Spin Gap, Electronic Crossover, and Charge Density Waves in Y-Ba-Cu-O Superconductors*

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This paper discusses recent NQR/NMR studies performed on Y-Ba-Cu-O superconductors at the University of Zürich. The work is concerned with normal state properties which are still controversial, for instance the spin-gap effect, i.e. the opening of a pseudo gap in the electron spin excitation spectrum at a temperature T^*, which lies above T_c. We will report on the detection of "anomalies" which are displayed in the temperature dependence of several NMR and NQR quantities measured in the normal state of $YBa_2Cu_4O_8$. These anomalies are interpreted as an electronic crossover which involves a charge redistribution in the CuO_2 planes and an enhancement of the charge fluctuations. As a possible mechanism of the crossover, a charge density wave instability is proposed.

Key words: NQR, NMR, High-Temperature Superconductors, Spin gap, Electronic Crossover.

1. Introduction

There is still no consensus of opinion about the mechanism of high-temperature superconductivity. It is commonly agreed that an understanding of the normal state of these materials is a prerequisite for the elucidation of the superconductivity mechanism. A typical question, not yet satisfactorily answered, concerns the origin of the spin pseudogap in underdoped cuprate superconductors, i.e. the opening of a pseudo gap in the electron spin excitation spectrum at a temperature T^*, which lies above T_c (see, e.g. [1]). Possible explanations have considered, for instance, intrinsic properties of the CuO_2 planes or the coupling between these planes. We are going to present new experimental facts from NMR/NQR studies that seem to link the spin gap to an electronic crossover which could be triggered by a charge density wave instability.

Therefore, we will start with a discussion of the spin-gap effect; then we will present the new data on the crossover, and, finally, we will discuss the theoretical work on the charge density wave instability. In the course of this presentation, we will note how nuclear quadrupole interactions play a crucial and fundamental role in these studies.

2. The Spin-Gap Effect

The spin-gap effect has been discovered in $YBa_2Cu_3O_{7-\delta}$ by neutron scattering [2]. Then, several NMR groups have regarded this effect to be responsible for the peculiar temperature variation of the spin-lattice relaxation rate, $1/T_1$, at least in the normal conducting state [1, 3]. The occurrence of a spin gap means that spectral weight in the electron spin fluctuations is transferred from lower to higher energy. The effect competes with the antiferromagnetic (AF) fluctuations which increase with decreasing temperature. These fluctuations are typical for high-temperature superconductors, since several of these materials are synthesized by doping an AF parent structure, e.g. $YBa_2Cu_3O_{7-\delta}$ is obtained by adding oxygen to $YBa_2Cu_3O_6$.

Below a temperature T^*, where the maximum of $(T_1T)^{-1}$ occurs, the spin-gap effect predominates and thus $(T_1T)^{-1}$ is decreasing. In the under-doped structures, T^* lies well above T_c while in over-doped compounds, T^* nearly coincides with T_c.

The spin-gap effect seems to have a widespread nature [4] and still attracts considerable attention in the NMR community [5]. In the absence of a detailed theory, it became common [1] to describe the temperature dependence of the "spin-lattice relaxation rate per temperature unit" in the following way:

$$\frac{1}{T_1T} = CT^{-\alpha}\left[1 - \tanh^2\left(\frac{\Delta}{2T}\right)\right], \qquad (1)$$

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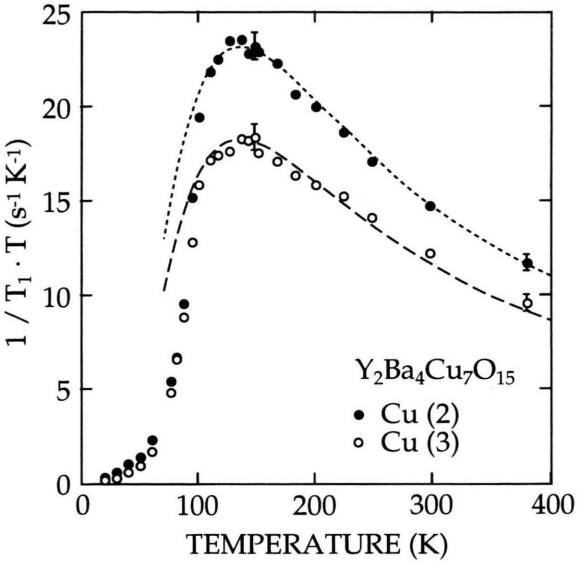

Fig. 1. Fit of Eqn. (1) to the Cu (2) and Cu (3) relaxation rates in $Y_2Ba_4Cu_7O_{15}$. From Ref. [6].

where Δ denotes the spin gap energy, C is a constant, and the factor $T^{-\alpha}$ has been introduced for greater fit flexibility.

An illustrative and also important example is given in Fig. 1 which shows the fit of (1) to the Cu (2) and Cu (3) relaxation rates of the "mixed-layer" compound $Y_2Ba_4Cu_7O_{15}$ [6]. The parameters for both fits 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 our Cu (2) data in $YBa_2Cu_4O_8$. The agreement of both Δ parameters is also in accord with our result of a spin-echo double resonance (SEDOR) experiment in this compound [7]. By measuring the ratio of two relaxation times, the intra-plane $T_{2G,ind}$ and the inter-plane T_{SEDOR}, we have directly confirmed the existence of an appreciable coupling between the two *inequivalent* CuO_2 planes. Among the several proposals for a possible origin of the spin gap, it had also been suggested [8] that the gap arises from an effective inter-plane coupling between adjacent CuO_2 planes. We therefore had taken our results as evidence for this model.

Recent photoemission studies [9, 10] brought into focus the instability phenomena as a possible origin of the pseudo gap, and it had been suggested that the normal-state pseudo gap is closely related to the superconducting gap below T_c. Our new NMR/NQR data for $YBa_2Cu_4O_8$ [11], which present evidence for an electronic crossover in that compound, provide an additional link to the instability problem; this will be discussed now.

3. Electronic Crossover in $YBa_2Cu_4O_8$

Our conclusion about the occurrence of an electronic crossover in $YBa_2Cu_4O_8$ is based on the fact that the temperature dependence of the following NMR/NQR parameters exhibits an anomaly at a temperature $T^{\dagger} = 180$ K: (i) Plane copper, Cu (2): frequency and linewidth of the NQR signal (see Fig. 2), total magnetic shift and linewidth of the NMR signal (see Fig. 3); (ii) Chain copper, Cu (1): frequency and spin-lattice relaxation rate of the NQR signal; (iii) Chain oxygen, O (4): spin-lattice relaxation rate of the NMR signal; and (iv) Ratio of the yttrium and plane oxygen spin-lattice relaxation rates.

The first question to be answered is whether these facts reflect the presence of a structural phase transition or a change in the electronic structure only. The occurrence of a *first-order* phase transition can be ruled out since neither $^{63}\nu_Q$ of Cu (1) nor $^{63}\nu_Q$ of Cu (2) show a "jump"

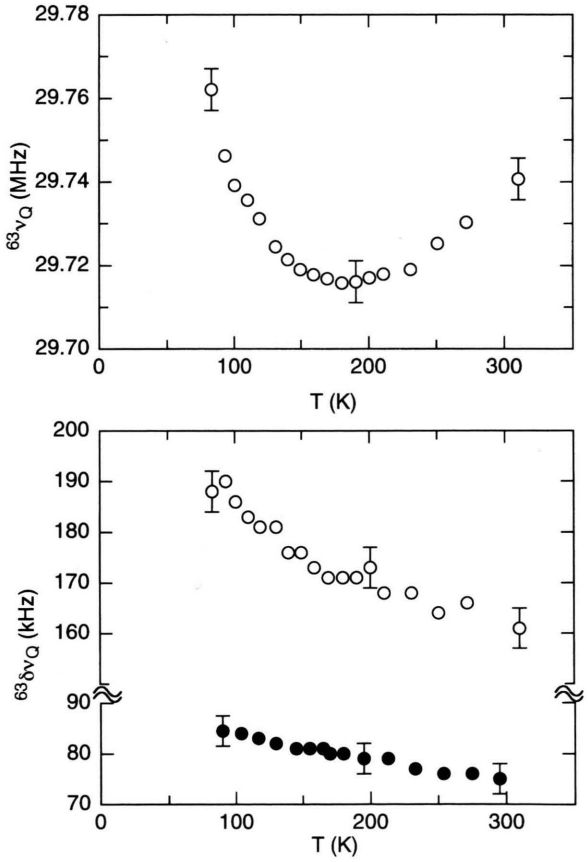

Fig. 2. Temperature dependence of frequency (top) and linewidth (bottom) of ^{63}Cu (2) NQR signal in $YBa_2Cu_4O_8$. From Ref. [11].

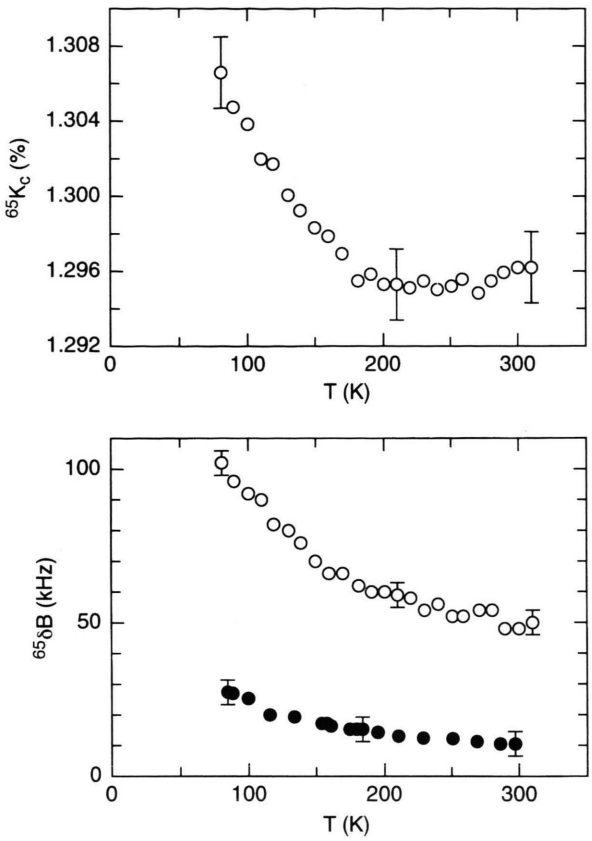

Fig. 3. Temperature dependence of total magnetic shift (top) and linewidth (bottom) of Cu(2) NMR signal ($c \| B_0$) in $YBa_2Cu_4O_8$. Full circles represent chain Cu(1) data. From Ref. [11].

at $T^\dagger$. In addition, the temperature dependence of ν_Q of ^{137}Ba from 17 K up to 400 K is perfectly "smooth" and the linewidth remains constant in that range [12]. Hence, the changes at $T^\dagger$ do not arise from a structural phase transition; instead, they can be attributed to a change in the *electronic* system. We suggested that this electronic crossover results in an opening of an additional relaxation channel for spin-lattice relaxation of both the chain Cu(1) and O(4) and that the mechanism of the additional relaxation is of quadrupolar origin due to charge fluctuations in the chain.

A close inspection of the temperature dependence of both $^{63}\nu_Q$ and K_c of Cu(2) reveals that a charge redistribution occurs below $T^\dagger$, namely a transfer of holes from the chains into the planes. Accepting this interpretation, one immediately understands the unusual temperature dependence of two ratios of relaxation rates, namely $^{17}(W_\| / W_{c,\perp})$ and $17W_c/^{89}W_c$; the latter exhibits a pronounced upturn below $T^\dagger$ and a saturation around 100 K. Following our model, the enhanced charge fluctuations in the chain and the plane, below $T^\dagger$, cause an increase of $^{17}W_c/^{89}W_c$ for decreasing temperatures, since only $^{17}W_c$ of O(2,3) is enhanced while yttrium, because of its spin 1/2, cannot couple to the charge fluctuations. As a possible mechanism of the crossover we propose a charge density wave instability to be discussed in the next section.

4. Charge Density Waves in $YBa_2Cu_4O_8$

At about the same time when studying the crossover effects, we discussed [13] the possibility whether these anomalies support the idea [14] that the spin gap phenomenon is caused, at least partly, by a transition due to a charge density wave (CDW). It is known that a quasi two-dimensional metal with strong anisotropic Fermi surface is unstable with respect to a CDW transition [15, 16]. According to photoemission data (see the review in [17]), Fermi surfaces in layered cuprates are really different from a perfect circle or cylinder. Therefore, the analysis of the CDW scenario as a possible origin for the opening of a pseudo gap in the normal state is desirable. Although this point has been emphasized by many authors, however, to our knowledge, numerical calculations have not been performed.

Starting from the t–J model and including electron-phonon interaction, Eremin et al. [13] derived the gap equation for a charge density wave in the CuO_2 plane, using the singlet correlated band in the normal state. The model allowed to explain the important features of the momentum and temperature dependences of the pseudo gap and the strong temperature dependence of the Cu(2) magnetic shift $^{65}K_{ab}$ ($B_0 \perp c$) which depends on the spin susceptibility.

A severe test, whether the CDW approach is correct, is the prediction of a relatively strong dependence of T^* on the isotope mass. An experimental verification of this prediction is in progress in our laboratory using a ^{18}O enriched $YBa_2Cu_4O_8$ sample.

The CDW approach has been developed further to explain electronic properties of the chains [18], where, due to the one-dimensional character, a Peierls instability is expected that leads to the formation of a CDW in the ground state. On the basis, one can understand the temperature dependence of (i) the Cu(1) NQR frequency in $YBa_2Cu_4O_8$ and $YBa_2Cu_3O_7$ and of (ii) the Cu(1) Knight shift in $YBa_2Cu_4O_8$.

In conclusion, the new experimental and theoretical results suggest a strong relation between the spin gap and the electronic crossover. It remains to be shown whether both effects are a manifestation of a common underlying mechanism and whether a charge density wave – or perhaps a *spin* density wave – is associated with this mechanism.

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