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An empirical model to calculate ^{19}F isotropic chemical shifts in alkali-hexafluoroaluminates

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ABSTRACT

As magic angle spinning solid-state NMR (MAS NMR) has become a powerful method in solid-state sciences, also models for the prediction of chemical shift values have become important topics in recent research.

In the present study, an empirical model to describe the cationic contribution to the ^{19}F isotropic chemical shift values in hexafluoroaluminates with isolated AlF_6-octahedra is presented. Using the corresponding alkali cryolites $M^I_3AlF_6$ (M^I = Li-Cs) as the basis of the calculation, this model is able to provide mean δ_{iso}-values for the whole series of Al-elpasolites used here in order to test the model. The achieved results are compared to experimentally derived values and values calculated using the superposition model developed by Bureau et al. [B. Bureau, G. Silly, J.Y. Buzaré, J. Emery, Chem. Phys. 249 (1999) 89–104] to demonstrate the quality of this new approach. It is shown that a proper choice of the calculation basis leads to values very close to the experiment.

As this model can be extended to other systems with isolated AlF_6-octahedra, it can be regarded as an additional possibility to the methods used so far.

1. Introduction

Magic angle spinning solid-state NMR (MAS NMR) has become an often used and powerful tool in fields like inorganic solid state chemistry and heterogeneous catalysis during the last decades. The main advantages of this method are its sensitivity on structural details often not accessible by other regularly used methods like for example powder X-ray diffraction (XRD). Similar to other analytical methods, models that are able to provide reliable values additionally to the experiment are of big interest. For aluminium oxy and hydroxy fluorides and fluorinated alumina respectively, chemical shift trend analyses were developed to assign the O/F-environment of aluminium to an observed ^{19}F chemical shift region [1–3]. As the position of the ^{19}F resonance strongly depends on the surrounding cations, several attempts in means of ab-initio methods have been made to describe this influence and thus to calculate single chemical shifts for ^{19}F corresponding to the present cationic environment [4–12]. Promising results can be obtained using the superposition model developed by Bureau et al. [13] proposed for purely ionic fluorides. Within this model the ^{19}F isotropic chemical shift δ_{iso} is calculated adding up one constant diamagnetic term and additional paramagnetic contributions due to cations in the neighbourhood of the respective fluorine atom. This model provides very reliable results if the crystal structures of the compounds of interest are known as the correct cation environment of ^{19}F is crucial for the calculations. In addition, the parameters strongly depend on the compounds used for their optimisation. Taking the second point into account, the phenomenological parameters α_1, d_0 and σ_{10} of each cation (s. Eq. (2)) have been refined consecutively several times to obtain optimal values for different classes of compounds [14–16]. Nevertheless, also examples exist where the original parameters have been used without optimisation [17,18].

Elpasolites, named after the mineral K_2NaAlF_6, are hexafluorometallates with the general formula $A^I_2B^IM^{III}F_6$ (with $r_A > r_B > r_M$) and a huge number of compounds with different cation combinations are known up to now. Depending on the ratio of the ionic radii expressed by the modified *Goldschmidt* factor $t' = \sqrt{2}(r_A + r_F)/(r_B + r_M + 2r_F)$ derived from perovskite lattices, different crystal types can be observed ranging from monoclinic over hexagonal to cubic [19]. Nevertheless, isolated MF_6-octahedra are the main building units in each compound. Naturally, this also holds with M = Al for Al-elpasolites and as well for Al-cryolites being a special class of elpasolites with $A^I = B^I$ (parts of the crystal structures of Na_3AlF_6, Cs_2NaAlF_6 and K_2NaAlF_6 are shown in Fig. 1).

All Al-compounds with alkali metals as A^I and B^I are easily accessible via a novel sol–gel synthesis route [20–22]. During structural investigations of these synthesis products it turned out

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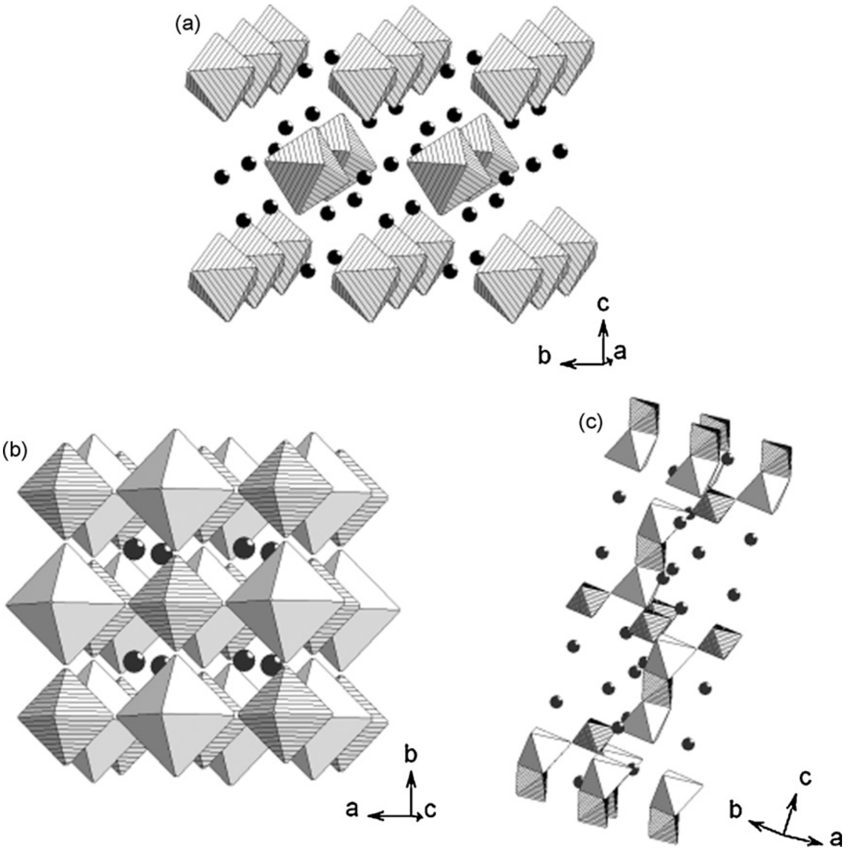

Fig. 1. Parts of the crystal structures of (a) Na_3AlF_6, (b) K_2NaAlF_6 and (c) Cs_2NaAlF_6. All AlF_6-octahedra are shown in the style of (a). Additional octahedra in (b) and (c) have Na-atoms in their centres. No polyhedral representation has been chosen for Na in (a), K in (b) and Cs in (c).

that the two compound classes are ideal candidates for the development of a model describing the cation contribution to the ^{19}F isotropic chemical shift within MAS NMR [23]. The observed chemical shifts for these compounds cover a large range and as the main building unit AlF_6 remains almost unchanged for all combinations, the influence of the alkali metals surrounding ^{19}F can be regarded as the only significant contribution to the observed position of the ^{19}F resonance. Here, we present an empirical model for the calculation of ^{19}F isotropic chemical shifts in hexafluoroaluminates using parameters derived from Al-cryolites. The obtained results will be compared to experimental and calculated values.

2. Results and discussion

In Fig. 2 the ^{19}F MAS NMR spectra (isotropic lines) of all investigated Al-elpasolites and Al-cryolites are shown. Although all compounds belong to the same structure class, the values of the measured shift cover a large range with a maximum difference between Cs_3AlF_6 and Na_3AlF_6 of 74 ppm. Although more sites could be expected corresponding to their crystal structures, only one isotropic line can be observed under the experimental conditions applied here regarding the cryolitic systems Li_3AlF_6 (Fig. 2a), Na_3AlF_6 (Fig. 2b) and the compound Na_2LiAlF_6 (Fig. 2f) in addition. The crystal structures at room temperature for K_3AlF_6 (Fig. 2c), Rb_3AlF_6 (Fig. 2d) and Cs_3AlF_6 (Fig. 2e) are unknown up to now, but TEM (K_3AlF_6) [24] and XRD [23] investigations have been able to show, that these compounds crystallize in a monoclinic cell in the space group $I2/a$. While only one resonance is observed for K_3AlF_6, the spectra of Rb- and Cs-cryolite tend to be more complicated.

Corresponding to their cubic crystal structure (K_2NaAlF_6-type [25], space group $Fm\bar{3}m$), one resonance can be detected for the compounds K_2NaAlF_6 (Fig. 2h), K_2RbAlF_6 (Fig. 2i), Rb_2NaAlF_6 (Fig. 2l), Rb_2KAlF_6 (Fig. 2m), Cs_2KAlF_6 (Fig. 2p) and Cs_2RbAlF_6 (Fig. 2q), while two resonances can be found for the hexagonal elpasolites K_2LiAlF_6 (Fig. 2g), $RbKLiAlF_6$ [21] (Fig. 2k) (the two resonances cannot be resolved due to structural disorder), Rb_2LiAlF_6 (Fig. 2j) and Cs_2NaAlF_6 (Fig. 2o) (Cs_2NaCrF_6-type [26], space group $R\bar{3}m$). The hexagonal structure of Cs_2LiAlF_6 (Fig. 2n; Cs_2LiGaF_6-type [27], space group $P\bar{3}m1$) slightly differs from those of the other hexagonal elpasolites possessing only one fluorine site. Thus, only one resonance can be found for this compound. It should be mentioned that additional small resonances have been observed for some elpasolitic compounds. These resonances belong to compounds not possessing the exact elpasolite-stoichiometry [23]. A special paper will be dedicated to these systems.

Considering all measured MAS NMR spectra, a clear trend can be observed: the resonances are continuously shifted into the low-field direction the more heavier alkali metals are present instead of lighter ones. This does not strictly hold when regarding Li-containing compounds (e.g. comparison of Na_3AlF_6 and Li_3AlF_6). Such findings have been discussed by Groß et al. [28] for the series of monovalent alkali metal fluorides in terms of electronegativy and polarizability.

Because all cations of interest are included in the superposition model of Bureau et al. [13], this methodology has been chosen to compare our experimental results with calculated values in order to find out if the described trend can be also found by calculation. The model of Bureau et al. is based on purely ionic fluorides and ^{19}F chemical shifts can be calculated in using the main formula (here given for the case of K_2NaAlF_6, taking into account the cationic environment of ^{19}F given by the crystal structure: $1 \times Al$, $1 \times Na$, $4 \times K$)

$$\delta_{iso/CFCl_3} = -293.1 - \sigma_{Al} - \sigma_{Na} - 4\sigma_{K} \quad (1)$$

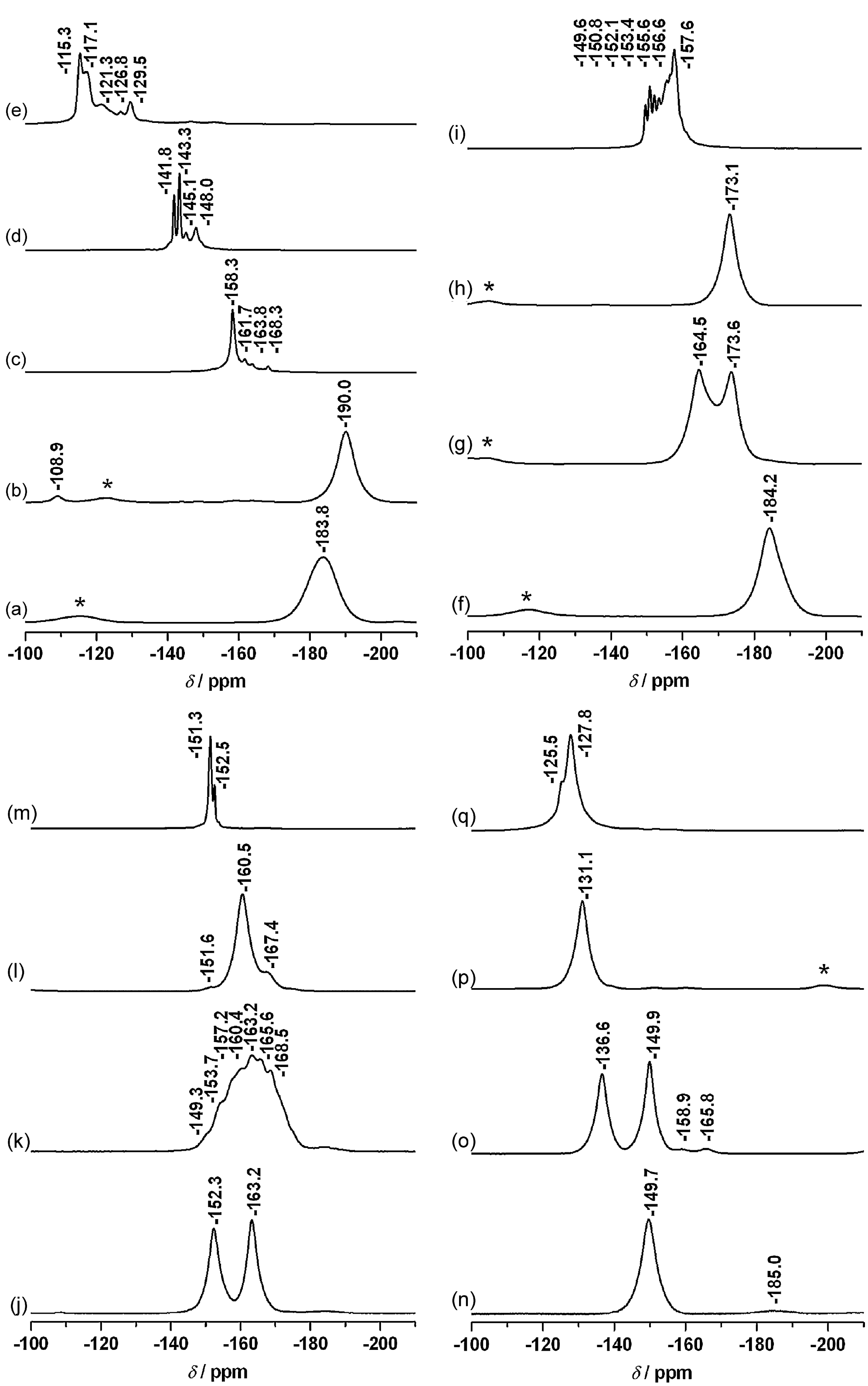

Fig. 2. ^{19}F MAS NMR spectra (isotropic lines, ν_{rot} = 25 kHz) of (a) Li_3AlF_6, (b) Na_3AlF_6 (unknown contamination at −108.9 ppm), (c) K_3AlF_6 (contaminated with $KAlF_4$ at −163.8 ppm, unknown contaminations at −161.7 and −168.3 ppm), (d) Rb_3AlF_6 (ν_{rot} = 30 kHz), (e) Cs_3AlF_6, (f) Na_2LiAlF_6, (g) K_2LiAlF_6, (h) K_2NaAlF_6, (i) K_2RbAlF_6 (contaminated with Rb_2KAlF_6, see (m); ν_{rot} = 30 kHz), (j) Rb_2LiAlF_6 (ν_{rot} = 30 kHz), (k) $RbKLiAlF_6$ (broad signal due to disorder; ν_{rot} = 30 kHz), (l) Rb_2NaAlF_6 (unknown contamination at −151.6 ppm), (m) Rb_2KAlF_6, (n) Cs_2LiAlF_6 (contaminated with Li_3AlF_6 at −185.0 ppm), (o) Cs_2NaAlF_6 (unknown contaminations at −158.9 and −165.8 ppm; ν_{rot} = 28 kHz), (p) Cs_2KAlF_6 and (q) Cs_2RbAlF_6; (*) = rotation side band.

Table 1

Experimental and calculated (superposition model of Bureau et al. [6]) ^{19}F chemical shifts of Al-elpasolites with known crystal structure.

Compound	δ_{iso} (ppm); experimental	δ_{iso} (ppm); calculated	Δ^a (ppm)	δ_{iso} (ppm); corrected^b	Δ^a (ppm)
Na_2LiAlF_6^{c}	−184.1	F1: −196.2 F2: −199.4 F3: −201.0 $\bar{F}$: −198.9	−14.8	F1: −208.9 F2: −211.6 F3: −213.0 $\bar{F}$: −211.2	−27.1
K_2LiAlF_6	F1: −164.4 F2: −173.4	F1: −146.3 F2: −160.9	F1: +18.1 F2: +12.5	F1: −165.5 F2: −178.1	F1: −1.1 F2: −4.7
K_2NaAlF_6	−173.1	−160.1	+13.0	−177.5	−4.4
Cs_2NaAlF_6	F1: −136.6 F2: −149.9	F1: −80.7 F2: −112.0	F1: +55.9 F2: +37.9	F1: −108.4 F2: −135.6	F1: +28.2 F2: +14.3

[a] $\Delta = \delta_{iso}$ (calculated) − δ_{iso} (experimental).

[b] The values σ_l used for the calculation of δ_{iso} (calculated) have been corrected by the factor 1.15.

[c] As only one resonance can be measured, also the mean values of the calculations are given. These mean values are also used for the calculation of Δ.

with σ_l representing the contribution of each surrounding cation to the ^{19}F isotropic chemical shift. The single values for σ_l can be calculated according to

$$\sigma_l = \sigma_{l0}\, e^{[-\alpha_l(d-d_0)]} \tag{2}$$

where σ_{l0}, deduced from measurements in the related basic fluoride, represents the order of magnitude of its cationic paramagnetic contribution to the shielding, d_0 stands for the M–F distance taken from the crystal structure of the related basic fluoride and α_l is connected to the exponential radial dependence of the cation contribution for each surrounding cation. d is the M–F distance in the compound of interest, and thus only cation contributions for systems with known crystal structure (or at least quite precise information on the surrounding cations and the corresponding distances) can be calculated.

In Table 1 the calculated δ_{iso} values for those elpasolites with known crystal structure are compared with the experimentally derived values. For this purpose the corresponding structural data published in recent literature have been used [26,29–31] and only cations with a maximum M–F distance of 3.5 Å have been taken into account. As Bureau et al. [13] state that the σ_l-values calculated with their model are usually overestimated by 15%, also the corrected results are given. It can be seen that the results either fit very good with the experimental values or strongly differ from them. While agreement is reached for K_2LiAlF_6 and K_2NaAlF_6, quite the opposite is observed for Na_2LiAlF_6 and Cs_2NaAlF_6. Taking into account that a new refinement of the parameters was performed when dealing with other systems [14,16], it becomes obvious that results of the superposition model depend on the basis chosen for the parameters used. Consequently, this results in the obvious differences observed for the systems investigated here. Hence, to improve the values for elpasolites a refinement on the basis of these compounds would be necessary. Instead of doing this, another methodology has been used in the present study.

The idea has been to set up a model on the basis of cryolites to obtain parameters for the calculation of chemical shift values for elpasolites. This has been done in a pure empirical way. As already mentioned, all elpasolites possess the same main building unit of AlF_6-octahedra and thus, the only parameter influencing the change of the ^{19}F chemical shift value can be seen to be the corresponding alkali metal combination in each compound. This also holds for the cryolitic system (Fig. 2) keeping in mind the slightly changed bonding situation when dealing with Li-containing compounds. In Table 2 the experimental shift values for the cryolites are presented. Regarding Rb_3AlF_6 and Cs_3AlF_6 the values given correspond to the mean values of the most intensive resonances observed as a precise assignment of the resonances is not possible due to the lack of crystal structures of these phases at room temperature. This has to be kept in mind, as substantial mistakes could arise from this assumption. In the next step the shift values have been normalised on Na_3AlF_6 resulting in a factor $F_{M^IAlF_6}$ for each compound. Using this factor, each shift value can be calculated from the value of Na_3AlF_6. Assuming that the changes for the five compounds are a result of the alkali metals present and taking into account that always the same alkali metal is present in each cryolite, $F_{M^IAlF_6}$ can be divided by 3 (the number of alkali metal ions in $M^I_3AlF_6$) resulting in a factor f_{M^I} for each single alkali metal ion. Using these factors, the ^{19}F shift values for elpasolites $A^I_2B^IAlF_6$ can be calculated according to

$$\delta_{iso}(A^IB^IAlF_6) = (2f_{A^I} + f_{B^I})(-190\,\text{ppm}) \tag{3}$$

based on the shift value of Na_3AlF_6 ($\delta_{iso} = -190.0$ ppm). Exemplarily, the calculation done for K_2NaAlF_6 would be

$$\delta_{iso}(K_2NaAlF_6) = (2f_K + f_{Na})(-190\,\text{ppm}) \tag{4}$$

In Table 3 the results based on this empirical model are compared with the corresponding experimental values. Fig. 3 shows a graphical representation of the combined alkali metal factor $(2f_{A^I} + f_{B^I})$ and the experimental values. In both cases a very good agreement of model and experiment can be clearly seen.

Thus, using a mean value for the ^{19}F chemical shift of Rb_3AlF_6 and Cs_3AlF_6 tends to be a good assumption to overcome the problem of not having information on the corresponding crystal structures at room temperature. A disadvantage of the developed model is the fact that it is not capable to deliver values for different fluorine sites regarding hexagonal elpasolites. Nevertheless, the corresponding mean values fit as well to the experiment as for single site compounds.

In applying the presented model, mean ^{19}F chemical shifts of Al-elpasolites can be calculated with a very good accuracy. It could be shown that such accuracy can be reached in choosing related compounds with structural features near to the systems of interest. This methodology is comparable easy and straightforward. This is mainly due to the way, how the parameters necessary for calculation are derived in this case, and of course to the fact, that

Table 2

Experimental ^{19}F chemical shifts for the Al-cryolites, together with the alkali metal factors f_{M^I} derived from these values.

Compound	δ_{iso} (ppm); experimental	$F_{M^I_3AlF_6}$	f_{M^I}
Li_3AlF_6	−183.8	0.967	0.322
Na_3AlF_6	−190.0	1.000	0.333
K_3AlF_6	−158.5	0.834	0.278
Rb_3AlF_6^{a}	−142.6	0.751	0.250
Cs_3AlF_6^{a}	−116.2	0.612	0.204

[a] δ_{iso} represents the mean value of the most intensive resonances observed.

Table 3
Experimental and calculated (using the alkali metal factors f_{M^I}) ^{19}F chemical shifts for all investigated Al-elpasolites.

Compound	$\sum f_{M^I}$	δ_{iso} (ppm); experimental	δ_{iso} (ppm); calculated	Δ^a (ppm)
Na_2LiAlF_6	0.988	−184.1	−187.7	−3.6
K_2LiAlF_6[b]	0.878	F1: −164.4 F2: −173.4 $\bar{F}$: −168.9	−166.8	+2.1
K_2NaAlF_6	0.889	−173.1	−168.9	+4.2
K_2RbAlF_6	0.806	−157.6	−153.1	+4.5
$RbKLiAlF_6$[c]	0.850	−163.2	−161.5	+1.7
Rb_2LiAlF_6[b]	0.822	F1: −152.3 F2: −163.2 $\bar{F}$: −157.8	−156.2	+1.6
Rb_2NaAlF_6	0.833	−160.5	−158.3	+2.2
Rb_2KAlF_6	0.778	−151.3	−147.8	+3.5
Cs_2LiAlF_6	0.730	−149.7	−138.7	+11.0
Cs_2NaAlF_6[b]	0.741	F1: −136.6 F2: −149.9 $\bar{F}$: −143.3	−140.8	+2.5
Cs_2KAlF_6	0.686	−131.1	−130.3	+0.8
Cs_2RbAlF_6	0.658	−127.7	−125.0	+2.7

[a] $\Delta = \delta_{iso}$ (calculated) − δ_{iso} (experimental).

[b] For the compounds with more than one fluorine site, also the mean value is given; in these cases, the calculation of Δ was performed with the mean value.

[c] Due to structural disorder δ_{iso} (experimental) represents the maximum of the resonance

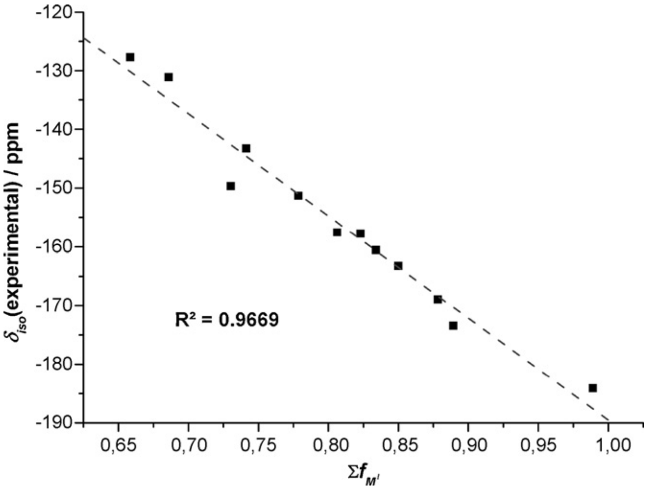

Fig. 3. Graphical representation of the experimental ^{19}F chemical shifts and the sums of alkali factors f_{M^I} for the elpasolites listed in Table 3.

the crystal structures of the investigated compounds are not the crucial point for this model.

3. Conclusion

An empirical model for the calculation of mean ^{19}F isotropic chemical shifts in hexafluoroaluminates of the elpasolite type has been developed. The parameters necessary to describe the influence of the cations surrounding ^{19}F have been deduced from the Al-cryolites $M^I_3AlF_6$. This is possible because the main building unit of AlF_6-octahedra is the same for all investigated compounds. The obtained chemical shift values are in very good agreement with the experimental results and thus, this methodology can be seen as an alternative to models used so far.

Regarding further applications it can be stated that this model can be easily expanded. For hexafluoroaluminates it is possible to include other cations like NH_4^+, Tl^+ or Ag^+. Additionaly, the methodology can be transferred to other hexafluorometallates like Ga- or Y-elpasolites. The only preconditions are the existence of the corresponding cryolites and the possibility to get reliable data within MAS NMR. Concluding, in applying the presented model, an average cationic contribution within ^{19}F MAS NMR of quite complex systems can be described in a comparable easy way.

4. Experimental

All Al-elpasolites and Al-cryolites have been synthesised via a sol–gel route described in ref. [20] using LiO^tBu, NaO^tBu, KO^tBu, RbO^tBu, CsO^tBu and $Al(O^iPr)_3$ as starting materials and HF dissolved in ^{i}PrOH as fluorinating agent. The synthesis products had to be annealed for 4 h in a tube-furnace under an Ar-atmosphere at temperatures between 430 and 550 °C in order to obtain samples suitable for MAS NMR experiments [23].

^{19}F MAS NMR ($I = 1/2$) spectra have been recorded on a Bruker AVANCE 400 spectrometer at rotation frequencies up to 30 kHz using a 2.5 mm MAS probe. The resonance frequency has been 376.4 MHz. The isotropic chemical shifts δ_{CS} of ^{19}F resonances are given in respect to the $CFCl_3$ standard. ^{19}F MAS NMR spectra were recorded with a $\pi/2$ pulse duration of p1 = 2.0 μs, a spectrum width of 400 kHz, a recycle delay of 10 s and an accumulation number of 64. Spectral changes for longer recycle delays were checked. Existing background signals of ^{19}F could be completely suppressed with the application of a phase-cycled depth pulse sequence according to Cory and Ritchey [32].

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