9 NMR/NQR Spectroscopy

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The NMR/NQR group has continued its general research plan of studying current problems of condensed matter physics by employing NMR (nuclear magnetic resonance) and NQR (nuclear quadrupole resonance) methods. These spectroscopies allow one to investigate electronic properties in solids at a *microscopic* level and thus provide an essential contribution for a better understanding of the materials studied. Our main interest is still devoted to (i) high–temperature superconductors, (ii) their antiferromagnetic parent compounds, (iii) superionic glasses, and (iv) high-pressure NMR/NQR using either the diamond-anvil cell or helium as the pressure medium.

9.1 High-temperature superconductors

Our research interest during the last year was mainly concerned with the following topics: (i) the nature of the pseudo gap in the normal state of high–temperature superconductors and its relation to other normal state electronic effects; (ii) calculation of the dynamic spin susceptibility under various circumstances; (iii) further experimental data for the coupling in the CuO_2 bilayers; (iv) electronic phase separation, and (v) the anomaly in the irreversible magnetization hysteresis curve.

9.1.1 Isotope effect of the spin gap

Recently, we have discovered an electronic crossover occurring in $YBa_2Cu_4O_8$ (1–2–4) around $T^\dagger = 180$ K [1]. The crossover, which is *not* a structural phase transition, involves enhanced charge fluctuations in planes and chains accompanied by a charge (hole) transfer from chain to plane. $T^\dagger$ is relatively close to another temperature, T^*, which is characteristic for underdoped high–temperature superconductors and which refers to the opening of a spin gap (as seen by NMR) in the electron spin excitation spectrum. In 1–2–4, $T^* \approx 150$ K which lies above $T_c = 82$ K. This spin gap effect explains the strong temperature dependence of the normal state susceptibility in 1–2–4. In collaboration with M. Eremin *et al.* from the Kazan State University, we have argued that the spin gap effect in 1–2–4 is caused by a transition due to a charge density wave (CDW) instability [2]. The proximity of $T^\dagger$ and T^* has been a trigger for these theoretical investigations.

The most crucial experimental verification whether the spin gap is related to or triggered by a CDW or spin density wave (SDW) instability, is probably the measurement of the isotope effect, *i.e.* the change, ΔT^*, of the temperature T^* resulting from a change, Δm, of the isotope composition and its dependence on doping level. We have calculated ΔT^* for the case that ^{16}O is replaced by ^{18}O [2]. The result may be expressed in the form of the isotope coefficient $\alpha = (-\Delta T^*/T^*)\,(m/\Delta m)$.

We have performed, together with susceptibility measurements, a high–accuracy NQR determination of the temperature dependence of the planar ^{63}Cu spin–lattice relaxation rate per temperature unit, $1/T_1T$, in several polycrystalline 1–2–4 samples, either enriched with

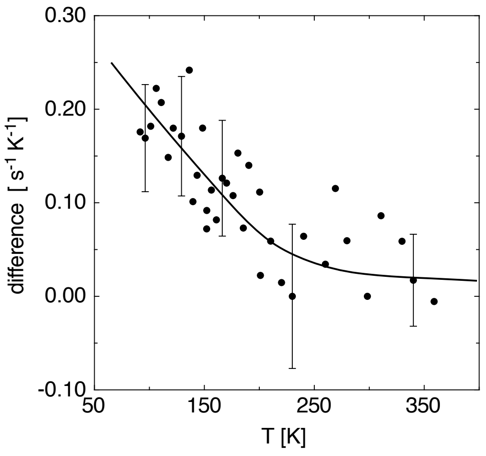

Figure 9.1: *Temperature dependence of the difference of the* ^{63}Cu $1/T_1T$ *values for either* ^{16}O *or* ^{18}O *enriched* $YBa_2Cu_4O_8$ *samples.*

^{16}O or ^{18}O. Figure 9.1 shows that a difference in $1/T_1T$ develops at lower temperatures. The analysis of the measurements reveals that the exponent α is finite and, within the experimental error, is the same for T^* and T_c. This important result implies that the lattice is also involved in the opening of the spin gap, and suggests that the superconducting and the spin gap have a common origin. Recently, it has been concluded [3], based on yttrium NMR Knight shift measurements, that no isotope effect exists. The fact that our relaxation data show a finite isotope effect on the spin gap, points to the necessity to distinguish between the behavior of the dynamic spin susceptibility at zero wavevector (as probed by the Knight shift) and at the antiferromagnetic wavevector (probed by spin–lattice relaxation).

9.1.2 Magnetic properties of Cu–O chains in $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$

It is well known that the CDW and SDW transitions become more pronounced in quasi-one dimensional (1D) systems. Therefore, the chains in the $YBa_2Cu_4O_8$ (1–2–4) and $YBa_2Cu_3O_{6+x}$ (1–2–3) compounds represent a convenient system for clarifying the question whether such transitions exist or not. For many years, the analysis of the spin dynamics in cuprates was hampered by the problem how to take into account effects due to electron correlation. To overcome this problem, one may use a Hubbard–like theory extended by including superexchange, to calculate the dynamic spin susceptibility in the so–called fast fluctuation regime. This approach has been successfully used [2] when dealing with the CDW instability scenario described above.

Within the framework of the $t - J$ model, we have now derived a new expression for the dynamic spin susceptibility, which, contrary to the random–phase approximation for usual metals, takes into account effects due to electron correlation. Our results demonstrate that the main features of the magnetic properties of chains in the 1–2–3 and 1–2–4 compounds can be described on the basis of this new expression; in particular, the temperature dependence of both the NMR spin–lattice relaxation rate and the magnetic shift tensor of the chain Cu(1) nuclei in the normal state can be explained this way. The anomalies (non-Korringa behavior) in the relaxation rate can be attributed to the strong temperature dependence of the amplitude of antiferromagnetic fluctuations at the wave vector $Q = \pi$.

Taking into account experimental data, we argue that the temperature dependence of the shift tensor in 1–2–4 provides evidence for the presence, in the double chains, of incommensurate CDW fluctuations, near the wave vector $2k_F$. In this picture, lattice anomalies in the chains, occurring around $T^\dagger = 180$ (see above), can be understood, for decreasing temperature, as a crossover from the region with one-dimensional to the region with quasi two-dimensional CDW fluctuations.

9.1.3 Calculation of the dynamic susceptibility

In the antiferromagnetic (AF) phase of the AF parent compounds of high–temperature superconductors, the Cu spins of the CuO_2 planes exhibit long range order and this order is gradually destroyed by doping. Therefore, the understanding of the evolution of the normal state magnetic properties of CuO_2 planes with doping is believed to be a key to elucidate the unusual properties of these superconductors. The hole dynamics in an AF background is perfectly described by the dynamic spin susceptibility which provides direct information about the low energy excitation spectrum and its evolution with doping.

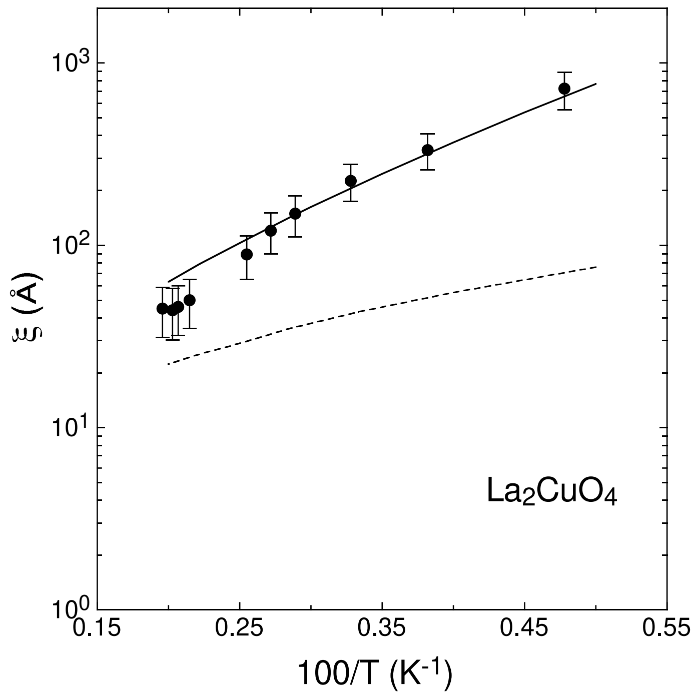

Figure 9.2: *The calculated temperature dependence (solid line) of the antiferromagnetic correlation length, ξ, compared with experimental data (closed circles) for* La_2CuO_4 *and with the result (dashed line) following from the Kondo–Yamaji procedure*

In contrast to other models and theories, we have investigated [4] the dynamic spin susceptibility within a constraint–free theory which may be based, as a natural starting point, on the presentation of the $t - J$ model in terms of Hubbard operators . This presentation obeys rotational symmetry of the spin correlation functions and automatically guarantees the exclusion of double occupancy. Moreover, such a technique allows to take into account the magnetic effects near half filling of the energy bands where the random phase approximation does not work. By taking into account both electron and AF spin correlations, we have calculated the dynamic spin susceptibility of CuO_2 planes in high–temperature superconductors. Our model is able to reproduce the main features of the temperature and doping dependence of the AF correlation length in doped compounds (*e.g.* $La_{2-x}Sr_xCuO_4$) and in the pure Heisenberg antiferromagnet like La_2CuO_4 (see Figure 9.2) where our model is superior to the old Kondo–Yamaji procedure.

9.1.4 Inter– and intra–plane coupling

Superconductivity in Y–Ba–Cu–O compounds takes place in the CuO_2 planes which form double planes or bilayers. The coupling between individual planes of a bilayer and its influence on the spin dynamics are one of the most important topics in present research. In the past, we have performed extensive NQR/NMR studies of $Y_2Ba_4Cu_7O_{15}$ (2–4–7) by measuring various planar Cu NQR/NMR parameters such as different relaxation times and the Knight shift. We found that all these parameters, which are related to the wavevector and frequency dependent electron spin susceptibility, exhibit a common temperature dependence in the normal phase of 2–4–7; this result had been interpreted as the signature of a coupling between adjacent planes within a bilayer.

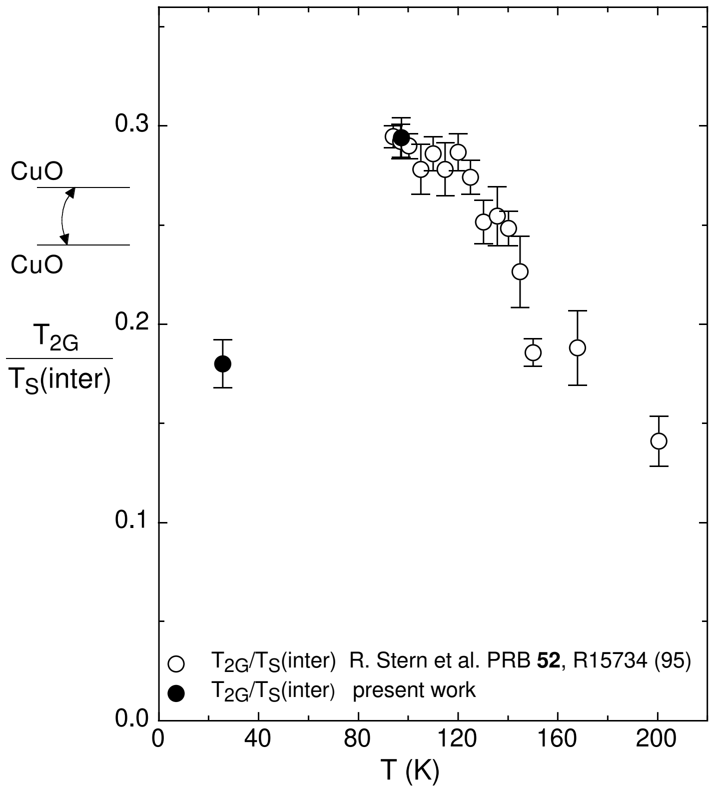

Figure 9.3: *Temperature dependence of the ratio of the relaxation rates* $1/T_{2G}$ *and* $1/T_S$ *which are measures for the intra– and inter–plane coupling, respectively.*

Then, by performing NQR spin–echo double resonance (SEDOR) experiments [5], we have confirmed independently and directly the existence of the inter–plane coupling in 2–4–7 and have determined the temperature dependence of the inter–plane component of the static electron spin susceptibility in the normal state. We have now extended those studies into the superconducting phase by again performing SEDOR NQR with the planar Cu sites in 2–4–7.

Our data (see Figure 9.3) suggest that, within a bilayer, the single planes, which are strongly coupled in the normal state, decouple in the superconducting state.

9.1.5 Electronic phase separation

Whether an electronic phase separation is present in some high–temperature superconductors is still a controversial topic. Extensive NQR studies to elucidate the problem have been performed by the group of M. Teplov of the Kazan State University. In particular, they have studied $TmBa_2Cu_4O_8$ (Tm124) which has a $YBa_2Cu_4O_8$ (Y124) structure and the same superconducting properties as Y124. Previous investigations of the Cu(2) NQR in Tm124 have revealed some specific features of the spectra which were interpreted in terms of an electronic phase separation.

To gain new insight into the inhomogeneous distribution of holes in the CuO_2 planes, we have performed, in collaboration with the Kazan group, Cu NQR studies in Zn doped $TmBa_2(Cu_{1-x}Zn_x)_4O_8$ [6]. Two samples were used, one with x=0 (Tm124) the sample already used before, the other with x=0.027. Among others, a sharp increase of the Cu linewidth in Tm124 was found when the sample became superconducting. Such an increase is also present in $YBa_2Cu_3O_7$ and $TmBa_2Cu_3O_7$.

The origin of this broadening can hardly be associated with crystal structure imperfections since, as known from literature, X-ray and neutron diffraction studies show no appreciable excess distortions of the crystal structure below T_c. On the other hand, the broadening of the Cu(2) NQR spectrum can be described fairly well by the following model. Cu(2) nuclei possess two slightly different NQR frequencies due to two different states differing by their hole concentration; the lifetimes for residing in these states are different. If one assumes a re-distribution of these lifetimes when the sample becomes superconducting, the broadening can be explained. The fit of the model to the experimental data is quite satisfying.

9.1.6 Checking the "fishtail" effect

There is an anomaly in the irreversible magnetization hysteresis curve in single crystals of 1–2–3, often referred to as "fishtail effect": the magnetization increases anomalously on increasing the magnetic field. This feature is still of particular interest since the high critical currents calculated from the maximum of the magnetization curve suggests that even at high fields large critical currents can be passed through the 1–2–3 material.

It is a striking feature of *highly pure single crystals* of $YBa_2Cu_3O_{6.9}$ (1–2–3–6.9) that the fishtail effect can be switched off and on in a reversible manner by changing the annealing temperature. Erb *et al.* [7] have proposed the following model. Annealing the crystal at 510 K (and 1 bar oxygen pressure) causes clustering of the oxygen vacancies and the clusters form pinning centers which then lead to the fishtail effect. However, annealing the same sample at 650 K (and 100 bar), produces a random distribution of the vacancies which are now too small to act as pinning centers. In $YBa_2Cu_3O_7$ (1–2–3–7), no fishtail effect could be observed due to the absence of vacancies.

Cu NMR is the appropriate method to check this hypothesis because the resonance frequency of copper nuclei depends on their oxygen coordination. In 1–2–3–7, only two very sharp lines have been found corresponding to planar Cu(2) and to four-fold coordinated chain Cu(1). This indicates filled chains and confirms the extremely low defect concentration of this state. In 1–2–3–6.9 annealed at 510 K, these two lines become much broader and the

Cu(2) signal even exhibits three distinct peaks. Furthermore, two additional lines were detected. One line has been assigned to two–fold coordinated Cu(1) which implies the presence of sections of empty chains. This clearly proves that part of the oxygen vacancies are now clustered. The assignment of the second additional line is still controversial; it could be related to the interface between filled and empty chains. These investigations and experiments with 1–2–3–6.9 annealed at 650 K are in progress.

9.1.7 Mixed magnetic and quadrupolar spin–lattice relaxation

In many of our recent relaxation time experiments in superconductors, we observed the presence of both magnetic and quadrupolar time dependent interactions, for instance in copper relaxation studies. This is a situation quite common in condensed matter NMR. The question arises whether it is possible to deduce, directly from the experiment, the admixture of a weak contribution, for instance due to quadrupolar interaction, to the overall relaxation. In other words, how sensitive is the form of the magnetization recovery law in respect to the two types of interactions?

We have now performed calculations for a static quadrupolar perturbed Zeeman Hamiltonian in the presence of mixed magnetic and quadrupolar time dependent interactions [8]. This is done for three cases differing by the initial conditions and for spins $I = 1$, $I = 3/2$, and $I = 5/2$; the spin $I = 7/2$ is treated for magnetic fluctuations only. Most results are exact; approximate solutions were found for the general case of $I = 5/2$. We analyzed the whole parameter space constructed by the probabilities for magnetic and quadrupolar induced transitions. This is a necessity when dealing with single crystals or partial oriented powders, since in these cases the different contributions of the fluctuations depend on the angle they form with the external magnetic field, so that extended parts of the parameter space are sampled. We also investigated how sensitive the form of the recovery law of the magnetization is in respect to additional fluctuations (*e.g.* additional quadrupolar fluctuations in the presence of predominantly magnetic fluctuations), in order to determine whether it is possible to extract directly from the recovery law the magnetic and quadrupolar contributions.

We found that, in a surprisingly large region of the transition probability parameter space, it is almost impossible, within experimental errors, to separate magnetic and quadrupolar contributions to the relaxation. Instead, the "dominant" contribution determines the time evolution of the recovery law, *i.e.* the system can approximately be described by a single time constant, T_1^{eff}. In other words, even if the initial assumption of the experimentalist is wrong (lets say, the assumption of pure magnetic fluctuations), the extracted T_1 is of the right order of magnitude.

Thus, to test any hypothesis about the origin of the spin–lattice relaxation in the system under consideration, additional information is necessary. This may be provided by the temperature dependence of the relaxation or by the differing results obtained from different isotopes of the respective element. If single crystals are available, the relaxation's angular dependence yields valuable information. Because of the different transformation behavior of the electric field gradient tensor and the external magnetic field, a certain relaxation channel may vanish for a given orientation.

9.2 Antiferromagnetic parent compounds

Our interest is focused on the electronic and magnetic structure of antiferromagnetic (AF) parent compounds from which many high–temperature superconductors are derived. In detail, we are studying (i) the degree of the quasi–2D character of the AF state and its relation to the exchange coupling constants; (ii) the spin dynamics of a S=1/2 2D quantum Heisenberg AF; (iii) low energy excitations induced by the presence of holes; and (iv) the "magnetic moment distribution" at the planar CuO site.

9.2.1 The paramagnetic phase of $YBa_2Cu_3O_6$

Although $YBa_2Cu_3O_6$ (1–2–3–6) is the AF parent compound of the whole Y–Ba–Cu–O superconductor family, an adequate NMR study of the planar Cu(2) site in the *paramagnetic* (PM) phase has still been missing. This is due to severe experimental difficulties like the extremely short spin–spin and spin–lattice relaxation of the Cu(2) nuclei as well as its disadvantageous quadrupole coupling. Our first attempts to study Cu(2) in the 1–2–3–6 PM phase were done on c–axis oriented polycrystalline powders [9], however the thermal instability of the epoxy resin, used to keep the oriented powder in its position, limited the investigation to a very narrow temperature range.

Because now sufficiently large single crystals are available (synthesized by A. Erb, University of Geneva), we have extended our studies to higher temperatures [10]. Among others, we have measured the Cu(2) spin–lattice relaxation rate, W_c, which decreases with rising temperature. This rate is related to the imaginary part of the electron spin susceptibility taken at the AF wavevector.

In the so–called renormalized classical (RC) regime, the low–energy spin dynamics of a S=1/2 2D quantum Heisenberg AF is described in terms of the spin–wave stiffness constant and the spin–wave velocity, both being linear functions of the intraplanar coupling constant, J. W_c can then be connected with the planar spin correlation length. Our data can be described quite well by this model (see Figure 9.4). Within the temperature range we studied (500 to 700 K), 1–2–3–6 behaves in a similar way as La_2CuO_4.

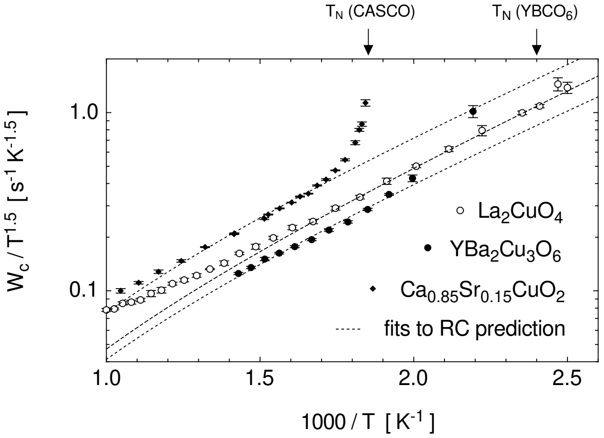

Figure 9.4: *Comparison of the plane* Cu(2) *spin–lattice relaxation rate, W_c, with theoretical prediction in the RC regime for various antiferromagnetic compounds.*

9.2.2 Internal magnetic field at oxygen sites in $YBa_2Cu_3O_6$

As to the AF phase of $YBa_2Cu_3O_6$, we are interested in the temperature dependence of the internal magnetic field which is created by the sublattice magnetization. While the internal field at the Cu site has been measured by other groups, we have studied, in previous work [11], the field at the Ba site and have now extended the investigation to the oxygen site; the reason is as follows.

When calculating the field at the Ba site, we found that assuming point like magnetic moments at the Cu(2) sites yields fields which are three times larger than the experimental value. In a second approach, extended $3d_{x^2-y^2}$ electrons are assumed and their dipolar field is computed by evaluating the integrals over the spherical functions of these electrons [12]. However, the effect of finite size and anisotropy of the Cu d electrons is only in the order of a few percent. A possible explanation of the discrepancy between these values and the experimental result could be the copper–oxygen covalence. If one assumes that part of the magnetic moment is located at oxygen ions, which corresponds to an extension of the "magnetic moment distribution", the dipolar field at the Ba site would be reduced.

To test this idea, we have measured the internal field at the two oxygen sites in the CuO_2 plane using a high–quality single crystal (synthesized by A. Erb, University of Geneva) with enriched ^{17}O [13]. The components of the magnetic field vector and the electric field gradient tensor have been determined. The magnetic field at the planar oxygen sites has a value of 0.6 Tesla which cannot be explained by assuming point like magnetic moments located at the Cu(2) sites. This result supports our conclusion from the Ba experiments and calls for an elaborate quantum mechanical calculation of the internal field. This then will provide further information on the basic question about the hybridization of copper and oxygen orbitals.

9.2.3 The antiferromagnetic phase of $Ca_{0.85}Sr_{0.15}CuO_2$

The present work in $Ca_{0.85}Sr_{0.15}CuO_2$ (CASCO) is a continuation of our previous NMR and NQR studies of its AF [14] and PM [15] phase. CASCO 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 and present investigations of the antiferromagnet $YBa_2Cu_3O_6$.

In CASCO, the intra-plane Heisenberg superexchange integral is $J \approx 1500$ K, as in the more popular La_2CuO_4 (LACO), while the relatively strong inter-plane coupling ($J' \approx 10$ K with respect to $J' \approx 5 \times 10^{-2}$ K in LACO) makes it peculiar in the category of layered cuprates. In particular, the large J' is expected to affect the Cu^{2+} spin-dynamics and is considered an important ingredient for a high value of T_c.

We have now performed the first complete study of the in-plane Cu nuclear spin-lattice and transverse relaxation in the AF phase of CASCO. We studied two different samples. From their T_N values and by information extracted from spin-lattice relaxation, we determined the presence of a small amount of holes introduced by Ca and Sr vacancies into the CuO_2 plane, namely about 4.9 $\times 10^{-4}$ and 1.1 $\times 10^{-4}$, respectively.

The spin-lattice relaxation is strongly affected by the low energy excitations induced by the presence of holes. In particular, the rate maximum at 40 K is induced by the diffusive motion of the holes. The values for the distribution of activation energies characterizing the diffusive process is the same for the two samples, and it is very similar to the one obtained for CuO:Li by Caretta *et al.* [16].

The transverse relaxation rate is mainly driven by the spin-spin indirect coupling, and this is true for the whole temperature range. The most surprising result of this work is the strong dependence of the spin–spin indirect coupling on the hole concentration. The reason for this probably is that the electronic spin susceptibility, taken at the AF wavevector, depends strongly on hole concentration, at least in the limit of very low doping.

9.3 Superionic glasses

9.3.1 Relaxation of the stationary ion

Our investigation of lithium conducting phosphate glasses of composition $x\mathrm{LiF}\cdot(1-x)\mathrm{LiPO_3}$, where the addition of the dopant salt, LiF, enhances the conductivity, have reached an important result. Our objective has been to monitor the ionic diffusion in these glasses from the point of view of both the stationary and the mobile ions. Relaxation time measurements, in particular, yield information about the correlation function of the fluctuating fields caused by ion diffusion. These advantages had been exploited when we used ^{7}Li, ^{6}Li and ^{19}F NMR to study these glasses (with $x = 0$; 0.30 and 0.35). However, all NMR studies in glasses are hampered by the intrinsic disorder of the structure. Hence, the temperature dependence of the spin-lattice relaxation is usually not described by the Bloembergen–Purcell–Pound (BPP) theory which is based on an exponentially decaying correlation function and which has been very successfully applied in liquids and some solids, including some *crystalline* superionic conductors.

We have circumvented the deviations from the BPP behavior by a modification of the BPP model which is physically obvious and results in a small number of adjustable parameters. Because of the intrinsic disorder of the glass, we have assumed a distribution of those activation energies which are associated with the ion diffusion process. We have obtained a consistent description of the relaxation rates of the stationary ^{31}P in the *undoped* glass, $\mathrm{LiPO_3}$, by covering a wide frequency range (from 34 kHz to 81 MHz) [17]. We have now applied the model to the ^{31}P relaxation in a *doped* glass, namely $0.35\mathrm{LiF}\cdot0.65\mathrm{LiPO_3}$. Choosing ^{31}P rather than ^{19}F simplifies the analysis of the data because so–called quadrupolar effects, which complicate the interpretation of ^{7}Li and ^{6}Li data, are absent. Our results agree quite well with conductivity data.

9.3.2 Magic angle spinning

We have now installed and tested our *magic angle spinning* (MAS) device. In this technique, one rotates the whole NMR sample about an axis which makes the "magic angle" α with the external magnetic field; α is determined by $3\cos^2\alpha = 1$. MAS makes the time averaged dipolar coupling to vanish, it eliminates chemical shift anisotropies and first–order quadrupole couplings. However, the signals obtained without MAS should not be too broad; therefore, in many of our superconductor studies, MAS could not be employed.

We have now obtained the first MAS spectra, namely in the superionic glass $x\mathrm{LiF}\cdot(1-x)\mathrm{LiPO_3}$. By introducing LiF, non–bridging P–F segments are created and a second ^{31}P signal appears which can be resolved from the signal obtained in the undoped glass only by MAS. Figure 9.5 shows these two signals and the dependence of their intensities on the amount of doping, *i.e.* the parameter x. Detailed experiments are in progress.

9.4 High–pressure NMR

After a long break due to a shortage of manpower, we have resumed our work with the diamond-anvil cell (DAC). We have improved the system and we intend to extend the exper-

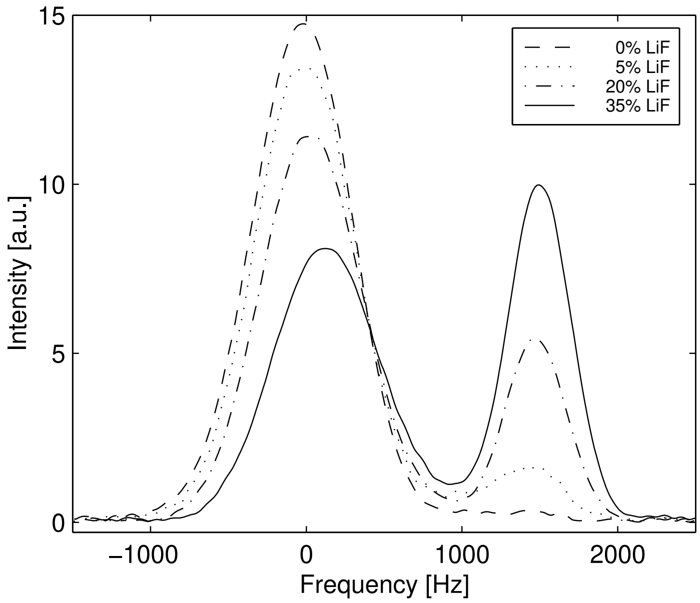

Figure 9.5: *MAS spectrum of the two* ^{31}P *signals in* xLiF$\cdot(1-x)$LiPO$_3$ *for various doping levels.*

iments with the antiferromagnet $Ca_{0.85}Sr_{0.15}CuO_2$ (CASCO) to pressures above 1 GPa.

9.4.1 Pressure induced shift of T_N in $Ca_{0.85}Sr_{0.15}CuO_2$

Using our helium-pressure device, we have measured the pressure variation of the temperature dependence of the sublattice magnetization of the antiferromagnet CASCO (see also above) by employing the internal magnetic field for doing ^{63}Cu NMR. In the temperature range 81 to 344 K, where we performed the experiment, the Cu Larmor frequency linearly increases proportional to the applied pressure, at least up to 0.6 GPa (see Figure 9.6). From the data we determined both the relative reduction of the magnetization for certain pressure and the relative reduction of the magnetization at ambient pressure. The difference between both magnetizations increases with increasing temperature. This is strong evidence that a pressure induced shift of T_N exists. By rescaling the temperature and assuming no change of the dimensionality, the relative shift of T_N has been estimated to be 0.018 (GPa)$^{-1}$. This value has the same order as that reported for La_2CuO_4. As a "by-product", we have determined the pressure dependence of the Cu quadrupole coupling.

9.4.2 Improvements of the diamond-anvil cell

A crucial part of the DAC is the gasket which houses the sample hole into which one places the substance under investigation together with the pressure transmitting mineral oil. In our earlier experiments, we used rhenium metal [18] and the beryllium–copper alloy Berylco [19]. We performed an extensive search for a better material including non-metallic substances which should not only resist high pressure but also should not suffer plastic deformation due to the applied forces. We settled on a Ni-Cr alloy and then investigated various geometrical arrangements of gasket and radio–frequency coil. We finally found a gasket with 0.7 mm hole diameter suitable to contain 300 μg of CASCO. This set–up yielded a sufficiently large signal–to–noise ratio of the ^{63}Cu NMR signal at ambient pressure. It should be noted that

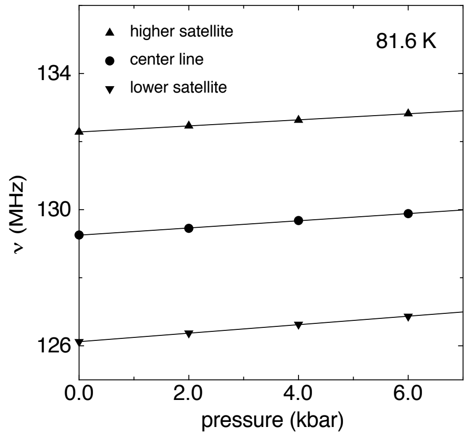

Figure 9.6: *Pressure dependence of the three lines of the quadrupole splitting of* ^{63}Cu *in* $Ca_{0.85}Sr_{0.15}CuO_2$*. The frequency of the "center" line is a measure for the sublattice magnetization.*

our previous DAC experiment were dealing with Na, Li, and Cs samples where *all* nuclei (or 92.5% in the case of Li) are NMR sensitive. In CASCO, only a fraction of nuclei contributes to the ^{63}Cu signal thus demanding a larger sample.

A second improvement concerns the optical system for pressure measurement where the old equipment has been replaced by a commercial spectrometer. The new DAC set–up is now ready for extending the above mentioned CASCO experiments into the pressure range beyond 1 GPa.

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