Isotropic and Anisotropic Nuclear Magnetic Shielding of $^{113}$Cd in Cadmiumhalides, Cadmiumchalcogenides and in Cadmiumcarbonate

A. Nolle
Physikalisches Institut der Universität Tübingen

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The NMR signals of $^{113}$Cd have been observed in powder samples of the cadmium halides CdF$_2$, CdCl$_2$, CdBr$_2$, CdI$_2$, of the cadmium chalcogenides CdO, CdS, CdSe, CdTe and of CdCO$_3$. For $^{113}$Cd in CdCl$_2$, CdBr$_2$, CdI$_2$, CdS and in CdSe anisotropies of the nuclear magnetic shielding have been detected. The shielding tensor in these powders is axially symmetric. For the other specimens no anisotropies of the magnetic shielding have been found. The principal values of the magnetic shielding tensor and the shielding constants are given in an atomic reference scale.

I. Introduction

In recent years some special techniques have been developed, which allow for the observation of high resolution NMR signals even in solid samples. Usually the papers concerning NMR in solid specimens deal with nuclear magnetic shielding [1—4] or with quadrupole interaction (see e.g. [5]). Nuclear magnetic shielding effects in solids are observable especially for nuclei without quadrupole moments, for example $^1$H, $^{13}$C, $^{113}$Cd or $^{207}$Pb.

The absolute size of the nuclear magnetic shielding is not easy to evaluate neither by theory nor by experiment, because always reference compounds are used and usually the absolute magnetic shielding of these references is not known. Mainly for the alkali nuclei in crystalline powders the absolute shielding has been determined [6, 7]. Relatively broad signals, however, are observed, because all stable alkali nuclei have quadrupole moments and therefore no alkali anisotropies of the magnetic nuclear shielding have been detected until now, as far as I know. Recently the anisotropy of the nuclear magnetic shielding of $^{207}$Pb in some powder specimens could be determined and could be related to the Pb$^{2+}$ ion in infinitely diluted aqueous solutions, for which the shielding referred to the free atom is known [8, 9].

In this paper $^{113}$Cd NMR signals in cadmium powder samples are reported. Single symmetrical lines have been observed as well as lineshapes due to an anisotropic nuclear magnetic shielding. All signals are referred to the $^{113}$Cd signal of an aqueous CdSO$_4$ solution, the absolute shielding of which is known [10].

In a solid sample, in which beside the Zeeman interaction only the magnetic shielding interaction must be taken into account, the Hamiltonian can be written as [4]:

$$ H = B_0 (E - \sigma) \gamma I $$

where $B_0$ is the static magnetic field, $E$ is the unit matrix, being the coupling matrix between the spin $I$ and the magnetic field $B_0$ and $\sigma$ the nuclear magnetic shielding tensor, which is real and to a good approximation symmetrical, $\gamma$ is the gyromagnetic ratio of the nucleus in question. The principal axis system of the shielding tensor is called {1, 2, 3}. Generally the observed influence of the shielding tensor changes with the orientation of the principal axis system relative to the static magnetic field. The isotropic shielding constant $\sigma$ is given by the trace of the shielding tensor $\sigma_{ii}$ for a nucleus are evaluated by comparing the resonance frequencies $\nu_i$ of a NMR experiment for orientations, in which one of the three principal axes of the shielding tensor is parallel to the static magnetic field with the Larmor frequency of the same nucleus in a solution $\nu_s$:

$$ \sigma_{ii} = (1 - \nu_i/\nu_s) \quad \text{for } i = 1, 2, 3. $$

In powder samples typical spectra due to the shielding interaction are obtained [4, 11]. For an axially symmetrical shielding tensor two principal values are equal, they are denoted by $\sigma_1$, and the third one by $\sigma_2$. The so-called shielding constant $\sigma$ is then $\sigma = \frac{1}{3} (\sigma_1 + 2 \sigma_2)$ and the shielding anisotropy $\sigma_2 - \sigma_1$. The lineshape for this case can be given by an analytical expression:

$$ I (\omega) \sim [ (\omega_1 - \omega_2) (\omega - \omega_2) ]^{-1/2} $$

for $\omega_1 \leq \omega \leq \omega_2$ or $\omega_2 \leq \omega \leq \omega_1$.
\[ I(\omega) = 0 \quad \text{elsewhere}, \]
where \[ \omega_\parallel = \gamma (1 - \sigma_\parallel) B_0 \]
and \[ \omega_\perp = \gamma (1 - \sigma_\perp) B_0 \]
is assumed.

For the general case a more complicated expression has been derived by Bloembergen and Rowland [11], but it needs not to be considered in this paper because only axially symmetrical shielding tensors have been observed for \(^{113}\text{Cd}\). From the theoretical lineshape of an axially symmetrical shielding tensor the main values can easily by evaluated [11]. But one really does not observe such ideal lineshapes, because line broadening occurs, which can be taken into account by calculating the convolution integral of \( I(\omega') \) with a broadening function \( L(\omega - \omega') \):

\[
\int_0^\infty I(\omega') L(\omega - \omega') \, d\omega'.
\]

\( L(\omega - \omega') \) is a Lorentzian or a Gaussian function or a mixture of both [12]. Theoretical lineshapes can be fitted to the experimental signals in a least-squares fit procedure by a computer program. Four different parameters can be changed: the shielding constant \( \sigma \), the anisotropy \( \sigma_\parallel - \sigma_\perp \), the linewidth of the broadening function and the type of the broadening function. In this paper only Gaussian or Lorentzian functions and no mixtures of both were used.

The orientation of the principal axis system of the shielding tensor relative to the crystal frame cannot be determined from measurements of powder samples. Hence with the shielding constant \( \sigma \) and the anisotropy \( \sigma_\parallel - \sigma_\perp \) the whole possible information about an axially symmetrical shielding tensor is extracted from the powder spectra.

The principal values of the nuclear magnetic shielding tensor \( \sigma_{ij} \) in solid samples can be given in the atomic shielding scale by: \( \sigma_{\text{ref}} = \sigma_{ij} + \sigma_{\text{ref}} \), using the shielding constant \( \sigma_{\text{ref}} \) of the reference solution which in the case of Cd is referred to the free Cd atom. This relation is true as long as quadratic terms in \( \sigma_{ij} \) and \( \sigma_{\text{q}} \) can be neglected and it has been used for the final evaluation of the principal elements \( \sigma_{\parallel} \) and \( \sigma_{\perp} \) of the nuclear magnetic shielding tensor in the atomic shielding scale. These values \( \sigma_{\parallel} \) and \( \sigma_{\perp} \) have a much better meaning than those \( \sigma_\parallel \) and \( \sigma_\perp \), which are related to an arbitrary reference. The shielding constant of the used reference, a 3 molal solution of CdSO\(_4\) in H\(_2\)O, can be determined from [10]:

\[
\sigma_{\text{ref}} \left( ^{113}\text{Cd in 3 molal CdSO}_4 \text{ in H}_2\text{O versus free Cd atom} \right) = -(1.100 \pm 0.005) \cdot 10^{-3}.
\]

### III. Experimental

The NMR signals of \(^{113}\text{Cd}\) were observed with a multinuclei Bruker pulse spectrometer SXP 4 - 100 MHz in a magnetic field of 2.114 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 Bruker B-NC 12 data unit.

\(^{113}\text{Cd}\) has a spin 1/2, the Larmor frequency in the given magnetic field is about 19.96 MHz and the receptivity is 1.3\cdot10^{-3} compared with 1 for the proton for an equal number of hydrogen and cadmium atoms in a natural abundant sample.

The shielding was measured relative to a 3 molal CdSO\(_4\) solution in H\(_2\)O by the sample exchange method. With the shielding constant \( \sigma_{\text{ref}} \) of the Cd\(^{2+}\) ion in this solution the observed frequencies of the solid samples can be referred to the free atom [10]. No bulk susceptibility corrections were made. The errors due to different susceptibilities were estimated to be less than 3 ppm. CdBr\(_2\), CdCl\(_2\), CdI\(_2\) and CdCO\(_3\) powders were purchased from Merck, Darmstadt, CdF\(_2\) and CdCl\(_2\) from Serva International, Heidelberg, CdO, CdS, CdSe and CdTe from Zinsser, Frankfurt. All samples were used without further purification.

### IV. Results and Discussion

The NMR signals have been observed in powder samples of the cadmium halides CdF\(_2\), CdCl\(_2\), CdBr\(_2\), CdI\(_2\), CdCl\(_2\) and of the cadmium chalcogenides CdO, CdS, CdSe, CdTe and further of CdCO\(_3\). Typical signals with experimental parameters are given in Fig. 1 and Figure 2. In the upper part of these figures the experimental spectrum is shown, and in the lower part the result of the least-squares fit, from which the shielding constant, the anisotropy of the shielding and the linewidth of the broadening function has been evaluated. In all cases with anisotropic nuclear magnetic shielding Gaussian functions were used for the convolution, because the fit with Lorentzian functions was worse. The results are given in Table 1. For the samples, for which no anisotropy of the shielding could be detected, the frequency of maximum intensity was used for the determination of the isotropic shielding and for these samples in Table 1 the observed linewidths are given. The errors of the shielding constants and of
Table 1. Results of the $^{113}$Cd NMR measurements in solid samples. A description of the quantities is given in part II of this work; some comments about the errors are given in part IV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absolute shielding $\sigma^*/10^{-6}$</th>
<th>Anisotropy of the shielding $(\sigma^<em>_\parallel - \sigma^</em>_\perp)/10^{-6}$</th>
<th>Typical linewidth in Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdF$_2$</td>
<td>$-877 \pm 6$</td>
<td>$-$</td>
<td>$2700$</td>
</tr>
<tr>
<td>CdCl$_2$</td>
<td>$-1311 \pm 7$</td>
<td>$115 \pm 8$</td>
<td>$650$</td>
</tr>
<tr>
<td>CdBr$_2$·4H$_2$O</td>
<td>$-1141 \pm 7$</td>
<td>$-127 \pm 9$</td>
<td>$1100$</td>
</tr>
<tr>
<td>CdI$_2$</td>
<td>$-428 \pm 6$</td>
<td>$-$</td>
<td>$2500$</td>
</tr>
<tr>
<td>CdO</td>
<td>$-1519 \pm 7$</td>
<td>$-$</td>
<td>$2000$</td>
</tr>
<tr>
<td>CdS</td>
<td>$-1792 \pm 8$</td>
<td>$-54 \pm 8$</td>
<td>$400$</td>
</tr>
<tr>
<td>CdSe</td>
<td>$-1650 \pm 7$</td>
<td>$-64 \pm 7$</td>
<td>$270$</td>
</tr>
<tr>
<td>CdTe</td>
<td>$-1383 \pm 5$</td>
<td>$-$</td>
<td>$300$</td>
</tr>
<tr>
<td>CdCO$_3$</td>
<td>$-1070 \pm 5$</td>
<td>$-$</td>
<td>$650$</td>
</tr>
</tbody>
</table>

The anisotropies are due to the statistical errors from at least four different spectra, the error of the shielding constant of the CdSO$_4$ solution, an estimated additional error of 3 ppm because of lacking bulk susceptibility corrections and a further error for the anisotropic signals, which takes into account the uncertainty of the determination of the parameters by the fit procedure. CdF$_2$ has a cubic [13] and CdI$_2$ a hexagonal lattice [14]. For $^{113}$Cd in both powders relatively broad signals were found (see Table 1). No anisotropy could be detected. The broad signals are certainly due to dipole-dipole interaction of the Cd nuclei with the $^{19}$F or $^{127}$I nuclei, which both have a natural abundance of 100% and relatively strong gyromagnetic ratios. The shielding constant of $^{113}$Cd in solid CdI$_2$ has a surprising value. But this fact is already indicated by the behaviour of concentrated aqueous CdI$_2$ solutions, which have been investigated by Kostelnik and Bothner-By [15]. Their results for aqueous solutions together with the results for solid samples of this work are given in Fig. 3 using the value of $\sigma^*_\text{Ref.}$ of [10].

CdCl$_2$ [14] has a hexagonal lattice and the structure of CdBr$_2$·4H$_2$O has not been published, as far as I know. The NMR data are given in Table 1. The isotropic shielding in both samples has values, which can be expected from the chemical shift in aqueous solutions [10, 15–20] (see Figure 3). For both powders anisotropies of the shielding could be observed. The sign of the anisotropy changes, the order of magnitude is the same for both samples. A typical signal of $^{113}$Cd in CdCl$_2$ is given in Figure 1. A decision, whether the deviation of the experimental and theoretical signal, which has been observed for all CdCl$_2$ spectra, is due to motional effects or not is only possible from measurements at different temperatures. The linewidth of the CdCl$_2$ signal is much smaller, because only nuclei with relatively small gyromagnetic ratios are present beside the cadmium nuclei.

For the cadmium chalcogenides CdO and CdTe — both have a cubic lattice [21] — no anisotropies of the shielding have been observed. Compared with
CdSe and CdTe have already been observed in single crystals [23, 24]. The values of the anisotropies of the nuclear magnetic shielding are in very good agreement. The values of the isotropic shift are related to a Cd(NO₃)₂ solution, the composition of which is not given, but the differences between the CdS, CdSe, CdTe samples of this work agree with those one determined by Krüger et al. [10]. Further temperature dependencies and theoretical studies of the Knight shift have been published [25, 28, 29, 33 – 37].

V. Conclusions

From the systematic investigation of the cadmium halogenides and cadmium chalcogenides some conclusions can be drawn: The Larmor frequency of concentrated aqueous solutions approaches the Larmor frequency of the solid specimens (see Figure 3). This could also be shown for ¹³³Cs NMR in powder samples [6]. The shift of CdCO₃ shows that the oxyanions indeed induce nearly the same shielding as the H₂O molecules. There is a large shift of the Larmor frequency between the halogenides and the chalcogenides of about 500 ppm (see Figure 4). This shift indicates that in the cadmium halides ionic bonding prevails, whereas the chalcogenides are more or less covalently bonded. Such differences between ionic and covalent compounds have already been observed for ²⁰⁷Pb [38, 39]. There is a remarkable similarity of the shielding as regards the dependence on the atomic number. This means that
The shift is mainly produced by the neighbours and is not determined by the crystal structure.

For the lightest and heaviest halogenides and chalcogenides no anisotropy of the shielding could be observed, whereas for the medium weight compounds the anisotropics were found to be of the order 100 ppm.

The linewidths vary by about one order of magnitude. These strong differences are partly due to differences in the dipole-dipole interaction. It is not quite clear, however, where the difference between CdTe and CdO comes from.

Studies of the shielding at different temperatures could presumably give further insight, but they are very time consuming (see Fig. 1 and 2).

Acknowledgement

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