NMR Spectra of Alkali and Halogen Nuclei in Alkali and Halogen Salts

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NMR signals of ^{7}Li, ^{23}Na, ^{35}Cl, ^{39}K, ^{79}Br, ^{87}Rb and ^{127}I have been measured in various alkali and halogen salt powders relative to well defined aqueous solutions. With the known shielding constants of some of these solutions the nuclear magnetic shielding constants of the alkali and chlorine nuclei in crystalline powders were evaluated in the atomic reference scale. The theoretical values of the shielding constants in alkali halides do not agree even in the order of magnitude with the experimental ones in some cases.

For ^{23}Na first-order and second-order quadrupole patterns have been observed and the quadrupole coupling constants are given.

Introduction

In NMR-spectroscopy chemical shifts of nuclei in condensed matter are usually referred to rather arbitrary reference compounds from the viewpoint of nuclear magnetic shielding. The understanding of nuclear shielding and the comparison with theory is therefore complicated by the usually unknown absolute size of the nuclear magnetic shielding of the reference compound. Also the meaning of the observed difference between the magnetic shieldings in different compounds — the chemical shift — cannot be valued in the light of the unknown range of nuclear magnetic shielding. Further it is well known that the range of observed chemical shifts is no basis for an estimation of the absolute shielding. For a few elements, however, the situation is more favourable; e.g. the nuclear magnetic shielding of the alkali nuclei in hydrated alkali ions is well established by experiment: ^{6}Li (Ref. [1]), ^{7}Li (Ref. [1]), ^{23}Na (Ref. [1]), ^{39}K (Ref. [2]), ^{40}K (Ref. [2]), ^{41}K (Ref. [1, 2]), ^{85}Rb (Ref. [3]), ^{87}Rb (Ref. [4–7]), ^{133}Cs (Ref. [7, 8]). Also the shielding of ^{35}Cl is known, though with lower accuracy [9].

Using these data it is possible to give the nuclear magnetic shielding of alkali and chlorine nuclei in all the compounds and environments the chemical shift of which has been measured versus a definite reference. For these nuclei it seems possible to get a deeper insight into the origin of nuclear magnetic shielding because now a more reliable comparison can be performed with theory. For crystalline halides Hafemeister and Flygare [10] and Ikenberry and Das [11] have calculated the nuclear magnetic shielding of some nuclei referred to the free ion. But often the experimental data of chemical shifts in alkali halide powders for the various nuclei are unfortunately not comparable because of unpractical referencing.

For ^{133}Cs, the nuclear magnetic shielding and quadrupole coupling in cesium salt powders have recently been reported [12].

In the following we describe investigations of the other alkali and halogen NMR signals in alkali and halogen salt powders which have been undertaken for an accurate evaluation of the nuclear magnetic shielding of these nuclei which can be compared with theoretical values [10, 11]. Further quadrupole coupling constants of ^{23}Na could be derived from some powder spectra.

Nuclear Magnetic Shielding

NMR experiments on diamagnetic ions or atoms, free and in condensed matter, yield different proportional constants — different gyromagnetic ratios — from the measurements of the appropriate $\boldsymbol{B}_0$, $\boldsymbol{\omega}$ and $\boldsymbol{\omega}'$ according to the relations

$$\boldsymbol{\omega} = \gamma_{\text{atom}} \cdot \boldsymbol{B}_0 \quad \text{or} \quad \boldsymbol{\omega}' = \gamma_{\text{cond.}} \cdot \boldsymbol{B}_0 \,.$$

This fact is due to the interaction of the electronic environment in condensed matter with the nucleus under observation and leads to the well known phenomenon of chemical shift.

A magnetic shielding constant σ^* is derivable by

$$\sigma^* = (\gamma_{\text{cond.}} - \gamma_{\text{atom}})/\gamma_{\text{atom}} \,.$$

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If σ^* is known for a definite sample, the chemical shift in all other measured environments can be referred to this atomic shielding scale. The atomic shielding scale is more meaningful for theoretical comparison than any other scale used in NMR spectroscopy basing on an arbitrary chemical compound. Between the experimental shielding constant σ^* of a compound, the diamagnetic shielding of the free atom σ_d and the absolute shielding σ of the compound (referred to the bare nucleus) the following relation holds:

$$\sigma = \sigma_d + \sigma^* .$$

σ_d and σ are defined by the relations:

$$\boldsymbol{\omega} = \gamma_I (1 - \sigma_d)\, \boldsymbol{B}_0 \quad \text{for free atoms and ions}$$

$$\boldsymbol{\omega}' = \gamma_I (1 - \sigma)\, \boldsymbol{B}_0 \quad \text{for condensed matter,}$$

where γ_I is the gyromagnetic ratio of the bare nucleus; for free atoms and ions σ_d can be calculated with reasonable accuracy (Ref. [13]).

Ikenberry and Das [11, 14, 15] and Hafemeister and Flygare [10] have calculated σ^* of some alkali and halogen nuclei in alkali halides and in infinitely dilute aqueous solutions of alkali halides. These authors used the Kondo-Yamashita-formalism [16] starting from wave functions of the free ion and found that σ^* is proportional to a sum of squares of overlap integrals between the orbitals of the neighbouring ions devided by the mean excitation energy.

The theoretical values of σ^* for the various alkali and halogen nuclei given by Ikenberry and Das [11, 14, 15] and Hafemeister and Flygare [10] could not be compared with experimental values of σ^* since the chemical shifts of the nuclei in condensed matter have not been available in the atomic reference scale at that time [2–9]. The chemical shifts of alkali and chlorine nuclei in alkali halides measured by several authors are referred to ambiguous aqueous solutions or solutions which contain paramagnetic ions [17–23]. The unknown shielding of the alkali and halogen nuclei by the water molecules, by the counter-ions and especially by the paramagnetic ions was usually underestimated.

The shielding constants σ^* of the nuclei in the ions at infinite dilution in H_2O used in this work are given in the heading of Tables 2 and 4. These values of σ^* are not at all negligible compared with the shielding constants in crystalline powders. Careful measurements of the chemical shifts δ of alkali and halogen nuclei in alkali and halogen salts relative to such solutions yield the shielding constants of the salts $\sigma^*_{\text{cryst.}}$ which can be compared with theoretical values.

Experimental

The NMR measurements on ^{7}Li, ^{23}Na, ^{35}Cl, ^{39}K, ^{79}Br, ^{87}Rb and ^{127}I were performed with a multinuclei Bruker pulse spectrometer SXP 4-100 at (298 ± 3) K in a magnetic field of 2.114 T, produced by a Bruker high-resolution magnet, which was externally NMR-stabilized. The free induction decays were accumulated and Fourier transformed by the Bruker B-NC 12 data unit. For large spectral widths the Bruker transi-store BC-104 was used.

Some essential NMR data of all observed nuclei are given in Table 1. By the sample exchange method the signals of the solid samples were measured relative to aqueous reference solutions the concentration of which was well known. With the concentration dependence of the chemical shift of the nuclei ^{7}Li (Ref. [24]), ^{23}Na (Ref. [25]), ^{35}Cl (Ref. [26]), ^{39}K (Ref. [2]), ^{79}Br (Ref. [26]), ^{87}Rb (Ref. [25]), and ^{127}I (Ref. [27]) the chemical shifts of the solid samples can be extrapolated to the respective aqueous solution with vanishing concentration. For these solutions the shielding constants in the atomic reference scale σ^* is known for the alkali nuclei [1–8] and for chlorine [9]. The measurements were performed on cylindrical or spherical samples with 10 mm outer diameter. Susceptibility corrections were not performed. Errors due to different susceptibilities are estimated

Table 1. NMR parameters of the observed nuclei.

Nucleus	Natural abundance in %	Spin	Quadrupole moment^a in 10^{-24} cm^2	Larmor-frequency at 2.114 *T* in MHz	Receptivity (proton = 1)
^{7}Li	92.6	3/2	-0.04	35.0	$2.7 \cdot 10^{-1}$
^{23}Na	100.0	3/2	$+0.10$	23.8	$9.3 \cdot 10^{-2}$
^{35}Cl	75.4	3/2	-0.10	8.8	$3.6 \cdot 10^{-3}$
^{39}K	93.1	3/2	$+0.049$	4.2	$4.7 \cdot 10^{-4}$
^{79}Br	50.5	3/2	$+0.37$	22.6	$4.0 \cdot 10^{-2}$
^{87}Rb	27.9	3/2	$+0.13$	29.5	$4.9 \cdot 10^{-2}$
^{127}I	100.0	5/2	-0.79	18.0	$9.4 \cdot 10^{-2}$

[a] Averaged values taken from Fuller [28].

to be smaller than 3 ppm, which is much smaller than the accuracy because the signals were broad. The Larmor frequency was assumed to be accurate for samples which yielded only symmetrical signals to about 5% of the linewidths even if the statistical error for different measurements was smaller. For signals with quadrupole splitting additional errors must be assumed.

Results and Discussion

The NMR signals of the alkali nuclei ^{7}Li, ^{23}Na, ^{39}K and ^{87}Rb have been measured in various crystalline samples versus definite solutions of LiCl, NaCl, KNO_2, or RbCl in H_2O and the chemical shifts relative to these solutions have been extrapolated to infinitely diluted aqueous solutions using the measurements of Ref. [2, 3, 7, 24—27]. With the shielding constants of the dilute solutions [1—8] the shielding constants of the solid samples can easily be evaluated. In Table 2 these shielding constants are given. A negative sign of the shielding constant means a higher Larmor frequency of the nucleus in the solid sample than for the free atom or ion in the same magnetic field.

Table 2. Results of the NMR measurements for the alkali nuclei in crystalline salts. The given shielding constants have been referred to the free ions by using the chemical shift of the respective salt relative to infinitely diluted aqueous solutions [2, 3, 7, 24—27] and the shielding constants of these diluted solutions: $\sigma^*(^7\mathrm{Li}) = -(11.0 \pm 0.7) \cdot 10^{-6}$ (Ref. [1]), $\sigma^*(^{23}\mathrm{Na}) = -(60.5 \pm 1.0) \cdot 10^{-6}$ (Ref. [1]), $\sigma^*(^{39}\mathrm{K}) = -(105.2 \pm 0.8) \cdot 10^{-6}$ (Ref. [2]), and $\sigma^*(^{87}\mathrm{Rb}) = -(211.6 \pm 1.2) \cdot 10^{-6}$ (Ref. [6]).

Nucleus	Salt	$\sigma^*_{\mathrm{cryst.}}$ in ppm	Typical linewidth in kHz	Type of spectrum[b]
^{7}Li	LiBr	-33 ± 9	5.7	s
^{7}Li	Li_2O[a]	1 ± 13	9.0	s
^{7}Li	Li_2S[a]	-11 ± 13	10.0	s
^{7}Li	Li_2MoO_4	-7 ± 8	5.8	s
^{23}Na	NaF	-70 ± 15	7.0	s
^{23}Na	NaCl	-69 ± 6	2.7	s
^{23}Na	NaBr	-69 ± 7	3.1	s
^{23}Na	NaI	-55 ± 6	2.6	s
^{23}Na	$NaNO_3$	-45 ± 4	2.0	f. o.
^{23}Na	$NaReO_4$	-41 ± 7	2.0	f. o./s. o.
^{23}Na	$NaBiO_3$	-24 ± 15	7.0	s
^{23}Na	$Na_2B_4O_7$	-48 ± 13	6.0	s
^{23}Na	Na_2MoO_4	-57 ± 9		s. o.
^{23}Na	Na_2WO_4	-64 ± 13		s. o.
^{23}Na	$Na_2S_2O_3$	-40 ± 17		s. o.
^{23}Na	Na_2SO_4	-55 ± 10		s. o.
^{39}K	K_2SnCl_6	-90 ± 2	0.05	s
^{87}Rb	RbCl	-338 ± 3	1.3	s
^{87}Rb	RbBr	-362 ± 3	1.6	s
^{87}Rb	RbI	-390 ± 5	1.6	s

[a] Samples have been enriched in ^{7}Li to 99.99% (Ref. [36]). This enrichment yields a linebroadening of about 2 kHz compared with naturally abundant samples.

[b] s means single line; f.o. means first-order quadrupole splitted signal; s.o. means second-order quadrupole splitted central line.

For ^{7}Li only a few signals have been observed and only very broad single signals were found. The shielding constant for these samples is relatively small.

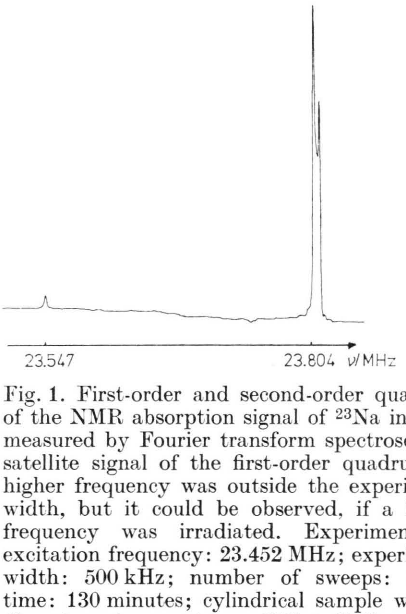

Fig. 1. First-order and second-order quadrupole splitting of the NMR absorption signal of ^{23}Na in $NaReO_4$ powder measured by Fourier transform spectroscopy. The second satellite signal of the first-order quadrupole splitting at higher frequency was outside the experimental spectrum width, but it could be observed, if a higher excitation frequency was irradiated. Experimental parameters: excitation frequency: 23.452 MHz; experimental spectrum width: 500 kHz; number of sweeps: 1500; measuring time: 130 minutes; cylindrical sample with 10 mm outer diameter; temperature: (298 ± 3) K; 600 data points were accumulated followed by 3496 points of zerofilling before the Fourier transformation of 4 K points.

For ^{23}Na in sodium halides and in $NaBiO_3$ and $Na_2B_4O_7$ single lines were measured. It is well known that for $NaNO_3$ a first-order quadrupole splitting can be detected [29]. For $NaReO_4$ a spectrum was observed which shows a first-order quadrupole splitting and a second-order quadrupole splitting of the central line. An example of this signal is shown in Figure 1. Only second-order quadrupole splitted central lines have been observed for ^{23}Na in Na_2MoO_4, Na_2WO_4, $Na_2S_2O_3$ and Na_2SO_4. The values of the quadrupole coupling constants and of the asymmetry parameter of the electric field gradient are given in Table 3. The spectra showing a second-order quadrupole splitting of the central line have been evaluated using the relations describing the positions of the shoulders and divergences, which have been given

Table 3. Quadrupole coupling constants of ^{23}Na in some solid samples.

Sample	$e^2 q Q/h$ in kHz	Asymmetry parameter	Type of observed spectra[a]
$NaNO_3$	336 ± 1	0.0 ± 0.1	single crystal and powder, f.o.
$NaReO_4$	1044 ± 2	0.0 ± 0.1	powder, f.o./s.o.
Na_2MoO_4	2573 ± 8	0.0 ± 0.1	powder, s.o.
Na_2WO_4	2479 ± 14	0.0 ± 0.1	powder, s.o.
$Na_2S_2O_3$	1728 ± 90	0.7 ± 0.1	powder, s.o.
Na_2SO_4	2620 ± 170	0.6 ± 0.1	powder, s.o.

[a] f.o. means NMR signal with first-order quadrupole splitting; s.o. means NMR signal with a second-order quadrupole splitted central line.

e.g. by Taylor et al. [30]. Afterwards with a computer program theoretical spectra were calculated using the parameters: Larmor frequency, quadrupole coupling constant and asymmetry parameter of the evaluation of the experimental spectra. With this program the resonance frequencies of about 65000 different orientations of the electric field gradient tensor have been calculated. We found no hints of an anisotropic nuclear magnetic shielding. With respect to the relatively small chemical shifts of ^{23}Na such effects can be estimated to have only minor significance. For ^{23}Na in Na_2MoO_4 and in Na_2WO_4 second-order quadrupole splittings have already been observed [31]; our results agree with this observation. For ^{23}Na in $Na_2S_2O_3 \cdot 5\,H_2O$ two crystallographic nonequivalent sodium ions have been found [32]. Our measurement was performed with a $Na_2S_2O_3$ sample, which contained no crystal water. Therefore the results are not comparable. Though two inequivalent sodium ions are also present, only one quadrupole spectrum was detected. Additional to the quadrupole coupling constants of ^{23}Na we have determined the shielding constants of the sodium samples, the results are given in Table 2. For the alkali halides NaF, NaCl, NaBr and NaI the absolute value of the shielding constant decreases with increasing atomic number of the halogen counterions, contrary to the behaviour found for ^{133}Cs incesium halides. For the sodium salts with oxyanions nearly always lower Larmor frequencies were measured than in dilute aqueous solutions. Recently precise measurements of the chemical shift of ^{23}Na in alkali halides versus a saturated aqueous NaBr solution have been published [17]. The values agree with ours within the limits of error, if the concentration dependence of the chemical shift of [25] is taken into account.

The magnetic shielding constants of ^{39}K in potassium halides have already been determined by Sahm and Schwenk [2]. We have measured the ^{39}K signal in a further compound: K_2SnCl_6. An example of the ^{39}K signal in this sample is shown in Figure 2. The linewidth of this signal is very small. The signal is observed at a lower Larmor frequency than the signals in aqueous solutions. The shielding constant for this sample is given in Table 2.

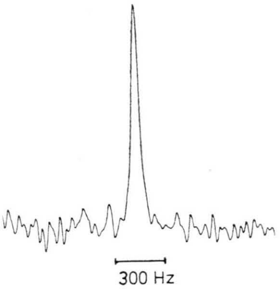

Fig. 2. Absorption signal of ^{39}K in K_2SnCl_6 powder at 4.200 MHz. Experimental spectrum width: 6 kHz; number of pulses: 300; measuring time: 5 minutes; cylindrical sample with 10 mm outer diameter; temperature (298 ± 3) K; 400 data points were accumulated followed by 15984 points of zerofilling before the Fourier transformation of 16 K points.

Single signals of ^{87}Rb have been observed in RbCl, RbBr and RbI crystalline samples. The results of the magnetic shielding constants are given in Table 2. With increasing atomic number of the halogen counterions the absolute value of the magnetic shielding constant increases. This tendency has also been found by other authors [16, 18, 19]. But the values of the shielding constants are not comparable, because the shielding constants of the respective reference solutions were not taken into account.

Further the chemical shifts of the halogen nuclei ^{35}Cl, ^{79}Br and ^{127}I have been determined in alkali halides relative to aqueous solutions with vanishing concentration of NaCl, NaBr or NaI. The results are given in Table 4. As only for chlorine the magnetic shielding constant of an infinitely dilute aqueous solution is known [9], only for ^{35}Cl in the alkali chlorides the nuclear magnetic shielding could be given. The chemical shift of the halogen nuclei ^{35}Cl, ^{79}Br and ^{127}I passes through a minimum as a function of the atomic number of the alkali

Table 4. Results of the NMR measurements of the halogen nuclei in crystalline alkali halides. The chemical shift data are given as $(\nu - \nu_{\text{Ref.}})/\nu_{\text{Ref.}}$ where $\nu_{\text{Ref.}}$ means the Lamor-frequency of sodium halide solutions with vanishing concentration in H_2O. For the evaluation of the shielding constant of ^{35}Cl in the alkali halides the shielding constant of ^{35}Cl in diluted aqueous solutions of Ref. [9]: $\sigma^*(^{35}\text{Cl}) = -(170 \pm 12) \cdot 10^{-6}$ has been used.

Nucleus	Salt	Chemical shift in ppm	$\sigma^*_{\text{cryst.}}$ in ppm	Typical linewidth in kHz
^{35}Cl	LiCl	$+\ \ 4 \pm 8$	-174 ± 14	1.3
^{35}Cl	NaCl	$-\ 44 \pm 5$	-126 ± 13	0.9
^{35}Cl	KCl	$+\ \ 4 \pm 1$	-174 ± 12	0.2
^{35}Cl	RbCl	$+\ 45 \pm 3$	-215 ± 12	0.4
^{35}Cl	CsCl	$+110 \pm 3$	-280 ± 12	0.5
^{79}Br	LiBr	$+109 \pm 9$		4.2
^{79}Br	NaBr	$-\ \ 6 \pm 5$		2.3
^{79}Br	KBr	$+\ 47 \pm 2$		1.0
^{79}Br	RbBr	$+118 \pm 3$		1.2
^{79}Br	CsBr	$+275 \pm 3$		1.4
^{127}I	NaI	$+213 \pm 4$		1.5
^{127}I	KI	$+179 \pm 3$		0.8
^{127}I	RbI	$+257 \pm 2$		0.9
^{127}I	CsI	$+548 \pm 4$		1.1

nuclei for sodium or potassium halides. This behaviour has also been found by [18, 20—22].

Some theoretical calculations of the nuclear magnetic shielding are known; all are using the Kondo-Yamashita formalism [16]. For ^{87}Rb the theoretical values are by about a factor 2.5 too small [10], indicating a decreasing paramagnetic shielding if the atomic number of the halogen counterion increases, contrary to the experimental tendency. From the values of the halogen nuclei only the value of ^{35}Cl in RbCl (Ref. [10]) can be compared with the experimental value. In this case the agreement between the theoretical and experimental value is remarkably good. The other values of the bromine and iodine nuclei [10, 15, 22] cannot be compared, because the atom related shielding constants of these nuclei in the respective compounds are not known.

When performing calculations with the overlap integrals of Hafemeister and Flygare [34] for all alkali and halogen nuclei in alkali halides we found no better agreement between the experimental and theoretical values. The difference amounts sometimes to nearly one order of magnitude. For ^{23}Na the theoretical values reproduce the decreasing paramagnetic shielding with increasing atomic number of the halogen counterions. But for the halogen nuclei the minimum value of the chemical shift, which is observed for sodium or potassium halides, as a function of the atomic number of the alkali nuclei, is not reproduced. This has also been shown for ^{19}F by Sears [35].

From these measurements one remarks that for all nuclei for which the shielding constant σ^* is known by experiment the Larmor frequencies of the nuclei in the solid and also the liquid state are shifted to higher frequencies relative to the free atom; this means that always a paramagnetic shielding is observed. The often reported shifts to lower frequencies result from the not at all negligible shielding constants of the reference solutions, which are in many cases aqueous solutions. The influence of the water molecules in aqueous solutions on the shielding of the hydrated ions (see Table 2) is often larger than the influence of the neighbour ions in the solid state. The dependence of the nuclear magnetic shielding in aqueous solutions on the concentration of the ions is due to both, the shielding by the water molecules and the shielding by the counter ions. From the measurements of this work the size of the latter effect is now also known and can be used for the evaluation of the concentration dependence of chemical shifts in aqueous solutions.

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