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Physica C 227 (1994) 225–229

PHYSICA C

Application of ^{199}Hg solid-state NMR to Hg based HTSC

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Received 29 March 1994

Abstract

It is proposed to study Hg-oxide ceramics, which are high-temperature superconductors, with ^{199}Hg NMR spectroscopy. As an exemplary application of this method first room-temperature ^{199}Hg spectra and spin–lattice relaxation times of samples with different macrostructure are presented. A spin–lattice relaxation time of $T_1 = 35$ ms is found. 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.

1. Introduction

With the discovery of high-temperature superconductivity (HTSC) of the system $HgBa_2CuO_{4+\delta}$ in 1993 [1], these materials have become a major object of HTSC investigations, $HgBa_2CuO_{4+\delta}$ is the first member of the homologous series of Hg based oxide ceramics [1–7]. They show maximum transition temperatures of 133 K [4] and under pressure T_c's > 150 K [5,8,9]. Since the first reports of HTSC in yttrium and thallium copper-oxide ceramic materials, nuclear magnetic resonance (NMR) spectroscopy was an important tool to study 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 – via relaxation measurements – of dynamic processes. Due to its spin of $\frac{1}{2}$ the mercury isotope ^{199}Hg is a convenient nuclear spin label (like ^{205}Tl in Tl HTSC's [14]) for the study of Hg based HTSC materials. Here we report first results of ^{199}Hg NMR studies of the $HgBa_2CuO_{4+\delta}$ and $HgBa_2CaCu_2O_{6+\delta}$ phases. The results are obtained using samples with different macrostructure.

2. Materials and methods

We investigated different samples of Hg based HTSC with a nominal composition $HgBa_2CuO_{4+\delta}$ (Hg-1201) and $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212). The $HgBa_2CuO_{4+\delta}$ compound is the first member of a homologous series of Hg based HTSC oxide cuprates which have transition temperatures in the range of

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SSDI 0921-4534(94)00261-D

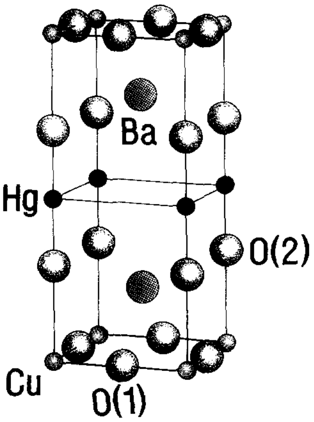

Fig. 1. Structure of $HgBa_2CuO_4$.

59 –94 K [1,7]. The samples were synthesized according to Ref. [1] in a two-step solid-state reaction, using $Ba_2CuO_{3+\delta}$ and HgO as primary reagents. The X-ray structure of Hg-1201 exhibits tetragonal symmetry. Fig. 1 shows the unit cell of the crystal. The Hg atoms are located at each corner of the unit cell [1].

3. Experimental details

The NMR data were obtained using a 7 T pulse Fourier transform solid-state NMR spectrometer (proton resonance frequency 297.75 MHz). All measurements were performed at room temperature. ^{199}Hg is a low abundant nucleus (16.8%) and the ^{199}Hg spectra typically exhibit a very broad width (approx. 300 kHz). Therefore we had to optimize the probe for high sensitivity and short 90° pulses, i.e. high B_1 field as well as short dead time requiring a low quality factor. As a compromise we chose a resonant circuit bandwidth of the probe of approximately 500 kHz. Using an amplifier power of 1 kW we optimized a 90° pulse width of 1.9 μs, which was sufficiently short to homogeneously excite the whole spectrum over the full spectral range.

To overcome the dead-time problem we recorded the spectra using the Hahn spin-echo sequence (90°–180°–echo) [16]. We applied a full 64 combination phase cycle of the sequence in order to suppress electronic artefacts and quadrature errors in the spectra. The pulse spacing was optimized by recording spectra for several different values and comparing them for minimal distortions by dead-time effects as well as minimum effects of T_2 relaxation. We took solid $HgCl_2$ as a convenient standard substance for calibrating the ^{199}Hg spectra and used the maximum of the powder spectrum 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 for the latter, the chemical shift depends strongly on the ionic concentration in the solution [17]. To get spectra with a reasonable signal-to-noise ratio we had to accumulate approximately 100 000 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. The experimental time for one spectrum came close to two days. To obtain a result in a reasonable time we restricted us to measure the spin–lattice relaxation time T_1, only of the sample with the largest amount of material (bulk sample), using 32 000 scans for each delay time.

4. Results and discussion

The superconducting properties of the samples were characterized by means of AC susceptibility measurements. The results of these experiments are shown in Fig. 2. From these measurements we extracted the transition temperature and the width of the phase transition, to get information about phase purity and granularity of the material. Sample 1, which was pressed into a small rod (bulk sample), showed a transition temperature of 71 K and a transition width of approximately 4 K. The relatively low transition temperature for the first sample can be explained due to a lower oxygen content than that for the second sample. Sample 2 (Hg-1201, fine-grained powder) exhibits a transition temperature of 92 K with a transition width of approximately 30 K. Compared to the first sample, the larger transition width is obviously due to a weaker intergranular coupling among different crystallites. The third sample, a $HgBa_2CaCu_2O_{6+\delta}$ HTSC (fine-grained powder), exhibits a transition temperature of 112 K. The low T_c at 112

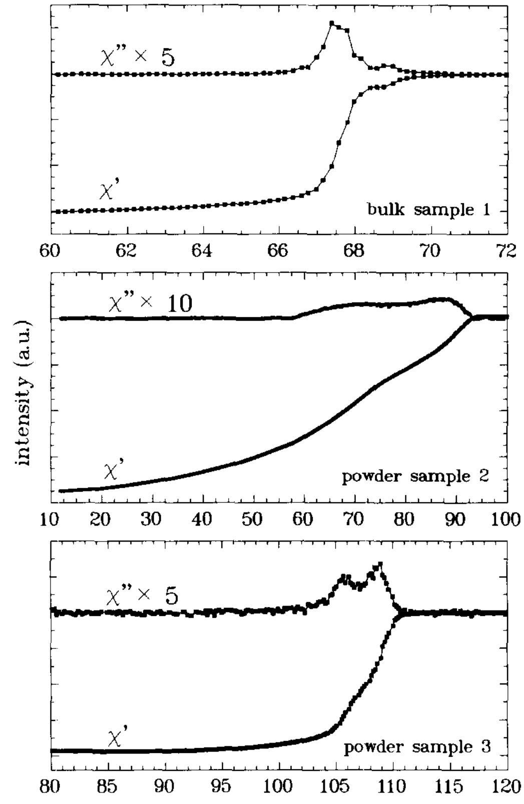

Fig. 2. AC susceptibility of Hg based HTSC.

Table 1
Superconducting properties of the samples

Sample	T_c (K)	Transition width (K)	Composition
1 (bulk)	71	4	$HgBa_2CuO_{4+\delta}$
2 (powder)	92	30	$HgBa_2CuO_{4+\delta}$
3 (powder)	112	8	$HgBa_2CaCu_2O_{6+\delta}$

K can be explained by the lower oxygen content than that in Hg-1212 with $T_c = 127$ K ($\delta = 0.22$). The superconducting properties are summarized in Table 1. The result of the room-temperature spin–lattice relaxation measurement for sample 1 is shown in Fig. 3. We obtained a value of $T_1 = 35 \pm 1$ ms. This value is comparable to results of spin–lattice relaxation measurements of other oxide ceramic HTSC compounds [14,18].

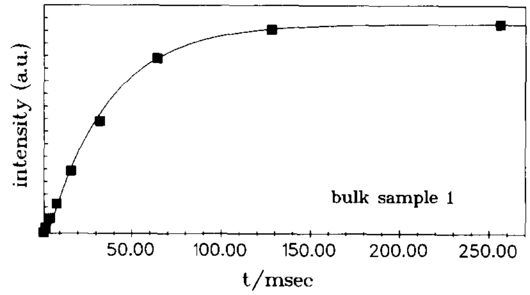

Fig. 3. Time-dependent spin polarization of sample 1. The spin–lattice relaxation time is 35 ± 1 ms.

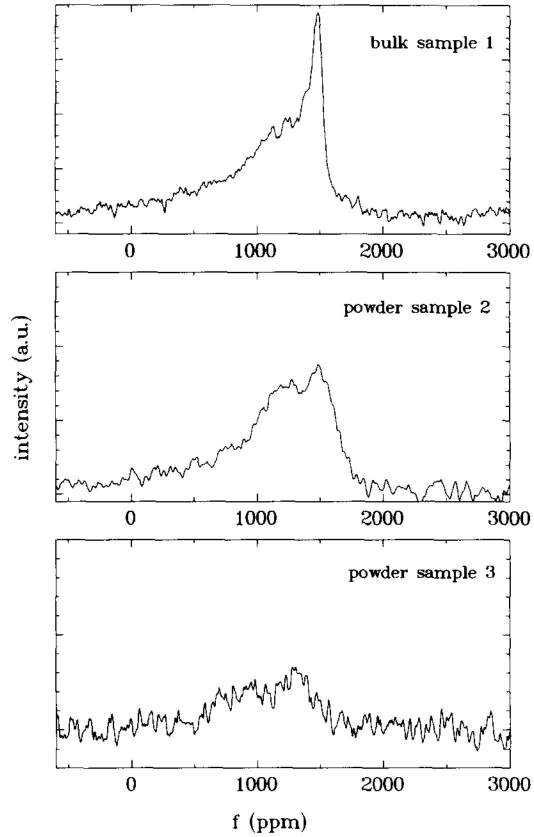

Fig. 4. ^{199}Hg NMR spectra for different Hg based HTSC (reference: $HgCl_2$).

The NMR spectra of the three samples are shown in Fig. 4. The poor signal-to-noise ratio of the $HgBa_2CaCu_2O_{6+\delta}$ sample (sample 3) was caused by the small amount of material. All spectra show similar line positions and line broadening. In particular line shifts and line broadening are neither affected 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., The spectra have the typical powder line shape of a spin $\frac{1}{2}$ nucleus under the influence of an axial 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 which has the best signal-to-noise ratio. These data show that the experimental line shape cannot be matched by a single tensor. Therefore we varied the fit and listed the calculated value which show the lowest deviation from the experimental spectrum. The best fit was obtained by superposition of 5 tensors with different anisotropy width (Table 2, Fig. 5).

The isotropic value of the resulting tensor is calculated to 1150 ppm. The principal values of the anisotropic tensors are in the range of $A_\perp = 1300$ to 1700 ppm, $A_\parallel = 900$ to -150 ppm. The variation of the anisotropic values results from a distribution of magnetic inequivalent environments of the Hg atoms in the sample, which might be caused by a distribution of the oxygen deficiency in the unit cells. Detailed measurements with the MAS technique and with oriented samples are necessary to support such an interpretation.These measurements are currently under progress.

Next we discuss possible ^{199}Hg interactions leading to the tensor. Since ^{199}Hg is a spin $\frac{1}{2}$ nucleus, it does not show any 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 origin for this tensor. Therefore the tensor seems to be attributed to chemical shift and/or Knight shift interactions [19,20]. Since these interactions both appear to be linear in the spin variable, they cannot be directly determined in room-temperature spectra. Measurements at different temperatures, which would allow one to discriminate the chemical shift from the Knight shift, are also under progress.

Table 2
Parameters of the powder lines used for the fit in Fig. 5

Line	$A_\perp$ (ppm)	$A_\parallel$ (ppm)	A_{iso} (ppm)
1	1300	900	1166
2	1400	700	1166
3	1500	500	1166
4	1600	300	1166
5	1700	-150	1083

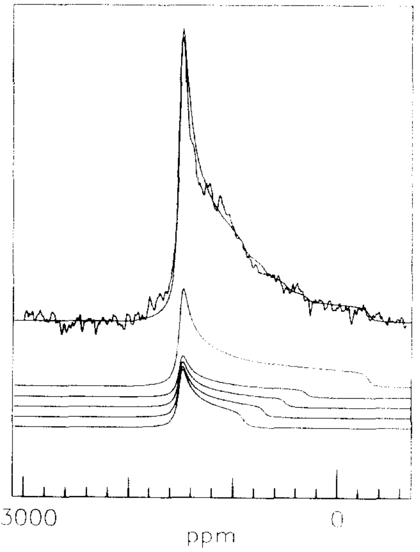

Fig. 5. Fit of the experimental spectrum (sample 1) by superposition of five theoretical anisotropic powder lines.

In summary, we have shown that ^{199}Hg NMR is a promising method to study the Hg based superconductors. Moreover we have obtained primary results of an application of this method to such samples.

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