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Magnetic-field dependence of planar copper and oxygen spin-lattice relaxation rates in the superconducting state of $YBa_2Cu_3O_7$

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The authors report nuclear spin-lattice relaxation rates, W_1, for planar copper and oxygen sites in the superconducting state of $YBa_2Cu_3O_7$. These measurements were made with the static magnetic field along the c axis at a variety of static magnetic-field strengths. The data show that the relaxation rate of ^{17}O depends on magnetic-field strength at low temperature and confirm a similar result for ^{63}Cu. The importance of these measurements is that they give the zero-field limit necessary for comparison with theory. The weak-field data at low temperature for both copper and oxygen have a temperature dependence close to T^3, which is the result expected for spin-singlet, orbital d-wave pairing and does not seem compatible with orbital s-wave pairing.

In a metal, NMR spin-lattice relaxation rates W_1 are strongly influenced by the transition to the superconducting state. Measurements of W_1 thus provide important tests of theories of superconductivity. Almost all such theories, however, apply to the limiting case of zero static applied magnetic field, whereas many NMR measurements, especially of type-II superconductors such as the cuprates, are made using nonzero applied magnetic field. Recently several groups have reported a magnetic-field dependence for nuclear spin-lattice relaxation rates for planar ^{63}Cu nuclei, $^{63}W_{1\alpha}$ (where α indicates the direction of the applied field), in the superconducting state of high-T_c superconductors. In our studies of $YBa_2Cu_3O_7$, with the magnetic field along the c axis at a temperature of 20 K, we observed a factor of 4 enhancement in the Cu(2) relaxation rate $^{63}W_{1c}$ when measured in a field of 8.30 T compared with measurements performed in zero field.[1] Similar enhancements of $^{63}W_{1c}$ for planar copper nuclei by strong magnetic fields have been reported by Borsa *et al.* for $YBa_2Cu_3O_7$ and for $La_{1.85}Sr_{0.15}CuO_4$,[2] and by Bankay *et al.* for $YBa_2Cu_4O_8$.[3] These results showed that the zero-field relaxation rate needed for comparison with theory could not be determined from data measured in strong magnetic fields. In particular, since all previous measurements of the planar oxygen spin-lattice relaxation rate $^{17}W_{1c}$ have been performed using strong magnetic fields, the zero-field relaxation rate was undetermined.

Recent theoretical calculations of zero-field properties indicated that the temperature dependences of $^{63}W_{1a}$, $^{63}W_{1c}$, and their ratio $^{63}W_{1a}/^{63}W_{1c}$ for the Cu(2) site may be a sensitive test of the nature of the orbital pairing state in $YBa_2Cu_3O_7$.[4,5] Knowledge of the orbital pairing state is significant because different mechanisms of superconductivity are believed to lead to different pairing states, such as orbital s state for phonon-mediated superconductivity and orbital d state for spin-fluctuation models. These theoretical calculations also made predictions for the temperature dependence of $^{17}W_{1c}$. Thus it became important to know the zero-field ^{17}O relaxation rates. In this paper we report such measurements.

While one can measure $^{63}W_{1c}$ in zero magnetic field using nuclear quadrupole resonance (NQR), for ^{17}O the NQR frequency would be prohibitively low. We have therefore measured $^{17}W_{1c}$ in a weak magnetic field (0.67 T) to obtain the true behavior of $^{17}W_{1c}$ in the superconducting state of $YBa_2Cu_3O_7$. We first show that $^{17}W_{1c}$ (as well as $^{63}W_{1c}$) depends on magnetic-field strength in the superconducting state, especially at low temperature, which confirms the necessity of using weak magnetic fields to obtain reliable measurements of superconducting-state relaxation rates. We then present our weak-field measurements of $^{17}W_{1c}$ and $^{63}W_{1c}$. These data demonstrate that at low temperature both $^{17}W_{1c}$ and $^{63}W_{1c}$ vary nearly as T^3, which is the temperature dependence expected for d-wave orbital pairing.[6]

We report measurements on two samples of $YBa_2Cu_3O_7$. Both were magnetically oriented powders sealed in epoxy, and both were isotopically enriched with ^{17}O. The sample preparation[7] and the enrichment procedure[8] have been described elsewhere. The value of T_c as measured in zero field by the change in inductance of an NQR coil was 92.5 K for both samples. Nuclear spin-lattice relaxation rates measured at 77 K and at 100 K for the planar oxygen sites in sample 1 have been previously reported in Ref. 9 (sample 6 in that paper). In order to improve the (S/N) signal-to-noise ratio, we made a second sample, sample 2, with a higher packing fraction (25% versus 13%) and more powder (750 mg versus 350 mg) than sample 1. This larger S/N ratio was necessary to conduct precise weak- (0.67 T) field measurements of $^{17}W_{1c}$. The NMR experiments were carried out with the magnetic field applied along the c axis for field strengths of 0.67, 4.14, and 8.30 T for sample 1 and of 0.67 T for sample 2. In addition, zero-field NQR measurements of $^{63}W_{1c}$ were also made for both samples. To avoid contributions from other sites, both the ^{63}Cu and ^{17}O relaxation rates were measured on the upper frequency $|m|=\frac{3}{2}-\frac{1}{2}$ or $|m|=\frac{5}{2}-\frac{3}{2}$ satellites, rather than on the central ($+\frac{1}{2}$ to $-\frac{1}{2}$) transition, and were measured using the inversion recovery technique.

We plot the data for both samples in Fig. 1. Figure 1(a) shows $^{63}W_{1c}$ as a function of temperature for various magnetic-field strengths, Fig. 1(b) the same for $^{17}W_{1c}$. We do not show the NQR results for $^{63}W_{1c}$ for sample 2 because we found no appreciable difference between the zero-field (NQR) and weak-field (0.67 T) data, which demonstrates that the 0.67 T field had no significant effect on the measurements. This is not the case for the strong magnetic fields, however. The low-temperature data for both $^{17}W_{1c}$ and $^{63}W_{1c}$ reveal the same effect as was previously observed—the presence of the strong magnetic field increases the relaxation rates, showing the importance of using weak magnetic fields to make measurements in the superconducting state. Furthermore, this result raises doubts about conclusions drawn from previous measurements of $^{17}W_{1c}$ at low temperature in the superconducting state since all previous data for $^{17}W_{1c}$ were obtained using strong magnetic fields.

There is an additional problem associated with previous measurements of the ratio $^{63}W_{1c}/^{17}W_{1c}$. Our result for this ratio using the weak-field data of sample 2 is shown in Fig. 2; it goes from 22 at 100 K to 7.5 at 17 K. Hammel *et al.* first reported that $^{63}W_{1c}/^{17}W_{1c}$ measured in strong field was independent of temperature for $20 \leq T \leq 110$ K with a value of approximately 19.[10] However, the strong-field data of Kohori *et al.*[11] and of Yoshinari, Yasuoka, and Ueda[12] showed this ratio was temperature dependent as did our strong-field measurements on sample 1. Kohori *et al.* reported that $^{63}W_{1c}/^{17}W_{1c}$ decreased from 20 at 100 K to 10 at 50 K. The result of Yoshinari, Yasuoka, and Ueda agrees qualitatively with our data in Fig. 2, showing a roughly temperature-independent value of 27 from 100 to 75 K followed by a decrease at lower temperature to 17 at 50 K. The difference in magnitude of $^{63}W_{1c}/^{17}W_{1c}$ near T_c for the various groups may be due to a difference in the oxygen content of the samples, but we do not understand why the result of Hammel *et al.* for the temperature dependence of the ratio differs from those of all other groups.

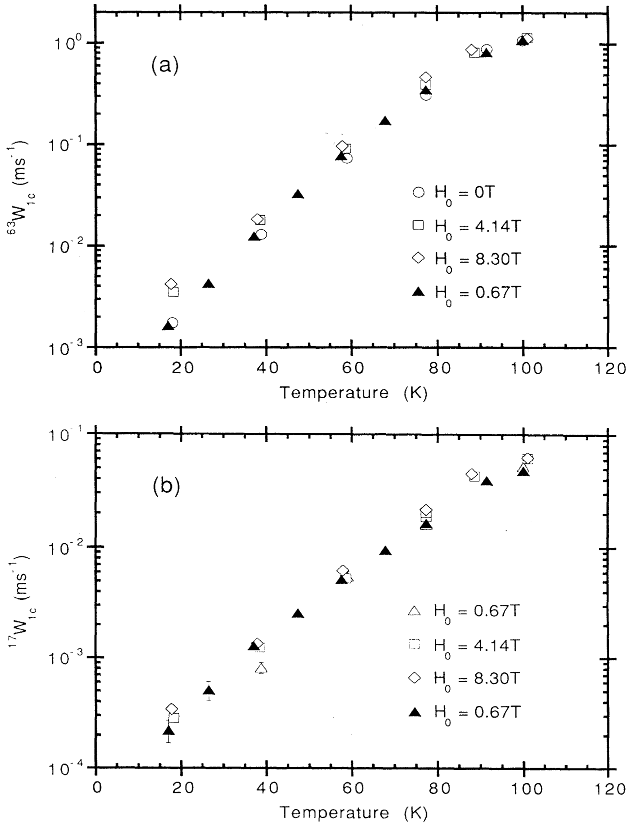

FIG. 1. W_{1c} vs temperature for (a) ^{63}Cu and (b) ^{17}O for different magnetic-field strengths. The open symbols are for sample 1 and the closed symbols for sample 2.

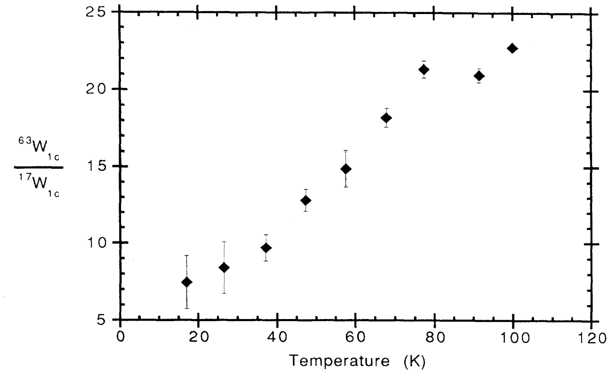

FIG. 2. The ratio of copper to oxygen spin-lattice relaxation rates vs temperature. These data from sample 2 were obtained in a 0.67 T field.

Figure 3 shows the weak-field (0.67 T) data for sample 2 on a log-log plot. For $^{63}W_{1c}$ for $T \leq 50$ K and for $^{17}W_{1c}$ for $T \leq 60$ K, the relaxation rate varies approximately as T^3 as indicated by the lines through the data. This result is similar to that previously reported by Imai *et al.*[13] and by Kitaoka *et al.*[14] for $^{63}W_{1c}$ measured by

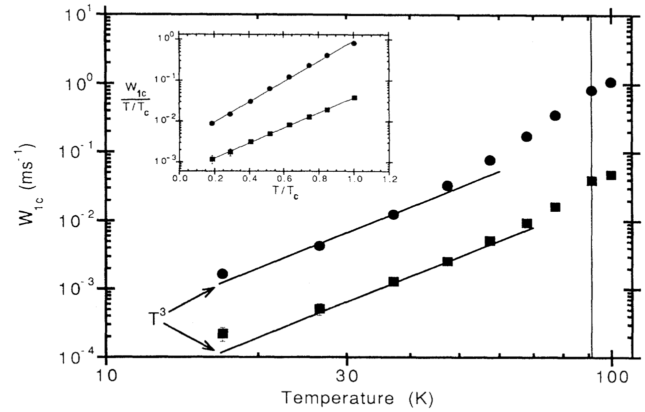

FIG. 3. W_{1c} from sample 2 measured in a 0.67 T field vs temperature on a log-log scale. The circles are ^{63}Cu, and the squares are ^{17}O. The vertical line is at $T_c = 91.2$ K for this field strength and orientation. Inset: The same data replotted in a form we have reported previously (Refs. 1 and 9), W_{1c} divided by T/T_c vs T/T_c. The lines through the data show the exponential behavior for this quantity.

NQR. The data in Fig. 3 show a slight deviation from T^3 at the lowest temperature, as was observed for ${}^{63}W_{1c}$.[13,14] Sample variations at temperatures below 20 K are frequently found in W_1 data for $YBa_2Cu_3O_7$ and are assumed to represent a nonintrinsic relaxation mechanism such as that due to impurities.[6,15] The additional relaxation may perhaps alter somewhat the temperature dependence for ${}^{63}W_{1c}$ and ${}^{17}W_{1c}$ at higher temperature, but because sample variability occurs primarily at or below 20 K, we believe it is unlikely that the nearly T^3 temperature dependence we have observed results from this nonintrinsic contribution.

In the superconducting state the temperature dependences of the Knight shifts and of the nuclear spin-lattice relaxation rates should in principle provide information about the orbital and spin pairing state of a superconductor. In $YBa_2Cu_3O_7$, Knight-shift measurements below T_c showed that the spin pairing is singlet.[16] In conventional orbital *s*-wave BCS superconductors such as aluminum, the nature of the orbital pairing state was revealed in the relaxation rates by the presence of the coherence peak[17] and by the $\exp(-\Delta/k_B T)$ temperature dependence at low temperature.[18] Neither of these orbital *s*-wave signatures has been observed in high-T_c materials. The nearly T^3 temperature dependence we have observed for both the copper and the oxygen is the result one expects for an energy gap with a line of nodes, the situation for *d*-wave orbital pairing, and is incompatible with the nodeless gap of an orbital *s* state. The conclusion that orbital *s* states should lead to a strong temperature dependence at low temperature, in contrast to orbital states with nodes, appears to be rather insensitive to the details of specific models.

Several groups have built the unusual physical properties of $YBa_2Cu_3O_7$ into calculations of the Knight shift and of the spin-lattice relaxation rates for the superconducting state which combine antiferromagnetic couplings between electron spins with BCS-like theories of superconductivity.[4,5] They have found that *d*-wave orbital pairing can provide a consistent account for all of the ^{63}Cu(2) NMR data, particularly for the unusual temperature dependence of the anisotropy ratio ${}^{63}W_{1a}/{}^{63}W_{1c}$, but that *s*-wave pairing cannot. Their calculations of ${}^{63}W_{1c}/{}^{17}W_{1c}$ are not in agreement with experiment, either predicting a relatively temperature-independent value or an increase in the ratio at lower temperature. These calculations, however, employed a closed Fermi surface for $YBa_2Cu_3O_7$. Since photoemission experiments show quite clearly an open Fermi surface,[19] Thelen, Lu, and Pines have extended the calculations to include an open Fermi surface.[20] By appropriate adjustment of the band parameters, they can account for the NMR data with a *d*-wave pairing state though not with *s*-wave pairing. They note that measurements of ${}^{17}W_{1c}$ should be a more telling indicator of the nature of the pairing state than ${}^{63}W_{1a}$ or ${}^{63}W_{1c}$ because ${}^{17}W_{1c}$ is less sensitive to the details of the band structure.

In summary, we have presented data for ${}^{63}W_{1c}$ and ${}^{17}W_{1c}$ in the superconducting state which show that both of these relaxation rates depend on magnetic-field strength at low temperature. By employing a weak 0.67 T magnetic field, we have presented data for ${}^{17}W_{1c}$ which should be free of magnetic-field effects. These data should represent the true superconducting-state behavior of ${}^{17}W_{1c}$. Our results show that both ${}^{63}W_{1c}$ and ${}^{17}W_{1c}$ have a temperature dependence close to T^3 at low temperature and thus appear to indicate *d*-wave orbital pairing.

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