

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

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The NMR signals of ^{113}Cd have been observed in powder samples of the cadmium halides CdF_2 , CdCl_2 , $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$, CdI_2 , of the cadmium chalcogenides CdO , CdS , CdSe , CdTe and of CdCO_3 . For ^{113}Cd in CdCl_2 , $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$, 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 ^1H , ^{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 anisotropies of the nuclear magnetic 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].

II. Theory

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]:

$$H = \mathbf{B}_0 (\mathbf{E} - \boldsymbol{\sigma}) \gamma \mathbf{I}$$

where \mathbf{B}_0 is the static magnetic field, \mathbf{E} is the unit matrix, being the coupling matrix between the spin \mathbf{I} and the magnetic field \mathbf{B}_0 and $\boldsymbol{\sigma}$ the nuclear magnetic shielding tensor, which is real and to a good approximation symmetrical, γ 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 σ is given by the trace of the shielding tensor $\frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$. The principal values of the shielding tensor σ_{ii} for a nucleus are evaluated by comparing the resonance frequencies ν_{ii} 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 ν_s :

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

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 σ_{\perp} , and the third one by σ_{\parallel} . The so-called shielding constant σ is then $\sigma = \frac{1}{3}(\sigma_{\parallel} + 2\sigma_{\perp})$ and the shielding anisotropy $\sigma_{\parallel} - \sigma_{\perp}$. The lineshape for this case can be given by an analytical expression:

$$I(\omega) \sim [(\omega_{\parallel} - \omega_{\perp})(\omega - \omega_{\perp})]^{-1/2} \\ \text{for } \omega_{\parallel} \leq \omega \leq \omega_{\perp} \quad \text{or} \quad \omega_{\perp} \leq \omega \leq \omega_{\parallel}$$

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$I(\omega) = 0$ 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}Cd . From the theoretical lineshape of an axially symmetrical shielding tensor the main values can easily be evaluated [11]. But one really does not observe such ideal lineshapes, because linebroadening 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 σ , 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 σ 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 σ_{ii} in solid samples can be given in the atomic shielding scale by: $\sigma_{ii}^* = \sigma_{ii} + \sigma_{\text{Ref}}^*$, using the shielding constant σ_{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 σ_{ii} and σ_{aq}^* can be neglected and it has been used for the final evaluation of the principal elements σ_{\parallel}^* and σ_{\perp}^* of the nuclear magnetic shielding tensor in the atomic shielding scale. These values σ_{\parallel}^* and σ_{\perp}^* have a much better meaning than those σ_{\parallel} and σ_{\perp} , which are related to an arbitrary reference. The shielding constant of the used reference, a 3 molal solution of CdSO_4 in H_2O , can be determined from [10]:

$$\sigma_{\text{Ref}}^* (^{113}\text{Cd} \text{ in } 3 \text{ molal } \text{CdSO}_4 \text{ in } \text{H}_2\text{O} \text{ versus free Cd atom}) = -(1.100 \pm 0.005) \cdot 10^{-3}.$$

III. Experimental

The NMR signals of ^{113}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}Cd has a spin 1/2, the Larmor frequency in the given magnetic field is about 19.96 MHz and the receptivity is $1.3 \cdot 10^{-3}$ 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_2O by the sample exchange method. With the shielding constant σ_{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. $\text{CdBr}_2 \cdot 4 \text{H}_2\text{O}$, 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 , $\text{CdBr}_2 \cdot 4 \text{H}_2\text{O}$, CdI_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

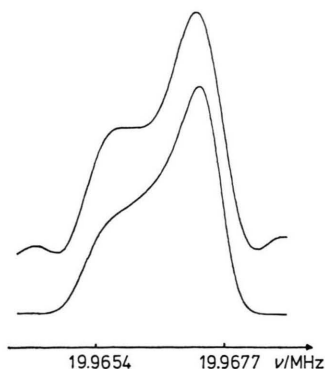


Fig. 1. ^{113}Cd absorption signal in CdCl_2 powder. The upper trace shows the experimental signal and the lower one of least-squares fit, by which an anisotropy of the nuclear magnetic shielding of $\sigma_{\parallel}^* - \sigma_{\perp}^* = (115 \pm 8)$ ppm has been evaluated. A Gaussian broadening function was used. Experimental spectrum width: 50 kHz; number of pulses: 9800; measuring time: 27 h; 100 data points were accumulated followed by 3996 points of zero filling before the Fourier transformation of 4 k points.

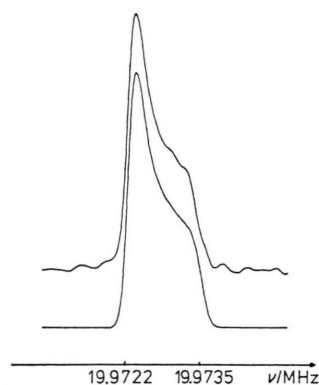


Fig. 2. ^{113}Cd absorption signal in CdSe powder. The upper trace shows the experimental signal and the lower one the least-squares fit, by which an anisotropy of the nuclear magnetic shielding of $\sigma_{\parallel}^* - \sigma_{\perp}^* = -(64 \pm 7)$ ppm has been evaluated. A Gaussian broadening function was used. Experimental spectrum width: 50 kHz; number of pulses: 8550; measuring time: 24 h; 400 data points were accumulated followed by 3696 points of zero-filling before the Fourier transformation of 4 k points.

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. 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.

Sample	Absolute shielding $\sigma^*/10^{-6}$	Anisotropy of the shielding $(\sigma_{\parallel}^* - \sigma_{\perp}^*)/10^{-6}$	Typical linewidth in Hz
CdF_2	-877 ± 6	—	2700
CdCl_2	-1311 ± 7	115 ± 8	650
$\text{CdBr}_2 \cdot 4 \text{H}_2\text{O}$	-1141 ± 7	-127 ± 9	1100
CdI_2	-428 ± 6	—	2500
CdO	-1519 ± 7	—	2000
CdS	-1792 ± 8	-54 ± 8	400
CdSe	-1650 ± 7	-64 ± 7	270
CdTe	-1383 ± 5	—	300
CdCO_3	-1070 ± 5	—	650

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 σ_{Ref}^* of [10].

CdCl_2 [14] has a hexagonal lattice and the structure of $\text{CdBr}_2 \cdot 4 \text{H}_2\text{O}$ 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

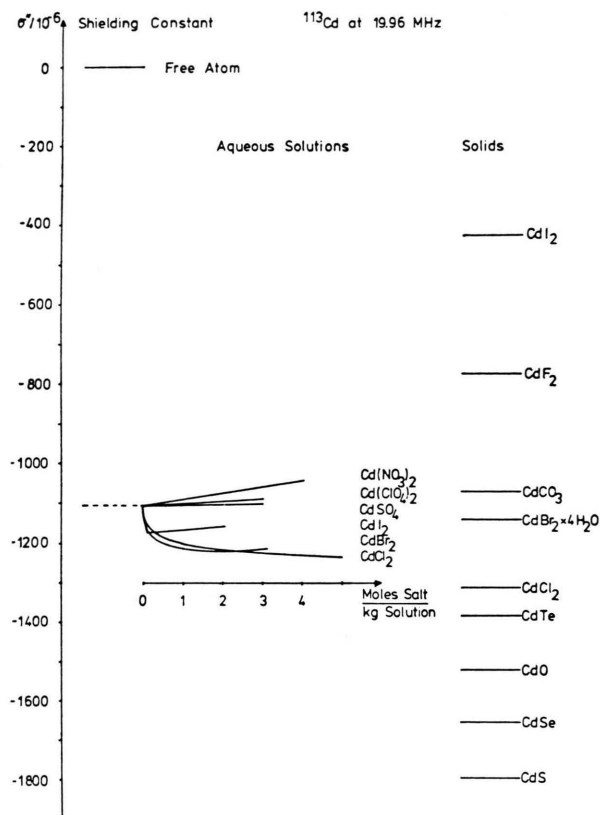


Fig. 3. Atomic reference scale of the nuclear magnetic shielding of ^{113}Cd . The following data were used: free atom: Ref. [40, 41], aqueous solutions: Ref. [15], solid samples: this work. Measurement of ^{113}Cd in metal or in alloys [25–37] are not given in this scale; they have been referred to the free atom in Ref. [10].

CdTe the linewidth of CdO seems rather large, though in a first approximation only the dipole-dipole interaction between the cadmium nuclei has to be taken into account, which is also effective in CdTe . Perhaps there is a small anisotropy, which was not resolved and which broadens the signal. Both spectra are observed at a resonance frequency, which is higher than the Larmor frequency of aqueous solutions.

CdS and CdSe crystallize in the hexagonal structure with ZnO arrangement [21], both samples yielded an anisotropic nuclear magnetic shielding the sign and the order of magnitude of which are very similar (see Table 1). A typical spectrum for the CdSe signal is given in Figure 2. The lower trace shows the result of the least-squares fit, which agrees fairly well with the experimental absorption

signal. The linewidths for the CdS and CdSe are very similar, for both samples much higher frequencies of ^{113}Cd were observed than in aqueous solutions.

For the CdCO_3 , which crystallizes in the rhombohedral calcite structure [22] only a symmetrical line was detected. The shielding constant is very similar to the shielding of the Cd^{2+} ion in aqueous solutions of vanishing concentration. This seems reasonable, because even concentrated solutions of Cd^{2+} and oxyanions in water show only slight chemical shifts of ^{113}Cd [10, 15–20] (see Figure 3).

For cadmium only a few measurements in the solid samples are known. The ^{113}Cd signals of CdS , 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 $\text{Cd}(\text{NO}_3)_2$ 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 Look [23]. ^{113}Cd signals have also been measured in metallic cadmium and in alloys [25–32]. An anisotropy of 480 ppm is found for the metallic cadmium [31]. These shifts have been referred to the shielding of the free atom 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 ^{133}Cs NMR in powder samples [6]. The shift of CdCO_3 shows that the oxyanions indeed induce nearly the same shielding as the H_2O 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 ^{207}Pb [38, 39]. There is a remarkable similarity of the shielding as regards the dependence on the atomic number. This means that

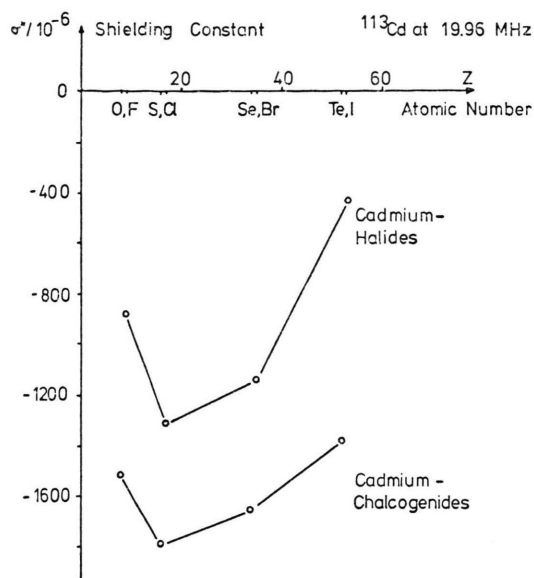


Fig. 4. Dependence of the absolute nuclear magnetic shielding of ^{113}Cd in crystalline halides and chalcogenides on the atomic number of the halides and chalcogenides. The straight lines connecting the experimental points are plotted only for clearness. They have no theoretical meaning.

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 anisotropies 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).

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