

^{199}Hg and $^{63,65}\text{Cu}$ NMR Studies of Mercury Based High- T_c Superconductors

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Abstract. Hg-oxide ceramic high temperature superconductors were studied by ^{199}Hg and $^{63,65}\text{Cu}$ NMR spectroscopy. Room temperature spectra, spin-spin and spin-lattice relaxation times of samples with different superconducting transition temperatures are presented. A spin-lattice relaxation time of $T_1 = 35$ msec and a spin-spin relaxation time of $T_2 = 1.6$ msec were found for the ^{199}Hg NMR. All samples exhibit similar characteristic powder spectra caused by an axially symmetric ^{199}Hg spin interaction. The isotropic value and the anisotropy of the tensor relative to solid HgCl_2 as a standard substance is estimated. Furthermore, results of $^{63,65}\text{Cu}$ NMR measurements at a temperature of 4.2 K which exhibit a typical powder line shape (for $I = 3/2$) are presented.

1. Introduction

With the discovery of high temperature superconductivity (HTSC) in Hg-based oxide ceramics $\text{HgBa}_2\text{CuO}_{4+\delta}$ in 1993 [1], these materials have become a major object of HTSC investigations [1–6]. $\text{HgBa}_2\text{CuO}_{4+\delta}$ is the first member of the homologous series of the Hg-based oxide cuprate system showing maximum transition temperatures of 133 K and T_c 's > 150 K [4–5, 7–9] under pressure. Ever since the first reports of HTSC in yttrium and thallium copper-oxide ceramic materials, nuclear magnetic resonance (NMR) spectroscopy has been an important tool in the study of these materials [10–14]. NMR allows one to obtain valuable information about the local environment, i.e. electronic structure and magnetic properties of the materials as well as dynamic processes via relaxation measure-

ments. Due to its spin of 1/2 the mercury isotope ^{199}Hg is a convenient nuclear spin label (such as ^{205}Tl in Tl-HTSC's [14]) for the study of Hg-based HTSC materials. With ^{199}Hg NMR we investigated different samples of Hg-based HTSC with a nominal composition of $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Hg-1201) and $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ (Hg-1212).

2. Experimental Details

The samples were synthesized according to [1] in a two-step solid state reaction, using $\text{Ba}_2\text{CuO}_{3+\delta}$ and HgO as primary materials. The X-ray structure of Hg-1201 exhibits tetragonal symmetry.

The NMR-data were obtained using a home built 7T pulse Fourier transform solid state NMR spectrometer (proton resonance frequency 297.75 MHz). The ^{199}Hg measurements were performed at room temperature. Using an amplifier power of 1 kW we optimized the probe until we achieved a 90° -pulse width of 1.9 μsec which was sufficiently short to homogeneously excite the whole spectrum over the entire spectral range. To overcome the dead time problem we recorded the spectra using the Hahn spin-echo-sequence (90° – 180° –echo) [16]. A full 64 combination phase-cycle of the sequence was applied in order to suppress electronic artifacts and quadrature errors in the spectra. Solid HgCl_2 was taken as a convenient standard substance for calibrating the ^{199}Hg spectra and the maximum of the powder spectrum was used as reference for the measurements (0 ppm, corresponding to 53.307 MHz in our spectrometer). It should be mentioned that solid HgCl_2 is more suitable as a reference standard than liquid solutions of mercury salts, because the chemical shift for the latter depends strongly on the ionic concentration in the solution [17]. In order to achieve spectra with a reasonable signal-to-noise ratio, we had to accumulate approximately 100000 scans for each spectrum which was possible because of the relatively short spin-lattice relaxation time. Spin-lattice relaxation measurements were performed using the saturation recovery pulse sequence, followed by the phase cycled echo-sequence to detect the signal. Obtaining a result within a reasonable time span was accomplished by restricting the measurement of the spin-lattice and spin-spin relaxation time only to the sample with most material (bulk sample), applying 32000 scans for each delay time. The $^{63,65}\text{Cu}$ NMR spectrum from Sample 3 was measured at 4.2 K by a field sweep method with a center-frequency of 64 MHz.

3. Results and Discussion

The superconducting properties of the samples were characterized by means of dc SQUID susceptibility measurements. The results of these experiments are shown in Fig. 1. From these measurements we extracted the transition tempera-

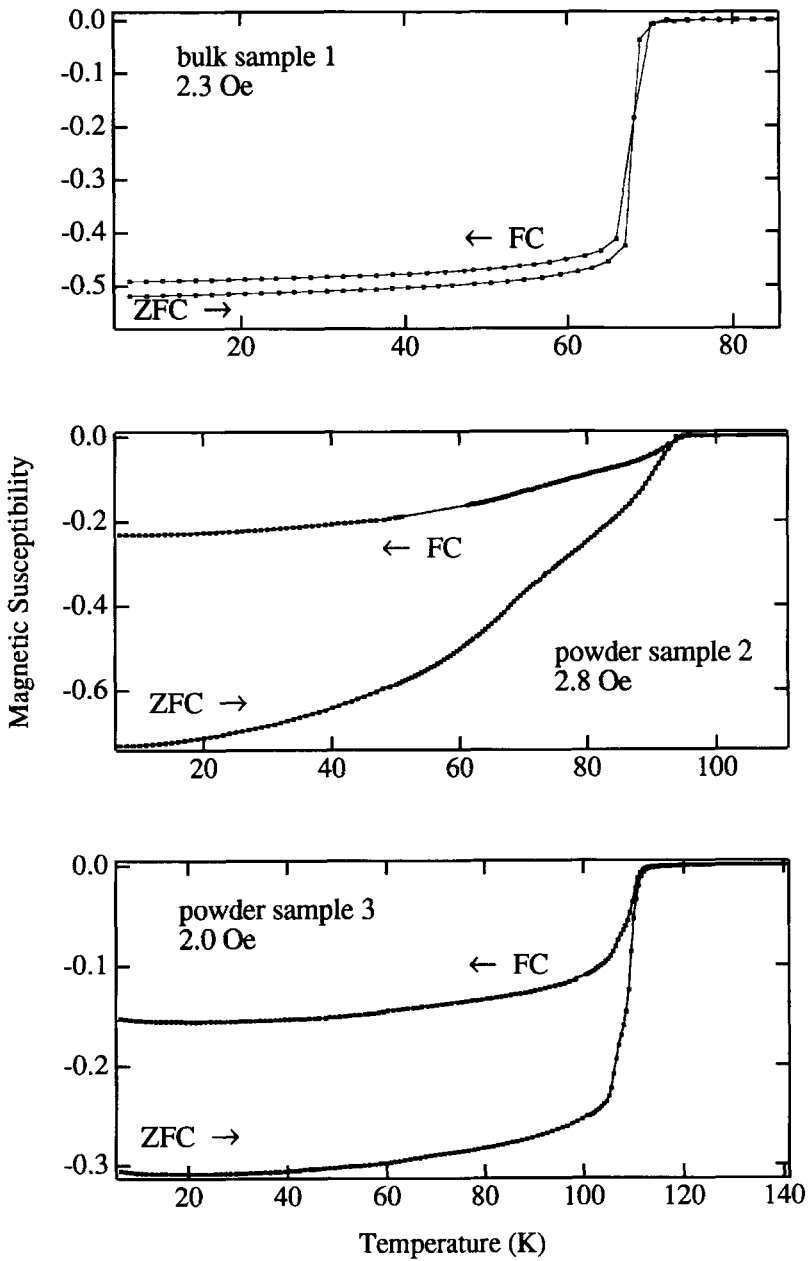
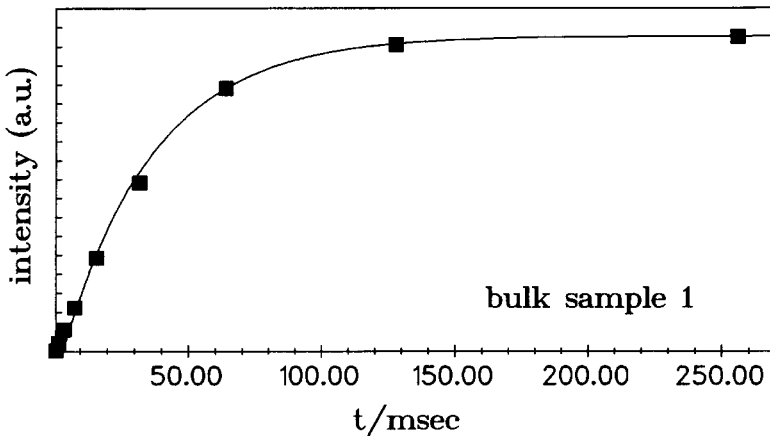


Fig. 1. Dc-magnetic measurements. The lower branches were recorded during warming after sample precooling in zero external field (ZFC). The upper curves are field cooling (FC).

Table 1. Superconducting properties of the samples with different macro structure and compositions.

Sample	T_c (K)	ΔT_c 10–90%	Max. shielding fraction (ZFC)	Max. Meissner fraction (FC)	Composition
1 (bulk)	71	5	0.52	0.49	$\text{HgBa}_2\text{CuO}_{4+\delta}$
2 (powder)	94	55	0.73	0.23	$\text{HgBa}_2\text{CuO}_{4+\delta}$
3 (powder)	112	26	0.31	0.16	$\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$

ture and the corresponding shielding fractions (Table 1). Sample 1, which was pressed into a small rod (bulk sample), showed a sharp transition at the temperature of 71 K. The relatively low transition temperature of this sample can be attributed to a lower oxygen content than that for Hg-1201, with high T_c (94 K). Sample 2 (fine grained powder) exhibits a transition temperature of 92 K. In comparison to the first sample, the larger transition width is obviously due to a weaker intergranular coupling among different crystallites. The third sample, $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ (fine grained powder), exhibits a transition temperature of 112 K. The low T_c compared to the Hg-1212 with $T_c = 127$ K ($\delta = 0.22$) can be explained by the lower oxygen content. The result of the room temperature spin-lattice relaxation measurement for Sample 1 is shown in Fig. 2. The magnetization decay is in good approximation monoexponential and we obtained a value of $T_1 = 35$ msec from the fit. This value is comparable to results of the spin-lattice relaxation measurements of other oxide ceramic HTSC compounds. [14, 18] The results of the spin-spin relaxation measurements are shown in Fig. 3 and Fig. 4. Again, a monoexponential decay of the spectral intensity was observed in good approximation and we obtained a value of $T_2 = 1.6 \pm 0.2$ msec.

**Fig. 2.** Time dependent spin polarisation of Sample 1. The spin-lattice relaxation time T_1 is 35 msec.

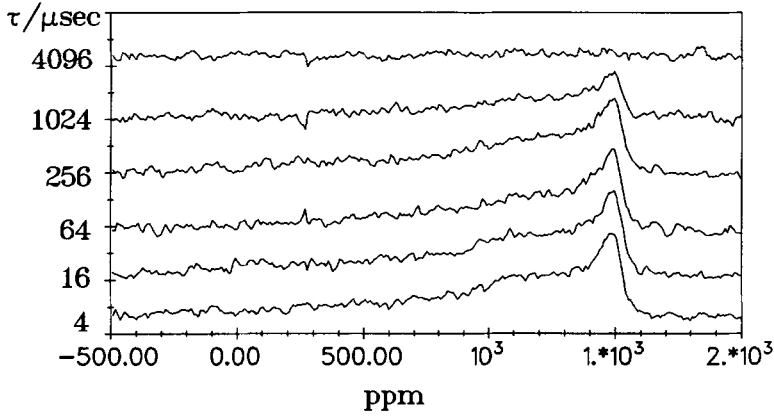


Fig. 3. Monoexponential decay of spin-spin relaxation in dependence of the delay time τ between the 90 degree and the echo-pulse.

The ^{199}Hg NMR spectra of the three samples are shown in Fig. 5. The poor signal-to-noise ratio of $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ (Sample 3) was caused by the small amount of material. All spectra have one thing in common; they show similar line positions and line broadenings, which are affected neither by the difference in granularity nor by the difference in the oxygen stoichiometry of the samples. The width of the spectra is approximately 2000 ppm and they have the typical powder line shape of a spin 1/2 nucleus under the influence of an axially symmetric second rank tensor interaction [14, 19], where the maximum of the line is given by one principal value and the width is determined by the anisotropy of the tensor. We estimated the principal values of this tensor by simulating the spectrum of the bulk sample possessing the best signal-to-noise ratio. These data

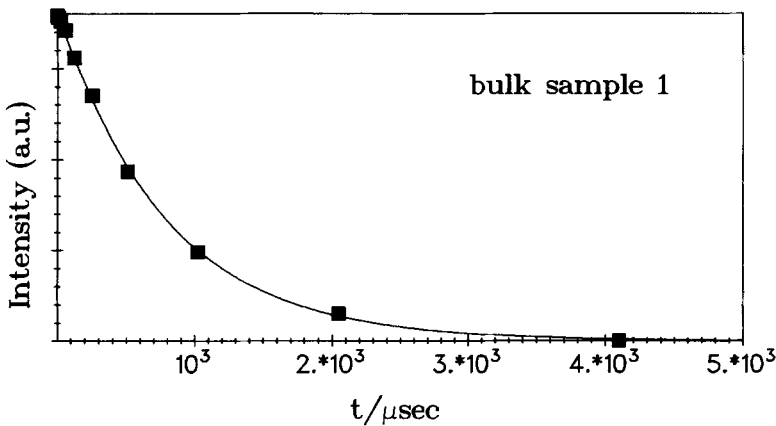


Fig. 4. Time dependent spin-spin relaxation of Sample 1. The spin-spin relaxation time T_2 is 1.6 msec.

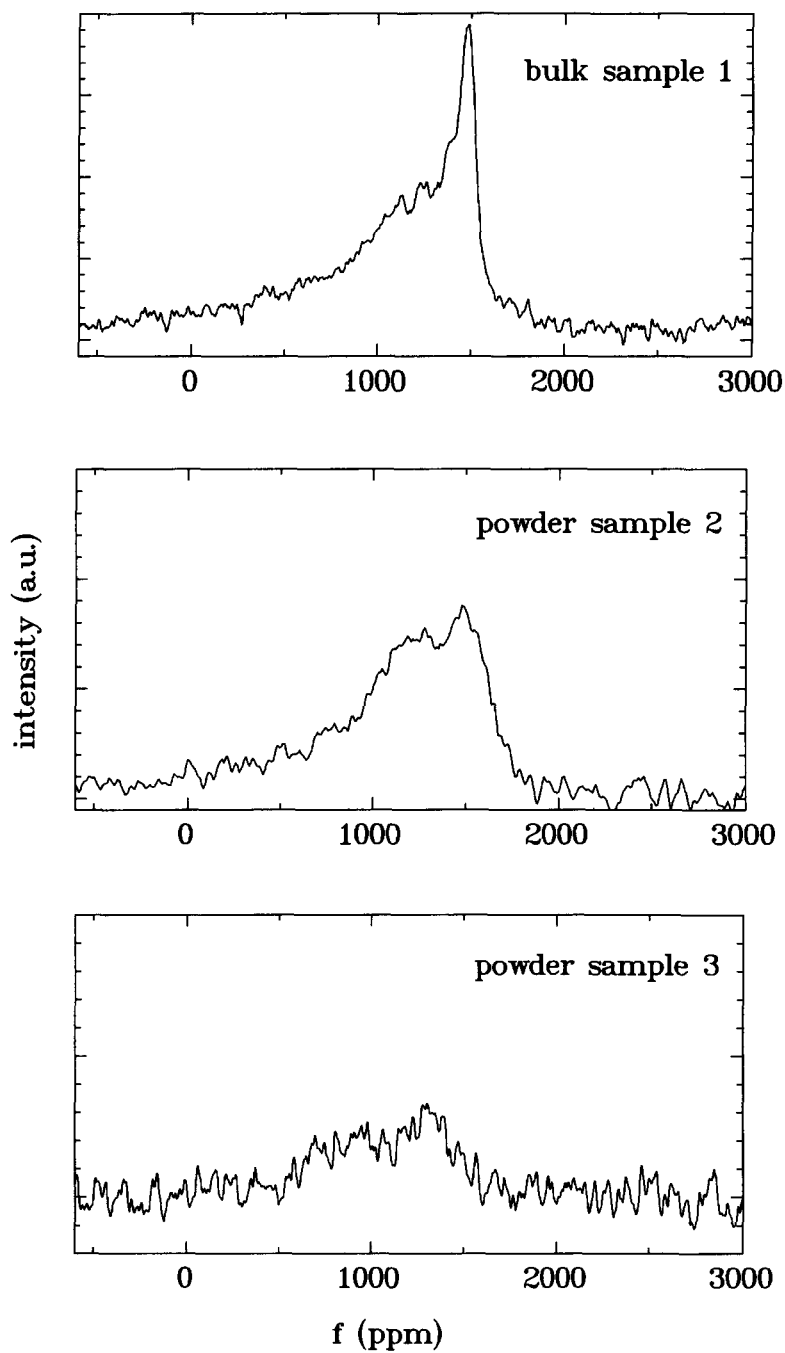
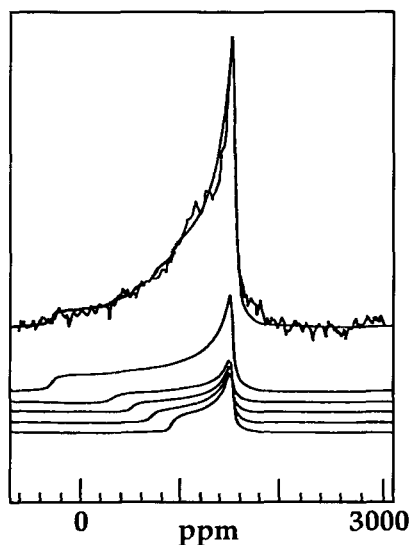


Fig. 5. ^{199}Hg NMR spectra for different Hg-based HTSC (reference: HgCl_2).

Table 2. Parameters of the powder lines used for the fit in Fig. 5; the superposition of these lines simulate the experimental spectrum (Sample 1).

Line	A_{\perp} (ppm)	A_{\parallel} (ppm)	A_{iso} (ppm)
1	1500	900	1266
2	1500	700	1200
3	1500	500	1133
4	1600	300	1066
5	1700	-300	1000

underline the fact that the experimental line shape cannot be matched by a single tensor, so we varied the fit and listed the calculated value showing the lowest deviation from the experimental spectrum. A good agreement between experimental data and simulated spectra was obtained by a superposition of a minimum of 5 tensors with differing anisotropy width (Table 2, Fig. 6). The isotropic values of the resulting tensors vary in the range of 1000 to 1270 ppm and the anisotropies in the range of 600 to 1800 ppm. We attribute the distribution of these tensor values to a distribution of magnetically inequivalent environments of the Hg atoms in the sample, which could be caused by a distribution of oxygen deficiency in the unit cells. Monoexponential decay for both T_1 - and T_2 -decay curves was found within experimental error, so we concluded that the relaxation times of the various spectral components are of comparable size and

**Fig. 6.** Simulation of the experimental spectrum (Sample 1) by a superposition of five theoretical anisotropic powder lines.

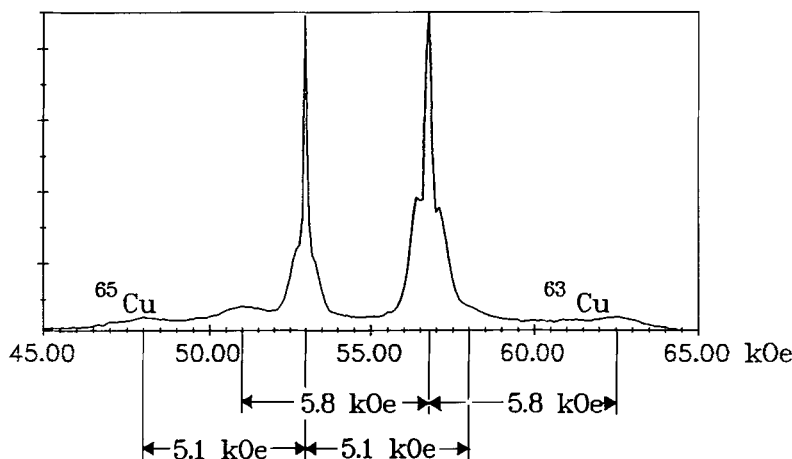


Fig. 7. $^{63,65}\text{Cu}$ NMR spectrum of $\text{HgBa}_2\text{CuO}_{4+\delta}$ (Sample 3) measured at 4.2 K.

therefore impossible to be resolved in the T_1 - and T_2 -decay curves. In other words, we interpret the resulting T_1 and T_2 times as being average values. Detailed measurements with MAS technique and on oriented samples are necessary for supporting such an interpretation. These measurements are currently in progress.

Following, we discuss possible ^{199}Hg interactions leading to the tensor. Since ^{199}Hg is a spin 1/2 nucleus, it shows no quadrupolar interaction. Due to the low gyromagnetic ratio of the ^{199}Hg nuclei as well as the relatively low abundance, dipolar interactions can be excluded as being the origin of this tensor. It is therefore reasonable to attribute the tensor to chemical shift and/or Knight shift interactions [19, 20]. As these interactions are both linear in the spin variable, they can not be directly distinguished in room temperature spectra. Measurements at varying temperatures which would allow discrimination of the chemical shift from the Knight shift interaction are also in progress.

The $^{63,65}\text{Cu}$ NMR spectrum shows a typical powder pattern for $I = 3/2$ nuclei with a symmetric EFG and interesting characteristic features (Fig. 7). The spectrum has strong central lines corresponding to the main transition $-1/2, 1/2$ of the copper nuclei. The Knight shift of these lines is equal to the Knight shift of metallic copper (the sharp peaks at the top of the central lines result from the copper coil). The central line of ^{63}Cu is weakly split by second order quadrupole interaction. According to the value of this splitting, one can estimate (by assuming an asymmetry parameter η close to zero) an NQR splitting of approximately 16 MHz. The shoulders of the NMR spectra corresponding to the $1/2-3/2$ transitions are not as sharp and narrow as for YBaCuO compounds [10]. This broadening could be caused by local disorder of the Cu-surrounding, leading to a wide EFG distribution. From the location of the shoulder we estimate an NQR

splitting of 13 MHz for ^{63}Cu . Our attempts to measure NQR spectra at 4.2 K directly depict the existence of the weak, broad ^{63}Cu NQR line in the frequency range of 13–20 MHz with very short T_2 (about 10–20 μsec). This matches the model of a wide EFG distribution at the Cu nuclei caused by the local structure disorder. Further evidence of similar local structure defects was recently found through high-resolved electron microscopy [21].

Summarizing, we have shown that ^{199}Hg and $^{63,65}\text{Cu}$ NMR are promising methods for studying the Hg-based superconductors. Moreover, we have shown primary results of the application of these methods to such samples.

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