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^{199}Hg- Solid State NMR and Susceptibility Studies of Mercury - based HTSC

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^{199}Hg- NMR Spectroscopy was applied to study Hg- oxide ceramic high temperature superconductors at room temperature. Spectra of samples with different macro- structure and transition- temperatures have been measured. A spin- spin relaxation time of T_2= 1.6 msec and a spin- lattice relaxation time of T_1= 35 msec was found. All spectra exhibit a characteristic powder line shape caused by an axially symmetric ^{199}Hg spin interaction.

1. INTRODUCTION

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 to investigate these materials [1]. Due to its spin of 1/2 the ^{199}Hg isotope is a convenient nuclear spin label for the study of Hg- based superconductors. With ^{199}Hg -NMR we investigated different samples of Hg- based HTSC with nominal compositions $HgBa_2CuO_{4+\delta}$(Hg1201) and $HgBa_2CaCu_2O_{6+\delta}$(Hg1212). $HgBa_2CuO_{4+\delta}$ is the first member of the homologous series of the Hg- based oxide cuprates and a single layered superconductor. The X- ray structure exhibits tetragonal symmetry, the Hg- atoms are located at each corner of the unit- cell [2]. The Hg atoms are coordinated to O-Hg-O chains linking the CuO planes [3]. The superconducting transition temperature varies between 54 and 95 K in dependence of the additional oxygen content (between 0.02 and 0.06 atoms per unit cell). The double CuO layered Hg 1212 compound exhibits maximum transition temperatures of 127 K.

2. EXPERIMENTAL DETAILS

The samples were synthesized in a two step solid state reaction, using the primary materials $Ba_2CuO_{3+\delta}$ and HgO according to [4]. The NMR- data were obtained using a 7 T NMR spectrometer. Solid $HgCl_2$ was used as an convenient standard substance, the maximum of the powder spectrum was taken as an reference (0 ppm, corresponding to 53.307 MHz). We optimized the B_1 field and obtained a 90°- pulse width of 1.9μsec to exite the whole spectra homogeneously. We recorded the spectra using the Hahn spin- echo- sequence (90°-180°-echo) and applied a full 64 combination phase- cycle of the sequence to suppress electronic artefacts and quadrature errors. Spin- lattice relaxation measurements were performed using the saturation recovery pulse sequence followed by the phase- cycled echo- sequence to detect the signal. To get spectra with reasonable signal- to- noise ratio we had to accumulate 100 000 scans

3. RESULTS AND DISCUSSION

We characterized the superconducting properties of the samples by means of SQUID measurements. The results are shown in table 1 and figure 1.

Table 1. Superconducting properties of the samples

SAMPLE	T_c/K	ΔT_c/K	Sf	Mf	Comp.
1(bulk)	71	5	0.52	0.49	Hg 1201
2(powder)	94	55	0.73	0.23	Hg 1201
3(powder)	112	26	0.31	0.16	Hg 1212

Sf is the maximum shielding fraction (ZFC),
Mf is the maximum Meissner fraction (FC)

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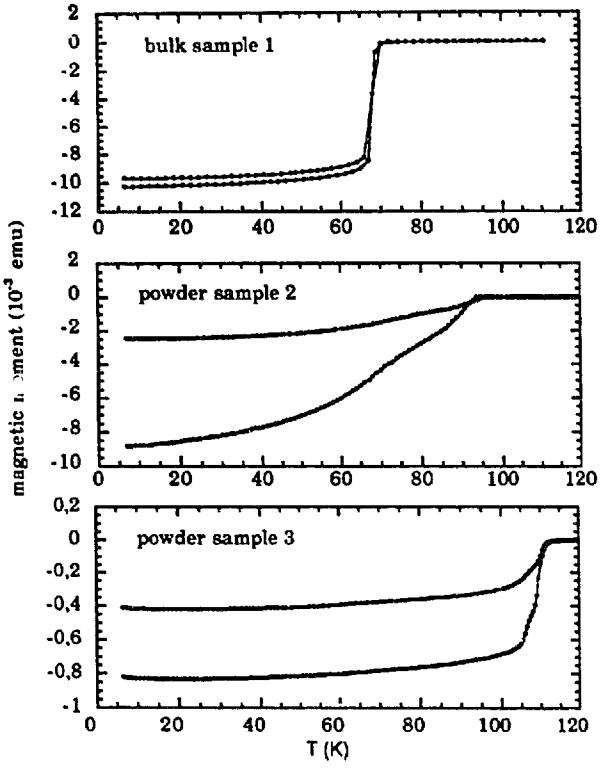
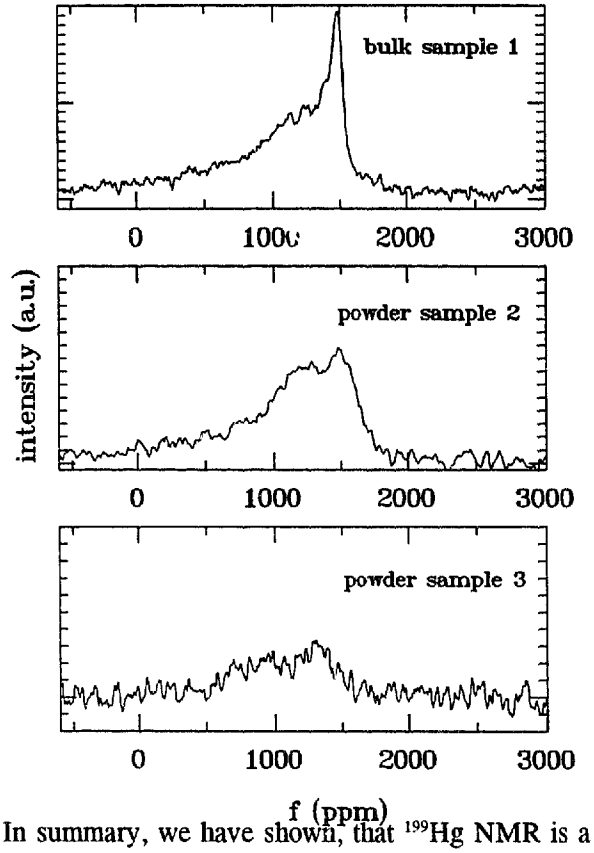
Figure 1. Dc- magnetic measurements.



Sample 1, which was pressed into a small rod (bulk-sample) showed a transition temperature of 71 K and a transition width of 5 K. The relatively low transition temperature of this sample may be attributed to a deficiency of the oxygen concentration in the sample. Sample 2 (fine grained powder) exhibits a transition temperature of 92 K and a transition width of 55 K. Compared to the first sample the large transition width is obviously due to a weak intergranular coupling between different crystallites. The third sample, a Hg-1212 HTSC, exhibits a transition temperature of 112 K, this value can be attributed to a lower oxygen content than that for Hg 1212 with highest T_c (127 K).

The NMR spectra of all samples are shown in figure 2. The poor signal- to- noise ratio of the third sample was caused just by the small amount of substance. All spectra show similar line positions and line broadening. The spectra have a typical powder line shape of a spin 1/2 nucleus under the influence of an axial second rank tensor interaction reflecting the O-Hg-O chain symmetry of the HTSC structure. The maximum of the line is given by one principal value and the width is determined by the anisotropy of the tensor. The dipolar interaction can be excluded as origin of the tensor because of the low gyromagnetic ratio of the ^{199}Hg nucleus as well as the relatively low abundance. Therefore we attribute the tensor to chemical shift and/or knight shift interaction. Since these interactions are both linear in the spin variable, we cannot discriminate them directly in room temperature spectra. Therefore measurements at different temperatures are under progress.

Figure 2. ^{199}Hg- NMR spectra of Hg-based HTSC



In summary, we have shown, that ^{199}Hg NMR is a promising method to study Hg-based HTSC and presented the first results of an application.

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