Anisotropic ^{63}Cu nuclear relaxation in magnetically oriented powdered samples of $YBa_2Cu_3O_7$

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Planar-site ^{63}Cu nuclear spin-lattice relaxation data are presented for a magnetically oriented sample of $YBa_2Cu_3O_7$ microcrystallites at temperatures 86 K $\leq T \leq$ 290 K and with the collective c axis at $\theta=0$ and $\pi/2$ relative to the applied field. These results yield a relaxation anisotropy in good agreement with previous data obtained with random powders. The anisotropy exhibits a small temperature dependence, suggesting the presence of dynamical correlations among the Cu(2) $3d$ spins.

Recently we reported[1] nuclear-magnetic-resonance (NMR) measurements on ^{63}Cu(2) (planar site) nuclei in $YBa_2Cu_3O_{7.0}$ (Y-Ba-Cu-O) which revealed that the spin-lattice relaxation rate T_1^{-1} is highly anisotropic, being $\sim$3.5 times greater with the quantization axis in the a-b plane then when it is along the c axis. The observations were limited to temperatures T in the range 100 K $\leq T \leq$ 300 K, and the anisotropy effect was found to be T independent within broad error limits. In this Brief Report we present a greatly refined and more accurate study of relaxation anisotropy covering the same temperature range, confirming our earlier value of the anisotropy and revealing that it has a barely resolved, but distinct temperature dependence. These improved data were obtained using magnetically oriented crystalline samples,[2,3] which offer NMR resolution within a factor 2 of the twinned crystalline materials[4] with an advantage in signal strength approaching 2 orders of magnitude.

Oriented crystallite samples were prepared from high-quality single-phase ceramic starting material prepared by the usual solid-state reaction methods. The source material gave a Meissner intercept of 89 $\pm$ 1 K and a Cu(2)-site nuclear-quadrupole-resonance (NQR) line at 31.5 MHz with a width $\Delta\nu\sim$300 kHz, both results characteristic of the best material reported.[5,6] The ceramic was ground in an agate mortar until the resulting powder consisted almost entirely of crystallites having average diameters $d \lesssim 25$ μm. The material is then mixed with a clear epoxy, loaded into a teflon sample container, inserted into the NMR probe, and placed in position in a field of 7.5 T to cure. Single crystallites are known to align with the c axis parallel to the field under these conditions.[2,3] Figure 1(b) shows the resulting NMR spectrum for field along the c axis ($\theta=0$) in the vicinity of the ^{63}Cu(2) $m=\pm\frac{1}{2}$ transition, which gives the tall narrow peak at 74.25 kG. The width of the peak is twice that observed with larger hand-oriented crystals.[4] That result, along with the absence of background intensity in Fig. 1(b), shows that a remarkable degree of orientation is achieved with this method.

The smaller line in Fig. 1(b) is the ^{63}Cu(1) resonance arising from the $(\frac{1}{2},\frac{3}{2})$ and $(-\frac{1}{2},-\frac{3}{2})$ transitions, which are nearly degenerate because of the accidental vanishing of the c-axis electric-field-gradient component.[7] For this line we estimate a full width of $\sim$450 kHz, comparable to that obtained with hand-oriented crystals.[4]

In Fig. 1(a) we show the ^{63}Cu(2) ($m=-\frac{1}{2},\frac{1}{2}$) resonance peak at $\theta=\pi/2$, which undergoes a quadrupolar shift to lower field and at FWHM $\sim$200 G is slightly broader than its $\theta=0$ counterpart in Fig. 1(b). The $\theta=\pi/2$ peak also exhibits a small misorientation smear on the high-field side. By confining our T_1 measurements to the peak intensity, we select crystallites with good $\theta=\pi/2$ orientation.

T_1 measurements on planar ^{63}Cu nuclei have been carried out at $\theta=0$ and $\pi/2$ over a temperature range 100 K $\leq T \leq$ 290 K at an NMR frequency $\nu=85$ MHz. Relax-

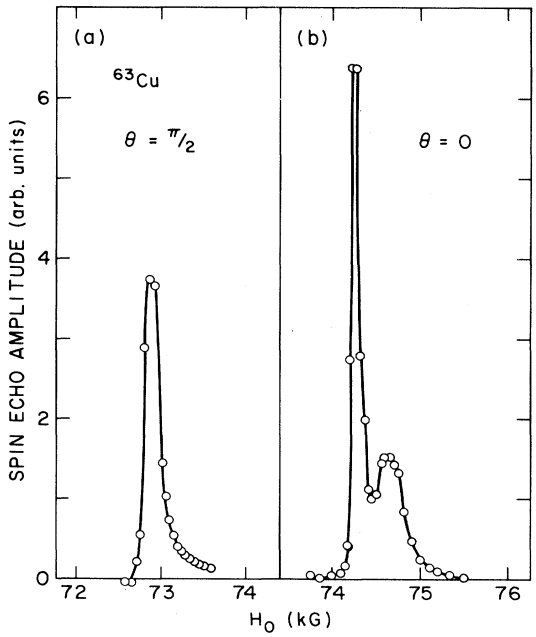

FIG. 1. Spectra of ^{63}Cu NMR spin-echo amplitudes taken at room temperature on a magnetically ordered powder sample of Y-Ba-Cu-O prepared as described in the text. (a) With c axis perpendicular to the applied field, the Cu(2)-site peak exhibits second-order quadrupolar shift to lower field. (b) With c axis parallel to the applied field. The Cu(2)-site peak is slightly overlapped by the "satellite" peaks from the Cu(1) site, which have a nearly vanishing quadrupole splitting.

ation data were obtained by measuring the spin-echo amplitude recovery following an inversion pulse. For a pulse which drives the $(m=-\frac{1}{2},\frac{1}{2})$ transition only, the signal recovery is given quite generally for magnetic dipole relaxation by

$$S(t)=S_{eq}-A[9\exp(-6t/T_1)+\exp(-t/T_1)], \quad (1)$$

where S_{eq} is the equilibrium signal amplitude and A is a parameter depending on the excitation pulse. For excitation with an exact π pulse $A=0.2S_{eq}$. Note that for NMR the "odd" mode with decay rate $3T_1^{-1}$ does not occur in $(m=-\frac{1}{2},\frac{1}{2})$ transition dynamics,[1] but is exclusively involved in the NQR T_1 process.[6]

Spin-echo recovery data were least-squares fitted to Eq. (1) as written as well as to a modified form where the coefficients of the two exponentials were both allowed to vary. The results of these two procedures agreed to well within the stated errors. T_1 values obtained with this scheme are plotted versus temperature T in Fig. 2 for $\theta=0$ and $\pi/2$. Data for these two orientations are plotted on separate amplitude scales, adjusted so as to make the T_1 curves coincide in the range $100\ \text{K}\leq T\leq 150$ K. The relative scale factor for the two orientations is 3.56, in good agreement with our previous data.[1] At the highest temperatures this simple scaling relationship breaks down noticeably, with the ratio of T_1's falling lower than 3.56. The significance of this effect is discussed below.

We note several other points about the data in Fig. 2.

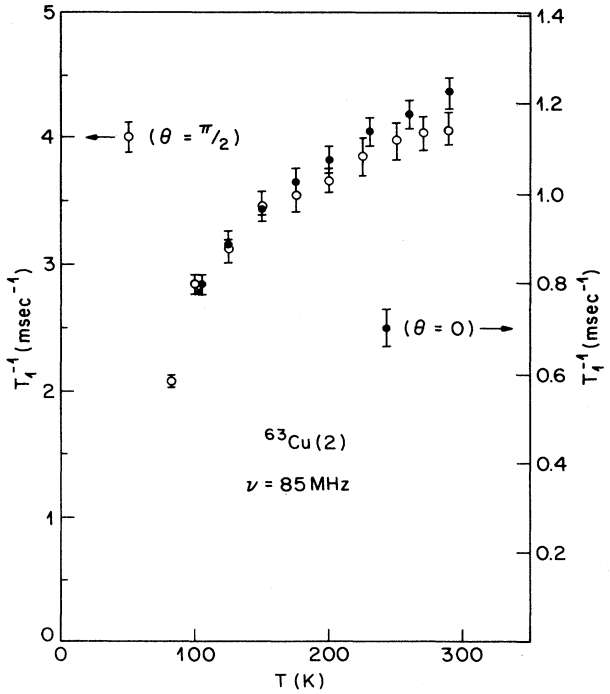

FIG. 2. ^{63}Cu(2) T_1 data for $\theta=0$ and $\pi/2$ plotted vs temperature T, where θ is the angle between the c axis and the applied field. Data are scaled to coincide for $100\ \text{K}\leq T\leq 150$ K. An NQR measurement of T_1 at $T=102$ K for this specimen is shown as an asterisk, in excellent agreement with the NMR value.

(1) The $\theta=0$ data are in good agreement with NQR T_1 data on this compound which have been previously reported.[8-10] (2) The NQR T_1 value for ^{63}Cu(2) ($\nu=31.5$ MHz) for this sample was measured at $T=100$ K and is seen (Fig. 2) to be in good agreement with the NMR value. (3) The NMR T_1 value was also measured below T_c ($T=86$ K) for $\theta=\pi/2$. The decline in T_1^{-1} relative to its value at $T=100$ K is similar to that found for NQR.[8,10]

The anisotropy of T_1 was discussed earlier[1] in terms of the conventional theory of relaxation by itinerant d electrons[11] assuming isotropic spin dynamics. The latter approach failed to give a satisfactory account of the data. Moreover, the T_1 anisotropy effect, which corresponds to a larger fluctuating hyperfine field along the c axis than in the a-b plane, was in apparent conflict with low-temperature NMR shift measurements,[3] which yield a vanishingly small static (spin) hyperfine interaction along the c axis. The answer to this seeming paradox is the presence of multiple (i.e., two or more) separate hyperfine terms which nearly cancel under uniform polarization, but which fluctuate either independently or with correlations (e.g., antiferromagnetic) which enhance the relaxation process.

A model hyperfine Hamiltonian which incorporates these features has been proposed by Mila and Rice.[12] By incorporating terms which couple the four nearest-neighbor Cu(2) spins and the neighboring Cu(1)-site spin to a given Cu(2)-site nucleus, in addition to the on-site spin hyperfine coupling, these authors have apparently reconciled the anisotropic spin and orbital shift data[1,3,13] with the observed T_1 anisotropy. Their treatment is based on a local-moment spin-Hamiltonian[14] viewpoint for the description of the (Cu^{2+}) hole state on the copper site. This is an approximation, however, because the Cu^{2+} d hole is in fact itinerant. As emphasized by these authors, the d-hole spins at the Cu(2) sites become paired at $T\ll T_c$.[15] The transferred hyperfine fields are presumed to arise through covalent admixture effects as in nonmetallic systems. Interestingly, the magnetic hyperfine Hamiltonian they derive for the 90-K superconductor also gives a reasonable account of the Cu(2)-site antiferromagnetic nuclear resonance frequencies in the insulating antiferromagnetic $YBa_2Cu_3O_6$.[16]

In the Mila-Rice treatment, the relaxation rate T_1^{-1} is given in terms of spin autocorrelation as well as first- and second-neighbor pair correlation functions. The spin-autocorrelation terms alone suggest a T_1 anisotropy slightly larger[12] than given by the data of Fig. 2. The latter data strongly suggest, however, that the pair correlation terms are important, because the T_1 anisotropy is temperature dependent. In this model, such a temperature dependence can only arise from that of the dynamical pair correlations. T_1 analysis based on the fluctuation-dissipation theorem[1] also suggests antiferromagnetic correlations.

To examine this point further, we evaluate the relaxation rate expression given for Cu(2) nuclei [Eq. (30) and (31) of Ref. 12], neglecting the $B_1(2)$ terms and assuming that correlations between mutually orthogonal spin components are also negligible. Further, we assign the same

correlation time τ to all terms and assume $\omega_{\mathrm{NMR}}\tau \ll 1$. The ratio of T_1 rates for $\mathbf{H}_0$ in the a-b plane and along the c axis is thus

$$\frac{(T_1^{-1})_{ab}}{(T_1^{-1})_c} = \frac{4.89 - 7.28\langle \mathbf{S}_0 \cdot \mathbf{S}_1 \rangle + 2.67\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle}{1 + 0.31\langle \mathbf{S}_0 \cdot \mathbf{S}_1 \rangle + 2.67\langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle} \quad (2)$$

in the subscript notation of Ref. 12. Since one expects $\langle \mathbf{S}_0 \cdot \mathbf{S}_1 \rangle < 0$ and $|\langle \mathbf{S}_0 \cdot \mathbf{S}_1 \rangle| > \langle \mathbf{S}_1 \cdot \mathbf{S}_2 \rangle > 0$, it is clear that Eq. (2) will give a ratio of T_1 rates rather larger than the experimental value of 3.56 in the limit of strong correlations. Considering the approximations of the model and uncertainties in the data used to determine its parameters, we regard the agreement with our present T_1 anisotropy data to be satisfactory. In terms of Eq. (2), the temperature dependence of the relaxation anisotropy effect seen in Fig. 2 is interpreted to mean that the pair correlation terms are themselves temperature dependent over this range. The trend of decreasing T_1 anisotropy with increasing temperature is at least consistent via Eq. (2) with a concomitant decrease in the strength of the correlations. A quantitative estimate of these correlations will clearly have to wait for a more accurate formulation of the problem as well as more extensive data.

In summary, magnetically oriented finely powdered ceramic samples of Y-Ba-Cu-O give NMR linewidths comparable to those obtained with hand-oriented twinned crystals. An accurate determination of the T_1 anisotropy for Cu(2) sites yields a low-temperature value smaller by $\sim 25\%$ than predicted by the Mila-Rice hyperfine tensor. The data show a distinct trend of decreasing anisotropy with increasing temperature (i.e., decreasing spin correlation), which is consistent with the formulation of the T_1 anisotropy given by these authors.

Note added in proof. As an alternative to the Mila-Rice picture, the temperature-varying anisotropy could be produced by the superposition of the two relaxation processes with disparate temperature dependences and anisotropies.

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[15] Clear evidence for this comes from the asymptotic vanishing of the intrinsic nuclear relaxation process at low temperatures.

[16] In the notation of Ref. 12 the Cu(2)-site hyperfine field is given by $H_f^{(2)} = 2[A^{ab}(2) = 4B(2)]\langle S_x \rangle$. From spin-wave theory we take $\langle S_x \rangle \sim 0.60S = 0.30$ for the $S = \frac{1}{2}$ antiferromagnetic ground state. With parameter values given in Ref. 12, one finds $H_f^{(2)} = -94.9$ kG. The value $|H_{f(\mathrm{exp})}^{(2)}| = 79.7$ kG has been reported by H. Yasuoka *et al.*, J. Phys. Soc. Jpn. **57**, 2659 (1988).