9 NMR/NQR Spectroscopy

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Guests: Prof. M. Eremin, Kazan State University, Kazan (Russia), June till September 1996; I. Eremin, Kazan State University, August till November 1996; Prof. M. Matsumura, Kochi University, Kochi (Japan), March till September 1996; Dr. Y. Uchida, National Institute for Research in Inorganic Materials (NIRIM), Tsukuba (Japan), November 1996; Prof. M. Teplov, Kazan State University, February 1997; P.C. Schmidt, Technische Hochschule Darmstadt, February 1997.

The NMR/NQR group has continued its general research plan which aims to the better understanding of current problems of condensed matter physics by the application of NMR (nuclear magnetic resonance) and NQR (nuclear quadrupole resonance) methods. These spectroscopies allow one to study electronic properties in solids at a microscopic level. Our main interest is still devoted to (i) high-temperature superconductors (HTSC) and the interplay with their antiferromagnetic parent compounds, (ii) superionic conductors (in particular glasses), (iii) high-pressure NMR/NQR using either the diamond-anvil cell or helium as the pressure medium. In doing so, we have kept up a strong collaboration with theorists from Kazan State University and with experimentalists from various international laboratories.

9.1 High-temperature superconductors and related antiferromagnets

Our research interest during the last year was mainly concerned with two essential topics in this field: (i) The nature of the so–called pseudo gap in the normal state of the HTSC and its relation to other normal state electronic effects; (ii) the electronic and magnetic structure of some antiferromagnetic (AF) parent compounds from which many HTSC are derived.

9.1.1 Electronic crossover in $YBa_2Cu_4O_8$

It is commonly agreed that an understanding of the normal state of the HTSC is a prerequisite for the elucidation of the superconductivity mechanism. A typical question not yet satisfactorily answered concerns the origin of the spin pseudo gap in underdoped cuprate superconductors. Recently, we have detected an anomalous behavior in the temperature dependences of various NMR/NQR parameters, all occurring around a temperature $T^\dagger = 180$ K; these anomalies seem to be related to the spin gap [1].

We summarize the NMR/NQR parameters for which these anomalies were found: (i) Plane copper, Cu(2): frequency and linewidth of the NQR signal [see Fig. 9.1], total magnetic shift and linewidth of the NMR signal [see Fig. 9.2]; (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. Obviously, we are not dealing with some artifact.

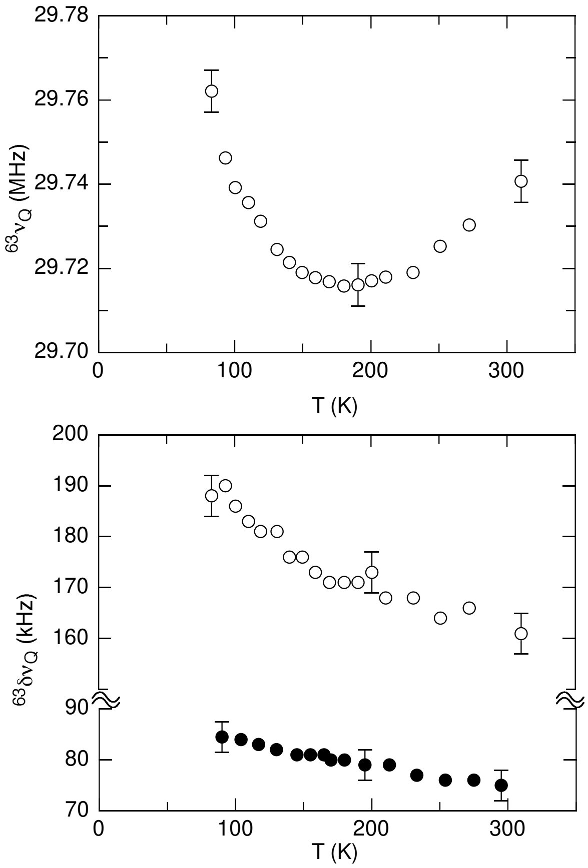

Figure 9.1: Temperature dependence of frequency (top) and linewidth (bottom) of ^{63}Cu(2) NQR signal in $YBa_2Cu_4O_8$.

Our analysis rules out a structural phase transition, either of first or second order, to be the origin of these anomalies. Instead, they are the signature of a change or a crossover in the electronic system that leaves the time–averaged spatial structure essentially untouched. The crossover occurs in both the planes and chains once the temperature is lowered below $T^\dagger$. The crossover reveals itself by enhanced charge fluctuations in planes and chains accompanied by a charge (hole) transfer from chain to plane.

As a possible mechanism of the crossover we propose a charge density wave instability. The occurrence of such instabilities in the normal state of cuprate superconductors has recently been discussed by Eremin *et al.* [2] (see next section). This model is able to explain some of the observed features, if one assumes that $T^\dagger$ is the temperature below which the charge density wave is formed.

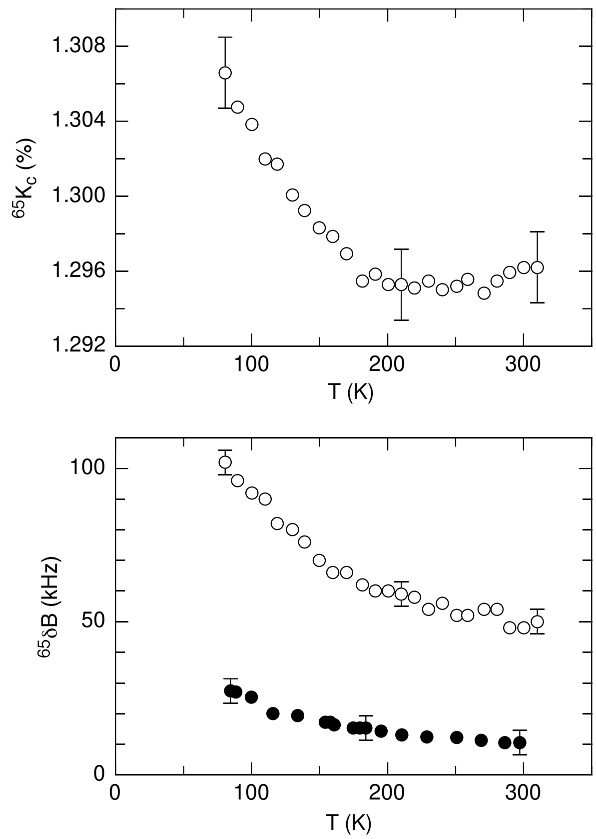

Figure 9.2: Temperature dependence of total magnetic shift (top)and linewidth (bottom) of Cu(2) NMR signal $c \parallel B_0$) in $YBa_2Cu_4O_8$. Bullets present chain Cu(1) data.

9.1.2 Charge density waves in $YBa_2Cu_4O_8$

As mentioned above, the origin of the spin pseudo gap in underdoped cuprate superconductors is still a matter of debate. The notion "spin gap" refers to the opening of a pseudo gap in the electron spin excitation spectrum at a temperature which lies above T_c. The effect manifests itself, among others, in a peak of the $1/T_1T$ data at a temperature T_S which is $\approx$ 150 K in $YBa_2Cu_4O_8$. In the past, we have studied this effect in great detail for $YBa_2Cu_4O_8$ and $Y_2Ba_4Cu_7O_{15}$.

Because of the proximity of $T^\dagger$ and T_S, we [2] have argued that the spin gap effect in $YBa_2Cu_4O_8$ is caused by a transition due to a charge density wave (CDW). It is known that a two–dimensional Fermi–like liquid is unstable with respect to a CDW transition if the chemical potential is located near the energy where the density of states exhibits the Van–Hove saddle singularity peak. Starting from the t–J model and including electron–phonon interaction, Eremin *et al.* derived the gap equation for a charge density wave in the CuO plane, using the singlet correlated band in the normal state. One could explain the important features of the momentum and temperature dependences of the pseudo gap and the strong temperature dependence of the magnetic shift $^{65}K_{ab}$ of Cu(2) [see Fig. 9.3].

The CDW approach predicts a relatively strong dependence of T_S on the isotope mass. Corresponding experimental work to check this prediction in $YBa_2Cu_4O_8$ with enriched ^{18}O is in progress in our laboratory.

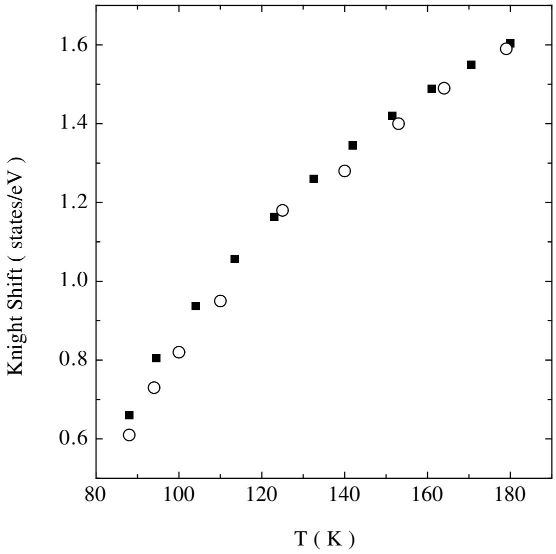

Figure 9.3: Temperature dependence of the spin susceptibility for Cu(2) ($B_0 \perp c$) in $YBa_2Cu_4O_8$. Squares: calculated values; circles: experimental data.

The CDW approach has been developed further to explain electronic properties of the chains [3], 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 this 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 Knight shift of Cu(1).

9.1.3 Inter-metallic $R_2X_2B_2C$ superconductors

The intermetallic superconductors RX_2B_2C with X = Ni, Pd, Pt and R = Lu, Y, La are based on tetrahedrally coordinated XB_2 layers which are separated by RC rocksalt layers. Although they are not HTSC since their T_c values are around and below 20 K, they are challenging substances because they are perhaps conventional electron-phonon coupled superconductors.

In a collaboration with Prof. K. Kumagai, Sapporo University (Japan), we have investigated, between 4 and 400 K, the $LaPt_2B_2C$ and YNi_2B_2C compounds by measuring the Pt and B NMR [4]. In YNi_2B_2C, the ^{11}B Knight shift and the spin-lattice relaxation rate per temperature, $1/T_1T$, increases with decreasing temperature; this contrasts with the behavior in $LaPt_2B_2C$ where both quantities are almost temperature independent. The value of $1/T_1T$ of ^{195}Pt in $LaPt_2B_2C$ is six times smaller than that of metallic Pt, indicating that the density of states of the $5d$ conduction electrons at the Pt site is small and there is no evidence of dominant antiferromagnetic correlations. Our NMR results are consistent with band structure calculations and suggest that, for these borocarbides, a conventional superconductivity mechanisms exists which is mediated by a possibly strong electron–phonon interaction with particular high phonon frequencies due to the light B and C atoms.

9.1.4 Cu coordination in B-Sr-Ca-Cu-O compounds

The work on these superconductors is a collaboration with Dr. Y. Uchida of the National Institute for Research in Inorganic Materials (NIRIM), Tsukuba (Japan), where this new family of structures has been synthesized under high pressure. When comparing these compounds with the Ga and Al systems, one notes that T_c is essentially governed by the structure of the CuO_2 plane and its carrier concentration. The *differently* coordinated Cu sites can be distinguished by NMR-NQR. Thus, probing the different Cu nuclei allows one to study how the various layers participate in superconductivity.

We have started our work with the B-1245 compound, *i.e.* $BSr_2Ca_4Cu_5O_{12.9}$, which has a T_c of about 105 K. The Cu NMR signals could be measured and we got first results for the NQR frequencies and relaxation times. This work is in progress.

9.1.5 Antiferromagnetic infinite-layer compound

The so-called infinite-layer compounds $Sr_xCa_yCuO_2$ contain the basic building blocks of the HTSC, the CuO_2 planes, and no apex oxygen ions. These "simpler" structures thus should help provide a better understanding of the HTSC, in particular the relation between magnetic order and superconductivity. $Ca_{0.85}Sr_{0.15}CuO_2$ is the undoped parent AF system of the infinite-layer superconductors with a Néel temperature of 539 K. This study is complimentary to our previous investigations of the antiferromagnet $YBa_2Cu_3O_6$.

(1) After studying the temperature dependence of the sublattice magnetization in $Ca_{0.85}Sr_{0.15}CuO_2$ [5], we have started to explore NMR parameters which reflect the electronic *spin dynamics* of the antiferromagnet [6]. The ^{63}Cu spin–lattice relaxation rate, $1/T_1$, exhibits an unusual temperature behavior [see Fig. 9.4]. Below 100 K, there is a clear presence of a maximum in $1/T_1$ centered at ≈ 40 K. We attribute the source of this peak to the presence of mobile holes in the CuO_2 plane. From about 100 to 350 K, $1/T_1$ is almost temperature independent. Because this relaxation rate is relatively large, low energy spin excitations induced by the presence of holes in the AF background seem to be the source of this relaxation. Finally, at temperatures higher than 350 K, $1/T_1$ diverges for $T \to T_N^-$ because of the slowing down of magnetic fluctuations on approaching the phase transition.

The investigation of the doping dependence of $1/T_1$ and the spin–spin relaxation time is in progress.

(2) In the meantime, we have finished our investigations of the paramagnetic phase of $Ca_{0.85}Sr_{0.15}CuO_2$ [7]. By measuring the temperature dependence of the magnetic shift, the quadrupolar frequency and the spin-lattice relaxation rate of copper nuclei, we have obtained a variety of information, in particular on the dimensionality and spin–degree crossovers of the magnetic structure.

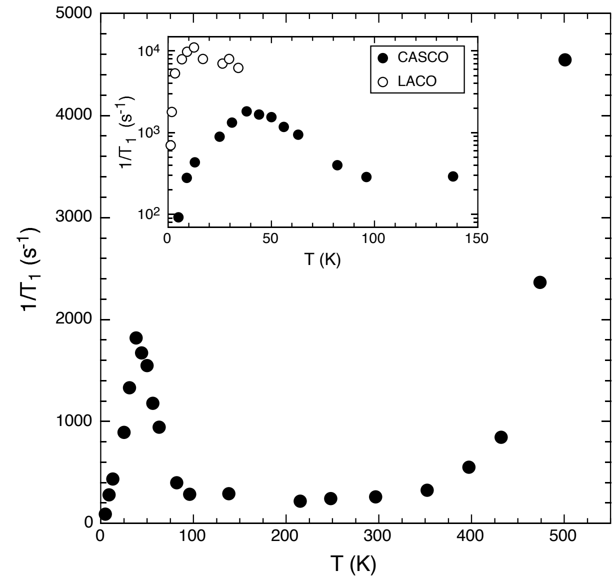

Figure 9.4: Temperature dependence of ^{63}Cu relaxation rate in $Ca_{0.85}Sr_{0.15}CuO_2$ (CASCO). Inset: Comparison with La_2CuO_4 (LACO) data.

In the paramagnetic phase, as well as in the AF phase, the electric field gradient at the Cu site increases with increasing temperature due to thermal lattice expansion. The relatively large lattice contribution to the field gradient reflects the considerable deviation from cubic symmetry of the oxygen ion configuration. There is no indication for any structural changes accompanying the magnetic phase transition.

As in other cuprate materials, the magnetic shift is very anisotropic. Above T_N, its spin part, which is proportional to the static electron spin susceptibility, is changing with temperature as expected for a 2D (2-dimensional) square-lattice Heisenberg AF with an in–plane AF exchange coupling constant, J, being larger than 1000 K.

Above ≈ 600 K, that is in the renormalized classical (RC) regime, the compound behaves as a spin–1/2 2D quantum Heisenberg AF. From the fit of the spin–lattice relaxation rate, W_c, to the RC prediction [see Fig. 9.5], a precise value for J was found, namely 1450(150) K. In the range from 600 K down to T_N+3 K, W_c can be fitted by a power law, $W_c = C[(T - T_N/T_N]^w$, with a critical exponent $w = -0.33(4)$ which agrees with the theoretical result, $w = -1/3$, for a 3D Heisenberg AF.

The ratio of the dynamical electron spin susceptibilities, χ_c''/χ_{ab}'', decreases to zero very close to T_N thus indicating a crossover from the isotropic Heisenberg to the XY–like exchange interaction antiferromagnetism. Thus, our main conclusion is that $Ca_{0.85}Sr_{0.15}CuO_2$, in its paramagnetic phase, undergoes, with decreasing temperature, two successive crossovers: A dimensionality crossover from a 2D to a 3D Heisenberg antiferromagnet followed, very close to T_N, by a spin–degree crossover from a 3D Heisenberg to a 3D XY antiferromagnet.

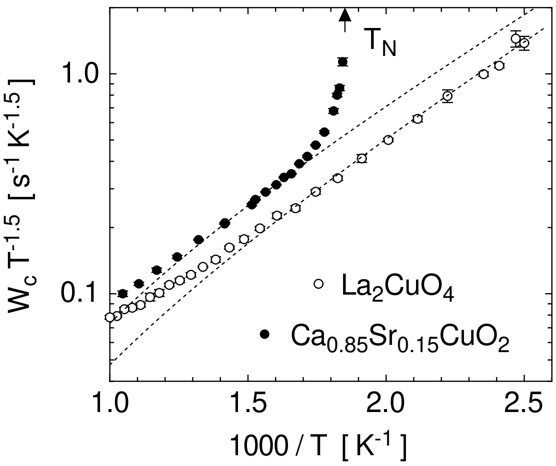

Figure 9.5: $\log(W_c T^{-1.5})$ for $Ca_{0.85}Sr_{0.15}CuO_2$ and La_2CuO_4 [data from M. Matsumura *et al.*, J. Phys. Soc. Jpn. 63 (1994), 4331] as a function of inverse temperature. The dotted lines represent the respective fits to the RC prediction. The arrow indicates the Néel temperature of $Ca_{0.85}Sr_{0.15}CuO_2$.

9.1.6 Antiferromagnet La_2CuO_4

This is the third compound in the series of antiferromagnets we have studied by NMR-NQR. Again, we are concerned with the fact that the 3D AF ordered state results from the interplay of a very strong quasi-2D exchange interaction with small J' and J_{xy} interactions. In La_2CuO_4, we encounter another "perturbing" interaction due to the structural transition, at $\approx$ 530 K, from the high–temperature tetragonal to the low–temperature orthorhombic phase accompanied by a small tilt of the CuO_6 octahedra. The lack of inversion symmetry in the orthorhombic phase introduces the antisymmetric intra-layer Dzyaloshinskii-Moriya (DM) interaction which causes a canting of the spin moments.

Probing the temperature dependence of the sublattice magnetization yields the microscopic information about the various couplings present in the AF structure. In La_2CuO_4 so far, the sublattice magnetization has been evaluated by elastic neutron scattering and by out-of-plane experiments like ^{139}La NQR. We have now studied the sublattice magnetization by probing directly the in-plane Cu nuclei by means of NMR [8].

Our major results are the following. The normalized NMR frequency, which is directly proportional to the decrease of the sublattice magnetization, follows the power law AT^{α} with A = (6.9 $\pm$ 0.5) $\times$ 10^{-6} and α = (2.00 $\pm$ 0.01) below about 100 K, while it is slightly suppressed above 100 K. Such a power law had already been found for $YBa_2Cu_3O_6$, for instance by our out–of–plane Ba site experiments. The good agreement of the various α values points to a common mechanism that diminishes the sublattice magnetization in all these AF compounds We therefore have calculated the sublattice magnetization numerically using a linear spin wave model. Good agreement with the experimental data is obtained by using the following coupling constants: The intra-plane exchange coupling $J = 1590$ K, the intra-plane x-y symmetric exchange coupling $J_{xy}/J = 1.5 \times 10^{-4}$, and the inter-plane exchange coupling $J'/J = 5 \times 10^{-5}$. In addition, we have determined the quadrupole frequency, the angle between the internal magnetic field and the axis of the maximum component of the electric field gradient (EFG) tensor, and the asymmetry parameter of the EFG.

9.2 Superionic conductors

Our collaboration with Prof. B.V.R. Chowdari (Physics Department, National University of Singapore) on lithium-fluorophosphate glasses of composition $xLiF \cdot (1-x)LiPO_3$ continues [9]. Our Li NMR studies revealed that the doping induced enhancement of the conductivity is probably due to an increased number of charge carriers. Furthermore, in LiF doped samples, we detected two "types" of Li ions. One type most likely consists of Li ions embedded in a more or less undisturbed $LiPO_3$ environment. Interestingly, it turned out that this type of site transforms into the other type after a period of about one year. Such an "aging" effect, which could not be detected by x–ray methods, seems to be a manifestation of the inherently metastable glass phase.

This effect has also been investigated via the stationary F ion; the results support the conclusion drawn from the Li study. We have now extended our experiments to the third "NMR isotope" of this glass, namely ^{31}P whose behavior should support previous conclusions and provide new information. In particular, we have measured the spin–lattice relaxation in both the laboratory and the rotating frame of references, in other words we have probed the spectral density of the fluctuating fields (due to the Li diffusion) over a wide range of frequencies, namely from 80 MHz down to 30 kHz [see Fig. 9.6]. To our knowledge, this is the first example of such a study in a superionic glass. The theoretical analysis of these results is in progress.

9.3 High-pressure NMR study of charge–transfer complexes

The neutral–to–ionic (N–I) transition is an unusual phase transition that takes place in some small–gap semiconducting organic charge–transfer complexes of mixed–stack architecture composed of electron donor (D) and electron acceptor (A) molecules. In collaboration with Dr. M. L. Le Cointe (Université de Rennes), we have studied the pressure–temperature phase diagram of the prototype compound of this family, tetrathiafulvalene-*p*-chloranil (TTF–CA) [10].

We have measured the pressure dependence (up to 0.7 GPa) of the ^{35}Cl NQR

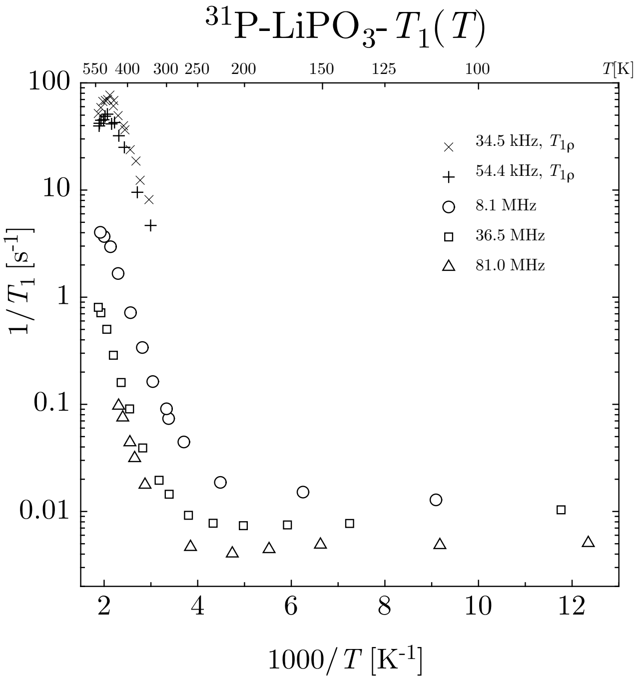

Figure 9.6: Spin-lattice relaxation rate in the laboratory frame, T_1, and in the rotating frame, $T_{1\varrho}$ of ^{31}P in $LiPO_3$.

spectrum at various temperatures between 80 and 220 K. The variation of the NQR frequency with pressure allows a very sensitive probing of the intramolecular change while the splitting of the lines in the I phase yields the symmetry breaking signature. Since the frequency shift for each chlorine nucleus is proportional, in a first approximation, to its local distortion, we can consider the splitting of the I lines to be proportional to the order parameter. In contrast to electronic and vibrational optical spectroscopies, NQR probes the thermal average of the degree of charge transfer, *i.e.* the true thermodynamic parameter.

Together with neutron diffraction experiments, this work suggests that the uncommon electronically driven structural transition can be described in terms of condensation and ordering (crystallization) of charge transfer excitations with a phase diagram analogous to the solid-liquid-gas diagram. To our knowledge, such a phase diagram has not been observed in other solid state systems.

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