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Accurate Determination of NMR Chemical Shifts in Alkali Halides and Their Correlation with Structural Factors

Shigenobu HAYASHI* and Kikuko HAYAMIZU
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305
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High-resolution solid-state NMR spectra of alkali halides have been measured using the magic angle spinning (MAS) of the sample, and chemical shifts of ^{7}Li, ^{23}Na, ^{87}Rb, ^{133}Cs, ^{35}Cl, ^{79}Br, and ^{127}I have been determined accurately. The ^{39}K chemical shifts have been determined by NMR without MAS. As the ratio of the cation radius to the anion radius (R_m) increases, the chemical shifts of halogen nuclei show an upfield shift when $R_m<0.6$, while they show a downfield shift when $R_m>0.6$. The chemical shifts of the halogen nuclei are explained in terms of the first and the second nearest neighbor interactions, both of which cause a downfield shift. On the other hand, the chemical shifts of alkali nuclei show a downfield shift for the ratio of the anion radius to the cation radius (R_x) less than 1.6, while they show an upfield shift for $R_x>1.6$. The chemical shifts of the alkali nuclei are expressed by the sum of the nearest neighbor interaction in the absence of the halogen-halogen interaction and the "isolation effect" caused by the halogen-halogen interaction. The "isolation effect" makes the chemical shifts approach to the values of the isolated ions.

Alkali halides have NaCl- and CsCl-type structures,[1] and their bonds are almost ionic. They are suitable for nuclear magnetic resonance (NMR) study, since they all contain components which can be easily observed by NMR; i.e., ^{7}Li, ^{23}Na, ^{39}K, ^{87}Rb, ^{113}Cs, ^{19}F, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, and ^{127}I. Although all the nuclei other than ^{19}F have quadrupole moments, the cubic structure leads to no quadrupolar broadening. Due to these favorable properties, NMR chemical shifts in alkali halides have been well studied in the past, both experimentally and theoretically.[2-10] Although the accuracy of the theoretical calculation was not very good, the basic ideas have been estabilished by Yoshida and Moriya[4] and by Kondo and Yamashita.[6] Yamagata[7] has improved the agreement between the experimental and the calculated shift values of the halogen nuclei by taking into account the second nearest neighbor interactrion in addition to the nearest neighbor interaction.

Since the pioneering work of Andrew et al.[11,12] and Lowe,[13] NMR techniques have been markedly developed, which makes it possible to obtain high-resolution spectra in solids. The technique called "magic angle spinning (MAS)" can narrow the resonance line, enabling the accurate determination of the isotropic chemical shift. The MAS technique is now used in a variety of fields.[14]

Much effort has been made to correlate the chemical shift with structural parameters.[15-32] ^{29}Si NMR in silicates and aluminosilicates has been studied intensively, and several correlations between the ^{29}Si chemical shift and structural factors have been presented.[15-25] The following factors have been proposed; the Si–O bond length,[15,20] the number of AlO_4 tetrahedra linked to the SiO_4 tetrahedron,[16] the cation–oxygen bond strength,[17] the Si–Si distance,[18] the Si–O–Si angle,[18,19,21,23,24] the number of neighboring silicon–oxygen tetrahedra,[22] and the group electronegativity.[25] Similar correlations have been presented for other nuclei such as ^{31}P,[26-31] ^{27}Al,[28] and ^{17}O.[32]

There are only a few reports on alkali halides studied by means of MAS NMR. Tabeta et al.[33,34] have recorded ^{23}Na MAS NMR spectra of inorganic salts including halides, and have attempted to relate the ^{23}Na chemical shift to the degree of electron transfer and to the Na–O distance. Weeding and Veeman[35] have determined ^{35}Cl and ^{37}Cl chemical shifts in alkali chlorides, and have tried to relate them with the electronegativity and the cation redius. The best correlation was obtained between the chemical shift and the electronegativity divided by the coordination number. The problem in their work is the missing of data of LiCl, which does not obey the above correlation, as had been pointed out by Yamagata.[7]

In the present work, we determine the chemical shifts in alkali halides accurately by means of MAS NMR, which can be used as shift references in solid-state NMR. A part of ^{23}Na shift values have been reported previously.[36] We discuss the correlation between the chemical shifts and structural factors, based partly on the established theories.[6,7] Finally, we propose empirical formulas which relate the chemical shifts with the structural factors.

Experimental

The materials were used as obtained commercially. NMR spectra were measured at room temperature by a Bruker MSL400 pulsed spectrometer, whose magnetic field was 9.40 T. ^{7}Li, ^{23}Na, ^{87}Rb, ^{133}Cs, ^{35}Cl, ^{79}Br, and ^{127}I NMR spectra were measured using the magic angle spinning of the sample, while ^{39}K spectra were measured for a static sample because of instrumental limitations. The ordinary single-pulse sequence was used. The spinning rates were varied in the range between 2 and 5 kHz. The chemical shifts are presented with respect to 1 M (=1 mol dm^{-3}) MCl (M=Li, Na, K, Rb, and Cs) aqueous solutions for alkali nuclei, and with respect to solid KX (X=F, Cl, Br, and I) for halogen nuclei. The higher-frequency side is expressed as positive.

Results

Figures 1 and 2 show ^{7}Li and ^{35}Cl MAS NMR spectra of alkali halides. The spinning rate of the sample is 4.0 kHz, unless otherwise stated. The spectra of the other nuclei have similar features, and thus they are not shown. Tables 1 and 2 summarize the chemical shifts. The experimental errors listed reflect the reproducibility of the measurements. Tables 3 and 4 list the line widths both in the MAS experiment and in the static sample. We explain the characteristics of the spectra below.

^{7}Li MAS NMR. Figure 1 shows ^{7}Li MAS NMR spectra of lithium halides. The spectrum of LiF is very broad, since the dipolar interaction with ^{19}F is large. The gyromagnetic ratio of ^{19}F is very large, and its natural abundance is 100%. Although spinning at 4.8 kHz is not enough to separate the center peak from

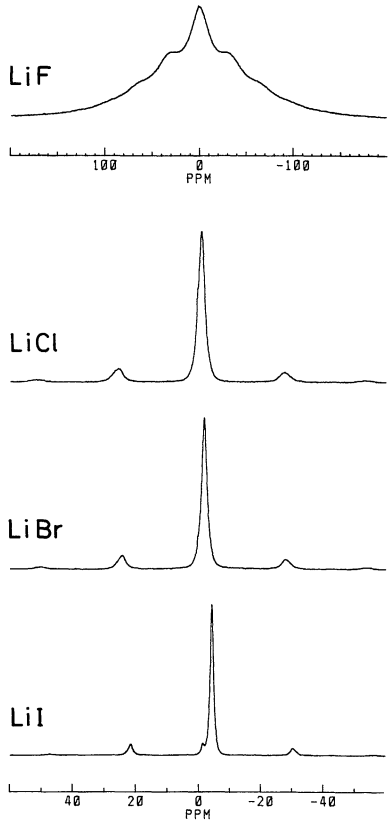

Fig. 1. ^{7}Li MAS NMR spectra of lithium halides, measured at a resonance frequency (ν_0) of 155.509 MHz. The spinning rate is 4.8 kHz for LiF, while it is 4.0 kHz for the other compounds. The ^{1}H high-power decoupling is carried out for LiI sample. The chemical shift is expressed with respect to 1 M LiCl aqueous solution.

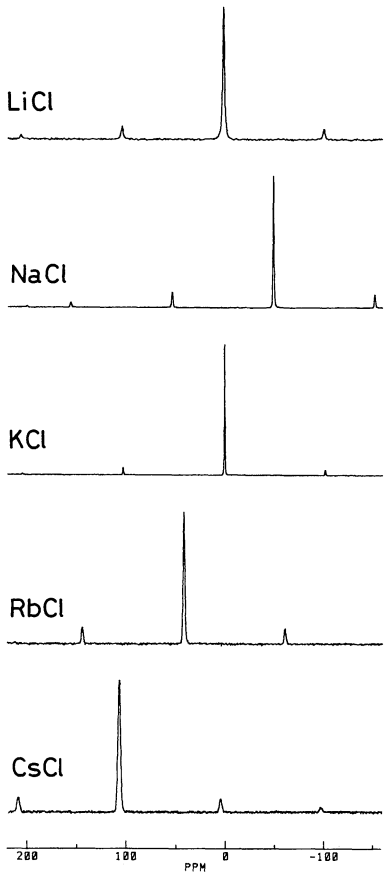

Fig. 2. ^{35}Cl MAS NMR spectra of alkali chlorides at ν_0=39.206 MHz. The chemical shift is expressed with respect to solid KCl.

Table 1. NMR Chemical Shifts of Alkali Nuclei in Alkali Halides

Halogen component	r_x[a]/Å	δ_m/ppm[b] ^{7}Li	^{23}Na	^{39}K[c]	^{87}Rb	^{133}Cs
F	1.33	−0.30	7.13	22.6	60.22	176.27
		(0.10)	(0.03)	(0.1)	(0.08)	(0.10)
Cl	1.81	−1.19	7.21[d]	47.8	123.43	218.52
		(0.03)	(0.03)	(0.1)	(0.06)	(0.14)
Br	1.96	−2.04	5.04[d]	55.1	149.51	250.97
		(0.03)	(0.02)	(0.1)	(0.08)	(0.09)
I	2.20	−4.57	−3.25[d]	59.3	177.08	271.05
		(0.03)	(0.06)	(0.1)	(0.06)	(0.14)

a) Ionic radius cited from Ref. 37. b) Shift from 1M MCl aqueous solution. Values in the parenthesis are experimental errors. c) Chemical shifts are determined from the static spectra. d) This value has already been reported in Ref. 30.

Table 2. NMR Chemical Shifts of Halogen Nuclei in Alkali Halides

Alkali component	r_m[a]/Å	δ_x/ppm[b]			
		^{19}F[c]	^{35}Cl	^{79}Br	^{127}I
Li	0.76	−74	1.31	64.74	215.28
			(0.06)	(0.12)	(0.35)
Na	1.02	−91	−49.73	−52.89	33.53
			(0.03)	(0.08)	(0.23)
K	1.38	0	0	0	0
Rb	1.52	42	41.13	71.66	76.91
			(0.09)	(0.15)	(0.12)
Cs	1.67[d]	122	105.96	227.43	368.69
	1.74[e]		(0.11)	(0.08)	(0.12)

a) Ionic radius cited from Ref. 37. b) Shift from solid KX. Values in the parenthesis are experimental errors. c) From Ref. 38. The chemical shift of hexafluorobenzene is −33 ppm with respect to solid KF. d) Sixfold-coordinated. e) Eightfold-coordinated.

Table 3. Line Widths in Alkali NMR of Alkali Halides

Halogen component	Mode	$\Delta\nu$/ppm[a]				
		^{7}Li 155.509 MHz	^{23}Na 105.844 MHz	^{39}K 18.672 MHz	^{87}Rb 130.928 MHz	^{133}Cs 52.484 MHz
F	MAS	40[b]	10.6	—	3.7	3.0
	Static	148	77	11.8	29	31
Cl	MAS	2.6	1.9	—	1.8	1.4
	Static	44	24	8.4	10.2	16.7
Br	MAS	2.1	1.9	—	4.2	5.0
	Static	41	29	14.7	12.5	18.3
I	MAS	1.3	1.8	—	7.0	7.5
	Static	32	27	13.3	11.7	16.3

a) FWHM. In the MAS mode, the line width of the isotropic peak at the spinning rate of 4 kHz is shown. b) The spinning rate is 4.80 kHz, but the isotropic peak is not separated completely from the sidebands.

Table 4. Line Widths in Halogen NMR of Alkali Halides

Alkali component	Mode	$\Delta\nu$/ppm[a]		
		^{35}Cl 39.206 MHz	^{79}Br 100.256 MHz	^{127}I 80.073 MHz
Li	MAS	1.8	3.9	19.4
	Static	32	32	31
Na	MAS	1.0	2.1	6.9
	Static	19.6	20.3	18.5
K	MAS	0.5	1.4	3.8
	Static	6.7	10.2	10.0
Rb	MAS	1.9	3.5	6.8
	Static	10.8	11.7	13.1
Cs	MAS	2.8	5.7	11.1
	Static	13.5	14.2	16.0

a) FWHM. In the MAS mode, the line width of the isotropic peak at the spinning rate of 4 kHz is shown.

the sidebands, the chemical shift can be estimated accurately to be −0.30±0.10 ppm with respect to 1 M LiCl aqueous solution. LiCl, LiBr, and LiI have chemical shifts of −1.19, −2.04, and −4.57 ppm, respectively. LiCl and LiBr have a small shoulder at about 0 ppm, which might be ascribed to hydrated species. LiI has the second small peak at −1.7 ppm. ^{1}H high-power decoupling enhances the relative height of the −1.7 ppm peak a little (The specrtum of LiI shown in Fig. 1 is measured under ^{1}H high-power decoupling). This fact suggests that the −1.7 ppm peak is ascribed to hydrated species like $LiI \cdot H_2O$.[39] The line widths of the isotropic peak in the MAS experiment are in the following decreasing order; LiF>LiCl>LiBr>LiI. In summary, an upfield shift is observed in ^{7}Li NMR of LiX, as the anion size increases.

^{23}Na MAS NMR. NaF has broad peaks because of the large dipolar interaction with ^{19}F, while NaCl, NaBr, and NaI have narrow peaks with full widths at half maximum (FWHM's) of about 1.9 ppm. The

chemical shifts are 7.13, 7.21, 5.04, and −3.25 ppm for NaF to NaI, respectively. The isotropic peak shifts towards upfield from NaCl to NaI, as the anion size increases. NaF is an exception, taking a value a little smaller than NaCl. NaI has a small second peak at about 2 ppm, which might be ascribed to hydrated species.

^{39}K Static NMR. ^{39}K spectra have been measured at ν_0=18.672 MHz in a static state because of the instrumental limitations. The FWHM's are between 8.4 and 14.7 ppm, and thus the accuracy of the shift values is somewhat worse than that in the MAS NMR spectra. However, this accuracy is enough to discuss the dependence of the chemical shift on structural factors. As is listed in Tables 1, a downfield shift takes place as the anion size increases.

^{87}Rb MAS NMR. Much more spinning sidebands are observed in the ^{87}Rb MAS NMR spectra, when compared with the MAS NMR spectra of the other alkali nuclei. The isotropic peak shifts towards downfield as the anion size increases, similarly to ^{39}K, although the change in the peak position is much larger. The line widths of the isotropic peak in the MAS experiment increase in the following order; RbCl<RbF<RbBr<RbI.

^{133}Cs MAS NMR. The intensity of the spinning sidebands is small. The peak shifts towards downfield with the anion size, similarly to ^{39}K and ^{87}Rb. Impurity peaks are detected at 73 and 101 ppm in CsF, and at about 240 ppm in CsBr. They might be ascribed to hydrated species, since hydrated species are expected to be observed at a position between the anhydrous species and the aqueous solution. The line widths in the MAS experiment are CsCl<CsF<CsBr<CsI.

^{35}Cl MAS NMR. Figure 2 shows ^{35}Cl MAS NMR spectra of alkali chlorides. A very sharp isotropic peak is observed, especially in KCl whose FWHM is only 0.5 ppm. The line widths in the MAS experiment increase as follows; KCl<NaCl<LiCl<RbCl<CsCl. A downfield shift is observed from NaCl to CsCl, as the cation size increases. LiCl is an exception, and takes a shift value between KCl and RbCl. To compare with literature data, the spectrum of 1M NaCl aqueous solution is measured, whose chemical shift is −3.90± 0.02 ppm. The shift values of NaCl to CsCl reported by Weeding and Veeman[35] agree to the present results.

^{79}Br MAS NMR. Many spinning sidebands accompany the isotropic peak, as has been reported in KBr by Frye and Maciel.[40] Similarly to ^{35}Cl, the isotropic peak shifts towards downfield from NaBr to CsBr, while LiBr has a shift value between KBr and RbBr. The line widths in the MAS experiment are expressed as KBr<NaBr<RbBr<LiBr<CsBr.

^{127}I MAS NMR. Many spinning sidebands are produced, similarly to the ^{79}Br MAS NMR spectra. The line widths of the isotropic peak are as follows; KI<RbI<NaI<CsI<LiI. As the cation size increases, a downfield shift takes place from KI to CsI, while an upfield shift from LiI to KI. Consequently, KI has the most upfield shift. The spectrum of 1 M KI aqueous solution is very broad, having a FWHM of 26 ppm, whose chemical shift is −169.1 ppm.

Table 5. The Parameters Obtained from the Simulation[a]

Nucleus	C/ppm	A/ppm	B	D/ppm
Li	0	0.0028	2.54	−0.1
Na	5	0.0009	4.5	0.9
K	76	0.00001	8.7	−51
Rb	208	0	—	−122
Cs	213	0	—	5
F	785	2100	2.93	−918
Cl	796	1970	4.02	−702
Br	2650	4530	2.74	−2520
I	9460	14200	1.48	−11550

a) The subscripts, m and x, are omitted.

Discussion

Shift References. The shift values in Tables 1 and 2 can be used as shift references in solid-state NMR. The ^{19}F shift values are added[38] to complete the tables. They have been determined by means of MAS NMR, in which the spinning rate was about 9 kHz and the static magnetic field was 11.7 T.

In NMR of alkali nuclei, MCl aqueous solution can be the first standards. In the present work, chemical shifts of 1 M MCl aqueous solutions are assumed to be 0 ppm. Alkali halides can be used as the second standards. Among them, solid MCl is the most adequate for the second standards, since the residual line width is small in the MAS NMR spectra.

On the other hand, some aqueous solutions have broad signals in NMR of halogen nuclei,[41] as is shown in the ^{127}I NMR results in this work. Hexafluorobenzene and 1 M NaCl aqueous solutions can be used as the first standards in ^{19}F and ^{35}Cl NMR. However, to unify the shift references, solid KX is used as the first standards in the present work. KX has the narrowest line width among the alkali halides, as shown in Table 4.

Correlation with Structural Factors. In order to elucidate what structural factors determine the chemical shift, we try to relate the chemical shifts with structural factors. Various structural factors have been used in the past as described above. We have attempted to apply them to the alkali halides, and among them ionic radius,[37] electronegativity,[42] and lattice constants[1] are found to be appropriate. In the discussion below, we adopt the ionic radius, although similar discussion is possible by utilizing the other factors.

The chemical shifts listed in Tables 1 and 2 are regarded as having tendencies described below:

(1) There is a basic tendency that the signal shifts

towards downfield with the increase in the radius of the counter ion. The upfield shift is regarded as an exception.

(2) In NMR of alkali nuclei, K, Rb, and Cs obey the basic tendency. Li is an exception, in which the upfield shift is observed. Na is in the intermediate case, in which NaCl has the most downfield shift value.

(3) In NMR of halogen nuclei, the basic tendency is applied in the region of the larger cation radius. On the other hand, the upfield shift takes place in the region of the smaller cation radius. Thus, the most upfield shifts are exhibited in NaF (^{19}F), NaCl (^{35}Cl), NaBr (^{79}Br), and KI (^{127}I).

Conclusively, the chemical shift is not linearly correlated with the ionic radius.

Theoretically, the magnetic shielding is separated into two parts; diamagnetic and paramagnetic terms. In alkali halides, the paramagnetic term plays an important role in the chemical shift. Thus, according to Kondo and Yamashita[6] the chemical shift is expressed as:[7]

$$\delta = \frac{16}{3} N\mu_B^2 \left\langle \frac{1}{r^3} \right\rangle \frac{A}{\langle \Delta E \rangle}, \quad (1)$$

where N is the number of nearest neighbors, μ_B the Bohr magneton, r the distance between the central nucleus and an outermost p-electron of the ion, A the overlap integral, and $\langle \Delta E \rangle$ the mean excitation energy of the electron. Among the above parameters, the overlap integral is varied largely from material to material. The overlap integral is expressed in the form as[7]

$$A = A \exp(-Br_a), \quad (2)$$

where r_a is the interatomic distance, and A and B are constants characteristic of the atomic components. Generally, as the size of the counter ion increases, the overlap integral increases, resulting in the downfield shift. This is called "the nearest neighbor interaction," which explains the basic tendency. Tabeta et al.[33,34] have proposed the concept of "electon transfer" to explain the ^{23}Na chemical shift. The concept of the "electron transfer" is equivalent to the meaning of the above overlap integral. In other words, the electron transfer from the ligand species to 3p orbital of Na^+ ion makes the overlap integral increase, resulting in a paramagnetic shift.

In the case of alkali halides, the radius of the counter ion does nor correlate linearly with the degree of the electon transfer. The upfield shifts with increase in the counter ion size cannot be explained only by the nearest neighbor interaction. This problem is solved as described below. In Figs. 3 and 4 we plot the chemical shifts as a function of the ratio of ionic radii instead of the ionic radius. One notes that the maximum or minimum always takes place at a certain ratio of the ionic radii. In NMR of alkali nuclei, the most downfield shifts are observed at R_x ($=r_x/r_m$)≈1.6, although only the ^{23}Na results exhibit the maximum.

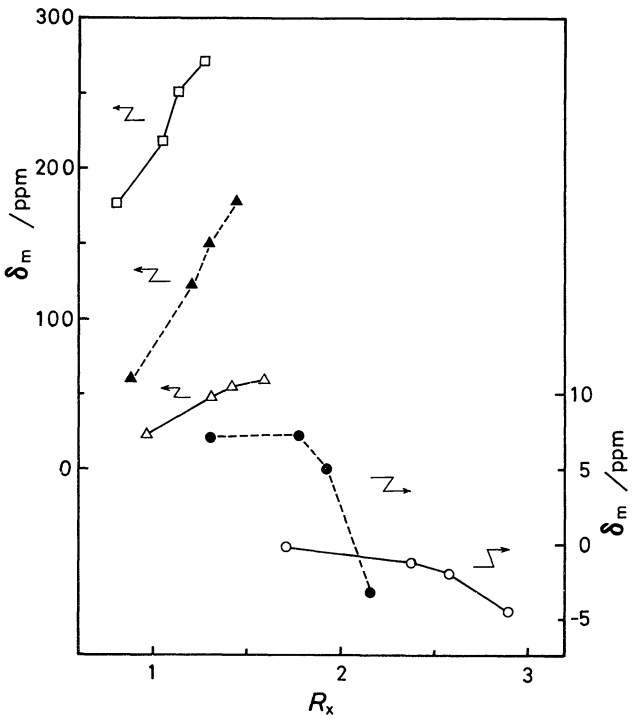

Fig. 3. Dependence of chemical shifts of alkali nuclei (δ_m) on the ratio of the ionic radii ($R_x=r_x/r_m$). ○: ^{7}Li, ●: ^{23}Na, △: ^{39}K, ▲: ^{87}Rb, and □: ^{133}Cs.

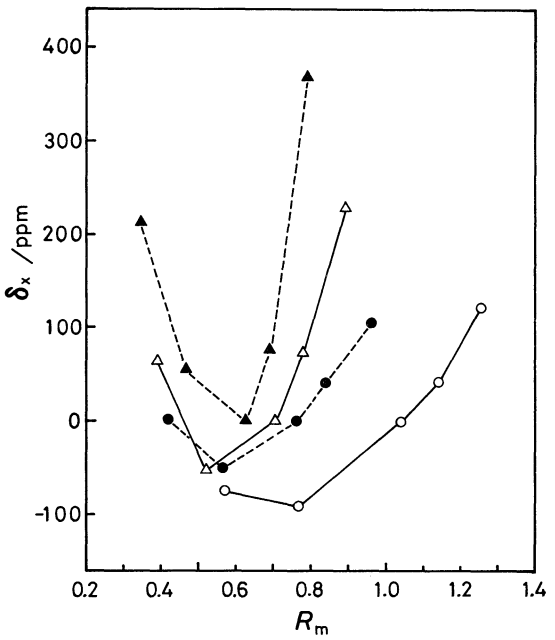

Fig. 4. Dependence of chemical shifts of halogen nuclei (δ_x) on the ratio of the ionic radii ($R_m=r_m/r_x$). ○: ^{19}F (from Ref. 38), ●: ^{35}Cl, △: ^{79}Br, and ▲: ^{127}I.

On the other hand, the halogen nuclei show the most upfield shifts at R_m ($=r_m/r_x$)$\approx$0.6. It is interesting that the product of the above R_x and R_m values is approximately 1. This means that the extremas locate at the same r_m/r_x ratio in alkali and halogen NMR, which suggests that similar mechanisms are applied to the irregularities in NMR of both alkali and halogen nuclei.

In the case of halogen NMR, Yamagata[7] has interpreted the irregularity in terms of the second nearest neighbor interaction. As R_m decreases, the interaction between halogen nuclei increases, which is the second nearest neighbor interaction. This effect causes paramagnetic shift, since the overlap integral between halogen atoms increases. The second nearest neighbor interaction is dominant when $R_m<0.6$.

According to the above discussion, the shift value of halogen nuclei is assumed to be the sum of the following terms:

$$\delta_x = C_x R_m + A_x \exp(-B_x R_m) + D_x, \qquad (3)$$

where C_x, A_x, B_x, and D_x are parameters characteristic of the halogen nuclei. C_x, A_x, and B_x are always positive. The first term expresses the nearest neighbor interaction, which is assumed to be linear with R_m from the results of the larger cation size. The second term expresses the interaction with the second nearest neighbor, i.e., the halogen-halogen interaction. The exponential form is derived from Eq. 2, since the parameters A and B are constants for a given nucleus. The most upfield shift is observed at

$$R_{m1} = \frac{1}{B_x} \ln \frac{A_x B_x}{C_x} \quad , \qquad (4)$$

where $R_{m1}\cong$0.6 experimentally.

A similar discussion is possible also in alkali NMR. The downfield shifts in the region of $R_x<1.6$ are explained in terms of the nearest neighbor interaction. The shifts caused by this interaction are assumed to be linear with the ratio of the ionic radii, R_x ($=r_x/r_m$). The deviation from the linear relation takes place in the region of high R_x ratios. The interaction between alkali nuclei, which is the second nearest neighbor interaction, is negligible because the cation radius is small compared to the anion radius. Especially when R_x is large, the interaction between the alkali ions is reduced nearly to zero. As the R_x ratio increases, the interaction between halogen atoms increases, and the interatomic distance might be restricted only by the anion radius. Consequently, the interatomic distance between an alkali atom and its nearest neighboring halogen atom might be longer than that expected from the sum of the cation and anion radii. This means that the overlap integral between the alkali and the halogen ions decreases when R_x increases. In other words, the alkali ions are slightly isolated from the nearest neighbor halogen ions by the strong halogen–halogen interaction. We call this effect as "isolation effect" for convenience. This effect makes the chemical shift approach to the values of the isolated alkali ion in the gas phase. In fact, the chemical shift of Na^+(gas) is -55.4 ppm,[34] which is shifted towards upfield very much. The "isolation effect" is the reverse side of the second nearest interaction in the halogen NMR.

According to the above discussion and by analogy with halogen NMR, we propose a formula which expresses the chemical shift of alkali nuclei:

$$\delta_m = C_m R_x + A_m (1 - \exp(B_m R_x)) + D_m \ , \qquad (5)$$

where C_m, A_m, B_m, and D_m are parameters characteristic of the alkali nuclei. C_m, A_m, and B_m are posivite. The first term expresses the interaction with the nearest neighbors expected when the halogen–halogen interaction is absent. The second term corresponds to the "isolation effect." The second term becomes zero when R_x approaches to zero, which behavior is reasonable. The most downfield shift takes place at

$$R_{x1} = \frac{1}{B_m} \ln \frac{C_m}{A_m B_m} \quad , \qquad (6)$$

where $R_{x1}\cong$1.6 experimentally.

The ionic radii (r_m, r_x) can be used in place of the ratios of the ionic radii (R_m, R_x) in Eqs. 3 and 5. In those cases, R_{m1} and R_{x1} depend on the halogen and alkali components.

To demonstrate the validity of the above discussion, the chemical shift data are simulated using Eqs. 3 and 5. The agreements between the experimental and the calculated values are good, although a small deviation remains in ^{127}I NMR. The coefficients obtained are listed in Table 5. There are two types of crystal structure, NaCl- and CsCl-types, in the alkali halides. The coordination numbers are six and eight, respectively. Although we did not take into consideration the difference in the crystal structure explicitly in the above discussion, no problems take place. The ionic radii are different for the different coordination, by which the crystal structure is taken into consideration implicitly.

We have tried to relate the coefficients with some structural parameters, but no linear correlations could be found. However, we can extract several trends. In both the alkali and the halogen NMR, the coefficient C in the nearest neighbor interaction increases with the atomic number. This is interpreted by that the magnitude of the overlap integral depends on the size of the observed nucleus itself as well as the size of the counter ion. In halogen NMR except for ^{19}F, A_x increases with the atomic number, while B_x decreases.

Hafemeister and Flygare[43] have calculated the overlap integral in the alkali halides lattices. According to them, the coefficients A and B in the Eq. 2 of the halogen–halogen interaction show the similar dependences on the atomic number. In the alkali NMR, with the increase in the atomic number A_m rapidly decreases while B_m increases. The magnitude of the "isolation effect" depends on B_m much more than on A_m. Therefore, this effect is in the following increasing order; Li<Na<K. This order is reasonable, since the overlap integrals between alkali ions show the similar increasing order.[43]

In summary, we have discussed the correlation between the chemical shifts and the structural factors in the alkali halides. In halogen NMR, the chemical shifts can be determined from the contributions of the first and the second nearest neighbor interactions. On the other hand, the chemical shifts of alkali nuclei can be expressed by the sum of the nearest neighbor interaction in the absence of the halogen–halogen interaction and the "isolation effect."

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