonances are shifted slightly from their values in the Y-Ba-Cu-O (22.07 MHz→ 22.5 MHz and 31.5 MHz→ 32.3 MHz). The spectra for both NQR signals were unaffected by the ordering of the gadolinium moments. This is consistent with the antiferromagnetic structure determined by neutron scattering[15] since this structure results in a dipole field which exactly cancels at both copper sites. This observation assures us that the resonances observed originate from copper nuclei in Gd-Ba-Cu-O as opposed to a spurious included phase. A spectrum of the 22.5 MHz line was taken at 100 K. There was no change in either signal upon cooling through the superconducting transition other

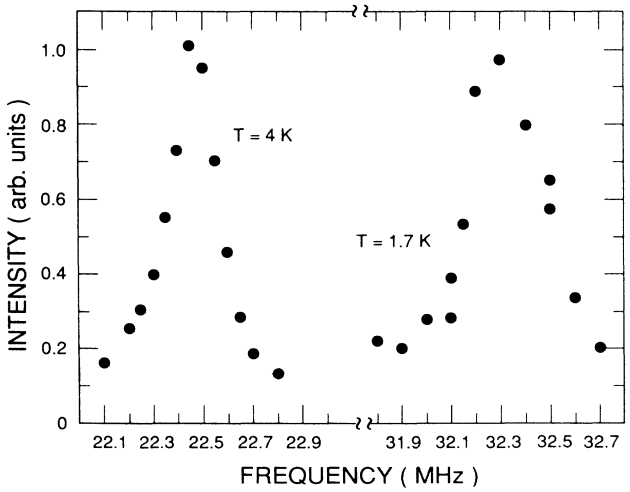

FIG. 3. ^{63}Cu spin-echo spectrum for $GdBa_2Cu_3O_{7-\delta}$ in zero applied field. The spectrum does not change upon cooling below $T_N=2.24$ K.

than the expected reduction of signal intensity due to flux exclusion.

We can write the copper relaxation rate in Gd-Ba-Cu-O, $(1/T_1)_{Gd}$, as the sum of a term, $(1/T_1)_Y$, which results from processes present in both the yttrium and gadolinium compounds and a term, $(1/T_1)_{4f}$, representing the contribution due to the dipolar coupling to the gadolinium moment: $(1/T_1)_{Gd}=(1/T_1)_{4f}+(1/T_1)_Y$. In Fig. 2, we show $(1/T_1)_{Gd}$ for both resonances along with the corresponding rates[2(a)] for Y-Ba-Cu-O. The contributions due to the $4f$ moment is quite evident. Above 20 K, this contribution is temperature independent, but it is suppressed at lower temperatures. This supression can be understood as the effect of short-range order among Gd moments because the dipolar fields in the ordered structure cancel at the copper sites. The magnitude of the temperature-independent $4f$ contribution to the relaxation of the 22.5 MHz resonance is 2.8×10^3 sec^{-1}. The uncertainty in $1/T_1$ at 32.3 MHz is probably $\pm30\%$ but the suppression of the relaxation at low temperatures is evident here as well. At 32.3 MHz, the $4f$ contribution to the relaxation rate is approximately $(1/T_1)_{4f}=5(\pm1)\times10^4$ sec^{-1}. The ratio of the two hyperfine rates is 18 ± 3.

The contribution from the (uncorrelated) $4f$ local moments to NQR relaxation rate well above T_N is[14]

$$\left[\frac{1}{T_1}\right]_{4f}=\frac{2\sqrt{2\pi}}{3}\frac{\gamma_n^2(g\mu_B)^2}{\omega_{ex}}S(S+1)\sum_j\frac{f(\alpha_j,\beta_j,\gamma_j,\eta)}{r_j^6}, \tag{1}$$

where $\gamma_n=2\pi\times1.1285\times10^3$ (sec^{-1}Oe^{-1}) is the ^{63}Cu gyromagnetic ratio, μ_B the Bohr magneton, $S=\frac{7}{2}$, $g=2$, and ω_{ex} is the exchange frequency of the $4f$ moments. $f(\alpha_j,\beta_j,\gamma_j,\eta)$ is a geometrical factor which depends on α_j, β_j, and γ_j, the direction cosines of r_j connecting the copper to the jth gadolinium site with respect to the principal axes, **x**, **y**, and **z**, of the electric field gradient (see Appendix). The asymmetry factor η is given by $\eta=(V_{xx}-V_{yy})/V_{zz}$. We follow the convention that $|V_{zz}|\geq|V_{yy}|\geq|V_{xx}|$. When $\eta=0$ it can be shown that $f=\frac{3}{4}(5-3\gamma_j^2)$.

Without including information about the largest field gradient and η, f_j cannot be calculated exactly. However, f_j depends on these quantities fairly weakly so we will make the arbitrary choice of $\eta=0$ for both sites and take an average over the directions of the largest field gradient. In this case, f_j is 3. [To verify the very weak dependence of the relaxation rates on the details of the electric field gradient, we calculate f_j using the gradient parameters determined by the high-field measurements.[6,7] In this case, the calculated relaxation rate $1/T_1$ for the Cu(2) sites is increased by 4% and $1/T_1$ for the Cu(1) sites is reduced by 7%.] The lattice sum is calculated from the known values of the crystal structure[15] to be

$$\sum 1/r_j^6=\begin{cases}1.79\times10^{44}\,\text{cm}^{-6}, & \text{Cu(1)},\\ 3.71\times10^{45}\,\text{cm}^{-6}, & \text{Cu(2)}.\end{cases}$$

We can estimate ω_{ex} by including only nearest-neighbor interactions among gadolinium moments in the *ab* plane:[10]

$$\omega_{ex}^2=\frac{2}{3}\left[\frac{J}{\hbar}\right]^2ZS(S+1),$$

where Z, the number of nearest neighbors, is 4. The magnitude of the exchange interaction J can be estimated from the Néel temperature ($T_N=2.24$ K)[13] by the mean-field relation[16]

$$T_N=\frac{|J|ZS(S+1)}{3k_B}.$$

These relations give $\omega_{ex}=0.91\times10^{11}$ sec^{-1} and $(1/T_1)_{4f}$ at each site can be calculated to be

$$(1/T_1)_{4f}=\begin{cases}2.7\times10^3\,\text{sec}^{-1}, & \text{Cu(1)},\\ 5.6\times10^4\,\text{sec}^{-1}, & \text{Cu(2)}.\end{cases}$$

Comparison of the measured with the calculated rates is reassuring: the ratio of the rates agrees with that expected from the lattice sums which are based on *well-known parameters* and the magnitude of the rates are in quite reasonable agreement with calculated values. The $4f$ contribution to the relaxation rate for the 32.3 MHz signal is approximately 18 (±3) times larger than for the 22.5 MHz signal. We can then clearly identify the higher-frequency resonance as originating from the Cu(2) site which is much closer to the gadolinium moment. This identification is based upon a simple geometrical argument, and so is relatively free of the ambiguity present in some of the reported site assignments. Thus, the identification of the higher frequency resonance with the Cu(2) site in Y-Ba-Cu-O is clear.

Note added in proof. Y. Kitaoka *et al.* and H. Lütgemeier reported in *Proceedings of the International Conference on High-T_c Superconductors: Materials and Mechanisms of Superconductivity, Interlaken, Switzerland, 1988,* edited by J. Müller and J. L. Olsen [Physica C (to be published)] that they have made measurements in Gd-Ba-Cu-O which lead them to the same site assignment as we report here.

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APPENDIX

The eigenstates of nuclear spin $\frac{3}{2}$ in an asymmetric field gradient are generally expressed as

$$|a\rangle=\alpha|\tfrac{3}{2}\rangle+\beta|-\tfrac{1}{2}\rangle,$$
$$|b\rangle=-\beta|\tfrac{3}{2}\rangle+\alpha|-\tfrac{1}{2}\rangle,$$
$$|a'\rangle=\alpha|-\tfrac{3}{2}\rangle+\beta|\tfrac{1}{2}\rangle,$$
$$|b'\rangle=-\beta|-\tfrac{3}{2}\rangle+\alpha|\tfrac{1}{2}\rangle,\ \alpha^2+\beta^2=1.$$

On the right-hand side of these equations, the state $|m\rangle$ denotes the state with $I_z = m$, z being parallel to the direction of the largest field gradient. $|a\rangle$ and $|a'\rangle$ are degenerate as are $|b\rangle$ and $|b'\rangle$. The coefficients α and β are determined by the asymmetry factor η. By calculating the transition probabilities between these eigenstates caused by the dipolar interaction it is easily shown that f_j in Eq. (1) is

$$f_j(\alpha_j,\beta_j,\gamma_j,\eta) = \left[\frac{\sqrt{3}}{2}(\alpha^2-\beta^2)+\alpha\beta\right]^2(3\alpha_j^2+1)+\left[\frac{\sqrt{3}}{2}(\alpha^2-\beta^2)-\alpha\beta\right]^2(3\beta_j^2+1)+4\alpha^2\beta^2(3\gamma_j^2+1)\,.$$

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