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Temperature-dependent anisotropy of Cu(2) nuclear-relaxation rate in $YBa_2Cu_3O_7$ below T_c

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We have measured the anisotropy of the Cu(2) nuclear-spin–lattice relaxation rate in the superconducting state of $YBa_2Cu_3O_7$ in a small magnetic field (0.44 T) and the temperature range 30–210 K. The anisotropy is almost temperature independent in the normal state but develops a nonmonotonic temperature dependence below T_c with a minimum near 70–80 K. The isotopic ratio of the relaxation rates shows that the nuclear relaxation is due to magnetic processes in this temperature range, although an extrinsic quadrupolar relaxation process appears below 30 K.

Nuclear-magnetic resonance[1–9] (NMR) and neutron-scattering[10–13] experiments have clarified the existence of antiferromagnetic (AF) dynamical spin correlations in the normal state of high-temperature superconductors. It is important to know how these AF correlations are affected by superconductivity. Hammel *et al.* observed that the ratio of the nuclear relaxation rate (W) at the Cu(2) site to that at the O(2,3) site in $YBa_2Cu_3O_7$ is independent of temperature below 120 K.[5] This suggests that the AF correlations, which grow with decreasing temperature, cease to grow around 120 K and remain unchanged in the superconducting state.

Recently, Barrett *et al.* reported that the anisotropy of W at the Cu(2) site in $YBa_2Cu_3O_7$ is only weakly temperature (T) dependent in the normal state but develops a significant T dependence below T_c and discussed the possibility that the spin fluctuations become anisotropic below T_c.[14] Most of their measurements were done at a relatively large magnetic field (8.1 T), which may introduce additional complications. For example, T_c at such a high field is different for different field directions and this field introduces a high density of vortices whose effect is also anisotropic. Barrett *et al.* measured the anisotropy in a weak field (0.446 T) at 77 K and reported that such field effects can be taken into account by using the reduced temperature scale $T/T_c(\mathbf{H})$.[14] In this paper, we report the T dependence of the anisotropy of the Cu(2) relaxation rate measured at a low enough field (0.44 T) to eliminate anisotropic effects of the magnetic field in a wider temperature range 30–210 K. Our results agree with Barrett *et al.* above 70 K but are significantly different at lower temperatures.

We performed NMR and nuclear-quadrupole resonance (NQR) measurements on a c-axis-oriented powdered sample imbedded in epoxy.[15] The sample exhibited a full shielding fraction with an onset $T_c=93$ K. Since the quadrupole splitting of the Cu(2) nuclear-spin levels is much larger than the Zeeman splitting for a small field, a special procedure is required to obtain the anisotropy of W correctly.

Figure 1 shows the frequency of various resonance lines as a function of (a) the magnetic-field applied parallel and (b) perpendicular to the c axis. For $\mathbf{H}\parallel c$, the nuclear spins are quantized along the c axis and the eigenstates are given by those of I_c, the c component of the nuclear spin, because the electric-field gradient (EFG) is symmetric around the c axis. In this case, the spin-lattice relaxation is caused only by the a and b components of the fluctuating hyperfine field $\mathbf{H}_{\rm hf}$, and the fundamental relaxation rate is given by

$$W_c=\frac{\gamma_n^2}{2}(J_a+J_b)=\gamma_n^2 J_a,\ \ J_a=\int_{-\infty}^{\infty}\langle H_{\rm hf}^a(t)H_{\rm hf}^a(0)\rangle dt\ , \tag{1}$$

where γ_n is the nuclear gyromagnetic ratio and we assume $J_a=J_b$. The actual measurements were done by recording the spin-echo intensity as a function of the delay-time t after a single saturating pulse, using either the NQR signal at zero external field or the ν_1 $(+\frac{1}{2}\leftrightarrow+\frac{3}{2})$ signal at a finite field (NMR). The delay-time dependence of the spin-echo signal is given by

$$M(t)=M_0(1-e^{-3W_ct})\ \ (\text{NQR})\ , \tag{2a}$$

$$M(t)=M_0(1-0.1e^{-W_ct}-0.5e^{-3W_ct}-0.4e^{-6W_ct})\ \ (\text{NMR})\ . \tag{2b}$$

The values of W_c obtained from NQR measurements in the temperature range 30–250 K agree quite well with the previous measurements.[4,14] The observed $M(t)$ is well fitted by Eq. (2a) above 30 K. At lower temperatures, however, a multiexponential behavior appears, which is evidence for inhomogeneous distribution of W_c caused by some kind of disorder.

In order to know the anisotropy of the hyperfine field fluctuations

$$R=J_c/J_a\ , \tag{3}$$

the value of J_c should be determined from the measurements with $\mathbf{H}\perp c$. Since the c component of $\mathbf{H}_{\rm hf}$ causes only the ν_3 transition when Zeeman frequency $\nu_0=\gamma_n H$ is much smaller than ν_Q (the zero-field NQR frequency), the ν_3 resonance must be monitored. The anisotropy of W in the high-field limit is given by $(1+R)/2$.

The value of R was determined as follows. Let $n_i(t)$ be

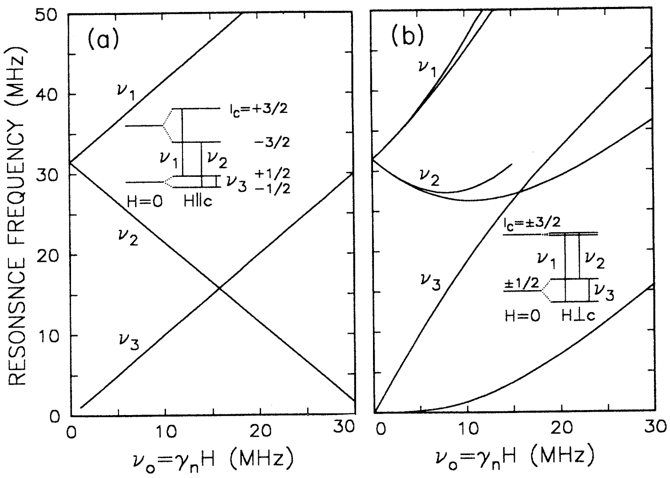

FIG. 1. Various resonance frequencies at the Cu(2) site are plotted against the Zeeman frequency with (a) the external-field parallel and (b) perpendicular to the c axis. The energy-level diagrams for both cases are also shown.

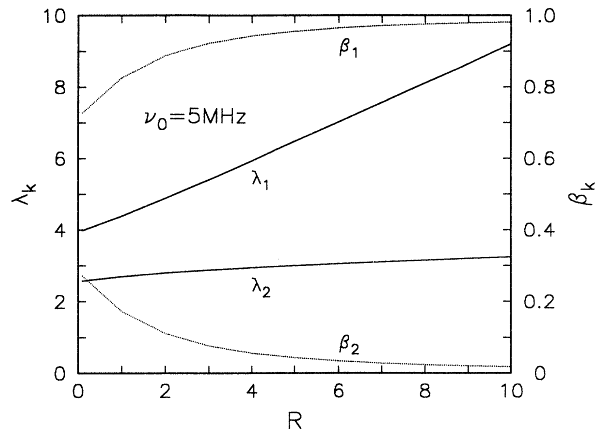

FIG. 2. Calculated R dependence of λ_k and β_k. The weight of the third component β_3 is almost zero ($<10^{-3}$) and not shown here.

the population of the ith eigenstate $|i\rangle$ of the nuclear-spin Hamiltonian for a magnetic-field perpendicular to the c axis. The transition probability Γ_{ij} from $|j\rangle$ to $|i\rangle$ is given by

$$\Gamma_{ij}=\gamma_n^2\sum_a J_a|\langle j|I_a|i\rangle|^2$$
$$=W_c(|\langle j|I_a|i\rangle|^2+|\langle j|I_b|i\rangle|^2+R|\langle j|I_c|i\rangle|^2)\,. \quad (4)$$

We then obtain the following rate equations

$$\frac{dp_i(t)}{dt}=\sum_{i\neq j}\Gamma_{ij}(p_i-p_j),\ p_i=n_i(t)-n_i^0\,, \quad (5)$$

where n_i^0 is the thermal equilibrium value of n_i. These equations are solved with the initial conditions,

$$p_1(0)=p_2(0)=0,\ p_3(0)=-p_4(0)=\tfrac{1}{2}\,, \quad (6)$$

for the present case of a single saturating pulse for the ν_3 resonance. The spin-echo intensity is proportional to $1-(p_3-p_4)$ and given in the form

$$p_3-p_4=\sum_{k=1}^{3}\beta_k\exp(-\lambda_k W_c t),\ \sum_{k=1}^{3}\beta_k=1\,. \quad (7)$$

Using the measured value of ν_Q (31.48 MHz at 100 K with a small T dependence), $\langle j|I_a|i\rangle$ is calculated numerically for a given value of the Zeeman frequency ν_0. Then β_k and λ_k are calculated as a function of R as shown in Fig. 2 for ν_0=5 MHz. As W_c is known from NQR or NMR measurements with H‖c, R can be determined from the requirement that the fitting of the H⊥c data to Eq. (7) gives the same value of W_c.

The T dependence of R, thus determined at H(⊥c) =0.44 T, is shown in Fig. 3. The two sets of data (solid and open circles) correspond to the values of W_c determined from zero-field NQR and small-field NMR (0.44 T) measurements, respectively. No appreciable discrepancy is seen between the two sets of data. We have done the same measurements at H(⊥c)=0.88 T and obtained the same values of R within the experimental error, which indicates that such a small magnetic-field perpendicular to the c axis has negligible effects.

The value of R is nearly T independent in the normal state (6.5±0.2 at 100 K) but decreases rapidly below T_c, in agreement with Barrett *et al.*[14] However, R shows a minimum at 70–80 K and increases again at lower temperature down to 30 K, which disagrees with the result by Barrett *et al.* obtained in a large magnetic field (8.1 T).[14]

We have also confirmed that the nuclear relaxation above 30 K is caused by magnetic processes by measuring the isotopic ratio of W_c. In Fig. 4, we show the ratio of W_c for two Cu isotopes obtained from NQR measurement. This ratio should be equal to the ratio of the squared-gyromagnetic ratio (1.147) for magnetic processes. But for quadrupolar processes (relaxation caused by the fluctuations of electric-field gradient), this should be the ratio of the squared-quadrupole moment (0.856). The relaxation process is almost purely magnetic above 30 K. However, the isotopic ratio decreases below 30 K, indicat-

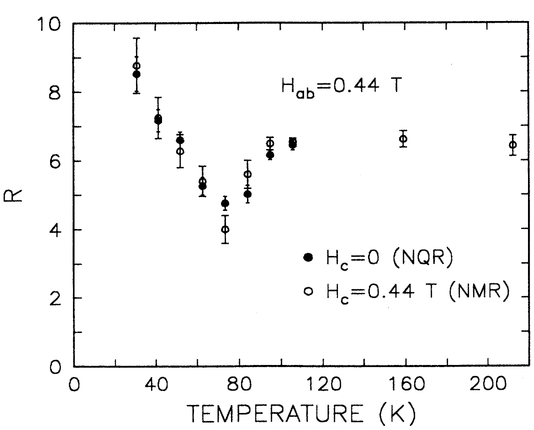

FIG. 3. Temperature dependence of R. The two sets of data correspond to the values of W_c determined from NQR and low-field NMR.

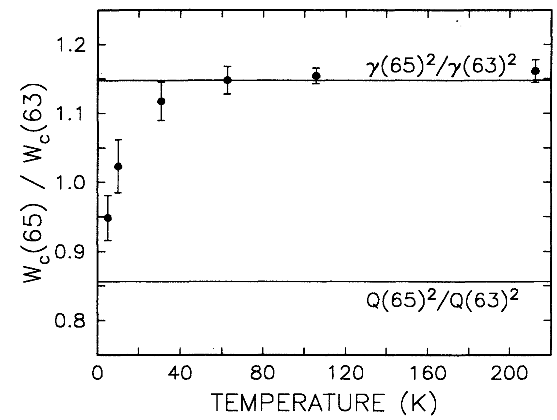

FIG. 4. Temperature dependence of the isotopic ratio of W_c. The ratios of the squared-gyromagnetic ratio and the quadrupole moment are also shown.

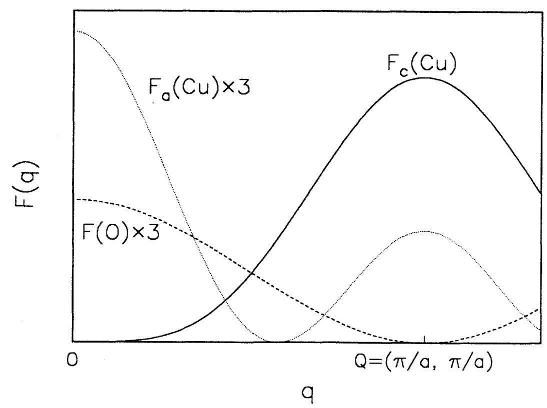

FIG. 5. The various form factors for the nuclear-relaxation rates are plotted as a function of the wave vector along the (q,q) direction.

ing that a quadrupolar process becomes dominant at lower temperatures. It should be noted that an inhomogeneous distribution of W_c is seen in the same temperature range, resulting in nonsingle-exponential recovery of $M(t)$. This suggests that the low-T quadrupolar relaxation is extrinsic and due to some kind of disorder.

A similar result has been reported by Kitaoka *et al.*[16] Imai *et al.* have discussed magnetic impurities as a possible source for the low-T extrinsic relaxation.[17] Our result shows that slow modulations of EFG, most likely caused by motion of oxygen or vacancies, are responsible for the low-T relaxation, even though ionic motion at such a low temperature is rather unexpected. Further efforts to obtain better stoichiometry may help to eliminate the extrinsic process and permit finding the intrinsic behavior down to lower temperatures.

We now discuss the possible implications of the T dependence of R. Generally, the nuclear-relaxation rate is determined from the hyperfine interaction and the dynamic spin susceptibility. The hyperfine interaction at the Cu(2) site in $YBa_2Cu_3O_7$, originally proposed by Mila and Rice[18] and widely used in subsequent works, takes the form

$$\mathcal{H}_{\rm hf}=\hbar\gamma_n\sum_{\alpha=a,b,c}I_\alpha H^\alpha_{\rm hf},\ \ H^\alpha_{\rm hf}=A_\alpha S_{0,\alpha}+B\sum_{j=1}^{4}S_{j,\alpha}\,, \qquad (8)$$

where A_α is the anisotropic on-site hyperfine coupling and B is the isotropic coupling to the nearest neighbor Cu spins. It should be emphasized that such an expression is strictly valid only for magnetic insulators. However, the Knight-shift results in $YBa_2Cu_3O_{7-y}$ with various oxygen content indicate that the hyperfine interaction does not change with doping,[6,7] and therefore, the ionic expression Eq. (8) is a good approximation. Then J_α is given by

$$J_\alpha=\sum_q F_\alpha(q)\frac{{\rm Im}\chi_\alpha(q,\omega)}{\omega}\,, \qquad (9)$$

where $F_\alpha(q)=[A_\alpha+2B(\cos q_x a+\cos q_x a)]^2$ is the form factor and $\chi_\alpha(q,\omega)$ is the dynamic susceptibility. The q dependences of F_a and F_c for the Cu(2) site are shown in Fig. 5 together with F(O) for the O(2,3) site. We made use of the fact that $A_c \simeq -4B$ derived from the Knight-shift measurement[19] and took $a=A_a/4B=0.25$. The F_c has a peak at the AF wave vector $Q=(\pi/a,\pi/a)$. The F_a has less weight at $q=Q$ than $q=0$ and F(O) vanishes at $q=Q$. Therefore AF correlations enhances R as well as W(Cu)/W(O). In fact, as pointed out by Monien, Pines, and Slichter[20] the value of R in the absence of AF correlations is given by $R=\sum F_c(q)/\sum F_a(q)=5/(4a^2+1)\leq 5$, which is smaller than the observed value in the normal state.

The initial decrease of R below T_c might be explained if the AF correlations are greatly lost below T_c. However, the almost T-independent ratio W_c(Cu)/W_c(O) gives strong evidence against the loss of AF correlations in the superconducting state.[5]

The T dependence of R could result if $\chi_\alpha(q,\omega)$ has a T-dependent anisotropy below T_c. In the long-range ordered antiferromagnetic states, a small XY anisotropy of the exchange interaction leads to an anisotropy in the spin-wave spectrum.[21] Although we do not expect such anisotropy to persist in the metallic phase, Rossat-Mignot *et al.* reported that, in the oxygen reduced $YBa_2Cu_3O_{7-y}$, ${\rm Im}\chi_a(Q,\omega)$ at a low temperature (5 K) decreases with increasing oxygen content more rapidly than ${\rm Im}\chi_c(Q,\omega)$ over a wide frequency range,[11] which may indicate anisotropy in $\chi(Q,\omega)$.

The upturn of R below 70 K is also hard to understand. Millis and Monien have suggested the existence of a second mechanism for nuclear relaxation, other than electronic spin fluctuations.[22] Since the relaxation rate due to electron spin is decreasing very rapidly below T_c, such a second process, which is unimportant above T_c, could be dominant at low temperatures. From the result of the isotopic ratio of W_c, the second mechanism must also be magnetic. Relaxation due to an orbital current could be responsible for this, because the symmetry allows the d_{xy} states to be mixed with the $d_{x^2-y^2}$ states at the Fermi-level leading to a finite orbital relaxation for $\mathbf{H}\perp c$.[23] However, this mixing is not likely to be large enough to account for the upturn of R.[23]

Bulut and Scalapino have extended the random-phase-approximation calculation of the nuclear-relaxation rate[8] into the superconducting state and found that the characteristic features of the T dependence of R are reproduced by a d-wave model having nodes in the gap.[24] In this model, the initial decrease of R below T_c is due to different coherence factor of $\chi(q,\omega)$ at $q\sim0$ and $q\sim Q$. The low-T upturn of R comes from the fact that $\mathrm{Im}\chi(q,\omega)/\omega$ at $q\sim Q$ does not go to zero at low temperatures since this wave-vector connects points where the gap becomes zero. Although this is remarkable, s-wave pairing remains supported by many other experiments.[25]

In conclusion, we have found an unusual temperature dependence of the anisotropy of the Cu(2) nuclear-relaxation rate in the superconducting states in $YBa_2Cu_3O_7$, which agrees with the previous results by Barrett *et al.* above 70 K but is significantly different at lower temperatures. Our result, when combined with the almost T-independent ratio of the Cu and O relaxation rates, is difficult to understand in the framework of the models that have been proposed to analyze the normal state NMR results.

Note added in proof. After submission of the manuscript, we were informed that similar measurements of the anisotropy of the Cu(2) relaxation rate at a small magnetic field have been done by J. A. Martindale, C. P. Slichter *et al.* and that they obtained a similar result to that shown in Fig. 3.[26]

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