Temperature-independent spin-lattice relaxation of Cu(2) nuclei in the normal state of $YBa_2Cu_3O_{7-\delta}$ single crystals

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The spin-lattice relaxation rate T_1^{-1} of Cu(2) nuclei has been measured in an $YBa_2Cu_3O_{7-\delta}$ single crystal over the temperature range 100–300 K for two directions of the magnetic field with respect to the crystallographic **c** axis: **H**||**c** and **H**⊥**c**. The independence of T_1^{-1} from the temperature, unusual for a metal, is discussed. The maximum near 210 K in the **H**⊥**c** case and the anisotropy of the relaxation are also discussed.

Numerous studies of the spin-lattice relaxation time T_1 of copper nuclei in $YBa_2Cu_3O_{7-\delta}$ have now been carried out, and they have provided much useful information.[1–3] All of the measurements, however, have involved polycrystalline samples, so the interpretation of the results has been complicated by the difficulty in distinguishing the magnetic and quadrupole components of the relaxation and by the inability to study the anisotropy of T_1. Most of the experiments have used the nuclear-quadrupole-resonance method, since NMR studies of polycrystalline samples run into additional difficulties because of the large width and superposition of the lines of chain copper, Cu(1), and of planar copper, Cu(2). A single crystal was used in measurements of the NMR relaxation in Ref. 4, but only for a single temperature, 100 K. In the present letter we are reporting a study of the spin-lattice relaxation of ^{63}Cu nuclei in the Cu(2) position in an $YBa_2Cu_3O_{7-\delta}$ single crystal over the temperature range 100–300 K, for two orientations of the magnetic field with respect to the crystallographic *c* axis: **H**||**c** and **H**⊥**c**. The most important result of this study is that the magnetic relaxation rate does not depend on the temperature.

In the measurements we used a mosaic of seven $YBa_2Cu_3O_{7-\delta}$ single crystal with a total weight of 28 mg. The (**a**,**b**) faces of the crystals were pressed against a plane quartz substrate, so the **c** axes of the crystals were oriented identically. The temperature and width of the superconducting transition of a given sample were found from the diamagnetic screening to be 91.5 K and 1.1 K, respectively. The NMR spectrum was recorded on a Bruker CXP-360 spectrometer in a static field $H = 8.5$ *T*, as described in Ref. 5. For the relaxation measurements we used the line of the central transition ($-1/2, 1/2$) and a saturation-recovery method. Saturation was achieved with the help of a train of 40 pulses with a total length of 350 μs.

In the NMR spectrum in the case **H**||**c** we see three lines (Fig. 1). The most intense of these lines (*a*) and also line *b* correspond to central transitions ($-1/2$, $1/2$) of Cu(2) and Cu(1), respectively. Line *c* corresponds to a noncentral transition ($\pm 1/2$, $\pm 3/2$) of the Cu(1) nucleus which is nearly degenerate in frequency. This

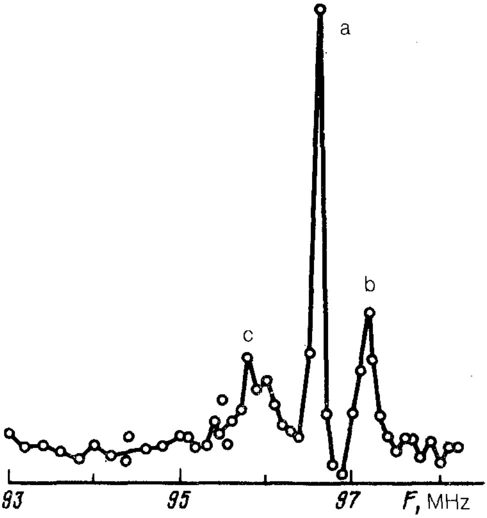

FIG. 1. NMR spectrum of ^{63}Cu in YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals in a field $H = 8.5$ T in the orientation **c**‖**H** at $T = 102$ K. *a*—The line $(-1/2, 1/2)$ of a Cu(2) transition; *b*—the line $(-1/2, 1/2)$ of a Cu(1) transition; *c*—the lines $(\pm 3/2, \pm 1/2)$ of Cu(1) transitions.

identification of lines follows unambiguously from the results of our previous determination of the parameters of the quadrupole interaction and the Knight shift for Cu(1) and Cu(2) (Ref. 5), since the transition frequencies calculated on the basis of these results agree with the positions of the corresponding lines in the spectrum in Fig. 1. The shape of the spectrum and the identification of the line are in complete agreement with Ref. 6. In the H⊥**c** case, the Cu(2) line shifts by a frequency of 97.7 MHz, while the Cu(1) line broadens and disappears because of the different orientations of the **a** and **b** axes in the different crystals of the mosaic.

In the case of the magnetic relaxation of the central transition of a quadrupole nucleus with a spin $I = 3/2$, the restoration of the magnetization is described by a sum of two exponential functions:

$$M(\infty) - M(t) = Ae^{-t/T_{11}} + Be^{-t/T_{12}}, \tag{1}$$

where $T_{12}/T_{11} = 6$. This expression no longer applies if quadrupole relaxation is also important.[7] The amplitude ratio A/B is determined by the length of the time interval over which the saturation is produced; its value is 9 if the interval is short in comparison with T_{11} (saturation by a short, intense pulse), or its value is 3/2 in the case of a steady-state saturation. The NMR relaxation process is described well by a sum of two exponential functions with $T_{12}/T_{11} = 6$, both in the case **c**‖**H** (Fig. 2) and in the case **c**⊥**H**. This result is evidence of a magnetic mechanism for this relaxation. As expected, the value found for the ratio, $A/B \approx 3$, lies between the values corresponding to these limiting cases, since the saturation time in our experiments was comparable to the relaxation time.

It can be seen from Fig. 3 that the relaxation rate is constant over the temperature range 100–300 K for both **H**‖**c** and **H**⊥**c**. The only exception to this statement is the narrow temperature interval 200–220 K in the **H**⊥**c** case, where we see a large maxi-

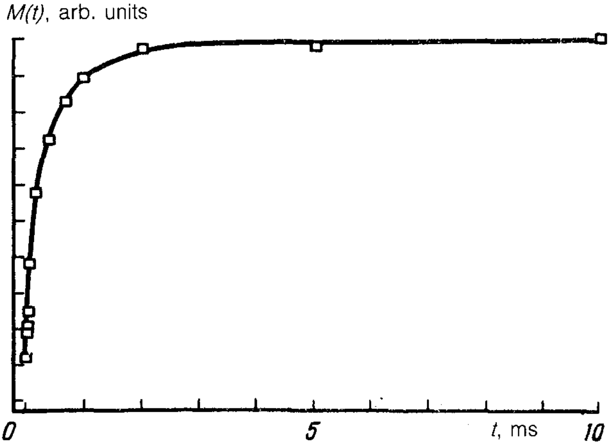

FIG. 2. Restoration of the nuclear magnetization of Cu(2) for the orientation **c**∥**H** at $T = 100$ K. The solid line was calculated from Eq. (1) with the parameter values $T_{12} = 0.936$ ms and $T_{12}/T_{11} = 6$.

mum due to relaxation by the quadrupole mechanism. The results of our measurements of the temperature dependence of the spectrum and spin-spin relaxation of the NMR also reveal anomalies near 200 K and will be reported separately. Here we simply note that structural studies[8] of the bending of Cu–O chains suggest the appearance of a superstructural distortion in this temperature interval.

The magnetic relaxation of the nuclei in a metal is determined by the temporal fluctuations of the components of the hyperfine field, $h_i(t)$ $(i = a, b, c)$, which are usually characterized by a correlation time[9] τ_0. The nuclear magnetization along the **a** axis (corresponding remarks hold for **b** and **c**) relaxes at a rate $T_{1a}^{-1} = \gamma_n^2(\overline{h_b^2} + \overline{h_c^2})\tau_0$, where $\overline{h_i^2}$ is the time average of h_i^2, and γ_n is the gyromagnetic ratio of the nucleus. Assuming $h_i^2 \propto K_i^2$, we find $(T_1^{\parallel}/T_1^{\perp}) = (K_a^2 + K_c^2)/(K_a^2 + K_b^2) = 2.98$, where the components of the Knight shift, K_a

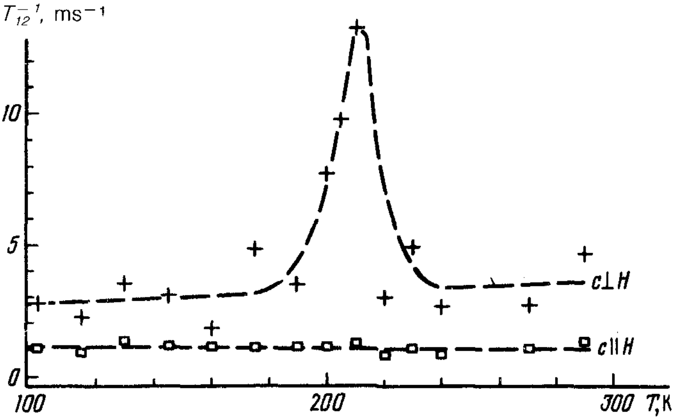

FIG. 3. Temperature dependence of the spin-lattice relaxation rate for the orientations **c**∥**H** and **c**⊥**H**.

$= K_b = 0.57\%$ and $K_c = 1.27\%$ were measured in Ref. 5. The calculated value is close to the observed anisotropy of the relaxation, $T_1^{\|}/T_1^{\perp} \approx 3$ (Fig. 3).

We turn now to the main result: the independence of the relaxation rate from the temperature. Our measurements show that the Knight shift has essentially no temperature dependence. In the case **H**||**c**, for example, the Knight shift is 1.2 MHz, and it increases by only 17 kHz when the sample is cooled from 300 K to 100 K. This combination of NMR properties is extremely unusual, and it deviates in a fundamental way from the Korringa relation $T_1^{-1} \propto TK^2$, which holds for simple metals. In transition metals and their compounds, it is customary to distinguish among three components of the Knight shift: one from the spins of *s*-electrons, one from the spins of *d*-electrons, and one from the orbital angular momenta of the latter.[10] The Korringa relation does not hold, and in several cases a weak temperature dependence T_1^{-1} has been observed (e.g., in[11] V_3Si), because of the presence of a narrow peak in the state density of the *d*-electrons at the Fermi level. However, in contrast with the case under consideration here, this effect is accompanied by a temperature dependence of the Knight shift. The exchange interaction of paramagnetic Cu^{2+} ions might play a governing role in nuclear relaxation. This interaction leads to an antiferromagnetic order in $YBa_2Cu_3O_{7-\delta}$ with a low oxygen content, $\delta = 0.7$, as we know. In the paramagnetic phase, above the Néel point, the behavior is[10] $T_1^{-1}(T) = \text{const}$, but the magnetic susceptibility and thus the Knight shift depend on the temperature in a Curie-Weiss fashion, in contrast with our case. The RVB theory also fails to describe our results, since that theory predicts a Korringa relaxation due to an interaction of nuclei with spinons.[12] A temperature-independent relaxation should be explained in a natural way by assuming that the electron spins of the Cu(2) are in a singlet state and form a 2*D* spin liquid with an exchange integral $J \gg 300$ K (Ref. 13). In this case, fluctuations of the local magnetic field should be of a quantum nature and should be temperature-independent.

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