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Temperature dependence of the anisotropy of the planar oxygen nuclear spin-lattice relaxation rate in $YBa_2Cu_3O_y$

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We report measurements of the full planar ^{17}O nuclear spin-lattice relaxation rate tensor in optimally and underdoped $YBa_2Cu_3O_y$ ($y=6.96$ and 6.63). The anisotropy varies strongly with temperature in both samples: for the $y=6.63$ sample, the ratio of the relaxation rate measured with the applied field in the ab plane and oriented parallel to the copper-oxygen bond axis to that measured with the applied field in the ab plane and oriented perpendicular to the bond axis changes by over 25% from room temperature to T_c. The consequences of these results for theoretical models are discussed. They suggest that a second spin degree of freedom independent of the $Cu(3d_{x^2-y^2})-O(2p\sigma)$ band exists in the CuO_2 planes of $YBa_2Cu_3O_y$.
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I. INTRODUCTION

A centrally important issue in understanding the cuprates has been determining the minimal number of degrees of freedom per unit cell, or number of electronic bands, which are necessary to adequately describe the crucial physics. It is clear that the planar $O(2p\sigma)$ and the $Cu(3d_{x^2-y^2})$ orbitals are strongly coupled and thus form a single, strongly hybridized Cu-O σ band. While this band is the fundamental element of the electronic structure of the cuprates, the existence of a second degree of freedom cannot be ruled out and is suggested by several experimental results. Even though the occupation of such a second band may be small, it could play a crucial role in determining normal state behavior and contribute to the pairing mechanism in the superconducting state. A microscopic probe of electronic structure, NMR has been an especially powerful tool in addressing this question due to its ability to selectively discern behavior of carriers in the $Cu(3d_{x^2-y^2})$ and the various $O(2p)$ orbitals in the planes.[1–5] Studies of the uniform $(q=0)$ spin susceptibility[1] have found no evidence for a second band of carriers. In the present study we focus on ^{17}O spin-lattice relaxation rate measurements because these provide sensitivity to the short wavelength $(q\neq 0)$ excitations of the carriers without being dominated by the strong antiferromagnetic spin fluctuations of the Cu moments.

Here we report the temperature dependence of the full (anisotropic) planar ^{17}O spin-lattice relaxation rate tensor in both optimally doped $(y=6.96)$ and underdoped $(y=6.63)$ $YBa_2Cu_3O_y$. Our central finding is that, in contrast to the uniform spin susceptibility, the various components of the relaxation rate tensor *have distinct temperature dependencies*, that is, the anisotropy is temperature dependent. The temperature independence of the anisotropy of the ^{17}O Knight shift $^{17}K_\alpha$ demonstrates that this is not the result of a temperature-dependent hyperfine coupling. This experimental result provides compelling evidence for the existence of a second band of carriers in the CuO_2 planes. The magnitude of the additional relaxation process increases strongly with decreasing temperature and becomes sufficiently large that the symmetry of the relaxation rate tensor is significantly altered at low temperatures where the effect of the second band is most evident; this indicates significant involvement of the $O(2p\pi)$ orbitals in the second carrier band.

The nature and importance of the Cu-O σ band have been well established. The very different temperature dependencies[2] observed for the nuclear spin-lattice relaxation rates at the copper and oxygen sites suggested independent spin degrees of freedom. However, it was pointed out[2] that since the hyperfine field from the antiferromagnetically correlated copper spins will cancel at the oxygen site centered between its two copper neighbors, these different temperature dependencies could be understood as arising from a single, antiferromagnetically correlated spin degree of freedom. Using the hyperfine Hamiltonian of Mila and Rice[6] and of Shastry[7] as a basis, and a single spin susceptibility which incorporated antiferromagnetic spin correlations between nearly localized copper moments, Bulut *et al.* showed that the different temperature dependencies for the copper and oxygen relaxation rates could occur within a one component picture.[8] Millis, Monien, and Pines (MMP) and co-workers[9] extended this framework to develop a powerful phenomenology capable of providing a quantitative understanding of a broad range of data. Through ^{63}Cu and ^{17}O Knight shift measurements, Takigawa *et al.*[1] demonstrated that the static, uniform susceptibilities associated with the $Cu(3d_{x^2-y^2})$ and all the various $O(2p)$ orbitals have identical temperature dependencies in $YBa_2Cu_3O_{6.63}$. This showed that the spin degrees of freedom located in the $O(2p\sigma)$ and the $Cu(3d_{x^2-y^2})$ orbitals are strongly coupled and placed stringent limits on the possible magnitude of the contribution of a second band to the *uniform* $(q=0)$ susceptibility.

There is evidence, however, that this picture is incomplete. Measurements of the anisotropy of the ^{17}O relaxation rate in oxygen deficient ($T_c\lesssim 60$ K) single crystals[3,4] revealed a temperature-dependent anisotropy, an important result which pointed to the existence of a second spin degree of freedom and motivated this work. Disturbingly, Horvatić *et al.*[4] reported that the temperature-dependent anisotropy was absent in fully oxygenated crystals. Walstedt *et al.*[5] have

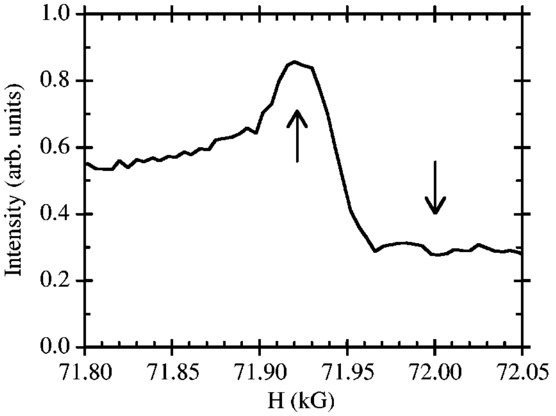

FIG. 1. We plot the spectrum for the first high-field planar oxygen quadrupolar satellite with the magnetic field H perpendicular to both the c-axis and the copper-oxygen bond axis. The arrows indicate the points where the peak (↑) and baseline (↓) measurements discussed in the text and Fig. 2 were made.

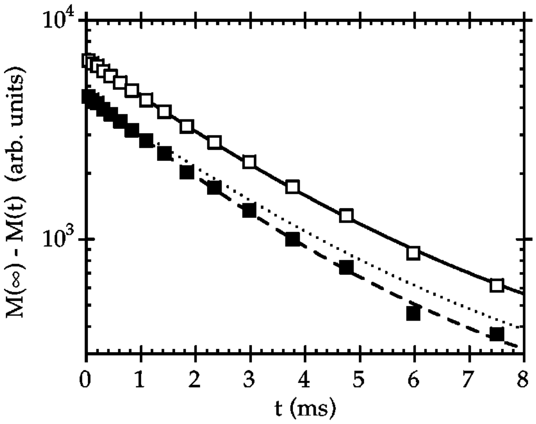

FIG. 2. An example of the baseline subtraction technique: we plot magnetization recovery curves for the peak data (open squares) and for the baseline-corrected data (closed squares) for the field perpendicular to the copper-oxygen bond axis at $T=100$ K. The solid (peak) and dashed (corrected) lines are fits to the appropriate theoretical expression for the magnetization recovery of the first satellite for an $I=\frac{5}{2}$ nucleus such as ^{17}O. The dotted line is the fit to the peak data scaled to agree in magnitude at the earliest time with the baseline-corrected data. Note that, although the fit to the uncorrected data is quite good, the fit yields parameters which are unphysical, namely, an inversion coefficient greater than the maximum value of 2.

recently performed a detailed ^{17}O and ^{63}Cu NMR study of $La_{2-x}Sr_xCuO_4$. Based on comparison of NMR data with inelastic neutron scattering data and on analysis of Cu-O nuclear spin-spin coupling, they have argued that a single band picture of the cuprates is inadequate. Finally, it has been pointed out[10,11] that the experimentally determined anisotropy of the ^{17}O orbital shift[10] is inconsistent with the picture of holes occupying the O($2p\sigma$) orbital alone.

II. EXPERIMENTAL METHOD

Our measurements were carried out on aligned powder samples using a home-built pulsed NMR spectrometer employing quadrature detection. The $y=6.96$ sample was prepared by the procedure described in Ref. 12 and enriched with ^{17}O as in Ref. 13. The oxygen content was determined by iodometric titration.[14] T_c was measured in zero field by the change in inductance of an NQR coil and was found to be 92.2 K. The $y=6.63$ sample ($T_c=62$ K) is the same one for which the Knight shift tensor[1] and other properties[15] have been reported. The spin-lattice relaxation rates were measured by inversion recovery utilizing a CYCLOPS phase cycling sequence which removed the effects of coil ringdown, gain imbalance, and stimulated echoes.[16] We shall use the notation $^{17}T_{1\alpha}^{-1}$ in discussing the ^{17}O(2,3) relaxation rates. For $\vec{H}\|\vec{c}$, $\alpha=c$; for $\vec{H}\|$ copper-oxygen bond axis in the ab plane, $\alpha=\|$; and for $\vec{H}$ in the ab plane, but perpendicular to the copper-oxygen bond axis, $\alpha=\perp$. For $\vec{H}\|\vec{c}$, $^{17}T_{1c}^{-1}$ was measured on the peak of the second high-field quadrupolar satellite. For measurements with $\vec{H}\perp\vec{c}$, however, the random alignment in the ab plane in the c-axis-aligned sample produces a powder pattern spectrum which created difficulties for the measurement of $^{17}T_1^{-1}$. Figure 1 demonstrates the problem. The peak shown arises from the first high-field satellite in those powder particles for which the field is perpendicular to the copper-oxygen bond axis. The signal at higher field, which is due to other satellites, other sites, and differently oriented particles, has a field-independent intensity in this field range and so extends underneath the peak. To remove this ''baseline'' contribution, we extended a technique which has been successful in handling small baseline problems in copper NMR measurements.[13] This technique involves the measurement of two magnetization recovery curves, one on the peak (the up arrow in Fig. 1) and the other on the baseline ~ 10 mT above the peak (down arrow), for the same set of sixteen recovery times. The integrated echoes for the baseline were then subtracted from the integrated echoes for the peak for each recovery time, and the difference was fitted to the theoretical recovery curve;[17] the high quality of these fits, one example of which is shown in Fig. 2, indicates the success of this procedure in removing signals having different recovery times. This correction to the peak data amounts to $\sim 15\%$ of the obtained relaxation rate. The rate $^{17}T_{1\|}^{-1}$ was also measured in this way using the first high-field satellite.

III. RESULTS

In Fig. 3 we show the temperature dependence of $(^{17}T_{1\alpha}T)^{-1}$ for both samples for all three orientations in both the normal and superconducting states. The normal state data alone are replotted in Fig. 4. Focusing on the data for $y=6.96$ in Fig. 4, $(^{17}T_{1\alpha}T)^{-1}$ increases with decreasing temperature down to $T\sim 150$ K, a hallmark of a slightly overdoped material. Below this temperature $(^{17}T_{1\alpha}T)^{-1}$ decreases, displaying the familiar ''spin-gap'' behavior characteristic of underdoped compounds. Just above 100 K, $(^{17}T_{1\alpha}T)^{-1}$ drops quite abruptly. The anisotropy observed at high temperature displays, as expected, nearly uniaxial symmetry with the copper-oxygen bond as the axis of symmetry. However, below 150 K the suppression of the rates measured with the field oriented perpendicular to the bond axis is more rapid with decreasing temperature than that obtained with field orientation parallel to the bond axis. This is the origin

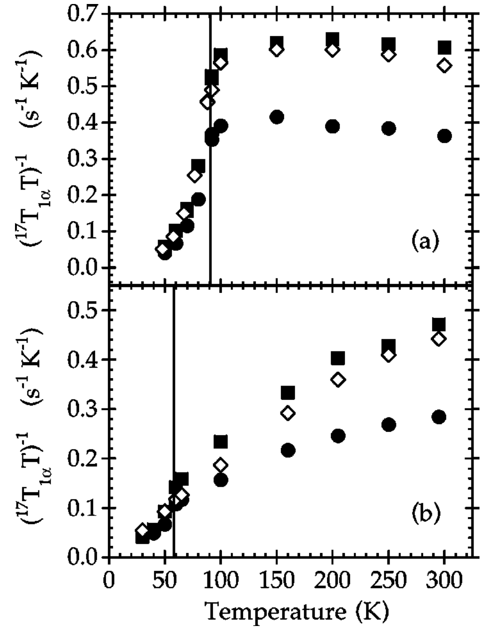

FIG. 3. We plot the temperature dependence of $({}^{17}T_{1\alpha}T)^{-1}$ in $YBa_2Cu_3O_y$ for $y=6.96$ (a) and $y=6.63$ (b): ${}^{17}T_{1\parallel}^{-1}$ (closed circles), ${}^{17}T_{1\perp}^{-1}$ (closed squares), and ${}^{17}T_{1c}^{-1}$ (open diamonds). The vertical lines show the location of T_c for each sample.

of the temperature dependence of the anisotropy. The $y=6.63$ data also show the expected uniaxial anisotropy at high temperature as well as the "spin-gap" suppression of $({}^{17}T_{1\alpha}T)^{-1}$ over the entire temperature range.

The relaxation of nuclear spins arises from hyperfine couplings to the imaginary part of the electron spin susceptibility $\chi''(\vec{q})$. If we allow for the existence of a second band, we can write the planar ${}^{17}O$ relaxation rate in the following form (because we are interested in ratios we drop constant factors):

$$({}^{17}T_{1\alpha}T)^{-1} \propto \sum_{\vec{q}} [{}^{17}F_{\alpha,\sigma}\chi''_{\sigma}(\vec{q}) + {}^{17}F_{\alpha,2}\chi''_{2}(\vec{q})]. \qquad (1)$$

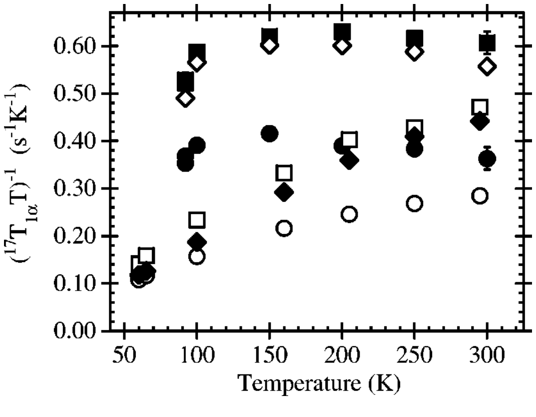

FIG. 4. We replot the data of Fig. 3 to show just the data from the normal state. The closed circles $({}^{17}T_{1\parallel}^{-1})$, closed squares $({}^{17}T_{1\perp}^{-1})$, and open diamonds $({}^{17}T_{1c}^{-1})$ are from the $y=6.96$ sample while the open circles $({}^{17}T_{1\parallel}^{-1})$, open squares $({}^{17}T_{1\perp}^{-1})$, and closed diamonds $({}^{17}T_{1c}^{-1})$ are from the $y=6.63$ sample.

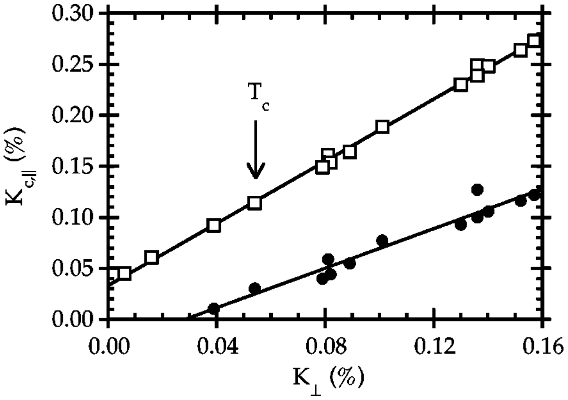

FIG. 5. This plot of ${}^{17}K_c$ (closed circles) and ${}^{17}K_\parallel$ (open squares) versus ${}^{17}K_\perp$ for $y=6.63$ demonstrates that each component of the shift has the same temperature dependence (as shown by the straight-line fits through the data) and therefore that temperature-dependent changes in the hyperfine coupling constants are not responsible for the changes we observe in the anisotropy of ${}^{17}T_{1\alpha}^{-1}$.

Here the subscripts σ and 2 indicate the copper-oxygen σ and the hypothesized second bands, respectively (both assumed isotropic), ${}^{17}F_\alpha$ is the form factor, and the $\vec{q}$ sum is over the first Brillouin zone. In the single band picture of the cuprates $\chi''_2(\vec{q})=0$, and the oxygen form factor is ${}^{17}F_{\alpha,\sigma} = [C^2_{\alpha'} + C^2_{\alpha''}]\cos^2(q_x a/2)$,[7] where $C_{\alpha'}$ and $C_{\alpha''}$ are the oxygen hyperfine coupling constants for directions orthogonal to α, and a is the lattice constant. Because the $\vec{q}$ dependence of ${}^{17}F_{\alpha,\sigma}$ is independent of α, it follows from Eq. (1) that ratios of relaxation rates will be given by ratios of hyperfine constants. If we define

$$\zeta_\perp \equiv C_\perp / C_c$$

and (2)

$$\zeta_\parallel \equiv C_\parallel / C_c ,$$

then,

$$R_{\parallel/\perp} \equiv {}^{17}T_{1\parallel}^{-1}/{}^{17}T_{1\perp}^{-1} = (\zeta_\perp^2+1)/(\zeta_\parallel^2+1) \qquad (3)$$

and

$$R_{\perp/c} \equiv {}^{17}T_{1\perp}^{-1}/{}^{17}T_{1c}^{-1} = (\zeta_\perp^2+1)/(\zeta_\perp^2+\zeta_\parallel^2). \qquad (4)$$

Because the hyperfine constants are determined by electronic energy scales (~eV), one expects these to be independent of temperature in the range studied. That this is indeed the case is confirmed by Knight shift $(K_\alpha \propto C_\alpha \chi_\alpha)$ measurements: all components of the Knight shift tensor have the *same* temperature dependence for all oxygen contents.[11,18] This is demonstrated in Fig. 5 for the particular $y=6.63$ sample for which we report ${}^{17}T_{1\alpha}^{-1}(T)$ here.[1] Values of ζ obtained from the Knight shifts predict the *temperature-independent* relaxation rate ratios given in Table I and shown in Fig. 6.

In Fig. 6 the temperature dependencies of the various components of ${}^{17}T_{1\alpha}^{-1}$ are contrasted by plotting ratios of rates $R_{\parallel/\perp}$ and $R_{\perp/c}$. Note that for the data displayed in Fig. 6(a), the applied field is in the planes for both measurements, and, because we have a uniaxially aligned sample, both measurements are obtained without altering the orientation of the sample with respect to the applied field. Shown as dashed

TABLE I. Relaxation rate ratios predicted by the measured, anisotropic Knight shifts [see Eqs. (3) and (4) and following text].

y	$\zeta_{\parallel}$	$\zeta_{\perp}$	$R_{\parallel/\perp}$	$R_{\perp/c}$	Refs.
6.96	1.42	0.91	0.61	1.06	11,18
6.63	1.54	0.98	0.58	1.01	1

($y=6.96$) and solid ($y=6.63$) lines are the values of the relaxation rate ratios one expects based on the ratios of the hyperfine constants (shown also in Table I) determined from the (temperature-independent) Knight shift ratios. The doping independence of the measured ratio $R_{\parallel/\perp}$ [Fig. 6(a)] is notable. However, using the prediction from the Knight shift ratios as a reference, we see that the deviation of the underdoped material is greater at all temperatures. We note the rough correlation between the magnitude of the spin gap and this deviation.

The striking feature of Fig. 6(a) is the ever more rapid increase of the ratio with decreasing temperature as T_c is approached. It appears, then, that the lower T_c in the $y=6.63$ sample allows the ratio to increase more dramatically before T reaches T_c; just above T_c it has become 25% greater than the room temperature value. The bottom panel of Fig. 6 shows the ratio $R_{\perp/c}$. In this case the temperature dependence is absent in the $y=6.96$ sample, but a strong temperature dependence is present for $y=6.63$. Once in the superconducting state, the anisotropy ratios are temperature independent for $y=6.96$ as shown in Fig. 7.[19] Thus, whatever its origin, the temperature dependence of $R_{\parallel/\perp}$ ceases in the superconducting state for $y=6.96$. For $y=6.63$ the results for the ratios in the superconducting state are less certain because the measurements of ${}^{17}T_{1\parallel}^{-1}$ and ${}^{17}T_{1\perp}^{-1}$ are quite difficult at low temperature ($T<T_c$) in that sample. It is our opinion that the ratios in the superconducting state for $y=6.63$ are likely independent of temperature as they are for $y=6.96$.

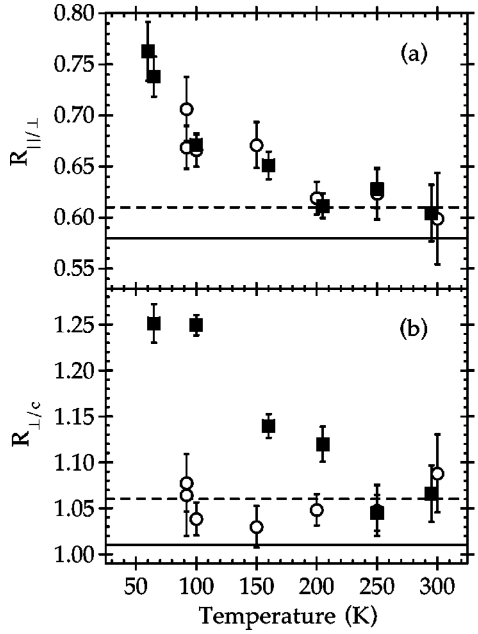

FIG. 6. We show the temperature dependence of the ratios $R_{\parallel/\perp}\equiv{}^{17}T_{1\parallel}^{-1}/{}^{17}T_{1\perp}^{-1}$ (a) and $R_{\perp/c}\equiv{}^{17}T_{1\perp}^{-1}/{}^{17}T_{1c}^{-1}$ (b) in the normal state of $YBa_2Cu_3O_y$ for $y=6.96$ (open circles) and $y=6.63$ (closed squares). Note that all data in (a) are taken with $\vec{H}\perp\vec{c}$ and, because the sample is uniaxially aligned, the orientation of $\vec{H}$ with respect to the sample is unchanged for the two measurements. The dashed (solid) lines are the predicted values for $y=6.96$ ($y=6.63$) as determined from the ratios of the Knight shifts (see text and Table I).

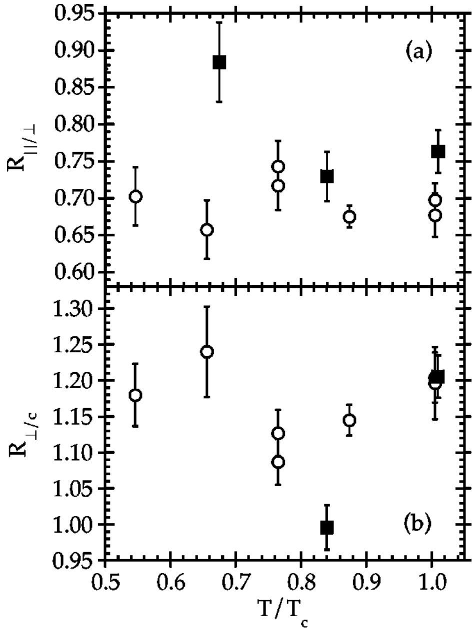

FIG. 7. We show the temperature dependence of the ratios $R_{\parallel/\perp}\equiv{}^{17}T_{1\parallel}^{-1}/{}^{17}T_{1\perp}^{-1}$ (a) and $R_{\perp/c}\equiv{}^{17}T_{1\perp}^{-1}/{}^{17}T_{1c}^{-1}$ (b) in the superconducting state of $YBa_2Cu_3O_y$ for $y=6.96$ (open circles) and $y=6.63$ (closed squares).

Our results agree in large measure with the earlier measurements[3,4] in oxygen-deficient crystals; on the other hand, there is important disagreement for the near-optimally doped samples. The latter is probably another example of the previously recognized sensitivity of the properties of $YBa_2Cu_3O_y$ to small variations in oxygen stoichiometry around $y\simeq6.95$.[20] Since no data for ${}^{17}T_{1c}^{-1}$ for oxygen-deficient samples were reported in Refs. 3 and 4 other than at room temperature in Ref. 3, comparison of our results with previous data is limited. However, where the data overlap, our $y=6.63$ results and the data of Refs. 3 and 4 for oxygen-deficient samples are in excellent agreement: the magnitude and temperature dependence of $R_{\parallel/\perp}$ are the same within the error bars for all three cases, and the value of 1.06 at room temperature for $R_{\perp/c}$ reported in Ref. 3 is indistinguishable from our result. For (near) optimally doped samples, our data disagree in some respects with the data of Ref. 4. Although $R_{\perp/c}$ was found to be independent of temperature in both cases, we observed $R_{\parallel/\perp}$ to be temperature dependent for $y=6.96$ whereas Horvatić *et al.* reported this ratio to be independent of temperature. However, as mentioned previously, the ${}^{17}T_{1\alpha}^{-1}$ data for the O_7 crystal of Ref. 4 show no evidence of spin gap behavior (and, in fact, show signs of being overdoped). If the spin gap and the temperature dependence of $R_{\parallel/\perp}$ are related, it may be that the absence of a spin gap in the O_7 Horvatić *et al.* sample[4] explains the temperature-independent anisotropy in that case.[21]

IV. DISCUSSION

We first examine possibilities for obtaining a temperature-dependent relaxation rate ratio within the context of a single band model. We have shown that a temperature-dependent hyperfine coupling cannot be responsible. Within any model of the oxygen hyperfine coupling, such as that of Mila-Rice-Shastry (MRS) in which the $\vec{q}$ dependence of $^{17}F_{\alpha,\sigma}(\vec{q})$ is independent of orientation (e.g., for which $F_\alpha = c_\alpha f(\vec{q})$, where the c_α are q independent), the relaxation rate ratios can have *no* temperature dependence. However, a temperature-dependent anisotropy could arise from an α dependence of $F(q)$; in this case the presence of the very strong and possibly temperature-dependent peak in the spin susceptibility at $q = \mathbf{Q} \equiv (\pi/a, \pi/a)$ means that such a dependence of $F(q)$ for $q \simeq \mathbf{Q}$ will most effectively introduce a temperature dependence into the anisotropy. The MRS model is based on an ionic picture; modifications of this taking itinerancy into account might be expected to have a weak q dependence.[22] To model the behavior of such a second hyperfine coupling, we consider the effect of a q-independent term E_α:

$$^{17}F_{\alpha,\sigma}(\vec{q}) \propto [2C_{\alpha'}\cos(q_x a/2) + E_{\alpha'}]^2 + [2C_{\alpha''}\cos(q_x a/2) + E_{\alpha''}]^2 . \qquad (5)$$

Utilizing Eqs. (1) and (5) and employing the MMP expression for $\chi''_\sigma(\vec{q},T)$ [i.e., a commensurate peak in $\chi''_\sigma(\vec{q},T)$] as the sole spin susceptibility with updated values of the parameters,[23] we calculated $R_{\parallel/\perp}$, $R_{\perp/c}$, and $^{63}T_{1c}^{-1}/^{17}T_{1c}^{-1}$ as functions of temperature in the normal state for $y = 6.96$. The C_α and E_α are tightly constrained by the Knight shifts and by the large value (~ 20) of the ratio $^{63}T_{1c}^{-1}/^{17}T_{1c}^{-1}$ of the copper and oxygen relaxation rates measured with $\vec{H} \parallel \vec{c}$. Within these constraints, the calculated temperature variation of $R_{\parallel/\perp}$ in the normal state cannot exceed 3%, whereas the experimental temperature variation is approximately 15%. Explaining the larger variation with temperature of $R_{\parallel/\perp}$ for $y = 6.63$ with this approach would seem to be even less likely.

Recently Zha *et al.*[24] have proposed that the temperature-dependent ratio $R_{\parallel/\perp}$ we observe for $y = 6.96$ can be explained in a single band model if one makes two assumptions: that the spin susceptibility has a temperature-dependent peak at an *incommensurate* wave vector $\mathbf{Q_i}$, and that the oxygen nuclear spin experiences a hyperfine coupling to the *next*-nearest-neighbor Cu moment whose magnitude is a quarter of that to nearest-neighbor moment. Within these assumptions, the fall off in $^{17}F_{\alpha,\sigma}(\vec{q})$ with increasing q can coincide closely with the incommensurate peak in $\chi''_\sigma(\vec{q},T)$. The size of the next-nearest-neighbor coupling determines the orientation dependence of the strength of the coupling to this peak. A variation in $R_{\parallel/\perp}$ similar to that we observe for $y = 6.96$ has been obtained,[24] however, $R_{\perp/c}$ was not discussed. The plausibility of this interesting proposal remains uncertain pending examination of the validity of the underlying assumptions, most notably the large value of the next-nearest-neighbor hyperfine coupling which is required. It also remains to be seen if this model can reproduce the observed temperature dependence of $R_{\parallel/\perp}$ for $y = 6.63$ and the different variation with temperature of $R_{\perp/c}$ for $y = 6.96$ and $y = 6.63$.

Suter *et al.* have inferred a significant quadrupolar contribution to the ^{17}O relaxation rate from the temperature dependence of the ratio of the ^{89}Y and ^{17}O spin-lattice relaxation rates ($^{17}T_1^{-1}/^{89}T_1^{-1}$).[25] A quadrupolar contribution could, in principle, lead to a temperature-dependent anisotropy since the anisotropy and temperature dependence of the quadrupolar contribution will, in general, be different from the magnetic contribution. There are several issues concerning this assertion which remain unclear, however. The temperature dependence of the inferred quadrupolar component must have a very specific form in order to be consistent with the known T dependence of the total $^{17}T_1^{-1}$. In particular it must drop off below the superconducting T_c very steeply, and, in fact *more steeply* than the very rapid drop off of the observed $^{17}T_1^{-1}$because the coherence factor for quadrupolar relaxation has the opposite sign from that for magnetic relaxation and is very small.[26] Direct observation of this coincidental similarity below T_c to the rather extreme behavior of the magnetic relaxation would be an important confirmation of this hypothesis. Closer examination of the T dependence of the inferred quadrupolar relaxation component of $^{17}T_1^{-1}$ reveals that it is quite different from that of the anisotropy we find and so cannot explain it. The inferred quadrupolar relaxation peaks around 130 K and decreases below this in contrast to the observation that the anisotropy of $^{17}T_{1\alpha}^{-1}$ is small down to 150 K, and then begins to increase rapidly below this. A relaxation mechanism due to the coupling to the nuclear quadrupole moment ^nQ is proportional to $^nQ^2$. Since $[^{63}Q/^{17}Q]^2 \simeq 40$ is comparable to the ratio $^{17}T_1^{\text{quad}}/^{63}T_1$, one expects that such a contribution would be detected in Cu nuclear spin relaxation, contrary to experimental findings.[27] For these reasons we believe it unlikely that our finding is the result of a quadrupolar contribution to $^{17}T_1^{-1}$.

The remaining possibility is that, in addition to the well known copper-oxygen σ band susceptibility χ_σ, the planar ^{17}O nuclear spins are coupled to a second, independent spin degree of freedom χ_2 having a distinct temperature dependence, by a hyperfine coupling $^{17}F_{\alpha,2}$ whose anisotropy is different from $^{17}F_{\alpha,\sigma}$. The symmetry of the relaxation rate tensor $^{17}T_{1\alpha}^{-1}$ at low temperature would indicate that spins in at least two oxygen orbitals contribute to relaxation there. Near room temperature, $^{17}T_{1\alpha}^{-1}$ is nearly uniaxial with the $\alpha = \parallel$ rate smallest, as expected if the holes occupy the σ orbitals solely. Just above T_c in the $y = 6.63$ compound, the symmetry is again nearly uniaxial, but here the *largest* relaxation rate ($\alpha = \perp$) is now unique. Because relaxation is due to fluctuating fields oriented perpendicular to the applied field [see Eq. (1) and following text], this suggests that spin fluctuations in *two* orbitals, O $(2pc)$ and O$(2p\sigma)$, must contribute to relaxation.

V. CONCLUSIONS

We have reported the temperature dependence of the full ^{17}O(2,3) relaxation rate tensor in optimally and underdoped YBa$_2$Cu$_3$O$_y$. We find that the temperature dependencies of the various components of this tensor are distinct. In contrast, all components of the ^{17}O Knight shift tensor display identical temperature dependencies, ruling out the possibility of a temperature-dependent hyperfine coupling. An anisotropic coupling to the temperature-dependent commensurate antiferromagnetic spin fluctuations cannot account for our observations. A model[24] which obtains agreement with our $R_{\parallel/\perp}$ data by assuming incommensurate fluctuations requires a very large *next*-nearest-neighbor coupling. However, neither agreement of this model with our $R_{\perp/c}$ data, nor the plausibility of the large second neighbor coupling which is assumed, have been demonstrated. The temperature-dependent anisotropy thus suggests the existence of a second spin degree of freedom independent of the copper-oxygen σ band and therefore of a second band of carriers in the planes of the cuprates. The symmetry of the relaxation rate tensor at low temperature where the contribution of the second band is most evident suggests that it involves the O$(2p\pi)$ orbitals.

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