Probing the Electronic Structure of Y–Ba–Cu–O Superconductors by Copper NQR/NMR

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The paper discusses some NQR/NMR studies performed on Y–Ba–Cu–O superconductors at the University of Zürich. It is shown how the resonance methods can yield information on electronic properties of quite different character. The review deals with: (1) the temperature and pressure dependence of Cu NQR frequencies in $YBa_2Cu_4O_8$ (1-2-4); (2) an NQR study of the properties of Ca substituted 1-2-4; (3) the temperature dependence of the Cu Knight shifts in 1-2-4; (4) the NMR of plane Cu2 in the paramagnetic state of $YBa_2Cu_3O_6$; (5) the dependence on temperature, pressure and orientation of the Cu spin-lattice relaxation in 1-2-4.

Key words: NQR, NMR, High-temperature superconductors, Knight shift, Spin-lattice relaxation.

1. Introduction

Nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) have proven to be excellent tools to probe electronic properties of the new high-temperature superconductors. In this paper we review several copper NQR and some NMR studies the NMR group of the Physik-Institut has performed in some representative compounds of the Y–Ba–Cu–O family of superconductors. A similar but more detailed account of these studies will appear elsewhere [1].

Our discussion will deal with quite different aspects of the electronic properties of Y–Ba–Cu–O compounds. Two topics will emphasize NQR studies: Cu NQR frequencies and their temperature and pressure dependence in $YBa_2Cu_4O_8$ (1-2-4), which has a transition temperature of $T_c = 82$ K, and the properties of Ca substituted 1-2-4. Then we will deal with the Knight shifts and their temperature dependence in 1-2-4; with NMR of plane Cu2 in the paramagnetic state of $YBa_2Cu_3O_6$ (1-2-6) and finally with the Cu spin-lattice relaxation and its dependence on temperature, pressure and orientation in 1-2-4.

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2. Electric Field Gradients in $YBa_2Cu_4O_8$

The importance of the Cu NQR transition frequencies ν_Q is that they yield direct access to the electric field gradient (EFG) through the relation $\nu_Q = (eQV_{zz}/2h)(1 + (1/3)\eta^2)^{1/2}$ since both Cu isotopes have a spin 3/2. Here, V_{ii} are the principal components of the EFG tensor present at the Cu site, η is the asymmetry parameter defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$, where $|V_{zz}| \geqq |V_{yy}| \geqq |V_{xx}|$, and eQ is the nuclear electric quadrupole moment of the respective Cu isotope. Thus, the study of ν_Q as a function of temperature (T) and pressure (p) can yield valuable information about the electronic properties of the superconductors.

Figure 1 shows the $\nu_Q(T)$ data of ^{63}Cu for both Cu sites in 1-2-4 [2, 3]. Since ab initio claculations of the EFG are not precise enough at the present time [4] we have estimated the subtle changes of $\nu_Q(T)$ by means of the point charge model, thereby taking into account a valence contribution originating from the holes in the open Cu 3d shell. The solid and dashed lines in Fig. 1 are fits to the data using the following ionic charges: Y^{+3}, Ba^{+2}, $Cu1^{+2}$, Cu^{+2}, $O1^{-2}$, $O2^{-1.917}$, $O3^{-1.917}$ and $O4^{-1.667}$, a Sternheimer factor -11.8 and a 0.8 occupancy of the Cu $3d_{x^2-y^2}$ orbital. That one may have some confidence in these calculations follows from the fact that the calculated asymmetry parameters η are in excellent agreement with data we obtained from high field NMR measurements [3, 5].

The pressure dependence of the ^{63}Cu2 NQR frequency at different temperatures is given in Figure 2.

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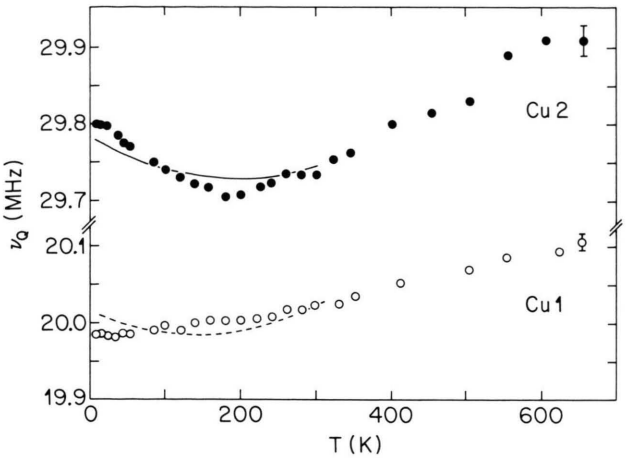

Fig. 1. Temperature dependence of the Cu NQR frequencies in $YBa_2Cu_4O_8$. The solid and dashed lines are fits discussed in the text. From [3].

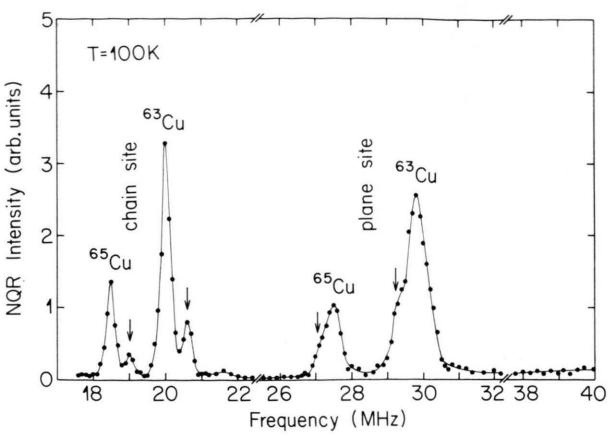

Fig. 3. Cu NQR spectrum in $YBa_{1.9}Ca_{0.1}Cu_4O_8$ at 100 K. The arrows indicate resonance lines that have not been detected in pure $YBa_2Cu_4O_8$. From [8].

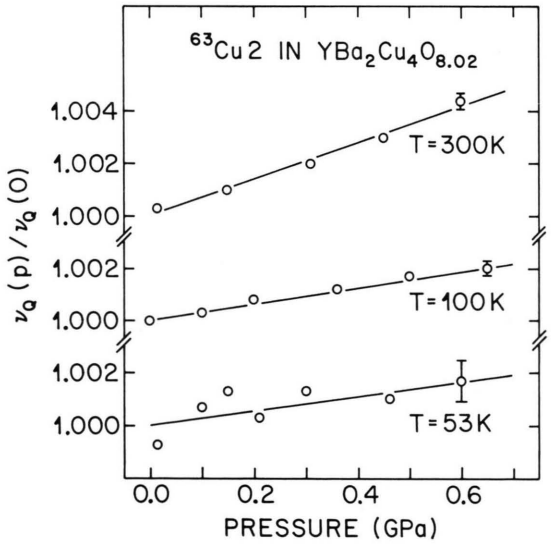

Fig. 2. Pressure dependence of the Cu2 NQR frequencies in $YBa_2Cu_4O_8$ at different temperatures. From [3].

As expected for small volume changes, the p dependence of ν_Q is linear. Cu1 exhibits a similar behavior, however, with a negative value for the slope $d\nu_Q/dp$. The data can be fitted using the point charge model with nominal valencies as mentioned above, provided one allows for a charge transfer dx/dp from the chains to the planes. Good agreement with the data is obtained for $dx/dp = 6\%/\text{GPa}$, which is compatible with the pressure dependence of the electric conductivity.

The slope $d\nu_Q/dp$ is nearly equal for 1-2-4 and 1-2-3-7 [6]. Thus, the question arises why the quantity dT_c/dp, which amounts to 5.7 K/GPa in 1-2-4, exceeds the value for 1-2-3-7 by a factor of 10. A similar difference is observed for 1-2-3-6.5 and 1-2-3-7. Since 1-2-3-6.5, which exhibits some similarities with 1-2-4, seems to have more two-dimensional (2d) character (in terms of charge carrier confinement) than 1-2-3-7, one could speculate that by applying pressure in the "2d structures" the interplane coupling on which T_c sensitively depends, is increased.

In summary, because the derivative $d\nu_Q/dT$ is so small over the whole temperature range we have studied, we conclude that no structural phase transition occurs and the valence at both Cu sites does not change significantly. In other words: the localized hole in the Cu $3d_{x^2-y^2}$ orbital retains its degree of localization between 10 and 750 K and up to 0.7 GPa.

3. Ca Doped $YBa_2Cu_4O_8$

Miyatake et al. [7] could increase T_c of 1-2-4 from 82 K to 90 K by doping 1-2-4 with 10% Ca. Because of the controversy, which site is substituted by Ca and what the mechanism of the enhancement of T_c is, we have studied at 100 K the Cu spectrum in Ca doped 1-2-4 (Ca-1-2-4) with $T_c = 91$ K and 10% Ca, between 18 and 40 MHz [8].

As shown in Fig. 3, in Ca-1-2-4 a new line at 20.600 MHz shows up whose intensity is $23 \pm 5\%$ of the main

Cu1 line at 20.000 MHz if the slight difference in frequency and T_2 is taken into account. Otherwise the new line exhibits a similar linewidth and T_2 value. We therefore identify the 20.600 MHz peak as a Cu1 resonance line arising from those Cu1 nuclei which are nearest neighbors of a lattice defect. A careful discussion of the signal intensities has revealed [8] that the defect is a Ca ion occupying a Ba site.

The next question is whether this type of substitution changes the hole concentration. It is known that ν_Q of the plane Cu2 nuclei is shifted towards higher values with increasing hole concentration. A rough estimate is a change of ν_Q of Cu2 by 26 MHz/ hole. Since ν_Q of Cu2 in Ca-1-2-4 remains in the limit of the linewidth unchanged with respect to pure 1-2-4, the increase of the number of holes is less than 0.013 per Cu. It therefore seems that the increase of T_c in 1-2-4 by Ca doping must be explained by another mechanism. It is important to note that the spin-lattice relaxation times, T_1, of both the Cu1 and Cu2 nuclei in 1-2-4 are not changed by 10% Ca doping [9].

4. Knight Shifts at Cu sites in $YBa_2Cu_4O_8$

We are now turning to NMR studies in 1-2-4. As a first example we will discuss Knight shifts whose temperature dependence and anisotropy provide insight into the behavior of the local spin susceptibilities.

The magnetic shift K is defined as the displacement of the NMR line with respect to the frequency in a non conducting reference sample. The principal components K_i (with the conventional crystal axes $i = a, b, c$) of the magnetic shift tensors for ^{63}Cu at Cu1 and Cu2 sites were determined [3, 10] by exact diagonalization of the Hamiltonian and taking into account the NQR frequency ν_Q; c-axis oriented samples were used. The temperature dependence of the magnetic shifts at Cu1 and Cu2 sites for $B \| a, b, c$ (K_a, K_b, K_c) is shown in Figs. 4 and 5, respectively, together with the data for 1-2-3-$\dot{7}$ of Barrett et al. [11]. The large difference between the double Cu1 chain 1-2-4 compound and the single chain 1-2-3-7 structure is evident; in the latter, K of both sites is temperature independent in the normal conducting phase.

The magnetic shift K_i is the sum of two contributions: $K_i(T) = K_i^{orb} + K_i^{spin}(T)$, where K^{orb} is the orbital or chemical shift generally being temperature independent, and $K^{spin}(T)$ is the spin or Knight shift. In order to determine $K_i^{spin}(T)$ we have assumed that

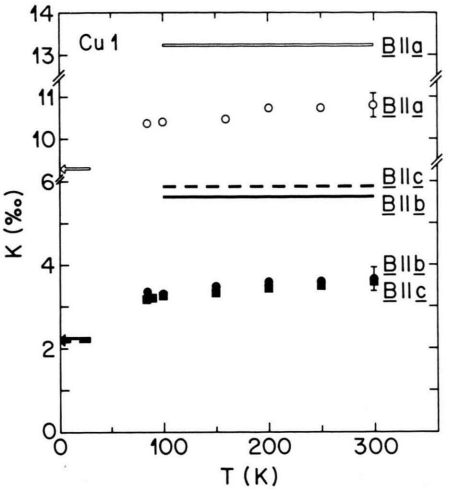

Fig. 4. Temperature dependence of Cu1 magnetic shift in $YBa_2Cu_4O_8$ (open and full symbols, from [3]). Solid and dashed lines denote values for $YBa_2Cu_3O_7$ (from [11]). The arrows indicate the orbital contribution to the magnetic shift in $YBa_2Cu_4O_8$.

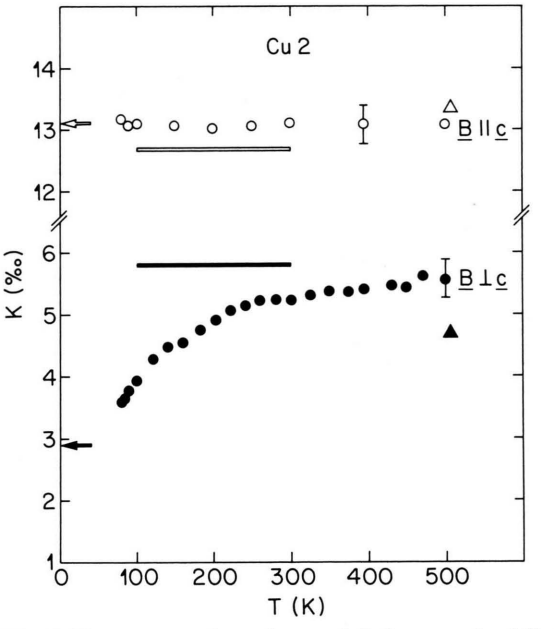

Fig. 5. Temperature dependence of Cu2 magnetic shift for $c \| B$ (open symbols) and $c \perp B$ (full symbols) in $YBa_2Cu_4O_8$ (circles), $YBa_2Cu_3O_6$ (triangles, [13]) and $YBa_2Cu_3O_7$ (lines, [11]). The arrows indicate the orbital contribution to the magnetic shift in $YBa_2Cu_4O_8$.

the *ratio* of the components of K^{orb} is the same as that in 1-2-3-7 [11].

For Cu1, it follows that K^{spin} must be isotropic. Because of the relation $K_i^{spin}(T) \propto A_i^{spin} \chi_i^{spin}$, where A denotes the hyperfine field and χ the susceptibility,

A_i^{spin} must be isotropic. This cannot be accomplished for a quasi-localized hole in the Cu $3d_{x^2-y^2}$ orbital by either direct coupling or transferred coupling. It turned out [3] that a one-component model can explain the data, i.e. one assumes that – extending a model due to Mila and Rice [12] – the shift is given by

$$K_i^{spin} \propto [(A_i + 2B) f_{Cu} + B^{hole} f_O] \chi^{spin}.$$

Here, A_i is the direct anisotropic hyperfine coupling of the nuclear spin with the on-site 3d spin, B is the isotropic transferred coupling with neighboring spins and B^{hole} is the indirect coupling to the O-2p system; the f's are the contributions to the spin susceptibilities.

When discussing the Cu2 Knight shifts, we keep in mind that the 1-2-3-7, 1-2-3-6.63 and 1-2-4-8 compounds are differently doped and exhibit different spin susceptibilities and, in addition, χ^{hole} can depend on doping. We therefore conclude that χ^{hole} and χ^{spin} are not independent of each other, i.e. they exhibit the same dependence on doping and temperature. Thus, the data are interpreted [3] in terms of a one-component spin susceptibility model. This yields among others the temperature dependence of the Cu2 spin susceptibility as shown in Figure 6. The 60% decrease of K_{ab}^{spin} between 500 and 100 K contrasts with the nearly temperature independent K_{ab}^{spin} in 1-2-3-7. Since the hyperfine coupling is temperature independent because of the absence of electronic changes in the temperature range we studied, we conclude that the strong temperature dependence of K_{ab}^{spin} is attributed to the changes of χ^{spin} with temperature. At present we have no explanation for this unusual behavior.

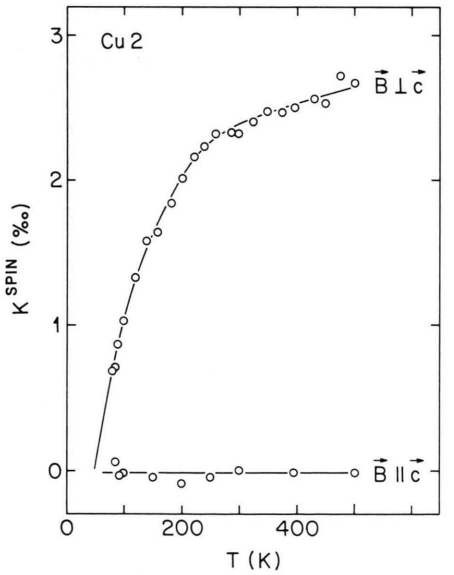

Fig. 6. Temperature dependence of the spin contribution of the Cu2 magnetic shift in $YBa_2Cu_4O_8$ for two orientations (from [3]).

5. Plane Cu NMR in Paramagnetic $YBa_2Cu_3O_6$

As an "interlude" we briefly comment on the first observation [13] of the Cu2 NMR in the paramagnetic state of $YBa_2Cu_3O_6$ (1-2-3-6). This compound with tetragonal crystal structure is an antiferromagnetic (AFM) insulator with a Néel temperature $T_N = 415$ K. In the past, the Cu2 in the AFM phase has already been studied intensively by NMR.

The Knight shift K_α of Cu2 nuclei is not very different from the values we measured in the normal conducting state of the superconductor 1-2-3-7. Of particular interest, however, is the anisotropy of the spin-lattice relaxation rate $1/T_1$. We denote by $T_1^{\parallel c}$ and $T_1^{\perp c}$ the relaxation rates for the orientations $c \parallel B_0$ and $c \perp B_0$, respectively, and we define the ratio $r = T_1^{\parallel c}/T_1^{\perp c}$. Our experimental result is $r = 2.6 \pm 0.4$, a value significantly smaller than 3.56 and 3.72 measured in 1-2-3-7 [14, 15]. The ratio $r = 2.6$ is very close to the 5/2 value expected for purely dipolar interaction between the nuclear spin and an isotropically fluctuating electronic spin of the Cu2 $3d_{x^2-y^2}$ hole. On the other hand, a consistent explanation of the anisotropies of the Cu2 relaxation and Knight shift in 1-2-3-7 was given by F. Mila and T. M. Rice [16] employing – as already mentioned above – an on-site hyperfine coupling to local Cu^{2+} electronic spins and a transferred hyperfine coupling to neighboring spins. It remains to be shown if their analysis is still compatible with our results obtained for 1-2-3-6. We will return to a discussion of r in the next paragraph.

6. Cu Spin-Lattice Relaxation in $YBa_2Cu_4O_8$

Direct probing of the nuclear and electronic spin dynamics is provided by investigating the relaxation behavior of the various nuclei involved. We have studied intensively the Cu spin-lattice relaxation in 1-2-4 [3, 5, 10]. The overall behavior of the NQR relaxation for chain and plane sites is plotted in Fig. 7 while in Fig. 8 we have shown the anisotropy r of the Cu2

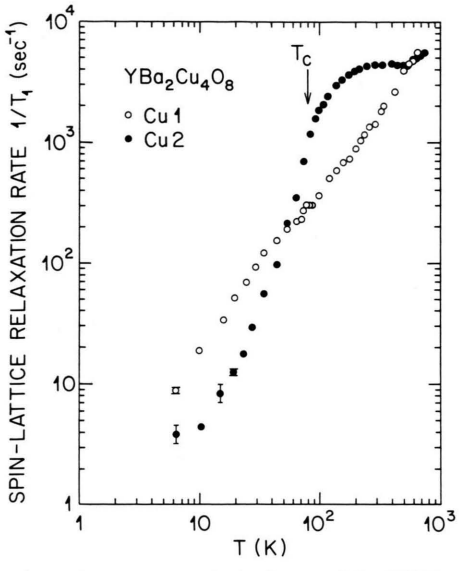

Fig. 7. Temperature dependence of the NQR spin-lattice relaxation rate $1/T_1$ of Cu1 and Cu2 in $YBa_2Cu_4O_8$ (from [5]).

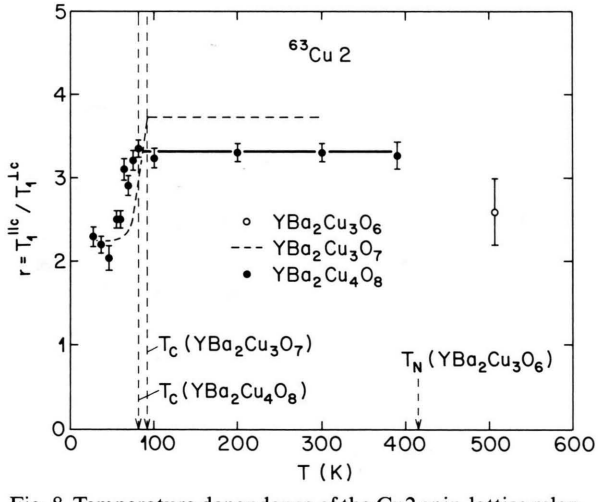

Fig. 8. Temperature dependence of the Cu2 spin-lattice relaxation rate anisotropy r in $YBa_2Cu_4O_8$ (full circles: [20]), $YBa_2Cu_3O_7$ (dashed line: [15]) and $YBa_2Cu_3O_6$ (open circle: [13]).

relaxation rate. For Cu1 at 100 K no anisotropy could be detected. Finally, Fig. 9 exhibits the field dependence of the Cu2 relaxation rate.

One notices immediately that neither the Cu1 nor the Cu2 relaxation rate exhibits a Bardeen-Cooper-Shriefer (BCS) behavior in the superconducting state. Instead, the Cu1 relaxation rate shows the typical

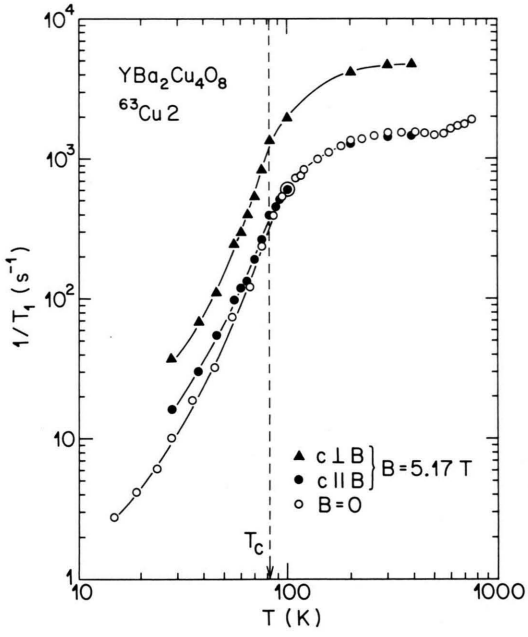

Fig. 9. Temperature dependence of the spin-lattice relaxation rate $1/T_1$ at Cu2 in $YBa_2Cu_4O_8$ determined by NMR in a magnetic field of $B = 5.17$ T oriented $c \parallel B$ (full circles) and $c \perp B$ (full triangles) and by NQR in zero magnetic field (open circles). The arrow indicates T_c in $B = 0$ (from [20]).

behavior of quasi-particles of a Fermi liquid. The parameter $T_1^{\mathrm{NQR}}\, T (K^{\mathrm{spin}})^2 = S B^{\mathrm{KORRINGA}}$ is nearly constant between T_c and 350 K and yields $B^{\mathrm{KORRINGA}} = 0.27$, which implies a weak AFM correlation of the quasi-particles. According to the formula for K_i^{spin}, the factor $f_{\mathrm{O}} B^{\mathrm{hole}}$ seems to play the dominating role. Thus, the data can be explained by the one-component "extended" Mila-Rice model. The free charge carriers seem to be composed of hybridized O-2p, Cu-3d and Cu-4s states.

For the Cu2 relaxation, the Korringa relaxation is not obeyed. Instead, the quantity $T_1^{\mathrm{NQR}}\, T (K_{\mathrm{ab}}^{\mathrm{spin}})^2$ increases linearly with rising temperature. At 100 K one measures $B^{\mathrm{KORRINGA}} = 0.05$, which is indicative of strong AF correlations. The contribution from AFM fluctuations to the relaxation has been taken into account explicitly in a phenomenological model due to Millis et al. [17]. The authors introduce for the wave number and frequency dependent susceptibility, $\chi(q, \omega)$, a mean field expression which contains the AFM correlation length ξ. One then obtains for the Cu relaxation rate $1/T_1 \propto T \chi_0 \langle 1 + (f(q, \xi)^2 \rangle$ where $\langle\rangle$ denotes the average over q space and $\langle f(q, \xi)^2 \rangle$ is roughly proportional to ξ^2 for large ξ. Since for the

Cu2 site K_{ab}^{spin} is proportional to $\chi(0)^{spin}$, $1/(T_1 T K_{ab}^{spin})$ is a measure of the AFM correlations. Introducing our experimental results, we obtain a growing AFM correlation length when approaching T_c from above. However, whether the correlation length as determined from neutron scattering experiments is temperature dependent is still a matter of debate. For example, Rossad-Mignod [18] measured a temperature independent correlation length in $YBa_2Cu_3O_{6.5}$. Thus, a final answer cannot be given at present.

A very different approach to understand relaxation has recently been made by Tachiki and Takahashi [19]. The authors have calculated Knight shifts and relaxation of Cu and O ions in the superconducting state using a layer model where superconductivity is generated by an isotropic pairing interaction acting between electrons in the CuO_2 layers. The authors obtained remarkable agreement with our experimental data. It remains to be seen how models proposed for the normal and the superconducting state can be "unified" to interpret the experimental data.

We now return to a discussion of the relaxation rate anisotropy r. Figure 8 shows our results for Cu2 in 1-2-4 [20] together with our 1-2-3-6 point mentioned above and 1-2-3-7 data from [15]. The temperature dependence of r in 1-2-4 and 1-2-3-7 are very similar. There is a lower constant value $r = 3.3$ in the normal conducting phase of 1-2-4 as compared to 3.72 in 1-2-3-7. This difference could be due to the lower charge carrier concentration in the Cu planes of 1-2-4. In 1-2-3-6, an insulator without charge carriers, r is the lowest, namely 2.6. It is tempting to assign the anisotropy in excess of 2.6 to the charge carriers, especially in view of the precipitous drop of r below T_c, approaching in 1-2-3-7 and 1-2-4 practically the same value of 2.3, which (in error bar limits) coincides with the 1-2-3-6 result.

Finally, we like to mention preliminary results on the field dependence of the Cu2 relaxation rate. Figure 9 presents $1/T_1$ for the two different magnetic field directions $c \parallel B$ and $c \perp B$ together with NQR data. NQR delivers $T_1^{\parallel c}$ in zero magnetic field. While $T_1^{\parallel c}$ is field independent at high temperature, it becomes field dependent already 15 K *above* T_c with a field dependence that is increasing the lower the temperature. At the moment we know neither the influence of B on $T_1^{\perp c}$ nor the eventual effect of different T_c on r for $c \parallel B$ and $c \perp B$.

[1] D. Brinkmann, Proc. Intern. Workshop on Electronic Properties and Mechanisms in High-T_c Superconductors, Tsukuba, 1991 (Elsevier Science Pub.).
[2] H. Zimmermann, M. Mali, I. Mangelschots, J. Roos, D. Brinkmann, J. Karpinski, S. Rusiecki, and E. Kaldis, J. Less-Common Metals **164, 165,** 132 (1990).
[3] H. Zimmermann, Ph.D. Thesis, University of Zürich, 1991.
[4] C. Ambrosch-Draxl, P. Blaha, and K. Schwarz, to be published in Phys. Rev. B.
[5] H. Zimmermann, M. Mali, D. Brinkmann, J. Karpinski, E. Kaldis, and S. Rusiecki, Physica C **159,** 681 (1989).
[6] K. Müller, M. Mali, J. Roos, and D. Brinkmann, Physica C 162–164, 173 (1989).
[7] T. Miyatake, S. Gotoh, N. Koshizuka, and S. Tanaka, Nature, London **341,** 41 (1989).
[8] I. Mangelschots, M. Mali, J. Roos, H. Zimmermann, D. Brinkmann, S. Rusiecki, J. Karpinski, E. Kaldis, and E. Jilek, Physica C **172,** 57 (1990).
[9] I. Mangelschots, M. Mali, J. Roos, H. Zimmermann, D. Brinkmann, J. Karpinski, E. Kaldis, and S. Rusiecki, J. Less-Common Metals **164, 165,** 78 (1990).
[10] H. Zimmermann, M. Mali, I. Mangelschots, J. Roos, L. Pauli, D. Brinkmann, J. Karpinski, S. Rusiecki, and E. Kaldis, Less-Common Metals **164, 165,** 138 (1990).
[11] S. E. Barrett, D. J. Durand, C. H. Pennington, C. P. Slichter, T. A. Friedmann, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B **41,** 6283 (1989).
[12] F. Mila and T. M. Rice, Phys. Rev. B **40,** 11382 (1989).
[13] M. Mali, I. Mangelschots, H. Zimmermann, and D. Brinkmann, Physica C **175,** 581 (1991).
[14] R. E. Walsted, W. W. Warren Jr., R. F. Bell, and G. P. Espinosa, Phys. Rev. B **40,** 2572 (1989).
[15] S. E. Barrett, J. A. Martindale, D. J. Durand, C. H. Pennington, C. P. Slichter, T. A. Friedmann, J. P. Rice, and D. M. Ginsberg, Phys. Rev. Lett. **66,** 108 (1991).
[16] F. Mila and T. M. Rice, Physica C **157,** 561 (1989).
[17] A. J. Millis, H. Monien, and D. Pines, Phys. Rev. B **42,** 167 (1990).
[18] J. Rossat-Mignod, L. P. Regnault, C. Vettier, P. Burlet, J. Y. Henry, and G. Lapertot, Physica B **163,** 4 (1990).
[19] M. Tachiki and S. Takahashi, preprint.
[20] H. Zimmermann, M. Mali, M. Bankay, and D. Brinkmann, Intern. Conf. M^2-HTSC III, Kanazawa 1991.