^{207}Pb Magnetic Shielding Anisotropy in $Pb(NO_3)_2$, $PbCO_3$, $PbCrO_4$, $PbMoO_4$ and $PbWO_4$ by Fourier Transform NMR

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The NMR signals of ^{207}Pb have been observed in powder samples of $Pb(NO_3)_2$, $PbCO_3$, $PbCrO_4$, $PbMoO_4$ and $PbWO_4$ using a Fourier transform apparatus. All the observed signals are asymmetrical, indicating anisotropies of the magnetic shielding $\sigma_{33}-\sigma_{11}$ with values between -56 ppm for $Pb(NO_3)_2$ and -884 ppm for $PbCrO_4$. The principal elements of the shielding tensors σ_{11}, σ_{22}, σ_{33} are given relative to the Pb^{2+} ion at infinite dilution in H_2O and can be referred to the free lead atom with the known shielding constant of earlier measurements.

Introduction

NMR investigations of nuclei in solid matter yield information about the generally anisotropic interactions: magnetic shielding, direct spin-spin coupling, indirect spin-spin coupling and quadrupole coupling. For nuclei with spin 1/2 no quadrupole interaction is possible because of lacking quadrupole moments. Further, if the nuclei with gyromagnetic ratios are very diluted in solids, direct and indirect spin-spin coupling mainly influence only the linewidths of the signals. If this influence can be ignored, NMR lines are observed which are essentially caused by the magnetic shielding interaction, the Hamiltonian of which can be written as

$$\mathcal{H} = \gamma_\mathrm{I}\, \boldsymbol{I}\, \underline{\sigma}\, \boldsymbol{B}_0 .$$

γ_I and $\boldsymbol{I}$ are the gyromagnetic ratio and the spin of the nucleus in question, $\boldsymbol{B}_0$ is the static magnetic field and $\underline{\sigma}$ is a second rank tensor, which is in first order symmetrical. As this interaction usually depends on the orientation of the principal axis system of this tensor to the magnetic field, the resonance frequencies in single crystals correlate with the orientation. For powder samples one gets typical lineshapes[1], from which the principal values σ_{11}, σ_{22}, σ_{33} of the shielding tensor can be determined but not the orientation of the principal axis system relative to the crystal frame (see for example References[2, 3]).

The NMR signal of ^{207}Pb has been observed earlier in a limited number of solid compounds[4–13]. The measured shielding constants which have been referred to different reference signals, have been used for a classification of the chemical bonds[4, 7, 8, 12]. Only in a few cases an anisotropic magnetic shielding has been reported[6, 9, 11–13].

In this work the ^{207}Pb NMR signals were investigated for powder specimens of $Pb(NO_3)_2$, $PbCO_3$, $PbCrO_4$, $PbMoO_4$ and $PbWO_4$ and were referred to the ^{207}Pb signal of an aqueous solution of $Pb(NO_3)_2$. As the chemical shift of $^{207}Pb^{2+}$ in this aqueous solution relative to the free atom is known[14–16], the tensor elements can be related to the free lead atom. For all samples an anisotropic magnetic shielding was found, also in $Pb(NO_3)_2$ for which in earlier investigations, which were performed at lower magnetic fields, no anisotropy was reported[4, 6, 7, 12].

Experimental

The ^{207}Pb NMR signals were observed with a multinuclei Bruker pulse spectrometer SXP 4 to 100 MHz in a magnetic field of 2.1 T in 10 mm cylindrical sample tubes at (300 ± 3) K. The magnetic field was externally stabilized by the Bruker B-SN 15 NMR stabilization. The free induction decays were accumulated and Fourier transformed by the BNC 12 data unit.

^{207}Pb has a spin of 1/2; the Larmor frequency in the given magnetic field is 18.8 MHz and the receptivity is $2.0 \cdot 10^{-3}$ compared with 1 for the proton for an equal number of hydrogen and lead atoms at natural abundance. The chemical shift of the solid samples was measured relative to the ^{207}Pb signal in a 1.1 molal solution of $Pb(NO_3)_2$ in H_2O. With the known dependence of the ^{207}Pb Larmor frequency on the concentration of the $Pb(NO_3)_2$ solution in

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water[14, 15] the Larmor frequency ν_s of the solid samples can be related to the Larmor frequency ν_0 of the Pb^{2+} ion at infinite dilution in water. The shielding is given as $\sigma^0_{zz} = (1 - \nu_s/\nu_0) \cdot 10^6$, where σ^0_{zz} is the component of the shielding tensor $\underline{\sigma}^0$ along the static magnetic field $\boldsymbol{B}_0$ in the laboratory frame. No bulk susceptibility correction was made. The absolute errors due to different susceptibilities are estimated to be less than 3 ppm. For the measurements of $Pb(NO_3)_2$ powders of Merck, Darmstadt and of Marquart, Bonn-Beuel * with purities of 99.5% and 99% were used. The $PbCO_3$ and $PbCrO_4$ powders were delivered by Merck, Darmstadt and the $PbMoO_4$ and $PbWO_4$ powders by Serva International, Heidelberg. The solid samples were used without further purification. The heating of a $Pb(NO_3)_2$ sample for several hours at about 370 K did not change the results.

Results and Discussion

The crystallographic data of the samples, for which ^{207}Pb NMR signals are reported in this work, are given in Table 1. For the ^{207}Pb signal in $Pb(NO_3)_2$ powder a very small anisotropic shielding was found. An example is shown in Figure 1. The shielding tensor of ^{207}Pb in this sample is axially symmetrical. The anisotropy is due to the local symmetry of the Pb^{2+} ion, which is only ambiguously known[17–19]. The principal values of the shielding tensor σ_{11}, σ_{22}, σ_{33} are given in Table 2.

The data of Table 2 are related to the Pb^{2+} ion surrounded only by water molecules. A positive principal value of the shielding tensor means a lower frequency for the ^{207}Pb nucleus in the solid specimen than in the infinitely diluted aqueous solution. The trace $\frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$ gives the isotropic part and $\sigma_{33} - \sigma_{11}$ the total anisotropy of the shielding tensor.

In former measurements of ^{207}Pb in $Pb(NO_3)_2$ no anisotropies of the ^{207}Pb NMR signal were reported. But all these measurements were performed in magnetic fields less than 0.9 T (Ref. [4, 6, 7, 12]). The isotropic part of the shielding tensor of Pb in $Pb(NO_3)_2$ in Table 2 shows, that the shielding of the Pb nucleus by water molecules is stronger than

Table 1. Crystallographic data of the used solid specimens.

Sample	Lattice	Space group	Cell dimensions $a_0/10^{-10}$ m	$b_0/10^{-10}$ m	$c_0/10^{-10}$ m	β	Molecules/ unit cell	Ref.
$Pb(NO_3)_2$	cubic	$Pa3 - T_h^6$ $P2_13 \quad T^4$	7.853				4	17 18, 19
$PbCO_3$	orthorhombic	$Pbnm - V_h^{16}$	8.468	6.146	5.166		4	20
$PbCrO_4$	monoclinic	$P2_1/n - C_{2h}^5$	7.118	7.434	6.794	102° 25′	4	21, 22
$PbMoO_4$	tetragonal	$I4_1/a - C_{4h}^6$	5.47		12.18		4	23
$PbWO_4$	tetragonal	$I4_1/a - C_{4h}^6$	5.44		12.01		4	23

Table 2. Principal values of the shielding tensor of ^{207}Pb in different powder samples. The measured tensor elements are related to the Larmor frequency ν_0 of the Pb^{2+} ion at infinite dilution in water ** and are given as $\sigma_{ii} = (1 - \nu_{\text{sample}}/\nu_0) \cdot 10^6$. No susceptibility corrections were performed.

Sample	σ_{11}	σ_{22}	σ_{33}	$\sigma_{33} - \sigma_{11}$	$\frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$
$Pb(NO_3)_2$	645 (4)	589 (4)	589 (4)	−56 (6)	608 (7)
$PbCO_3$	204 (13)	−394 (4)	−566 (8)	−770 (15)	−252 (16)
$PbCrO_4$	−174 (7)	−572 (4)	−1058 (8)	−884 (11)	−601 (11)
$PbMoO_4$	−823 (4)	−823 (4)	−1004 (5)	−181 (6)	−883 (8)
$PbWO_4$	−823 (4)	−823 (4)	−1025 (6)	−202 (7)	−890 (8)

** The principal values of the shielding tensor have been measured relative to a 1.1 molal $Pb(NO_3)_2$ solution in H_2O. The shielding constant of this solution relative to the Pb^{2+} ion at infinite dilution is 75 ± 15 and was taken from Reference [15]. The error of this extrapolation was not taken into account. The errors are calculated from the standard deviations of at least 4 measurements and from an estimated error due to different susceptibilities of 3 ppm.

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* I like to thank the Firma Marquart for the generous gift of a $Pb(NO_3)_2$ sample.

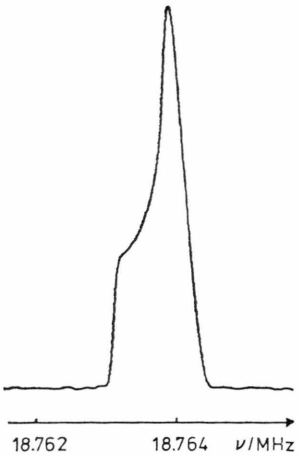

Fig. 1. ^{207}Pb NMR signal in $Pb(NO_3)_2$ powder at 18.76 MHz: Experimental spectrum width: 50 kHz, number of pulses 55 000, measuring time: 15 hours, 500 data points were accumulated followed by 7692 points of zero filling before the Fourier transformation of 8 K points. This absorption signal can very well be fitted by a convolution of the theoretical powder lineshape of an axially symmetrical shielding tensor (see for example Ref. [2]) with a Gaussian broadening function.

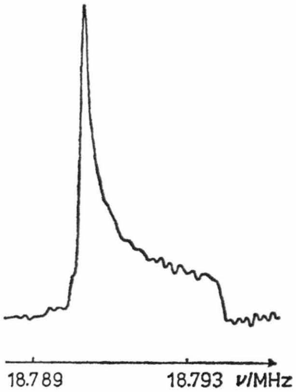

Fig. 2. ^{207}Pb NMR signal in $PbWO_4$ powder at 18.79 MHz: Experimental spectrum width: 50 kHz, number of pulses 9500, measuring time: 8 h, 500 data points were accumulated followed by 7692 points of zero filling before the Fourier transformation of 8 K points.

by nitrate ions. This behaviour has also been detected for alkali nuclei [24].

Much stronger anisotropies of the order of magnitude of $1^{0}/_{00}$ have been found for ^{207}Pb in $PbCO_3$ and $PbCrO_4$ powders. The shielding tensor is not axially symmetrical for these two samples. The principal values are given in Table 2. Because of the very broad pattern the obtained signal-to-noise ratio is only about 15. Hence the accuracy is worse than for the other spectra. From measurements of single crystals Rocard et al. [6] estimated an anisotropy of ^{207}Pb in $PbCO_3$ of about $1^{0}/_{00}$. For $PbCrO_4$ no earlier measurements were performed, as far as I know.

$PbMoO_4$ and $PbWO_4$ have almost identical crystal data (see Table 1). According to this fact the NMR spectra are very similar. The shielding tensor is axially symmetrical. The data are given in Table 2. A typical spectrum for $PbWO_4$ is given in Figure 2. Lauterbur [9] has determined the principal values of the shielding tensor of ^{207}Pb in $PbMoO_4$ in a single crystal. His result of the anisotropy agrees with the data of the powder spectra. The isotropic parts cannot be compared, as Lauterbur used a saturated aqueous solution of $Pb(NO_3)_2$ as reference sample. For $PbWO_4$ no further measurements are known.

One can relate the measured values of the shielding tensor to the free atom, using the shielding constant of the Pb^{2+} ion in water which has been determined by Lutz and Stricker [14, 15] to $-1.781(6)\%$ and by Hawk and Sharp [16] to -1.754%. Compared with the large isotropic shielding referred to the free atom the total anisotropies are relatively small, about 5% for the $PbCrO_4$ which yielded the strongest anisotropy. But it is essential to bear in mind this relation of the isotropic and anisotropic shielding if further conclusions are drawn from these results.

Using the chemical shifts for a classification of the chemical bonds, as it has been done in the earlier papers [4, 7, 8, 12], all measured samples seem to be ionic crystals.

Conclusions

In this work the principal elements of the shielding tensor of ^{207}Pb of some solid samples have been determined relative to the Pb^{2+} ion surrounded only by water molecules. ^{207}Pb is one of the first nuclides for which these elements can be given in an atomic reference scale of the magnetic shielding. Compared with the strong shielding constant of the Pb^{2+} ion in water the anisotropy is relatively small.

For the future, single crystal measurements are planned to elucidate the orientation of the shielding tensor and to correlate it with the crystal sructure.

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