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# The Infrared Absorption Spectra of a Number of Sodium Fluoroaluminates in the Wavenumber Region Between 500 and 800 $cm^{-1}$

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Infrared absorption data on $AlF_3$, $NaAlF_4$, natural chiolite and cryolite are given, together with those of a number of synthetic cryolites, commercially available, in the composition range between chiolite and cryolite.

The dependency of the frequencies of the deformational vibrations on the $NaF/AlF_3$ ratio is discussed.

An attempt is made to designate specific vibrations in accordance with the asymmetry of the $AlF_6^{3-}$ octahedron.

The infrared absorption pattern of the synthetic cryolites is due to an integral effect of small particle-sized separate mineral phases (chiolite and cryolite), not to mixed-crystal formation.

The group of known sodium fluoroaluminates with the naturally occurring compounds cryolite ($Na_3AlF_6$) and chiolite ($Na_5Al_3F_{14}$), together with $NaAlF_4$ (Howard [2]) offers an opportunity to gain some knowledge of the nature of infrared frequency shifts in relation to the $NaF/AlF_3$ ratio.

Attention is also given to a number of commercially available synthetic cryolites, having a chemical composition intermediate between cryolite and chiolite (Table 1).

Although these cryolites are inhomogeneous according to their XRD patterns, which persistently show mixtures of cryolite and chiolite, it appears that they behave as being homogeneous solid solutions with respect to infrared absorption. A possible explanation will be suggested.

The sample of $NaAlF_4$ has been obtained from Howard shortly after its synthetization. Since the compound slowly decomposes into chiolite and $AlF_3$, for this study the sample was re-heated in aluminium foil at about 500°C in order to secure total decomposition. After quenching $NaAlF_4$ was restored, as verified by X-ray diffraction.

The samples of cryolite and chiolite, used in this study, are the naturally occurring minerals from Ivigtut in Greenland.

*Table 1.* Chemical analyses of a number of synthetic cryolites, in weight per cent.

| | a | b | c | d | e | f | g |
|---|---|---|---|---|---|---|---|
| Na | 25.69 | 27.35 | 29.10 | 29.97 | 30.08 | 32.29 | 30.70 |
| Al | 16.60 | 15.68 | 14.92 | 13.73 | 13.36 | 13.00 | 12.14 |
| F | 56.35 | 55.57 | 55.57 | 50.18 | 55.30 | 54.20 | 51.10 |
| Ca | tr. | tr. | 0.16 | 1.31 | 0.21 | 0.26 | 0.12 |
| Mg | nil | nil | tr. | tr. | 0.11 | n.d. | n.d. |
| $Fe_2O_3$ | 0.02 | 0.06 | 0.04 | 0.52 | 0.04 | 0.64 | 0.03 |
| $SiO_2$ | 0.41 | 0.48 | 0.02 | 0.43 | 0.30 | n.d. | 0.10 |
| $SO_4^{2-}$ | tr. | nil | 0.09 | 1.29 | 0.11 | 0.28 | nil |
| $Cl^-$ | tr. | tr. | 0.04 | 0.80 | 0.16 | tr. | n.d. |
| $CO_3^{2-}$ | nil | nil | nil | nil | nil | n.d. | n.d. |
| $H_2O$ −110°C | 0.15 | 0.05 | 0.04 | 0.52 | n.d. | n.d. | n.d. |
| $H_2O$ +110°C | 0.89 | 0.57 | 0.09 | 0.17 | n.d. | 5.9 | 0.14 |
| Insoluble | n.d. | n.d. | n.d. | 0.99 | n.d. | 0.20 | n.d. |
| Total | 100.11 | 99.76 | 100.07 | 99.91 | 99.37 | 100.81 | 100.29 |
| $NaF/AlF_3$ mol % | 1.80 | 2.03 | 2.28 | 2.55 | 2.63 | 2.90 | 2.94 |
| Analyst | E-L.M. | E-L.M. | H.B. | H.B. | H.B. | H.B. | H.B. |

E.-L. M.: E.-L. Mortensen. H. B.: H. Buchwald. The analyses were obtained from 1954 to 1959.

a. Synthetic cryolite, China National Chemicals, P. Brøste, Copenhagen, Denmark.
b. Synthetic cryolite, Malmsten och Bergvall, Göteborg, Sweden.
c. Nalf Blue Extra synthetic cryolite, Kingsley & Keith, Ltd., Kinglochleven Research Dept., G. B. (sample ref. 112 F).
d. Cryolita sintetica pura, Drogas Sam. S.A., Spain.
e. Cryolita sintetica, Bonelli, Italy.
f. Synthetic cryolite "Montecatini", Joseph Weil & Son, Ltd., London (through J. G. Gregory & Son, Ltd., Newcastle, G.B.).
g. Cryolita sintetica macinata, Montecatini, Milano, Italy.

The observed infrared vibrational frequencies have been compared to those found in $AlF_3$. The sample of anhydrous $AlF_3$ was obtained from Rolin.[6]

In a paper by Peacock and Sharpe [4] it is noted that the main $AlF_6^{3-}$ deformation of the cryolites generally is split into several components of approximately equal intensities. The departure from ideality in the octahedral arrangement of the $MF_6^{n-}$ anion may point to anisotropic vibration in one plane,[1] or to compositional effects in the spatial arrangement of the $MF_6^{n-}$ octahedron.[4]

In $K_3AlF_6$, for example, the main absorption peak at 587 $cm^{-1}$* shows additional absorptions at 605 and 574 $cm^{-1}$. In natural cryolite the main absorption occurs at 599 $cm^{-1}$ with overlapping peaks having nearly equal intensities, at 625 an 585 $cm^{-1}$.

The infrared data obtained from the study of the compounds $AlF_3$, $NaAlF_4$, $Na_5Al_3F_{14}$, and $Na_3AlF_6$, together with 7 apparently homogeneous synthetic cryolites, are plotted in Fig. 1. The ordinate represents the $NaF/AlF_3$ molar ratio, the abscissa the wavenumber scale. The chemical analysis of the synthetic cryolites are given in Table 1.

* Peacock and Sharpe [4] find 570 $cm^{-1}$.

The infrared absorption spectrum of $AlF_3$ reveals 4 absorption maxima between 500 and 800 $cm^{-1}$: at 548, 667, 690, and 720 $cm^{-1}$ (Fig. 2).

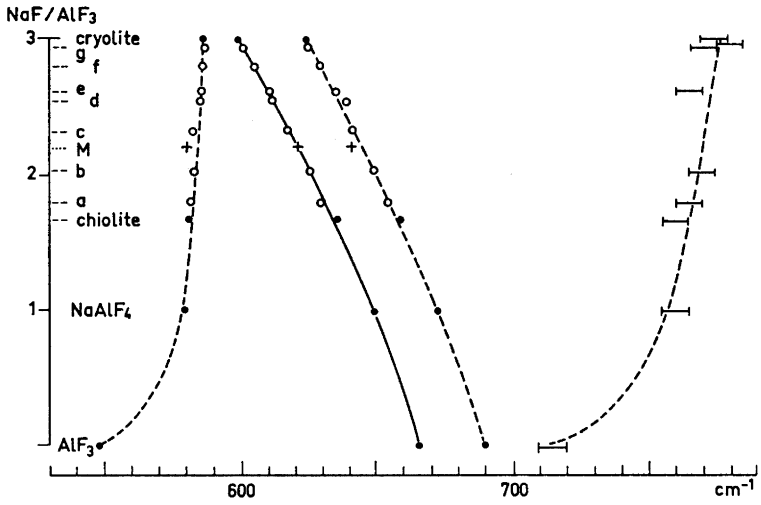


*Fig. 1.* The position of the infrared absorption maxima of the deformational vibrations, expressed in wavenumbers, of anhydrous aluminium fluoride and the sodium fluoroaluminates, *versus* the $NaF/AlF_3$ ratio of the compounds. Solid dots (●) represent the pure compounds, open dots (○) the group of synthetic cryolites (a–g), and crosses (+) the absorption maxima of the mechanically prepared sample (M), heated to 850°C (see the text).

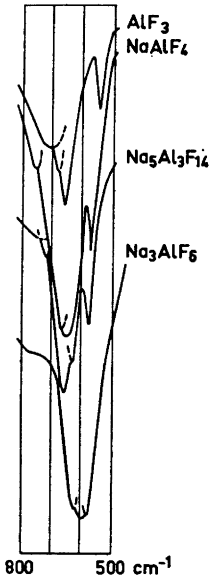


*Fig. 2.* The shape of the infrared transmission spectra of $AlF_3$, $NaAlF_4$, chiolite, and cryolite, between 800 and 500 $cm^{-1}$.

Of these only the 548 and the 667 $cm^{-1}$ absorption maxima are well defined, while the absorption peak at 690 $cm^{-1}$ appears as a shoulder on the 667 $cm^{-1}$ maximum absorption. The 720 $cm^{-1}$ absorption maximum is an overlapping, broad one of rather low absorbance.

Fig. 2 also shows the development of the above-mentioned absorption maxima in the spectra of $NaAlF_4$, chiolite and cryolite.

Structurally the series of sodium fluoroaluminates comprises the subsequent change from a framework structure ($AlF_3$) over sheet-structures ($NaAlF_4$ and chiolite) to separate $AlF_6$ octahedra (ino-structure) in cryolite.[3] The structure of chiolite has been classified as "interrupted" sheets by Pabst.[3]

By analogy with gaseous molecules $MF_6$, the main absorption in the frequency interval 500 to 800 $cm^{-1}$, represents deformational vibration (Peacock and Sharpe [4]). In the case of $AlF_3$, the main deformation ($\nu_3$) is represented by the 667 $cm^{-1}$ absorption maximum.

Due to a difference in the interatomic distance $Al-F_1$: 1.70 Å, $Al-F_2$: 1.89 Å (Wyckoff [8]), the symmetry of the $AlF_6^{3-}$ octahedra is non-ideal.

The occurrence of the 548 $cm^{-1}$ absorption band may presumably also be interpreted as a deformation frequency band. This view is supported by the further development of the band in the sodium fluoroaluminates. It has a nearly stable frequency already in a sheet-like arrangement of the $AlF_6^{3-}$ octahedra in $NaAlF_4$, being 580 $cm^{-1}$, while this peak gradually attains a lower transmission level in the sodiumfluoroaluminates with a higher $NaF/AlF_3$ ratio. Tentatively it could be termed the "axial" deformation, thus having the direction of a $4/m$ symmetry axis. In $Na_3AlF_6$ the octahedra are completely separated: the "gaseous" state has been obtained and the vibration components have reached nearly equal transmission levels, closely spaced.

Table 2 gives the interatomic $Al-F$ distances in $AlF_3$, chiolite and cryolite, according to Wyckoff.[8] The magnitude of the deformation of the $Al-F$ symmetry may be expressed by the difference in interatomic distance.

*Table 2.*

| | $Al-F_1$ | $Al-F_2$ | $d(Al\text{-}F_2-Al\text{-}F_1)$ | $NaF/AlF_3$ |
|---|---|---|---|---|
| $AlF_3$ | 1.70 Å | 1.89 Å | 0.19 Å | 0 |
| $Na_5Al_3F_{14}$ | 1.82 | 1.94 | 0.12 | 1.6 |
| $Na_3AlF_6$ | 1.79 | 1.83 | 0.04 | 3.0 |

The shift of the main deformation absorption band is nearly proportional to the $NaF/AlF_3$ ratio (Fig. 1). The vibrational frequency changes from 667 $cm^{-1}$ in $AlF_3$, *via* 650 $cm^{-1}$ in $NaAlF_4$ and 646 $cm^{-1}$ in chiolite to 599 $cm^{-1}$ in cryolite. The "axial" deformation frequency, on the other hand, is nearly constant in the interval between $NaF/AlF_3$ equals 1 and the same ratio being 3.

The secondary deformation which appears as a shoulder on the main deformation peak has exactly the same distance from the main absorption frequency in all the investigated compounds. Its appearance may be explained by the asymmetry of electron density distribution around the F-atom, similar to that

revealed by the Fourier analysis of $(NH_4)_3ScF_6$ by Bode and Voss.[1] For this scandium cryolite, Bode and Voss [1] considered the observed asymmetry of the electron density around the F-atom as being caused by anisotropic vibration of the $F_{II}$ atoms in the *xy*-plane. Perpendicular on this plane, the electron density is diminishing rapidly (Ref. 1, p. 10). It is noteworthy that the absorption of the duplicate deformation bands in chiolite is reversed in comparison to those of the other compounds. This may be due to a mechanical effect, which implicates that the doublet has no particular significance as to the Al – F modes, other than the asymmetry of the F-vibrations.

The nature of the absorption band at the highest frequency in the frequency interval under observation, being 720 $cm^{-1}$ in $AlF_3$, is not fully understood. The general frequency shift of this absorption band throughout the sodium fluoroaluminates follows the pattern of the axial deformation band shift between $AlF_3$ and cryolite with a slight deviation of direction. However, as the absorbance of the axial deformation bands increases with increasing $NaF/AlF_3$ ratio, the absorption band at the higher frequencies, occurring over a rather wide frequency range, decreases relatively in intensity in the sodium fluoroaluminates to a comparatively low value in $Na_3AlF_6$ (Fig. 2). The "axial" deformation of the $AlF_6^{3-}$ octahedra may be influenced by dimeric sodium fluoride groups: a certain resonance appears which damps the vibrational intensities.

The regularity of the decrease in frequency of the infrared absorption of the main deformation band, compared to the increase of the $NaF/AlF_3$ ratio, becomes somewhat puzzling in the group of commercially produced synthetic cryolites, since X-ray diffraction reveals that always two crystalline phases are present: chiolite and cryolite.

Thus it cannot be a random stuffing of $Na^+$ in the available $AlF_6^{3-}$ structures that produces the frequency dependency of the $NaF/AlF_3$ ratio, but the integral effect of infrared absorption in both crystalline structures.

A mechanically prepared mixture of 50 mol % natural cryolite and 50 mol % natural chiolite produced an infrared absorption spectrum in which the two compounds could be detected by careful weighing of the absorbances. The particle size of the mixture was less than 5 $\mu$m (designated with M in Fig. 1).

The sample was heated for 4 h at 550°C and at 850°C, that is near the inversion temperature and somewhat below the melting point of the mixture, after which it was quenched.

The absorption spectrum revealed that a certain homogenization was reached after heating at 550°C – broad absorption maxima – while homogenization was accentuated when heated to 850°C. The absorption maxima being, in order of increasing frequency, 580, 620 and 640 $cm^{-1}$ ($\pm$ 5 $cm^{-1}$).

As could be expected, the X-ray diffraction patterns of the heated samples still showed separate crystalline phases.

From these observations it seems likely that the infrared absorption dependency of the $NaF/AlF_3$ ratio in synthetic cryolites is due to a fusion effect, giving an integral infrared absorption pattern, as if the synthetic cryolite-chiolite intermixtures were a series of solid solution compounds.

Structurally the existence of a mixed-crystal series between cryolite and chiolite has been considered, taking into account the pseudo-cubic character of cryolite (Wrinch [7]), which may be brought to fit approximately the tetragonal lattice of chiolite. However, the X-ray diffraction diagrams of the synthetic cryolites have so far not revealed any deviations from the known diffraction patterns of the pure members of the mixtures, which could justify the assumption of having mixed-crystal structures, although the use of a focusing camera may give further clues on the possibility of an intermixture of the cryolite-chiolite structures. The molar proportion in which the two mineral phases were present in the synthetic cryolites is linearly proportional to the intensities of the 3.89 Å and 3.51 Å reflections of cryolite and chiolite, respectively.

*Experimental data.* Pressed KBr discs with about 1 % solids were prepared to fit the instrumental requirements of the Beckmann IR-9 infrared spectroscope.

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*Note added after completing the manuscript.* In a recent paper Povarennykh and Lebedeva [5] have obtained the infrared absorption spectra of a number of naturally occurring fluoroaluminates from the cryolite deposit at Ivigtut in Greenland. Although the authors do not recognise the doublet character of the main absorption in the 600 to 700 $cm^{-1}$ region, it appears from their published data that the difference between the absorption maxima of the main deformational vibration in cryolite and chiolite is 53 $cm^{-1}$, while the present author finds 47 $cm^{-1}$. The "axial" deformation band is given as 578 and 579 $cm^{-1}$ for both compounds in the above order.

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