ELECTRONIC PROPERTIES OF Y-Ba-Cu-O SUPERCONDUCTORS AS SEEN BY Cu and O NMR/NQR

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Abstract Nuclear Magnetic Resonance (NMR) and Nuclear Quadrupole Resonance (NQR) allow the investigation of electronic properties at the atomic level. We will report on such studies of typical members of the the Y-Ba-Cu-O family such as $YBa_2Cu_3O_{6+x}$ (1-2-3-(6+x)), $YBa_2Cu_4O_8$ (1-2-4) and $Y_2Ba_4Cu_7O_{15}$ (2-4-7) with many examples of recent work performed in our laboratory. In particular, we will deal with Knight shift and relaxation studies of copper and oxygen. We will discuss important issues of current studies such as: (1) Existence of a common electronic spin-susceptibility in the planes (and perhaps in the chains) of 1-2-4. (2) Strong evidence for the existence of a pseudo spin-gap of the antiferromagnetic fluctuations in 1-2-4 and 2-4-7. (3) Evidence for d-wave pairing in 1-2-4. (4) Strong coupling of inequivalent Cu-O planes in 2-4-7 and possible origin for the high T_c value of this compound. (5) The possibility to describe NMR data in the framework of a charge-excitation picture.

1. Introduction

While there is not yet a generally accepted theory of the mechanism of high-temperature superconductivity (HTSC) experiments have provided a wealth of sound data and relevant information which wait for proper and adequate interpretation. Among the techniques which probe properties on the *atomic* scale, are Nuclear Magnetic Resonance (NMR) and Nuclear Quadrupole Resonance (NQR). How these disciplines obtain their informations and what the results and issues are, at least for the Y-Ba-Cu-O and the La-Sr-Cu-O families of HTSC, has been reviewed recently [1]. A collection of articles on NMR/NQR applications in HTSC from many leading groups in the field may be found in a special issue of Applied Magnetic Resonance [2]. Recent short reviews of our work emphasizing Y-Ba-Cu-O compounds deal with either crystallographic and materials science aspects [3] or relaxation [4].

In this paper we review some of the results gathered in our laboratory. They are concerned with several issues presently under debate in the HTSC community: (i) the existence of a single-spin fluid in the Cu-O planes and chains; (ii) the spin-gap effect; (iii) the orbital symmetry of the pair-wave function; (iv) the coupling between CuO_2 planes; (v) the possibility to describe NMR data within the framework of a charge-excitation picture. Our answers are based on new Knight shift and NMR/NQR spin-lattice and spin-spin relaxation data for $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{15}$.

2. The single-spin fluid model

Many properties of the cuprates are intimately connected with the fact that the parent structure of these compounds is an anti-ferromagnet, namely $YBa_2Cu_3O_{6+x}$ which has a Néel temperature of $T_N = 415$ K for x = 0. Introducing oxygen destroys the long-range anti-ferromagnetic (AF) order. However, the Cu electron spins still exhibit short-range AF spin fluctuations which give rise to a frequency (ω) and wave-vector ($\vec{q}$) dependent dynamic electronic susceptibility $\chi(\vec{q}, \omega)$.

The question arises whether the susceptibilities associated with the Cu spin and the oxygen hole are independent of each other or not. This can be answered by Knight shift measurements. The NMR line shift due to magnetic interactions is expressed by the *magnetic shift tensor* K, whose components (in a reference frame $\alpha = x, y, z$), can be decomposed into a spin, an orbital and a diamagnetic part:

$$K_{\alpha\alpha}(T) = K_{\alpha\alpha}^{spin}(T) + K_{\alpha\alpha}^{orb} + K_{\alpha\alpha}^{dia} .$$

In HTSC compounds, K^{orb} is predominantly temperature independent, whereas the temperature dependent K^{spin} is expected to vanish in the superconducting state due to singlet spin pairing. K^{dia} is small and can be neglected quite often.

Each tensor can be expressed by the respective hyperfine interaction tensor and the *static* electronic susceptibility (*i.e.* at zero wave vector and zero frequency) as:

$$K_{\alpha\alpha}^{spin} = \frac{1}{g\mu_B} \sum_j (A_j)_{\alpha\alpha} (\chi_j)_{\alpha\alpha}$$

For the analysis of the data, we introduce the following notations. K_{cc} denotes the tensor component perpendicular to the CuO_2 planes ($B_0 \parallel c$), while the in-plane components of the shift are given by $K_\parallel$ and $K_\perp$, where B_0 is parallel and perpendicular to the CuO–bond axis, respectively. We define the axial spin part of K as $K_{ax}^{spin} = (1/3)(K_\parallel^{spin} - K_\perp^{spin})$. The equivalent definition for the isotropic spin part of K is $K_{iso}^{spin} = (1/3)(K_\parallel^{spin} + K_\perp^{spin} + K_c^{spin})$.

The new measurements of the planar Cu and O Knight shifts [5] enlarge and improve our previous data [6,1]. Various Cu and O shift components can be calculated from the data, the result is shown in Fig. 1. While in a "classical" superconductor like aluminum the Knight shift stays constant in the normal state and starts to decline at T_c, the Knight shift components of $YBa_2Cu_4O_8$ begin to decrease already well above T_c. This behavior is typical for under-doped HTSC [1], *i.e.* for compounds whose doping level is below the value that corresponds to a maximum T_c. In addition, all components exhibit the same temperature dependence. These facts support the "single-spin fluid" model which states that the Cu-d holes and the doped holes (which mainly go into O-$2p$ states) have one spin degree of freedom.

Our $YBa_2Cu_4O_8$ shift data resemble very much those for $YBa_2Cu_3O_{6.63}$ [7] thus demonstrating again that both compounds are under-doped. Similar ^{17}O

shift data for $YBa_2Cu_4O_8$ were reported by Machi *et al.* [8] and similar Cu Knight shift data were obtained in $Bi_2Sr_2CaCu_2O_8$ [9]. The existence of a planar single-spin fluid had also been deduced from Y and Tl NMR [1]. The concept is now well established.

A single-spin fluid seems to exist also in the chains of $YBa_2Cu_4O_8$ [5]. The components of both the Cu1 and O1 Knight shift decrease below T_c although this is less pronounced for the K_a component. All K components of Cu1 are proportional to the respective component of O1, which again points to the existence of a single-spin fluid. However, the susceptibilities of planes and chains are different.

3. The spin-gap effect

The study of spin-lattice (and spin-spin) relaxation in HTSC is intimately connected with the question about the origin of superconductivity in these materials, although not in a simple straightforward manner. For instance, some groups have proposed that superconductivity is induced by electron spin fluctuations [10]. The relevance of these fluctuations in neutron scattering and NMR relaxation experiments is well established [1]. Nearly all mechanisms which are responsible for spin-lattice relaxation in HTSC are based on electron-nuclear interactions. The only exception seems to be the Ba relaxation in $YBa_2Cu_4O_8$ [1,11] which is due to the two-phonon Raman process, *i.e.* a coupling between phonons and the Ba quadrupole moment.

Thus, for Cu, O and Y the relaxation is described by the Moriya formula which relates the relaxation rate to the hyperfine fields and the dynamical electron susceptibility:

$$^i(\frac{1}{T_1})_\alpha = \frac{\gamma_i^2 k_B T}{2\mu_B^2} \sum_{\vec{q},\alpha\neq\alpha'} |^i A_{\alpha'}(\vec{q})|^2 \frac{\chi''_{\alpha'\alpha'}(\vec{q},\omega_i)}{\omega_i} \qquad (1)$$

Here, i denotes the nuclear species and ω_i is its NMR frequency. The magnetic field B_0 is oriented along the α direction which coincides with one of the crystallographic axes (a,b,c). $\chi''_{\alpha'\alpha'}(\vec{q},\omega_i)$ is the imaginary (dissipative) part of χ. $A_{\alpha'}(\vec{q})$ are formfactors related to the hyperfine fields. Eq.(1) demonstrates that the spin-lattice relaxation provides a tool to probe the average over the *q-dependent* electron susceptibility.

As an example, Fig. 2 shows the temperature dependence of the relaxation rate per Kelvin for the planar Cu and O nuclei in $YBa_2Cu_4O_8$ [5]. $^{63}(T_1 T)^{-1}$ reaches a maximum around 130 K and rapidly decreases towards lower temperatures. On the other side, $^{17}(T_1 T)^{-1}$ displays a monotonous decrease with lowering temperature. These are typical behaviors found in oxygen-deficient $YBa_2Cu_3O_{6+x}$ and, thus, may be taken as signature of under-doped material.

A good starting point for explaining these data is the the phenomenological Millis-Monien-Pines model [12,1]. It is assumed that there is a direct hyperfine interaction between the Cu2 nuclei and an electron of the on-site $3d_{x^2-y^2}$ orbital

and a transferred interaction with electrons of the $3d_{x^2-y^2}$ orbitals of the four neighboring copper ions. For the planar oxygen nuclei, there exists a transferred hyperfine coupling. The electron spins themselves interact anti-ferromagnetically. The electronic spin fluctuations peak near $\vec{Q} = (\pi/a, \pi/a)$ which is the AF ordering point in $\vec{q}$-space. Since the O and Y formfactors entering into Eq.(1) vanish at $q = Q$, the different behavior of Cu, O and Y relaxation rates can be explained.

Further progress in understanding the Cu relaxation behavior was triggered in two ways. First, Millis and Monien [13] suggested that the spectral weight in the spin fluctuations decreases as the temperature is lowered. This missing spectral weight must reappear at a higher energy in the form of a transition over a "spin pseudo-gap", Δ. While the AF fluctuations increase with falling temperature and hence increase $1/T_1 T$, there will be a temperature where the spin gap effect wins and $1/T_1 T$ will decrease; this explains the maximum of $1/T_1 T$ for Cu. Secondly, Rossat-Mignod $et\ al.$ [14] were the first to discover the spin-gap effect in $YBa_2Cu_3O_{6+x}$ by neutron scattering where the results for $\chi''(\vec{Q}, \omega)$ resemble very much the $1/T_1 T$ data.

When describing the spin-lattice relaxation rate in terms of the spin-gap effect it became customary [1,15,16] to use the following $ad\ hoc$ formula:

$$\frac{1}{T_1 T} = \left(\frac{A_0}{T}\right)^{\alpha} \left[1 - \tanh^2\left(\frac{\Delta_{AF}}{2T}\right)\right] \tag{2}$$

Here, A_0 is a constant. Δ_{AF} denotes the spin-gap energy at Q. The factor $T^{-\alpha}$ is introduced to assure a reasonable description of the high–temperature behavior.

We have fitted Eq.(2) to the planar Cu relaxation data of both the $YBa_2Cu_4O_8$ [5] and the $Y_2Ba_4Cu_7O_{15}$ [1,16] structure, the latter case is shown in Fig. 3. The fit parameters for both Cu sites, Cu2 and Cu3, are $\Delta = 240 \pm 20$ K and $\alpha = 1.25$ and thus agree within the error limits with $\Delta = 260 \pm 10$ K and $\alpha = 1.25$ we obtained for the fit to the Cu2 data in $YBa_2Cu_4O_8$. We will return to this point later.

The Knight shift data have also been fitted by a spin-gap formula, similar to Eq.(2), namely by

$$K = K_0 \left[1 - \tanh^2\left(\frac{\Delta_0}{2T}\right)\right] \tag{3}$$

where Δ_0 refers to the gap at zero wave vector. Our fit to the $YBa_2Cu_4O_8$ data yields $\Delta_0 = 180$ K which is in good agreement with the neutron scattering result. If the temperature variation of the Knight shift is really due to the opening of a spin-gap and Eq.(3) is appropriate for analyzing the data, the result implies that a spin-gap opens also at $q = 0$ and that this values is different from the Δ_{AF} value.

4. The symmetry of the pair-wave function

Whether the spatial symmetry of the pairing state is a s-wave or d-wave is a controversial topic. This is not the place to deal with all the aspects of this

problem, we just focus on various possibilities NMR/NQR offer to check this symmetry, in particular in $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$.

One way is to study the anisotropy of the relaxation rate, that is the ratio $r = {}^{63}T_1^c/{}^{63}T_1^{ab}$ of the Cu relaxation rate in the superconducting state where c and ab specify the orientation of the applied magnetic field, B_0. Detailed theoretical analyses of the relaxation data for $YBa_2Cu_3O_7$ [17,18] revealed that the temperature variation of r is not compatible with s-wave pairing and favors d-wave symmetry. Our $YBa_2Cu_4O_8$ data [19] are in qualitative agreement with the $YBa_2Cu_3O_7$ data and thus also favor d-wave symmetry.

A very promising check of the pairing state symmetry is the measurement of the copper and oxygen relaxation rates at very low temperatures. Both rates display a power-law behavior, $i.e.$ $1/T_1 \propto T^n$ with n between 2.5 and 3 as recently observed for $YBa_2Cu_3O_7$ [20] and $YBa_2Cu_4O_8$ [5]. This points to the existence of nodes in the superconducting gap as one expects, for instance, for d-wave pairing superconductivity [21].

Last but not least, the Knight shift may reveal the pairing state symmetry provided the data are accurate enough. For instance, the chain Cu1 Knight shift data in $YBa_2Cu_3O_7$ [22] and $YBa_2Cu_4O_8$ [5] can not satisfactorily be fitted by an s-wave expression while an d-wave fit is perfect for the $YBa_2Cu_3O_7$ data. Although the theoretical expression for $YBa_2Cu_4O_8$ has not yet been calculated the similarity between data of both structures suggests that in both cases the d-wave expression provides the better fit. Thus, one may conclude that NMR/NQR data favor d-wave symmetry at least in the $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$ structures of the Y-Ba-Cu-O family.

5. Inter-plane coupling

One of the key issues in understanding HTSC is the question whether a coupling between CuO_2 planes favors or impedes superconductivity. Before speculating in one or the other direction, it is necessary to prove that an inter-plane coupling exists. As far as NMR/NQR is concerned, the multi-layer structure $Y_2Ba_4Cu_7O_{15}$ with its alternating 1-2-3 and 1-2-4 blocks offers the unique possibility to study the coupling between $inequivalent$ CuO_2 planes.

We have studied the relaxation rates and the Knight shifts of the Cu2 and Cu3 sites in the 1-2-3 and 1-2-4 block, respectively, of the $Y_2Ba_4Cu_7O_{15}$ compound [1,16]. It turned out that the ratios of these quantities are constant above T_c. Thus, both the static and the dynamic electron spin susceptibilities of the individual planes of a double-plane are governed by the $same$ temperature dependence. This implies the existence of common spin dynamics in both planes, and hence these planes must be strongly coupled. Despite their coupling, their spin susceptibilities retain a distinct q dependence. The presence of the coupling has also been demonstrated by performing SEDOR (spin-echo double resonance) experiments on the Cu2 and Cu3 nuclei [23].

Below T_c, the common temperature dependence is lost, which could arise from the opening of two superconducting energy gaps that differ in the individual planes, thus revealing the different plane charge carrier densities of the 1-2-3 and 1-2-4 block. This difference in doping levels had also been inferred from the temperature dependence of the Cu2 and Cu3 NQR frequencies. We found that the 1-2-3 block is less doped than the pure $YBa_2Cu_3O_7$ compound, hence the doping level of the 1-2-3 block is closer to optimal doping. If one simply assumes that the block with the highest T_c "wins", then this would explain the high T_c, namely 93 K, of the $Y_2Ba_4Cu_7O_{15}$ compound.

As mentioned above and shown in Fig. 3, the Cu2 and Cu3 relaxation rates in $Y_2Ba_4Cu_7O_{15}$ could be fitted by the spin-gap formula Eq.(2) with the same parameters for both data sets. The fact that these values are the same as those used for the fit of the $YBa_2Cu_4O_8$ relaxation data, demonstrates the very similar spin dynamics in $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{15}$ and that the doping level of the blocks in $Y_2Ba_4Cu_7O_{15}$ are close to optimal doping.

6. Hubbard model with magnetic exchange

The excellent fit of the spin-gap expression to the planar Cu relaxation data in $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{15}$ certainly cannot "prove" that the relaxation arises from the spin-gap effect. Other physical phenomena in HTSC need to be explained by this effect. As an alternative to explain Knight shift and relaxation data we conclude our survey by drawing the attention to an approach which is a variant of the Hubbard model comprising magnetic exchange in second order between copper and oxygen holes [24]. The exchange gives rise to a new singlet correlated band separated from the oxygen band. The energy spectrum has been calculated. The low energy physics is determined by a high density of charge excitations in the singlet impurity band together with spin excitations in the lower Hubbard band. Taking an idealized density of states, an analytical form is obtained for the temperature dependent susceptibility:

$$\chi'' \propto \frac{1}{T}\left[1 - \tanh^2\left(\frac{\mu_0 - \alpha T}{k_B T}\right)\right]$$

where the factor $\alpha = 0.4 \times 10^{-4}$ eV/K of the chemical potential is *not* a fit parameter. This expression perfectly describes the Cu2 relaxation rate in $YBa_2Cu_4O_8$ from T_c up to 600 K.

These examples clearly show that the debate about the proper description of spin-lattice relaxation in HTSC, at least of the Y-Ba-Cu-O type, is not yet closed.

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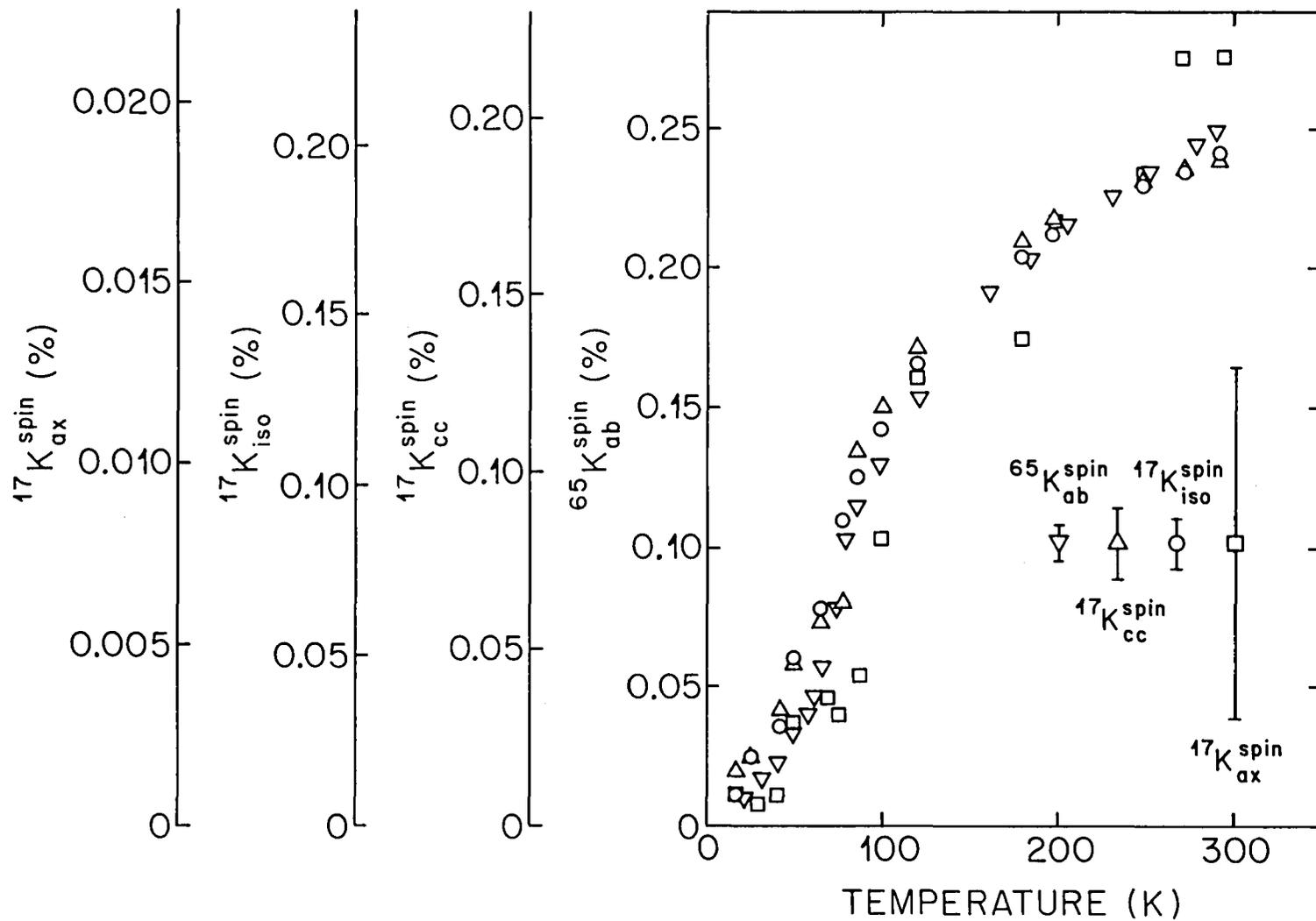
Figure 1.- Various Knight shift components of planar copper and oxygen nuclei in $YBa_2Cu_4O_8$ are plotted vs temperature (with different vertical scales). From Ref. [5].
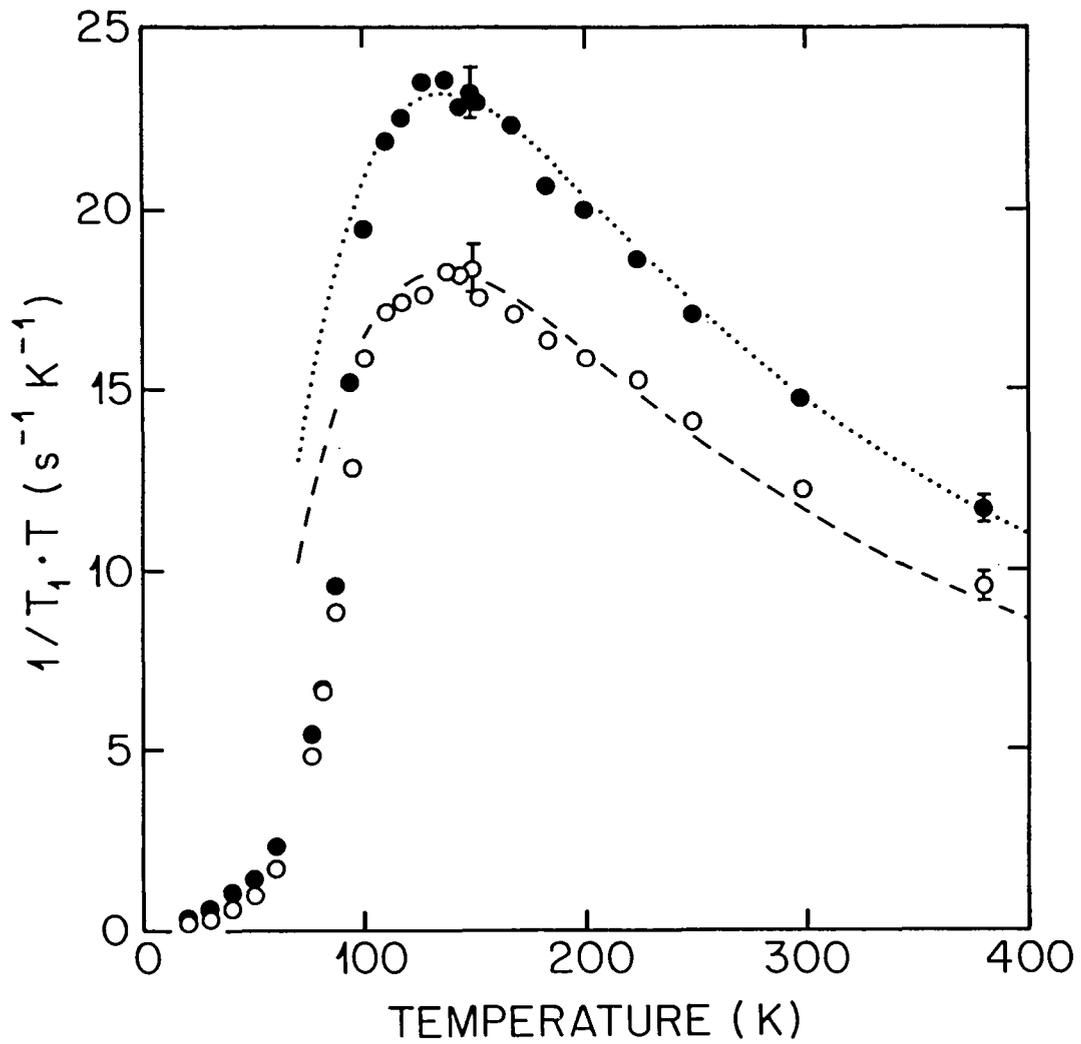
Figure 2.- The temperature dependence of the relaxation rate per Kelvin for the planar
Cu and O nuclei in $YBa_2Cu_4O_8$. From Ref. [5].
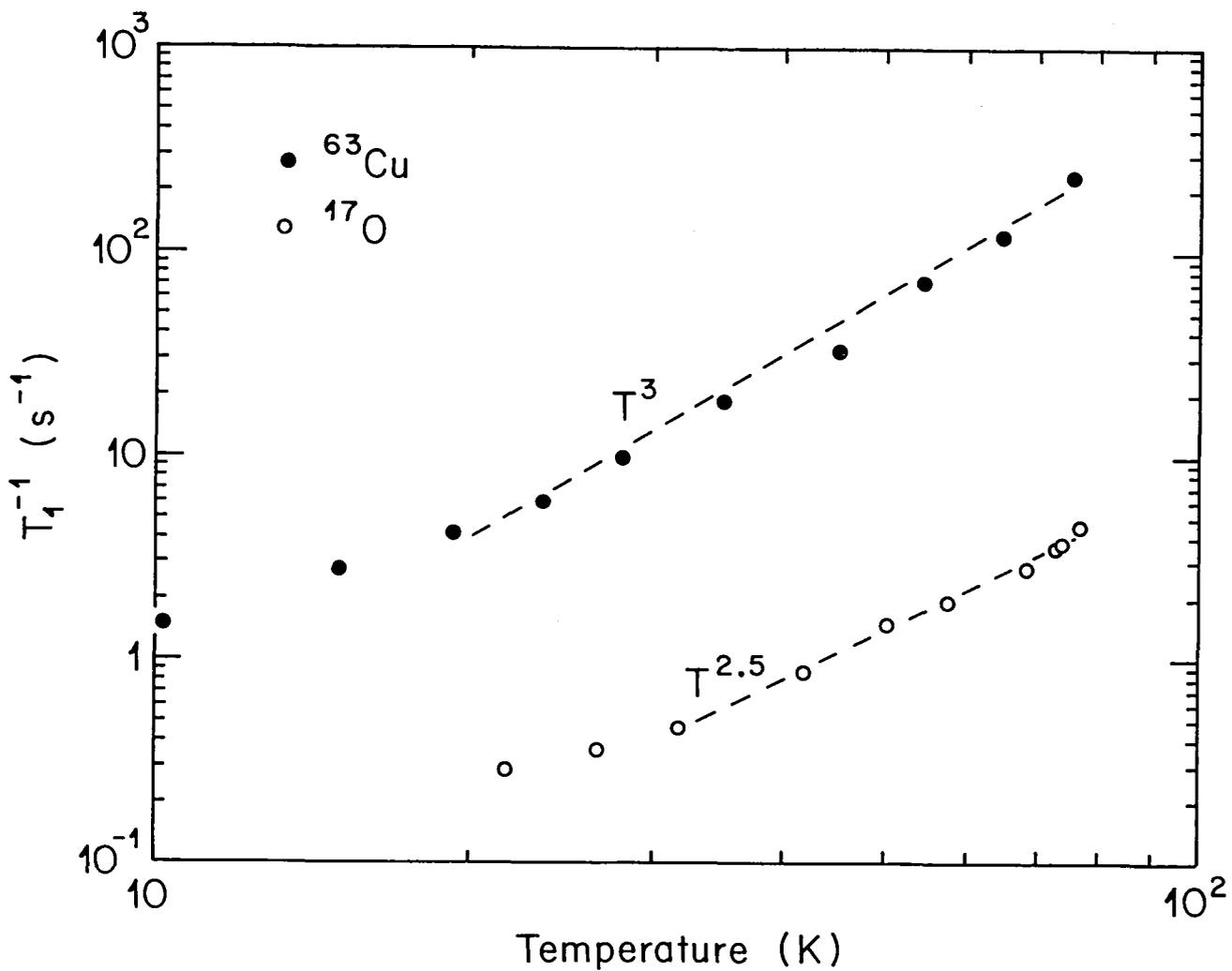
Figure 3.- Fit of Eq.(2) to the relaxation data of the two planar Cu Nuclei in
$Y_2Ba_4Cu_7O_{15}$. From Ref. [16].