American Mineralogist, Volume 77, pages 718–724, 1992

Influence of octahedral polymerization on ^{23}Na and ^{27}Al MAS NMR in alkali fluoroaluminates

PETER J. DIRKEN, J. BEN H. JANSEN, ROELOF D. SCHUILING
Institute of Earth Sciences, Department of Geochemistry, University of Utrecht, Budapestlaan 4,
P.O. Box 80.021, 3508 TA Utrecht, The Netherlands

ABSTRACT

Solid state ^{23}Na and ^{27}Al MAS NMR spectra of NaF, α- and β-AlF_3, cryolite (Na_3AlF_6), chiolite ($Na_5Al_3F_{14}$), and elpasolite (K_2NaAlF_6) have been studied. Structures and chemical compositions have been checked by X-ray diffraction, DTA-TGA, and wet chemical analyses (ICP-AES, AAS, ISE). The ^{27}Al NMR isotropic chemical shifts range from -13.2 to $+1.4$ ppm, indicating octahedral coordination by F, which is in agreement with crystallographic data. Compared to AlO_6 octahedra in aluminates, the AlF_6 octahedra in fluoroaluminates are at least 20 ppm more shielded. The ^{27}Al results show that Al chemical shifts become more shielded as the degree of polymerization of the AlF_6 octahedra increases. S^0 structures with isolated AlF_6 octahedra fall into a region around 0 ppm with a spread of only 2 ppm. Sheet structures with S^2 and S^4 octahedra have Al resonances at -1 to -3 ppm, and Al in network structures resonates at -12.5 to -13.2 ppm. This trend is explained by a decrease in the number of nonbridging F atoms per octahedron (NBF/O). Consequently, ^{23}Na NMR depends on the type of AlF_6 polymerization. Na that is octahedrally coordinated stepwise becomes more shielded from 7.2 ppm for NaF, to 2.4 ppm for cryolite, to -6 ppm for chiolite. Eightfold-coordinated Na resonates at more negative chemical shifts than sixfold-coordinated Na, -9.3 ppm in cryolite and -21 ppm in chiolite. The observation of the ^{27}Al and ^{23}Na signals of two closely related structures, cryolite and elpasolite, indicates that both ^{27}Al and ^{23}Na NMR are insensitive to cationic substitution within the lattice, probably because of the ionic character of the Al-F and Na-F bonds.

INTRODUCTION

Magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy is an important technique in determining the coordination state and local symmetry of structural units such as $(Si,Al)O_4$, AlO_5, or AlO_6 polyhedra within crystalline and amorphous solids. In general, increased shielding of a nucleus by its ligands and an increase in coordination number results in a more negative chemical shift. In the case of Al, chemical shifts for fourfold, fivefold, and sixfold coordination fall into the range 50–80, 35–40, and -10 to $+15$, respectively (Müller et al., 1981; Kirkpatrick, 1988; Akitt, 1989).

The degree of polymerization of SiO_4 tetrahedra in crystalline as well as in amorphous solids can be determined with one-dimensional ^{29}Si NMR experiments (Smith et al., 1983; Magi et al., 1984; Stebbins, 1987; Kirkpatrick, 1988). Increased polymerization causes an increased shielding of the Si nuclei. The chemical shifts of Al in AlO_4 are considered to be insensitive to polymerization effects and shift to higher fields if the tetrahedra are connected to SiO_4 tetrahedra (Müller et al., 1986). Müller and Bentrup (1989) studied various hydrous alkali fluoroaluminates and concluded that ^{27}Al NMR is hardly affected by differences in condensation of AlF_6 octahedra. Sodium (and lithium) fluoroaluminates were not considered, although the Na-Al-F system is particularly suited for the study of AlF_6 condensation, as a variety of structures exists in this system with a similar cationic second sphere of Na atoms. Furthermore, ^{23}Na NMR chemical shifts can be compared to give additional information on polymerization phenomena.

In this paper one-dimensional solid state ^{23}Na and ^{27}Al magic angle spinning NMR spectroscopic results on compounds in the system Na-Al-F are presented. The first aim is to determine if chemical shift data of ^{23}Na and ^{27}Al correlate with structural features within these phases. In this way it may be possible to discriminate among various Al-F structure types. For this purpose, a crystallographic review of all compounds considered is presented prior to any NMR data. Recently, Kohn et al. (1991) reported the existence of $^{[5]}$Al and $^{[6]}$Al complexes in melts of jadeite + NaF and jadeite + cryolite (Na_3AlF_6) compositions with ^{27}Al and ^{27}Al-^{19}F CP NMR at 22 and -5 ppm, respectively. They, among others (Manning, 1981; Mysen and Virgo, 1985), suggest that Al and F are present in F-rich aluminosilicate melts as Na-Al-F complexes. In this study we use magic angle spinning NMR spectroscopy to distinguish Al-O complexes from Al-F complexes

0003–004X/92/0708–0718$02.00

directly by ^{27}Al chemical shifts. Whether or not Al and F form clusters with Na that resemble crystalline sodium fluoroaluminates, ^{23}Na NMR can give useful information. Cationic effects on ^{27}Al chemical shifts are investigated by comparing ^{27}Al NMR data of two almost isostructural compounds (cryolite, Na_3AlF_6 vs. elpasolite, K_2NaAlF_6) and combining these with previous work on alkalifluoroaluminates (Müller and Bentrup, 1989).

CRYSTALLOGRAPHY

In the system NaF-AlF_3, NaF, AlF_3, and $Na_5Al_3F_{14}$ exist as stable phases in addition to the well-known mineral cryolite (Na_3AlF_6). NaF and $Na_5Al_3F_{14}$ occur in nature as the minerals villiaumite and chiolite, respectively. The crystal structures of these compounds have been determined and refined. Villiaumite (NaF) has the halite structure (Barth and Lunde, 1927), a simple cubic closest packing of F with Na in the octahedral interstices.

AlF_3 has a stable α form; a β phase has been obtained by dehydration of α-$AlF_3 \cdot 3H_2O$, a γ phase by thermal decomposition of NH_4AlF_4 (Shinn et al., 1966). Le Bail et al. (1988) reexamined the β phase prepared from dehydrating α-$AlF_3 \cdot 3H_2O$, assuming that it was identical to the γ phase. No structure determination has been carried out for γ-AlF_3. The stable α-AlF_3 crystallizes as a rhombohedral structure (Hoppe and Kissel, 1984). It can be regarded as a VF_3-type structure (Hepworth et al., 1957) that is built up by a distorted closest packing of F atoms, with Al in octahedral sites. The highly regular AlF_6^{3-} octahedra share corners in a three-dimensional network. The metastable β-AlF_3 phase consists of a three-dimensional network of very regular AlF_6^{3-} octahedra with two distinct Al sites. The structure can be regarded as a slightly modified hexagonal tungsten bronze (HTB) structure (Magnelli, 1953), in which sheets of interconnected AlF_6^{3-} octahedra parallel to the **a-b** plane are stacked along the **c** axis. At 500 °C, β-AlF_3 irreversibly transforms to α-AlF_3 (Le Bail et al., 1988). The crystal structure of cryolite (Na_3AlF_6) is made up of isolated AlF_6^{3-} octahedra linked by sixfold-coordinated Na, forming a regular octahedron, and eightfold-coordinated Na, creating a highly distorted cubic antiprism (Hawthorne and Ferguson, 1975). The AlF_6^{3-} octahedra are very regular. The structure has a pseudocubic, monoclinic symmetry, attaining true cubic symmetry in the β cryolite phase, above the reversible transformation temperature of 561 °C (Majumdar and Roy, 1965).

Elpasolite (K_2NaAlF_6) has the cryolite structure with the two eight-coordinated Na atoms replaced by K. It has cubic symmetry, with undistorted AlF_6 octahedra (Sabelli, 1987).

Chiolite ($Na_5Al_3F_{14}$) is a tetragonal phase, whose structure was refined by Jacoboni et al. (1981). Two types of octahedra form independent $[Al_3F_{14}]_n^{5n-}$ layers perpendicular to the **c** axis. Within each layer octahedra having $2/m$ or $4/m$ symmetry alternate with each fourth octahedron replaced by a Na atom. Two Na atoms are coordinated by eight F, the other eight Na atoms by six F. One AlF_6 octahedron shares corners with four octahedra; the other octahedron with two octahedra.

In general, the structures involved can be divided into three types, depending on the polymerization of the octahedra. The α- and β-AlF_3 phases are three-dimensional networks of AlF_6 units. $Na_5Al_3F_{14}$ is a sheet structure, and Na_3AlF_6 can be considered as a nesostructure since its AlF_6 octahedra are entirely isolated.

EXPERIMENTAL

Samples

Na_3AlF_6 and $Na_5Al_3F_{14}$ are available as the minerals cryolite and chiolite, respectively, both from the Ivigtut deposit, Greenland (Bøggild, 1953). The synthetic equivalents and elpasolite (K_2NaAlF_6) were prepared using the methods described by Cowley and Scott (1948). The compound β-AlF_3 was prepared by decomposing NH_4AlF_4 at 315 °C under a N_2 flow, a method described by Shinn et al. (1966) and by dehydrating α-$AlF_3 \cdot 3H_2O$ (Christoph, U.S. Patent 3 178 483). NaF was available as analytical grade reagent from Merck (Merck no. 6449); α-AlF_3 was provided by the Billiton Ore Company. All compounds were checked for impurities by X-ray diffraction with a Philips PW 1050/25 diffractometer using Cu*K*α radiation.

Chemical analyses of all the fluorides were carried out by dissolving them in a 40 mol% Li_2CO_3–60 mol% K_2CO_3 flux at 550 °C. The flux was then dissolved in H_2O and analyzed for K and Al by ICP-AES (ARL 34000), for Na by atomic absorption spectroscopy (Perkin Elmer 460), and for F by means of a F selective electrode (Orion, fluoride electrode model 9409 and reference electrode model 9001). Analytical errors are 5% for F and Na, and 10% for K and Al.

DTA-TGA measurements were conducted under a N_2 atmosphere with a Du Pont Instruments 1090 thermal analyzer at a heating rate of 10 °C/min. The temperatures are correct within 5 °C.

NMR spectroscopy

The one-dimensional solid state NMR spectra were obtained using Bruker CXP-300, AM-500, and AM-600 solid-state high-resolution spectrometers, operated at 7.1, 11.7, and 14.1 T, respectively. To ensure relative saturation of the ^{27}Al and ^{23}Na resonances, the spectra were measured with short pulse excitations, using typical pulse lengths of 1–2 μs, relaxation delays of 0.25–0.5 s, and spectral widths of 40–100 kHz. Per measurement, 100–12000 free induction decays were collected. The ^{27}Al and ^{23}Na chemical shifts were measured relative to an external standard of aqueous $AlCl_3$ and NaCl solution, respectively. Spinning rates were typically 12 kHz, unless stated otherwise.

The ^{23}Na and ^{27}Al isotropic chemical shifts (δ_{iso}) and quadrupole coupling constants (QCC) were determined by calculating the quadrupolar induced shift at different magnetic fields (7.1, 11.7, and 14.1 T), assuming that $\eta = 0$ and that the lines are symmetric. Contributions of

TABLE 1. Data for ^{27}Al NMR

Compound	S^{η}(Al)	δ_{iso} (ppm)	QCC (MHz)	η	Width (Hz)	QB* (Hz)
Na_3AlF_6	0	1.4	2.0	0	1050	220/60
K_2NaAlF_6	0	0.8	1.4	0	1000	110/30
$Na_5Al_3F_{14}$	2	−1	8.2	0	—	—
	4	−3	6.5	1	—	—
α-AlF_3	6	−13.2	2.8	0	1450	430/100
β-AlF_3	6	−12.5	3.4	0	1200	640/160

* QB: calculated second-order quadrupole broadening for $\eta = 0$ and 0.75, respectively.

the quadrupole broadening to the line width can be calculated (Engelhardt and Michel, 1987). In some cases the calculated broadening exceeded the experimental line width, which is an indication that the asymmetry parameter must be closer to 1. The asymmetry parameter has no influence on δ_{iso} in the calculations, as a change in η from 0 to 1 is compensated by a change in QCC of approximately 15%. Peak positions and δ_{iso} are correct within 1 ppm. Taking the error in peak position into account, the error in the QCC increases to 1 MHz. In the case of chiolite, δ_{iso} and the QCC were extracted from the spectra by using the frequencies for the singularities (Müller, 1982; Engelhardt and Michel, 1987) at two (^{23}Na) and three magnetic fields (^{27}Al). A computer program called Powder, based on Aspect 3000 (Müller and Bentrup, 1989), was used to check the calculations on the ^{23}Na and ^{27}Al spectra of chiolite.

RESULTS

X-ray diffraction

The diffraction patterns of NaF, α-AlF_3, natural cryolite, synthetic and natural chiolite, and synthetic elpasolite did not contain reflections of impurities. The XRD pattern of cryolite showed that it contained approximately 5 wt% chiolite. This impurity was not detected in the ^{23}Na and ^{27}Al NMR spectra. The XRD patterns of the β-AlF_3 phases were identical, so the NMR study was limited to the β-AlF_3 phase obtained by dehydration of α-$AlF_3 \cdot 3H_2O$.

DTA-TGA

All phases were studied by thermal analyses to obtain additional chemical and structural information. NaF displays no thermochemical effect in the temperature range 25–750 °C. The α-AlF_3 DTA spectrum has a small endothermic peak at 450 °C and a larger one at 750 °C. TGA results for α-AlF_3 show a 10% weight loss over the temperature region 450–780 °C. The onset of this volatilization corresponds to the first endothermic peak in the DTA. At this temperature the α phase transforms to a high temperature phase (Robie et al., 1978). The peak at 750 °C has not been reported in the literature. The β-AlF_3 phase displays an exothermic reaction at 720 °C. The reaction represents the structural transformation to α-AlF_3. This result is in good agreement with the temperature of 720 °C claimed by Shinn et al. (1966). However, Le Bail et al. (1988) reported a transformation temperature of 500 °C for their β-AlF_3. DTA on the β-AlF_3 obtained by dehydration of α-$AlF_3 \cdot 3H_2O$ does not display a transformation at 500 °C. It further justifies rejecting γ-AlF_3 as a separate phase.

Both natural and synthetic cryolite display an endothermic peak at 562 °C. The peak represents the reversible transformation of monoclinic α cryolite to cubic β cryolite. The temperature is in excellent agreement with the temperature of 561 °C reported by Majumdar and Roy (1965). Additionally, the synthetic cryolite loses a few percent H_2O at 125 °C. Elpasolite displays only one small DTA-peak at 113 °C, most probably caused by a H_2O loss of approximately 1 wt% from the sample. The DTA curve of natural chiolite shows a melting temperature of 700 °C, 75 °C lower than that reported by Mesrobian et al. (1972). Their experiments were conducted under nonatmospheric pressures up to 400 bars, however, so an absolute comparison is not entirely justified. The synthetic chiolite displays one small peak at 175 °C, resulting from the loss of a few percent H_2O.

TABLE 2. Data for ^{23}Na NMR

		δ_{iso} (ppm)		QCC (MHz)		η		Width (Hz)	QB** (Hz)
Compound	CN*	1	2	1	2	1	2	1	1
NaF	6	7.2		0		0		600	0
Na_3AlF_6	6	2.4	4	0	0.9	0	1.0	400	0
	8	−9.3	−8	2.3	1.45	0.75	0.25	700	1400/330
K_2NaAlF_6	6	2.1		0		0		500	0
$Na_5Al_5F_{14}$	6		−6		3.2		0.15	—	—
	8		−21		1.5		0	—	—

Note: 1 = this study; 2 = J.F. Stebbins and X. Xue, written communication.

* CN: Na coordination number.

** QB: calculated second-order quadrupole broadening for $\eta = 0$ and 0.75, respectively.

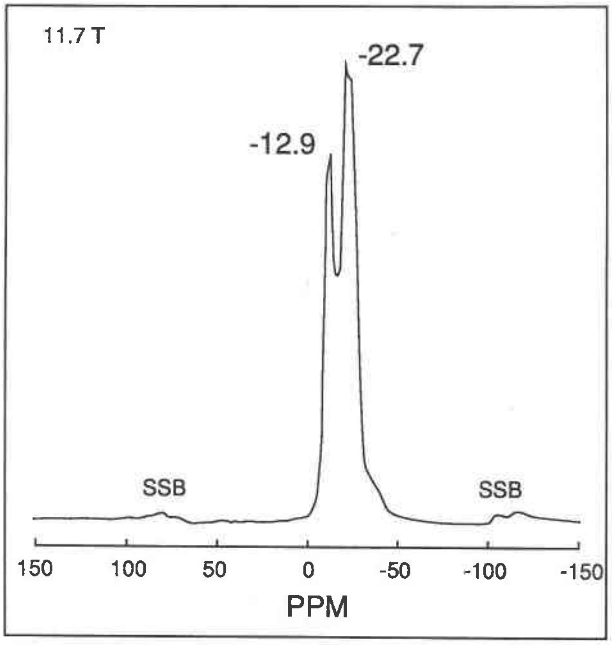

Fig. 1. The ^{23}Na MAS NMR spectrum of chiolite ($Na_5Al_3F_{14}$). SSB = spinning sideband.

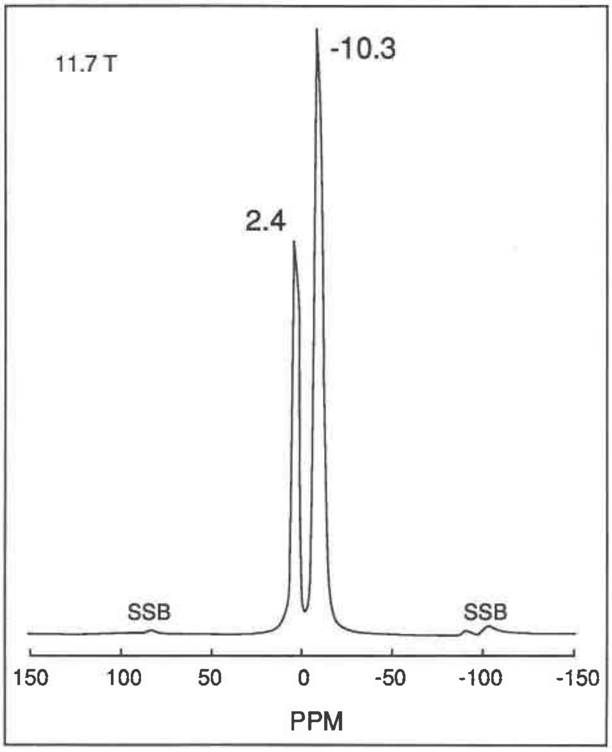

Fig. 2. The ^{23}Na MAS NMR spectrum of cryolite (Na_3AlF_6). SSB = spinning sideband.

Chemistry

The F content of α-AlF_3 is low, probably because of less than 5 wt% impurity corundum, which is the X-ray detection limit. Additional F was lost during analysis, because of the high vapor pressure of AlF_3. It is not to be expected that the impurity in any way influences the ^{27}Al NMR results. All samples acquired by precipitation from an aqueous solution, i.e., synthetic cryolite, chiolite, and elpasolite, have a weight percent sum smaller than 100%. This is due to uptake of some H_2O as evidenced by DTA-TGA. The stoichiometric compositions corrected for possible H_2O losses are within analytical accuracy.

^{27}Al and ^{23}Na NMR

The ^{27}Al and ^{23}Na NMR data for α- and β-AlF_3, NaF, Na_3AlF_6, K_2NaAlF_6, and $Na_5Al_3F_{14}$ are listed in Tables 1 and 2, respectively. The symbol S^n is used by analogy with Müller et al. (1986), with Q (of Quaternary) replaced by S (of Senary). The superscript n indicates the number of bridging F atoms per octahedron. If n = zero, the structure consists of isolated AlF_6 octahedra. If $n = 6$, the octahedra are condensed into a three-dimensional network. The intermediate types of octahedra, with $n = 2$ and $n = 4$, alternate in chiolite and form a sheet structure. The ^{27}Al isotropic chemical shifts in these fluoroaluminates range from -13.2 to $+1.4$, indicating octahedral coordination of Al by F in all Al-bearing phases (Müller et al., 1981; Kirkpatrick, 1988; Akitt, 1989). This is in agreement with crystallographic data and with earlier studies on alkalifluoroaluminates (alkali = NH_4, K, Rb, Cs) by Grimmer et al. (1982) and Müller and Bentrup (1989). Results from synthetic and natural samples are identical. In some cases more than one set of values is presented in Tables 1 and 2, indicating more than one crystallographic site. In the ^{23}Na and ^{27}Al spectra of chiolite, the central transitions have complex line shapes. They are reconstructed by using the frequency equations for the singularities at two or three magnetic fields (Engelhardt and Michel, 1987), the field dependent second-order quadrupole shift, and the computer simulation program Powder (Müller and Bentrup, 1989). The ^{23}Na spectrum of chiolite (Fig. 1) has a line shape that is characteristic of a crystallographic site with an asymmetry parameter of 0 (Kentgens et al., 1983). The high intensity of the right singularity points to an additional site, with a small intensity overlapping the other site. The data in Table 2 are from J. F. Stebbins and X. Xue (written communication), who obtained spectra at 9.4 T. The lower magnetic field allows a more accurate estimation of the NMR data. We used these data to simulate our spectra and obtained very good results. In the case of cryolite (Fig. 2), our variable field data are combined with the computer simulation data of Stebbins and Xue in order to compare the two approaches. The data correspond well within estimated errors. The lack of structure in the 4-ppm peak, even in the 9.4-T spectra, is responsible for the spread of η. The starting point for the analysis of the ^{27}Al spectra of chiolite (Fig. 3) was the assumption that the outermost signals correspond to a site with $\eta = 0$, whereas the signal in the middle corresponds to a site with $\eta = 1$. Calculating QCC and δ_{iso} at the three magnetic fields re-

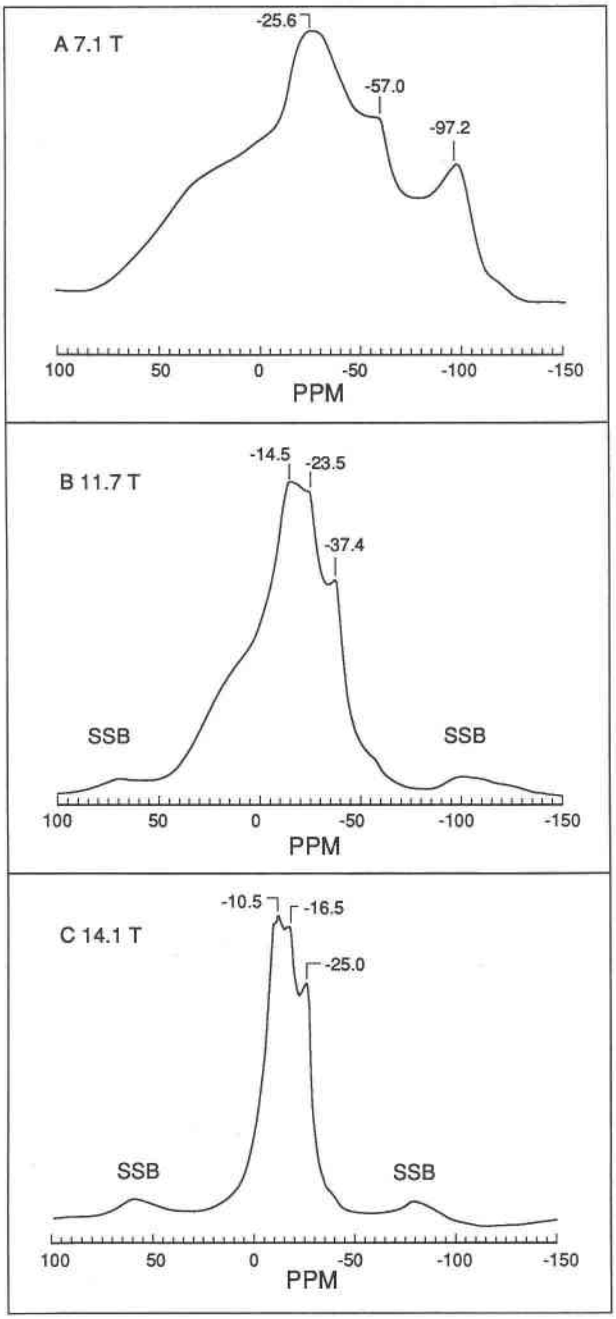

Fig. 3. Some ^{27}Al MAS NMR spectra of chiolite ($Na_5Al_3F_{14}$) at different magnetic fields. Spinning speeds are (**A**) 13.9, (**B**) 9, and (**C**) 11 kHz, respectively. SSB = spinning sideband.

sulted in three sets of data that are mutually consistent. This data set was then refined in a computer simulation. The shoulder at the low-field side of the spectrum is the result of a background signal from the probe, for which we did not make a correction. Line widths (full width at half height) are 1000–1500 Hz for ^{27}Al and 400–700 Hz for ^{23}Na. If the second-order quadrupole broadening is subtracted from these values and other contributions to the line width are ruled out, the broadening due to the coupling of Al and F and of Na and F becomes 600–1000 and 100–600 Hz, respectively.

DISCUSSION

^{27}Al

The ^{27}Al spectrum of α-AlF_3 displays one peak at −16 ppm at 11.7 T, which shifts to −15 ppm at 14.1 T, corresponding to δ_{iso} of −13.2 ppm. The −16 ppm has previously been reported by Kimura and Satoh (1989) and Satoh and Kimura (1990), who did not consider quadrupole-induced shifts. Their value of −16 ppm may indicate that the minor impurity in our α-AlF_3 has no influence on the NMR results. The compound β-AlF_3 has an isotropic chemical shift of −12.5 ppm, with only one peak at both fields of 11.7 and 14.1 T. The structure of β-AlF_3 has two Al sites, which are almost identical. The differences between these two sites are too small to be detected as two separate NMR resonances.

$Na_5Al_3F_{14}$ has ^{27}Al chemical shifts of -1 ± 2 ppm and -3 ± 2 ppm. This is in agreement with the two different octahedral Al sites in chiolite known from structure determinations. Crystallographic data show that the S^4 site is occupied by 33% of the Al and should have the lowest intensity in the ^{27}Al spectra. The Al site with a chemical shift = −3 ppm, with QCC = 6.5 ± 0.5 MHz, and with $\eta = 1$ can be identified as the S^4 site. The S^2 site must then be represented by the −1 ppm signal, with QCC = 8.2 ± 0.5 MHz and $\eta = 0$. The isolated AlF_6 octahedra in cryolite (Na_3AlF_6) have an ^{27}Al isotropic chemical shift of 1.4 ppm. Previously, Müller and Bentrup (1989) reported ^{27}Al chemical shifts of −0.6 and −0.1 ppm in similar compounds, $(NH_4)_3AlF_6$ and K_3AlF_6, respectively. The cubic elpasolite (K_2NaAlF_6) structure is closely related to the (pseudocubic) monoclinic cryolite structure. Two of the three Na atoms are replaced by K atoms. Like cryolite, the ^{27}Al NMR isotropic chemical shift is ±1 ppm. The spread in peak positions of these four hexafluoroaluminates is only 2 ppm. This observation leads us to the conclusion that second-sphere influences of Na, K, or NH_4 on the shielding of Al by F are of very little importance in alkalifluoroaluminates.

The cation effects are even smaller than the 6.4-ppm range for interconnected AlO_4 tetrahedra in potassium, lithium, and sodium aluminates (Müller et al., 1986). The Al nucleus is more effectively shielded from its surroundings and less sensitive to second-sphere substitutions, because of the more ionic character of the Al-F bond.

Figure 4 is a graphical presentation of the isotropic chemical shifts of Al in alkalifluoroaluminates. The ^{27}Al chemical shifts decrease from 1 ppm in S^0 to −1 in S^2, to −3 in S^4, and to −13 to −15 in S^6 structures. It follows that ^{27}Al chemical shifts decrease as the degree of polymerization increases, analogous to ^{29}Si results in aluminosilicates (Engelhardt and Michel, 1987). The number of nonbridging F atoms per octahedron (NBF/O, equal to $6 - n$) decreases from six in S^0 to four in S^2, to two in S^4, and to zero in S^6 structures. Nonbridging F atoms

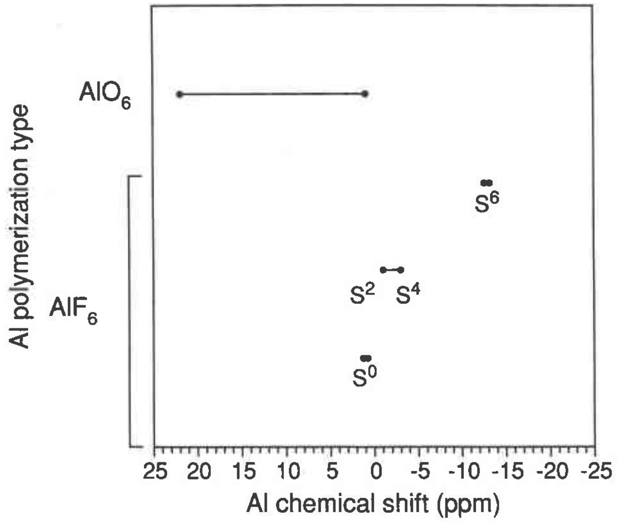

Fig. 4. Graphical representation of the ^{27}Al chemical shifts of AlX_6 octahedra in oxoaluminates and fluoroaluminates. S^0 = cryolite or elpasolite; S^2 and S^4 = chiolite; S^6 = α- and β-AlF_3.

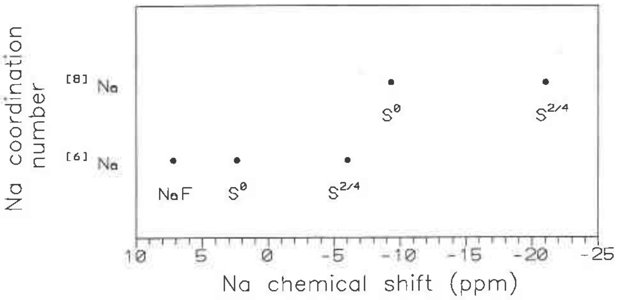

Fig. 5. Graphical representation of the ^{23}Na chemical shift of sixfold- and eightfold-coordinated Na in fluoroaluminates. S^0 = cryolite or elpasolite (our data); S^2 and S^4 = chiolite (data from J.F. Stebbins and X. Xue, written communication).

control the residual charge on the Al nucleus and thereby its shielding. The observed trend in the ^{27}Al chemical shift can be explained by a decrease in NBF/O with polymerization.

^{23}Na

The ^{23}Na NMR data can add important information to elucidating polymerization effects of AlF_6 octahedra in alkali fluoroaluminates. It is possible to assign specific resonances of Na to crystallographic sites. In the case of NaF, the 7.2-ppm peak obviously results from a very regular octahedral coordination of Na by six F atoms. According to the crystallographic data, the cryolite structure contains twice as much eightfold- as sixfold-coordinated Na. As a result, the ^{23}Na resonance with the lowest intensity should be assigned to sixfold-coordinated Na (Fig. 2). Therefore, the 2.4-ppm peak represents sixfold-coordinated Na and the peak at −9.3 ppm represents eightfold-coordinated Na. This is in accordance with the general observation that more shielded nuclei with more ligands resonate at higher fields (Engelhardt and Michel, 1987). Moreover, sixfold-coordinated Na in NaF resonates at 7.2 ppm, which is reasonably close to the value of 2.4 ppm of cryolite. Compared with cryolite, two eightfold-coordinated Na sites are occupied by K in elpasolite. The remaining octahedrally coordinated Na resonates at 2.1 ppm, very close to the value of 2.4 ppm of cryolite, which is another reason for assigning the 2.4-ppm peak to the sixfold-coordinated site. In chiolite, the sixfold-coordinated Na has a chemical shift of −6 ppm. Again, the eightfold-coordinated Na atoms are more shielded and have a peak position of −21 ppm. Clearly, ^{23}Na NMR is sensitive to the coordination number, just as ^{29}Si and ^{27}Al NMR are. Previously, Phillips et al. (1988) observed a much more continuous change in chemical shift with a change in the Na/(Na + K) ratio in an alkali feldspar solid solution. The continuous change in the Na/(Na + K) ratio causes the effective Na coordination number to increase, causing a continuous decrease in chemical shift. As for Al, the graphical representation of the ^{23}Na chemical shifts (Fig. 5) evidently shows that the chemical shifts of sixfold- and eightfold-coordinated Na are determined by the number of AlF_6 octahedra per Na atom in the structure. In NaF, with a chemical shift of 7.2 ppm, no AlF_6 octahedra are present. The chemical shift of ^{23}Na decreases to 2.4 ppm in cryolite (0.3 AlF_6 octahedron on 1 Na) and −6 ppm in chiolite (0.6 AlF_6 octahedron on 1 Na). In the case of eightfold-coordinated Na, the trend is from −9.3 ppm in cryolite to −21 ppm in chiolite.

The fact that both ^{27}Al and ^{23}Na chemical shifts correlate with the degree of polymerization of the AlF_6 octahedra points to a complex interaction of Al-F polymerization and Na-F bonds. More study is needed to elucidate the physical background of these empirical dependencies.

Comparison of $^{27}AlF_6$ with $^{27}AlO_6$

Isotropic ^{27}Al chemical shift data of octahedrally coordinated Al in compounds other than silicates are available only for the Al_2O_3 polymorph corundum (16.0 ppm; Skibsted et al., 1991) and yttrium aluminum garnet (0.8 ppm; Massiot et al., 1990). Peak positions in oxoaluminates other than Na have been reported by Müller et al. (1981) and range from 5 ppm for $BaO \cdot 6Al_2O_3$ to 22 ppm for spinel, $MgAl_2O_4$. When Al-O compounds are compared with Al-F compounds, ^{27}Al isotropic chemical shifts of oxoaluminates are at least 20 ppm less shielded than ^{27}Al chemical shifts of fluoroaluminates. The three-dimensional network structures Al_2O_3 and AlF_3 have chemical shifts of 16 and −13 ppm, respectively. This difference must be explained by the more ionic character of the Al-F bond compared with the Al-O bond. This is reflected by the mean bond lengths of $^{[6]}$Al-O and $^{[6]}$Al-F. The interatomic distances for $^{[6]}$Al-O are approximately 0.07 Å longer than for $^{[6]}$Al-F (Shannon and Prewitt, 1969).

CONCLUSIONS

1. Isotropic ^{27}Al chemical shifts systematically decrease with the increase in the degree of polymerization

of AlF_6 octahedra in sodium fluoroaluminates. This trend can be explained by considering the number of nonbridging F atoms per octahedron (NBF/O).

2. Na coordinated by eight F atoms has more negative isotropic chemical shifts than Na coordinated by six F atoms.

3. Isotropic ^{23}Na chemical shifts of sixfold- and eightfold-coordinated Na become more shielded as the AlF_6 polymerization increases.

4. Al nuclei in AlF_6 octahedra are at least 20 ppm more shielded than Al nuclei octahedrally coordinated by O.

5. Second coordination sphere effects of alkali cationic substitution on ^{23}Na and ^{27}Al NMR are of very small influence.

ACKNOWLEDGMENTS

We gratefully acknowledge the assistance we received from G. Nachtegaal and A. Kentgens in obtaining the NMR spectra at the HF-NMR facility at Nijmegen. We thank Jonathan F. Stebbins and Xianyu Xue from Stanford University for providing the Na data and for their critical review of this paper. A. van der Eerden is thanked for technical assistance in our HPT laboratory. V. Govers and T. Zalm are thanked for the provision of the XRD and DTA-TGA analyses, respectively. A. Kentgens, T. Kloprogge, J. van Beek, P. Buining, and G. Lieftink are thanked for their inspiring discussions and helpful comments during the course of this study. This paper is a contribution of the Debije Institute.

REFERENCES CITED

Akitt, J.W. (1989) Multinuclear studies of aluminium compounds. In J.W. Emsley, J. Feeney, and L.H. Sutcliffe, Eds., Progress in magnetic resonance spectroscopy, vol. 21, p. 1–149. Pergamon Press, Oxford.

Barth, T., and Lunde, G. (1927) Über das Mineral Villiaumit. Zentralblatt für Mineralogie, Geologie und Petrologie, A, 57–66.

Bøggild, O.B. (1953) The mineralogy of Greenland. Meddelelser om Grønland, 149 (3), 1–442.

Cowley, J.W., and Scott, T.R. (1948) The nature of precipitated fluoroaluminates. Journal of the American Chemical Society, 69, 2596–2598.

Engelhardt, G., and Michel, D. (1987) High resolution solid state NMR of silicates and zeolites. Wiley, Chichester, England.

Grimmer, A.-R., Müller, D., Bentrup, U., and Kolditz, L. (1982) ^{19}F und ^{27}Al-NMR-spektroskopischer Nachweis von Bewegungsvorgängen in Alkalihexafluoroaluminaten. Zeitschrift für Chemie, 22, 43.

Hawthorne, F.C., and Ferguson, R.B. (1975) Refinement of the crystal structure of cryolite. Canadian Mineralogist, 13, 377–382.

Hepworth, M.A., Jack, K.H., Peacock, R.D., and Westland, G.J. (1957) The crystal structures of the trifluorides of iron, cobalt, ruthenium, rhodium, palladium and iridium. Acta Crystallographica, 10, 63–69.

Hoppe, R., and Kissel, D. (1984) Zur Kenntnis von AlF_3 und InF_3. Journal of Fluorine Chemistry, 24, 327–340.

Jacoboni, C., Leble, A., and Rousseau, J.J. (1981) Détermination précise de la structure de la chiolite $Na_5Al_3F_{14}$ et étude par R.P.E. de $Na_5Al_3F_{14}$: Cr^{3+}. Journal of Solid State Chemistry 36, 297–304.

Kentgens, A.P.M., Scholle, K.F.M.G.J., and Veeman, W.S. (1983) Effect of hydration on the local symmetry around aluminum in ZSM-5 zeolites studied by aluminum-27 nuclear magnetic resonance. Journal of Physical Chemistry, 87, 4357.

Kimura, K., and Satoh, N. (1989) High resolution solid state NMR of $^{27}AlF_3$ particles observed by a conventional Fourier-transform spectrometer. Chemistry Letters (2), 271–274.

Kirkpatrick, R.J. (1988) MAS NMR spectroscopy of minerals and glasses. In Mineralogical Society of America Reviews in Mineralogy, 18, 341–403.

Kohn, S.C., Dupree, R., Mortuza, M.G., and Henderson, C.M.B. (1991) NMR evidence for five- and six-coordinated aluminum fluoride complexes in F-bearing aluminosilicate glasses. American Mineralogist, 76, 309–312.

Le Bail, A., Jacoboni, C., Leblanc, M., De Pape, R., Duroy, H., and Fourquet, J.L. (1988) Crystal structure of the metastable form of aluminum trifluoride β-AlF_3 and the gallium and indium homologs. Journal of Solid State Chemistry, 77, 96–101.

Magi, M., Lippmaa, E., Samoson, A., Engelhardt, G., and Grimmer, A.R. (1984) Solid-state high resolution silicon-29 chemical shifts in silicates. Journal of Physical Chemistry, 88, 1518–1522.

Magnelli, A. (1953) Studies on the hexagonal tungsten bronzes of potassium, rubidium and cesium. Acta Chemica Scandinavica, 7, 315–324.

Majumdar, A.J., and Roy, R. (1965) Test of the applicability of the Clapeyron relationship to a few cases of solid-solid transitions. Journal of Inorganic and Nuclear Chemistry, 27, 1961–1973.

Manning, D.A.C. (1981) The effect of fluorine on liquidus phase relationships in the system Qz-Ab-Or with excess water at 1 kb. Contributions to Mineralogy and Petrology, 76, 206–215.

Massiot, D., Bessada, C., Contures, J.P., and Taulelle, F. (1990) A quantitative study of the ^{27}Al MAS NMR in crystalline YAG. Journal of Magnetic Resonance, 90, 231–242.

Mesrobian, G., Rolin, M., and Pham, H. (1972) Étude sous pression des mélanges fluorure de sodium-fluorure d'aluminium riches en fluorure d'aluminium. Revues Internationales des Hautes Températures et des Refractaires, 9, 139–146.

Müller, D. (1982) Zur Bestimmung chemischer Verschiebungen der NMR—Frequenzen bei Quadrupolkernen aus den MAS-NMR-Spektren. Annalen der Physik, 39, 451–460.

Müller, D., and Bentrup, U. (1989) ^{27}Al-NMR-Untersuchungen an alkalifluoroaluminaten. Zeitschrift für anorganische und allgemeine Chemie, 575, 17–25.

Müller, D., Gessner, W., Behrens, H.-J., and Scheler, G. (1981) Determination of the aluminium coordination in aluminium-oxygen compounds by solid-state high-resolution ^{27}Al NMR. Chemical Physics Letters, 79 (1), 59–62.

Müller, D., Gessner, W., Samoson, A., Lippmaa, E., and Scheler, G. (1986) Solid-state aluminium-27 nuclear magnetic resonance chemical shift and quadrupole coupling data for condensed AlO_4 tetrahedra. Journal of the Chemical Society, Dalton Transactions, 1277–1281.

Mysen, B.O., and Virgo, D. (1985) Structure and properties of fluorine-bearing aluminosilicate melts: The system Na_2O-Al_2O_3-SiO_2-F at 1 atm. Contributions to Mineralogy and Petrology, 91, 205–220.

Phillips, B.L., Kirkpatrick, R.J., and Hovis, G.L. (1988) ^{27}Al, ^{29}Si and ^{23}Na MAS NMR study of an Al,Si ordered alkali feldspar solid solution series. Physics and Chemistry of Minerals, 16, 262–275.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1978) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin, 1452.

Sabelli, C. (1987) Structure refinement of elpasolite from Cetine mine, Tuscany, Italy. Neues Jahrbuch für Mineralogie Monatshefte, 11, 481–487.

Satoh, N., and Kimura, K. (1990) High-resolution solid-state NMR in liquids. 2. ^{27}Al NMR study of AlF_3 ultrafine particles. Journal of the American Chemical Society, 112, 4688–4692.

Shannon, R.D., and Prewitt, C.T. (1969) Effective ionic radii in oxides and fluorides. Acta Crystallographica, B25, 925–946.

Shinn, D.B., Crocket, D.S., and Haendler, H.M. (1966) The thermal decomposition of ammonium hexafluoroferrate(III) and ammonium hexafluoroaluminate. A new crystalline form of aluminum fluoride. Inorganic Chemistry, 5 (11), 1927–1933.

Skibsted, J., Nielsen, N.C., Bildsoe, H., and Jakobsen, H.J. (1991) Satellite transitions in MAS NMR spectra of quadrupolar nuclei. Journal of Magnetic Resonance, 95, 88–117.

Smith, K.A., Kirkpatrick, R.J., Oldfield, E., and Henderson, D.M. (1983) High-resolution silicon-29 nuclear magnetic resonance spectroscopic study of rock-forming silicates. American Mineralogist, 68, 1206–1215.

Stebbins, J.F. (1987) Identification of multiple structural species in silicate glasses by ^{29}Si NMR. Nature, 330, 465–467.

MANUSCRIPT RECEIVED AUGUST 20, 1991
MANUSCRIPT ACCEPTED FEBRUARY 21, 1992