RSC Advances



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PAPER

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Cite this: RSC Adv., 2020, 10, 25856

Received 31st May 2020 Accepted 1st July 2020 DOI: 10.1039/d0ra04804f

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Introduction

Cryolite, Na₃[AlF₆], occurs naturally as a rare mineral.¹ Historically, it was used as a source of aluminium but this has been superseded by bauxite (a mixture of the Al₂O₃ containing minerals boehmite, diaspore and gibbsite), largely because of the higher Al content of bauxite (\sim 50%) *vs.* cryolite (13%) and the scarcity of the latter. However, cryolite remains essential to aluminium production because alumina is readily soluble in molten cryolite. This is crucial to the economics of aluminium production because cryolite melts at 1012 °C whereas alumina melts at 2072 °C. As the melt is ionic, it also conducts electricity efficiently making the electrolytic reduction of alumina feasible. This is the basis of the Hall–Héroult process, which was invented independently by Hall and Héroult in 1886 and it is still the method of production today.²

The liquid phase of cryolite has been extensively investigated by a variety of techniques including multinuclear (¹⁹F, ²³Na, ²⁷Al) NMR,³⁻⁵ Raman spectroscopy⁶⁻⁸ and quasielastic neutron scattering.^{9,10} There are also a large number of molecular dynamics studies *e.g.*¹¹⁻¹⁵, some of which calculate the Raman spectra^{13,14} in the melt. Surprisingly, the solid state has been much less investigated, with only one paper on the infrared spectroscopy of Na₃[AlF₆]¹⁶ and one on that of the isostructural K_3 [AlF₆].¹⁷ Cryolite is the end member of the elpasolite family,¹⁸ the archetype is K_2 Na[AlF₆], and this is the most abundant prototype in the Inorganic Crystal Structure Database.¹⁹ The spectroscopy of elpasolite itself has been studied,²⁰ as has Cs₂Na [AlF₆].²¹ Materials of the type Li₃[InX₆] (X = Cl,²² Br²³) are of current interest as lithium ion conductors.²⁴

The structure and vibrational spectroscopy of cryolite, Na₃AlF₆

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Cryolite, Na₃[AlF₆], is essential to commercial aluminium production because alumina is readily soluble in molten cryolite. While the liquid state has been extensively investigated, the spectroscopy of the solid state has been largely ignored. In this paper, we show that the structure at 5 K is the same as that at room temperature. We use a combination of infrared and Raman spectroscopies together with inelastic neutron scattering (INS) spectroscopy. The use of INS enables access to all of the modes of Na₃[AlF₆], including those that are forbidden to the optical spectroscopies. Our spectral assignments are supported by density functional theory calculations of the complete unit cell.

In view of the technological importance of cryolite, we have carried out a comprehensive spectroscopic investigation and report new infrared and Raman spectra over extended temperature and spectral ranges and the inelastic neutron scattering (INS) spectrum. The last of these is observed for the first time and enables access to all of the modes of Na₃[AlF₆]. Our spectral assignments are supported by density functional theory calculations of the complete unit cell.

Results

Structure

At room temperature cryolite crystallizes in the monoclinic α phase, space group $P2_1/n$ (no. 14) with two formula units in the primitive cell,²⁵⁻²⁷ Fig. 1. The non-standard setting is used because it highlights the relationship to the high temperature (above 823 K) face centered cubic β -phase, $Fm\bar{3}m$ (no. 225).^{27,28}

The structure in the α -phase is shown in Fig. 1 and it can be seen that there are two types of sodium ion: one (Na1, orange) on the Wyckoff site 2c and two (Na2, purple) on the Wyckoff site 4e. These are six- and eightfold coordinated by fluorine atoms, respectively. The $[AlF_6]^{3-}$ ion is on the Wyckoff site 2d and has C_i symmetry. Thus the compound is better formulated as: (Na₂)(Na)[AlF₆] and is an example of a double perovskite.²⁷

We are unaware of any structural studies below room temperature. Heat capacity measurements from 7–350 K,²⁹ do not show any evidence of a phase transition in that range, apart from the melting of a liquid inclusion at 268 K in the natural sample of cryolite that was used. However, the INS spectrometer used in this work, VISION,³⁰ also has a neutron diffraction capability. Fig. 2 shows a two-phase (cryolite plus the aluminium can) Rietveld fit of the neutron diffractogram measured at 5 K. Scale factors were refined for both phases in obtaining the fit to the data. Lattice parameters have been allowed to refine, to allow for cell contraction, but atomic

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Fig. 1 The room temperature structure of cryolite in the monoclinic space group $P2_1/n$ (no. 14).²⁶ Key: Na1 = orange, Na2 = purple, Al = magenta, F = turquoise.

positions have been held at the room temperature values.²⁵ An excellent fit to the data is obtained, even though the atomic positions and temperatures factors of the cryolite have not been refined. Table 1 lists the lattice parameters determined here together with room temperature and estimated values. It is apparent that, apart from the expected lattice contraction on cooling, that the $P2_1/n$ structure is retained to at least 5 K.

Table 2 compares selected observed and calculated bond distances (all of the *cis* F–Al–F bond angles are 90 \pm 1°, all the *trans* angles are 180° by symmetry). As might be expected from the very small difference between the room temperature and 5 K lattice parameters there is little change in the interatomic distances. The calculation does slightly overestimate the Al–F distances. The Na–F distances are slightly shorter than found in NaF (2.318 Å (ref. 31)).

Vibrational spectroscopy

Fig. 3 shows the infrared, Raman and INS spectra of cryolite. The Raman spectrum at 13 K is seen in Fig. 3c, unfortunately, because of sample fluorescence, only the Al–F symmetric stretch mode at 554 cm^{-1} was observable. However, apart from a marked narrowing, there is no shift in transition energy or additional peaks apparent. The lattice mode region, shown in the lower part of Fig. 3, shows coincidences between the INS and the infrared and Raman data. Thus the vibrational spectroscopy suggests (but does not prove) that there is no phase change between room temperature and 5 K, consistent with the diffraction results.

An isolated octahedral, $O_{\rm h}$, $[{\rm AlF}_6]^{3-}$ ion has six Al–F stretch modes: ν_1 (A_{1g}), ν_2 (E_g), ν_3 (T_{1u}) and nine F–Al–F bend modes: ν_4 (T_{1u}), ν_5 (T_{2g}), ν_6 (T_{2u}). ν_1 , ν_2 and ν_5 are Raman active, ν_3 and ν_4 are infrared active and ν_6 is forbidden in both forms of spectroscopy.³² However, all of the modes are allowed in the INS spectrum. To go beyond this requires more detailed analysis and to this end we use the correlation method.³³ The results are shown in Table 3.

With two formula units in the primitive cell, there are 20 atoms present hence there are 60 modes, which are given by the sum of the last column in Table 3: $12 A_g + 12 B_g + 18 A_u + 18 B_u$. This includes the three acoustic translational modes, which have $A_u + 2 B_u$ representations and have zero energy at the

Brillouin zone Γ -point, where the infrared and Raman modes are observed. Modes that have A_u or B_u symmetry are infrared active, those with A_g or B_g are Raman active. Two deductions are immediately obvious: all of the degeneracies are formally lifted



Fig. 2 A two-phase Rietveld fit (solid line) to the VISION neutron data (open circles) in the *d*-spacing range 2.0 to 0.8 Å (upper panel) and 4.0 to 0.8 Å (lower panel). Blue tick marks indicate the reflection positions for cryolite, whilst green tick marks indicate the reflections associated with the aluminium sample can. An excellent fit to data is obtained, even though the atomic positions and temperatures factors of the cryolite have not been refined.

Table 1 Lattice parameters of cryolite

	5 ^{<i>a</i>} K	$0^b K$	0 ^{<i>c</i>} K	295 ^d K	295 K ^e
<i>a</i> /Å	5.3917(5)	5.381	5.42	5.4139(7)	5.4054(1)
b/Å	5.6010(5)	5.581	5.63	5.6012(5)	5.5934(1)
c/Å	7.7556(8)	7.693	7.83	7.7769(8)	7.7672(1)
$\alpha/^{\circ}$	90.000	90.000	90.0	90.000	90.000
$\beta/^{\circ}$	90.253(8)	90.285	90.2	90.183(3)	89.81(1)
$\gamma/^{\circ}$	90.000	90.000	90.0	90.000	90.000
$V/Å^3$	234.21(4)	232.6	238.9	235.8	234.84

^{*a*} This work. ^{*b*} Extrapolated from ref. 25 by ref. 14. ^{*c*} Calculated by molecular dynamics.^{14 d} From ref. 25. ^{*e*} From ref. 26.

and because the centre of symmetry is preserved, the free ion selection rules will still apply, except that v_6 is now allowed in the infrared spectrum. As stated earlier, all modes are allowed in the INS spectrum.

The analysis in Table 3 enables some of the modes to be assigned. The intense, broad mode at 559 cm⁻¹ with shoulders at 596 and 608 cm⁻¹ in the infrared spectrum must be v_3 . Previous work¹⁶ on the infrared spectrum of cryolite found v_3 at 599 cm⁻¹ with shoulders at 580 and 630 cm⁻¹, the lower energy modes were not reported. We can only ascribe the difference in the transition energy of v_3 to either a calibration error in the older (pre-FTIR) work or that the natural sample of cryolite used there was impure.

The strong mode at 554 cm⁻¹ in the Raman spectrum must be v_1 and the two weaker modes at 396 and 344 cm⁻¹ in the Raman spectrum are v_2 and v_5 respectively. This is in excellent agreement with the previously reported Raman spectrum of cryolite.⁸ Cryolite melts⁶⁻⁸ show a strong band at ~550 cm⁻¹ assigned to v_1 . In the infrared spectrum the mode at 396 cm⁻¹ is assigned as v_4 . The coincidence with v_2 is surprising because one is an Al–F stretch mode and the other an F–Al–F bending mode, but the selection rules are unambiguous. The assignment is supported by the INS spectrum, which shows a mode at 407 cm⁻¹, that is much stronger than v_5 , consistent with it being the unresolved sum of the two modes. The optically silent mode v_6 is not apparent, so it must occur below 300 cm⁻¹.

			5
Distance/Å	295 ^{<i>a</i>} K	5 K initial ^b	5 K opt ^c
Al–F	2 imes 1.799	2 imes 1.812	2 imes 1.825
	2 imes 1.820	2 imes 1.825	2 imes 1.834
	2 imes 1.830	2 imes 1.836	2 imes 1.836
Na1–F	2 imes 2.211	2 imes 2.205	2 imes 2.219
	2 imes 2.271	2 imes 2.256	2 imes 2.257
	2 imes 2.272	2 imes 2.264	2 imes 2.274
Na2–F (min)	2.292	2.287	2.276
(max)	2.816	2.806	2.807
(ave)	2.498	2.494	2.564

Table 2 Comparison of observed and calculated structure of cryolite

 a From ref. 26. b Structure used for the fits in Fig. 2. c 5 K structure after geometry optimization.

It is only in the region $<300 \text{ cm}^{-1}$ in the INS spectrum that the low symmetry of the system is readily apparent. In the infrared spectrum, there are three weak features, which Table 3 shows must be ν_6 and the translational modes of the ions, although there is no way to assign which is which. In the Raman spectrum there is a weak mode at 94 cm⁻¹, which is presumably the [AlF₆]³⁻ ion librational mode.

Computational studies

In order to assign the low energy region and to confirm the assignments for ν_1 to ν_5 we use periodic density functional theory (DFT) of the primitive cell and calculate the vibrational transition energies across the entire Brillouin zone (see: Materials and methods for details). The resulting dispersion curves are shown in Fig. 4 and the INS spectrum generated from the calculation is shown in Fig. 5.

It can be seen that the calculated INS spectrum is in almost quantitative agreement with the experimental data. The Al–F stretch modes are calculated slightly softer than is observed, this is probably because the bond lengths are calculated slightly too long: observed:^{25–27} 1.799, 1.820, 1.830 Å; calculated: 1.825, 1.834, 1.836 Å. However, the overall pattern of the experimental data is very well reproduced. In



Fig. 3 Vibrational spectra of cryolite: (a) infrared at room temperature, (b) Raman at room temperature (1064 nm excitation), (c) Raman at 13 K (785 nm excitation) and (d) INS at 5 K recorded on VISION. The lower panel shows the lattice mode region on expanded scales. Relative to the top panel the spectra are ordinate expanded: (a) \times 10, (b) \times 40 and (d) \times 1.5.

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Table 3 Correlation table for cryolite

				Crystal								
		Free ion			Translatic	suc	Librations		Intramole	ecular	Factor group	
lon	и	$\mathrm{Sym.}^b$	Rep.	Site^{c}	Rep.	No.	Rep.	No.	Rep.	No.	$C_{2\mathrm{h}}$	Total^{a}
Na1	2			$c_{\rm i}$	$A_{\rm u}$	3					$(A_u + B_u)$	$3(A_u + B_u)$
Na2	4			C_1	A	3					$(A_{g} + B_{g} + A_{u} + B_{u})$	$3(A_{g} + B_{g} + A_{u} + B_{u})$
AIF_6	2	$O_{ m h}$	T_{1u}	C ⁱ	$\mathbf{A}_{\mathbf{u}}$	3					$(A_u + B_u)$	$3(A_u + B_u)$
	2	$O_{ m h}$	T_{1g}	C _i			\mathbf{A}_{g}	ŝ			$(A_g + B_g)$	$3(A_g + B_g)$
	2	$O_{ m h}$	${ m A_{1g}}\left({ u _1} ight)$	$C_{\rm i}$)		\mathbf{A}_{g}	1	$(A_{g} + B_{g})$	$(\mathbf{A}_{\mathbf{g}}^{'} + \mathbf{B}_{\mathbf{g}})$
	2	$O_{ m h}$	$\mathrm{E_g}(u_2)$	$C_{\rm i}$					Åg	2	$(\mathbf{A_g} + \mathbf{B_g})$	$2(\mathbf{A_g} + \mathbf{B_g})$
	2	$O_{ m h}$	$T_{1u}(\nu_3)$	C _i					A_{u}	3	$(\mathbf{A_u} + \mathbf{B_u})$	$3(A_u + B_u)$
	2	$O_{ m h}$	$T_{1u}(\nu_4)$	$C_{\rm i}$					\mathbf{A}_{u}	3	$(\mathbf{A}_{\mathbf{u}} + \mathbf{B}_{\mathbf{u}})$	$3(A_u + B_u)$
	2	$O_{ m h}$	$\mathrm{T_{2g}}\left(\nu_{5} ight)$	$C_{\rm i}$					\mathbf{A}_{g}	3	$(A_g + B_g)$	$3(A_g + B_g)$
	2	$O_{ m h}$	$T_{2u}(\nu_6)$	$C_{ m i}$					$\mathbf{A}_{\mathbf{u}}$	3	$(\mathbf{A_u} + \mathbf{B_u})$	$3(\mathbf{A_u} + \mathbf{B_u})$
^{<i>a</i>} Total is th in the cryst	e product 11.	t of the colum	n "No." and the f	actor group. ^b	Sym. = symr	netry, Rep. =	irreducible re	presentatior	ı of the point	group, No. =	number. ^c Symmetry of the	site occupied by the ion



Fig. 4 Dispersion curves of cryolite in the monoclinic space group $P2_1/n$ (no. 14).

particular, the splitting of ν_3 is clearly seen and Fig. 4 shows that this is the result of the combination of the site group and factor group splitting combined with significant vibrational dispersion (variation with wavevector). The dense manifold of modes below 300 cm⁻¹ occurs because the low symmetry removes all the degeneracies and results in the complex structure seen experimentally.

The transition energies at the Brillouin zone Γ -point, (0,0,0), are given in Table 4 with the assignments based on visualization of the modes. This confirms the assignments for v_1 to v_5 and in particular that v_2 and v_4 are coincident. The "missing" mode v_6 is calculated at 254–288 cm⁻¹ and is seen to occur weakly in the infrared spectrum at 239/253 cm⁻¹. This is the first time that v_6 has been observed experimentally.

Fig. 5 also includes the individual contributions to the INS spectrum from each element. As expected, the fluorine contribution accounts for most of the intensity and it confirms that the librational modes account for the peaks at \sim 85–150 cm⁻¹. However, the librations have the same symmetry, A_g and B_g , as some of the translational modes of Na2 which results in extensive mixing of the two vibrations. Thus the lower energy modes around 100 cm⁻¹ are more librational in form while the higher energy ones around 210 cm⁻¹ are more translational. Na2 has modes of both gerade and ungerade character, Table 3, and this results in the modes occurring in a broad band from 50–300 cm⁻¹. In contrast, the Na1 modes are much more localized and largely occur in the narrower range of 200–300 cm^{-1} . This is a consequence of the more regular coordination polyhedron of Na1: the Na-F distances vary by less than 0.06 Å, by contrast those around Na2 vary by nearly ten times as much, 0.5 Å (Table 2).

Discussion

This work provides the first complete assignment of the vibrational spectra of cryolite. In particular, the forbidden (in



Fig. 5 Observed and calculated (CASTEP) spectra of cryolite. Top panel: infrared spectra (a) observed, (b) calculated. Raman spectra: (c) observed, (d) calculated. Lower panel: INS spectra. The individual element contributions to the calculated spectrum are also shown.

 $O_{\rm h}$ symmetry) mode ν_6 has been observed. This is very rare:³² (pp. 216–218) lists the spectra of over 30 $[MF_6]^{x-1}$ ions; for none of them is v_6 given, although it is known for a few neutral MF₆ systems. Assignment of librational modes is equally rare. To our knowledge, the only examples for which this is known are for $K_2[MCl_6]$ (M = Pt, Ir,³⁴ Re³⁵) where the librational transition energies are 55 cm^{-1} (Pt), 48 cm^{-1} (Ir) and 28 and 68 cm^{-1} (Re). Making the naive assumption that it is only the difference in the moment of inertia between the $[AlF_6]^{3-}$ and $[PtCl_6]^{2-}$ ions that accounts for the difference in transition energy would predict that $[AlF_6]^{3-}$ occurs at 87 cm⁻¹. This is on the lowest edge of the band of the librational modes (Table 4) and suggests that other factors are also relevant, the most likely being the difference in charge of the ions.

The only unassigned band in the spectra shown in Fig. 3 is the shoulder at 533 cm⁻¹ on the low energy side of v_1 that is clearly resolved at 13 K. We considered the possibility that it may be the Bg symmetric Al-F stretch mode that was miscalculated, however, there is no corresponding mode in the INS spectrum, which also argues against it being an overtone or combination. The calculated Raman intensity of this mode is almost zero which also militates against this assignment. Inspection of the Raman spectra of cryolite in the literature^{4,6,8} does not show the band in the solid or liquid phase. This suggests that it is an impurity, despite the stated purity being >99%, and the most likely candidate is chiolite, Na₅Al₃F₁₄. This mineral occurs naturally with cryolite³⁶ and consists of sheets of corner-sharing AlF₆ octahedra,³⁷ it has a very strong totally symmetric Al–F stretch mode at 530 cm⁻¹.³⁸

			D 4	Observed ^a			
CASTEP/cm ⁻¹	Sym ^b	mol^{-1}	Raman Int/A amu ⁻¹	INS/cm^{-1}	Raman/cm ⁻¹	Infrared/cm ⁻¹	Description ^b
0	Bu	0	0				Acoustic
0	Au	0	0				Acoustic
0	$\mathbf{B}_{\mathbf{u}}$	0	0				Acoustic
86	Ag	0	0.02	75s			Lib + Na2 trans
87	Å	13.62	0				AlF6 trans
90	B_u	103.00	0				AlF6 trans
92	A_{g}	0	0.02	87s	86sh		Lib + Na2 trans
93	$\mathbf{B}_{\mathbf{g}}$	0	0	96s	94w		Lib + Na2 trans
128	Bg	0	0	109s	109w		Lib + Na2 tran
137	Åg	0	0.02	136m			Lib + Na2 trans
138	$\mathbf{B}_{\mathbf{g}}$	0	0				Lib + Na2 tran
142	Au	32.79	0				Na2 trans
149	Au	9.73	0				AlF6 trans
150	B_u	36.73	0			146w	Na2 trans
165	Au	55.50	0			154w	Na2 trans
167	B_u	163.52	0	164s		163w	Na2 trans
175	A_{g}	0	0.02				Na2 trans + Lil
175	$\mathbf{B}_{\mathbf{g}}$	0	0.01				Na2 trans + Lil
178	$\mathbf{B}_{\mathbf{u}}$	226.57	0			178w	Na2 trans
191	Au	5.47	0			183w	Na1 trans
198	Au	100.07	0				Na2 trans
209	$\mathbf{B}_{\mathbf{g}}$	0	0	198w			Na2 trans + Lil
209	A_{g}	0	0.02	210m			Na2 trans + Lib

CASTEP/cm ⁻¹ Sym ^b Rama int/ mol ⁻¹ Rama int/ amu ⁻¹ INS/cm ⁻¹ Raman/cm ⁻¹ Infrared/cm ⁻¹ Description ^b 219 A_u 59.53 0 209m 209w Na1 trans 219 B_u 96.45 0 Na2 Na2 trans + Li 225 B_g 0 0.02 226m Na2 trans + Li 226 A_x 0 0.02 23m Na2 trans + Li 232 A_u 1.86 0 243m Na1 trans 240 B_u 37.39 0 243m Na1 trans 242 B_u 56.98 0 243w Na1 trans 258 A_u 1.46 0 257m 252w r_6 264 B_u 199.11 0 278th r_6 r_6 271 A_u 161.49 0 278th r_6 r_6 280 A_u 161.49 0 257m r_6			TD 1 4 (1	\mathbf{D}	Observed ^a			
219 A_u 59.53 0 209m 209m Nat trans 215 B_g 0 0.02 Nat trans Nat trans 226 A_g 0 0.02 Nat trans Nat trans 232 A_u 1.36 0 23m Nat trans 240 B_u 56.98 0 23m Nat trans 242 B_u 56.98 0 25m 243w Nat trans 244 B_u 73.93 0 25m 25w v_6 v_6 258 A_u 16f.49 0 25m v_6 v_6 v_6 264 B_u 73.93 0 25s v_6 v_6 v_6 271 A_u 7.19 0 v_6 v_6 v_6 v_6 292 B_u 38.42 0 v_6 v_6 v_6 v_6 314 B_g 0 0.01 325s v_6 v_6 v_6 335 A_g 0<	CASTEP/cm ⁻¹	Sym ^b	mol^{-1}	amu ⁻¹	INS/cm ⁻¹	Raman/cm ⁻¹	Infrared/cm ⁻¹	Description ^b
219B _u b b g c96.4500.02Na1 trans Na2 trans + Li Na2 trans + Li 	219	Au	59.53	0	209m	209w		Na1 trans
225 B_k 00.02226mNa2 trans + Li Na2 trans + Li Na1 transNa2 trans + Li Na2 trans + Li Na1 trans232 A_k 00.02Na1 trans240 B_u 37.390243mNa1 trans242 B_u 56.980257m243wNa1 trans258 A_u 1.460257m252w r_6 264 B_u 199.110257m78 r_6 268 B_u 73.930265sh r_6 r_6 271 A_u 161.490278h r_6 r_6 292 B_u 38.420 r_6 r_6 r_6 314 B_g 00.07 r_5 r_5 r_5 326 A_g^* 00.1636s,br343m r_6 341 B_g 00.1636s,br $343m$ r_6 357 A_g^* 00.62 r_4 r_4 397 B_u 129.310 $96h$ $395m$ r_4 400 A_g^* 00.50 r_2 r_4 404 A_g^* 00.50 r_2 r_4 404 A_g^* 00.50 r_2 r_4 406 A_g^* 00.50 r_2 r_4 406 A_g^* 00.50 r_2 r_4 407 A_g^* 00.50 r_2 $r_$	219	Bu	96.45	0				Na1 trans
226 A_g^P 0 0.02 Nat trans Nat trans 232 A_0 1.86 0 243m Nat trans 240 B_u 37.39 0 Nat trans 242 B_u 56.98 0 253m Adu Nat trans 258 A_u 1.46 0 257m 252w P_6 264 B_u 199.11 0 P_6 P_6 268 B_u 73.93 0 265sh P_6 P_6 271 A_u 71.91 0 P_6 P_6 P_6 280 A_u 161.49 0 278sh P_6 P_6 292 B_u 38.42 0 P_6 P_6 P_6 304 A_g 0 0.18 P_5 P_5 P_5 314 B_g 0 0.24 P_6 P_6 P_6 341 B_g 0 0.86 P_6 P_6 P_6 3497 B_u <td>225</td> <td>B_o</td> <td>0</td> <td>0.02</td> <td>226m</td> <td></td> <td></td> <td>Na2 trans + Lib</td>	225	B _o	0	0.02	226m			Na2 trans + Lib
232 $A_u^{}$ 1.860243mNat trans Nat trans240 B_u 37.390Nat trans242 B_u 5.680243wNat trans258 A_u 1.460257m252w r_6 264 B_u 199.110252w r_6 268 B_u 7.300255h r_6 r_6 271 A_u 71.910 r_6 r_6 280 A_u 161.490278sh r_6 r_6 292 B_u 3.420 r_6 r_6 304 A_g 00.01325s r_6 r_5 314 B_g 00.18 r_6 r_5 r_5 335 A_g 00.18 r_6 r_6 341 B_g 00.16336s,br343m r_6 379 B_u 108.530 r_6 r_4 380 A_u 95.400 r_6 r_4 397 B_u 108.530 r_6 r_4 398 A_g 00.62 r_6 r_4 404 B_g 0.400.56h r_6 r_4 414 B_g 0.400.56h r_6 r_6 415 P_6 P_6 P_6 r_6 r_6 416 P_6 P_6 P_6 r_6 r_6 397 B_u 0.62 P_6 P_6 r_6 416	226	Å	0	0.02				Na2 trans + Lib
240Bu u37.390Nal trans242Bu <bt></bt> b56.980243wNal trans258Au1.460257m252wr6264Bu199.110r6r6268Bu73.930258hr6r6268Bu71.910r6r6r6271Au161.490278hr6r6280Au161.490278hr6r6292Bu38.420r7r6r6304Ag00.01325sr5r5314Bg00.24r5r5r5326Ag00.42r5r5r5341Bg00.62r6r4r4341Bg00.62r6r4r4370Bu108.53395mr4r5380Ag00.62r6r4r4397Bu129.310395mr4r4400Ag00.62r6r4r4404Ag00.62r6r4r4405Ag00.62r6r4r44060.620r6r4r440700.55r595r4r4408Bg00.55r595r4r4414Ag	232	Au	1.86	0	243m			Na1 trans
242Bu a56.980243wNal trans258Au1.46025m252w v_6 264Bu73.930265sh52w v_6 268Bu73.930265sh v_6 v_6 271Au71.910 v_6 v_6 280Au161.490278sh v_6 v_6 292Bu38.420 v_6 v_6 314Ag00.01325s v_6 v_5 326Ag00.18 v_7 v_5 v_5 335Ag00.46 v_8 v_5 v_5 341Bg00.18 v_8 v_6 v_5 341Bg00.68 v_8 v_6 v_6 341Bg00.68 v_8 v_8 v_8 357Bu108.530 v_8 v_8 v_8 36000.62 v_8 v_8 v_8 v_8 379Bu108.530 v_8 v_8 v_8 397Bu108.530 v_8 v_8 v_8 404Ag00.62 v_8 v_8 v_8 398Ag00.62 v_8 v_8 v_8 404Ag00.55 v_8 v_8 v_8 404Ag00.55 v_8 v_8 v_8 404Ag </td <td>240</td> <td>Bu</td> <td>37.39</td> <td>0</td> <td></td> <td></td> <td></td> <td>Na1 trans</td>	240	Bu	37.39	0				Na1 trans
258 A_u 1.460257m252w μ_6 264 B_u 199.110 μ_6 268 B_u 73.930265sh μ_6 271 A_u 71.910 μ_6 280 A_u 161.490278sh μ_6 292 B_u 38.420 $275sh$ μ_6 304 A_g 00.01325s μ_5 314 B_g 00.18 μ_5 335 A_g 00.16343m μ_5 341 B_g 00.16 μ_6 379 B_u 108.530 μ_4 380 A_u 95.400 μ_4 397 B_u 129.310 μ_6 398 A_g 00.36 μ_4 398 A_g 00.36 μ_4 404 A_g 00.50 μ_7 405 A_u 0.240 μ_6 408 B_g 0.00.50 μ_7 418 B_g 0.00.50 μ_7 419 A_u 0.24 μ_1 μ_1 541 B_g 00.559 μ_1 541 B_g 0.0 <t< td=""><td>242</td><td>Bu</td><td>56.98</td><td>0</td><td></td><td></td><td>243w</td><td>Na1 trans</td></t<>	242	Bu	56.98	0			243w	Na1 trans
264 B_u 199.11 0 y_6 268 B_u 73.93 0 255h y_6 271 A_u 71.91 0 y_6 280 A_u 161.49 0 278h y_6 292 B_u 38.42 0 y_6 304 A_g 0 0.01 325. y_6 314 B_g 0 0.18 y_5 y_5 326 A_g 0 0.24 y_5 y_5 335 A_g 0 0.62 y_6 y_6 341 B_g 0 0.62 y_6 y_6 341 B_g 0 0.62 y_6 y_6 341 B_g 0 0.62 y_6 y_6 379 B_u 198.53 0 y_6 y_6 380 A_g 0 0.62 y_6 y_6 404 A_g 0 y_6 y_6 y_6	258	Au	1.46	0	257m		252w	ν ₆
268Bu a73.930265sh p_6 271Au71.910 p_6 280Au161.490278sh p_6 292Bu38.420 p_6 304Ag00.01325s p_5 314Bg00.07 p_5 326Ag00.18 p_5 335Ag00.16336s,br343m p_5 341Bg00.16336s,br343m p_5 341Bg00.16336s,br343m p_5 341Bg00.68 p_6 p_6 379Bu108.530 p_4 380Au95.400396sh395m p_4 397Bu129.310 p_6 p_4 398Ag00.62 p_6 p_4 400Bu0.62 p_6 p_4 404Ag00.36 p_4 405Au2.09 q_6 p_4 408Bg00.50 q_7 p_1 418Bg0 q_6 p_6 p_1 541Ag0 q_6 p_5 p_1 541Bg0 q_6 p_6 p_1 541Bg0 q_6 p_6 p_1 543Bu q_6 q_6 q_6 p_6 544Bg0 q_6 p_6 <td< td=""><td>264</td><td>Bu</td><td>199.11</td><td>0</td><td></td><td></td><td></td><td>ν_6</td></td<>	264	Bu	199.11	0				ν_6
271 a_u 71.91 0 n_6 280 A_u 161.49 0 278sh p_6 292 B_u 38.42 0 p_5 314 B_g 0 0.01 325s p_5 314 B_g 0 0.18 p_5 p_5 326 A_g 0 0.24 p_5 341 B_g 0 0.08 p_5 341 B_g 0 0.08 p_5 341 B_g 0 0.08 p_4 380 A_u 108.53 0 p_4 397 B_u 108.53 0 p_4 397 B_u 108.53 0 p_4 398 A_g 0 0.62 395m p_4 400 B_u 0.62 p_5 p_4 404 q_g 0 q_6 p_4 404 q_g 0 q_6 p_4 400 0.4 q_6 <	268	B	73.93	0	265sh			ν_6
280 A_u 161.49 0 278sh n_6 292 B_u 38.42 0 n_6 304 A_g 0 n_6 314 B_g 0 n_5 n_5 326 A_g 0 n_7 n_5 335 A_g 0 0.18 n_5 341 B_g 0 0.24 n_5 341 B_g 0 0.68 n_5 341 B_g 0 0.08 n_4 380 A_u 95.40 0 n_4 380 A_u 95.40 0 n_4 397 B_u 129.31 0 $395m$ n_4 398 A_g 0 0.62 $395m$ n_2 400 B_u 0.24 n_2 n_2 404 A_g 0 0.50 $395m$ n_2 404 A_g 0.29 n_1 n_2 404 A_g </td <td>271</td> <td>A</td> <td>71.91</td> <td>0</td> <td></td> <td></td> <td></td> <td>ν₆</td>	271	A	71.91	0				ν ₆
292 B_u 38.42 0 n_6 304 A_g 0 0.01 325s r_5 314 B_g 0 0.07 r_5 326 A_g 0 0.18 r_5 335 A_g 0 0.24 r_5 341 B_g 0 0.08 r_5 341 B_g 0 0.08 r_4 379 B_u 108.53 0 n_4 380 A_u 95.40 0 n_4 397 B_u 129.31 0 $395m$ n_4 398 A_g 0 0.62 $395m$ n_4 404 A_g 0 n_4 n_4 404 A_g 0 n_5 n_4 405 A_u 0.50 <	280	Au	161.49	0	278sh			ν ₆
304 A_g 00.01 $325s$ v_5 314 B_g 00.07 v_5 326 A_g 00.18 v_5 335 A_g 00.24 v_5 3314 B_g 00.16 $336s,br$ $343m$ v_5 341 B_g 00.16 $336s,br$ $343m$ v_5 341 B_g 00.08 v_5 v_6 341 B_g 00.08 v_4 380 A_u 95.400 v_4 397 B_u 129.310 $396sh$ $395m$ v_4 398 A_g 00.62 $395m$ v_2 400 B_u 0.62 0 v_4 404 A_g 0 0.50 $407s$ v_2 405 A_u 0.209 0 13.80 v_1 448 B_g 0 0.55 $554s$ v_1 448 B_g 0 0.55 $559s$ v_3 565 B_u 562.08 0 $559s$ v_3 574 A_u 762.85 0 v_3 v_3 577 A_u 21.77 0 $01m$ v_3 597 A_u 21.77 0 0 0 </td <td>292</td> <td>B</td> <td>38.42</td> <td>0</td> <td></td> <td></td> <td></td> <td>ν₆</td>	292	B	38.42	0				ν ₆
314 B_g 0 0.07 y_5 326 A_g 0 0.18 y_5 335 A_g 0 0.24 y_5 341 B_g 0 0.16 $336s, br$ $343m$ y_5 341 B_g 0 0.08 y_5 y_6 379 B_u 108.53 0 y_4 y_6 380 A_u 95.40 0 y_6 y_6 397 B_u 129.31 0 $395m$ y_2 400 B_u 0.62 $395m$ y_2 400 B_u 0.62 $395m$ y_2 400 B_u 0.62 y_2 y_2 400 B_u 0.62 y_2 y_2 404 A_g 0 0.550 $407s$ y_2 404 A_g 0 0.559 $554s$ y_1 448 B_g 0 $0.559s$ $559s$	304	A	0	0.01	325s			ν_5
326 A_g 0 0.18 y_5 335 A_g 0 0.24 y_5 341 B_g 0 0.16 $336s, br$ $343m$ y_5 341 B_g 0 0.08 y_5 341 B_g 0 0.08 y_5 379 B_u 108.53 0 y_4 380 A_u 95.40 0 y_4 397 B_u 129.31 0 $396sh$ $395m$ y_4 398 A_g 0 0.62 $395m$ y_2 400 B_u 0.62 0 y_2 400 B_u 0.62 y_2 y_2 400 B_u 0.62 y_2 y_2 400 B_u 0.62 y_1 y_2 404 A_g 0 y_2 y_2 405 A_u 0.26 y_1 y_2 406 B_g 0 0.50 $407s$ y_2 408 B_g 0 0.50 $425sh$ y_2 $4138h$ y_4 y_2 y_1 y_1 541 A_g 0 0 $559s$ $559s$ y_3 574 A_u 762.85 0 y_3 y_3 578 B_u 657.32 0 $580m$ y_3 597 A_u 21.77 0 $601m$ y_3 597 A_u 336.00 0 $590m$ y_3	314	B _o	0	0.07				ν_5
335 A_g 00.24 v_5 341 B_g 00.16336s,br343m v_5 341 B_g 00.08 v_5 379 B_u 108.530 v_4 380 A_u 95.400 v_4 397 B_u 129.310396sh395m v_4 398 A_g 00.62395m v_2 400 B_u 0.620 v_4 404 A_g 00.36 v_4 405 A_u 0.240 v_4 408 B_g 00.050407s v_2 409 A_u 2.090413sh v_4 448 B_g 013.80 v_1 v_1 541 B_g 00559s559s v_3 541 B_g 00 v_5 v_3 555 B_u 562.080559s559s v_3 578 B_u 657.320601m v_3 597 A_u 21.770601m v_3	326	Å	0	0.18				ν_5
341 B_g 00.16 $336s,br$ $343m$ v_5 341 B_g 00.08 v_5 379 B_u 108.530 v_4 380 A_u 95.400 v_4 397 B_u 129.310396sh395m v_4 398 A_g 00.62395m v_2 400 B_u 0.620 v_2 v_4 404 A_g 00.36 v_2 405 A_u 0.240 v_4 408 B_g 00.50 $407s$ v_2 408 B_g 00.05 $425sh$ v_4 448 B_g 013.80 v_1 541 B_g 00559s559s v_3 541 B_g 00 $559s$ $559s$ v_3 565 B_u 562.080 $59sh$ v_3 578 B_u 657.320 v_3 v_3 597 A_u 21.770 $601m$ v_3	335	Å	0	0.24				ν_5
341 B_g 0 0.08 v_1 379 B_u 108.53 0 v_4 380 A_u 95.40 0 v_4 397 B_u 129.31 0 $396 sh$ $395 m$ v_4 398 A_g 0 0.62 $395 m$ v_2 400 B_u 0.62 0 v_2 v_4 404 A_g 0 0.36 v_2 v_4 405 A_u 0.24 0 v_4 408 B_g 0 0.50 $407 s$ v_4 409 A_u 2.09 0 $413 sh$ v_4 448 B_g 0 0.55 $425 sh$ v_1 541 A_g 0 0.55 $559 s$ v_3 541 B_g 0 0 $559 s$ v_3 574 A_u 762.85 0 v_3 v_3 578 B_u 657.32 0 $601m$ v_3 597 A_u 21.77 0 $601m$ v_3 $596 sh$ v_3 v_3 v_3 v_3 597 A_u 21.77 0 $601m$ v_3	341	B _o	0	0.16	336s,br	343m		ν_5
379 B_u^5 108.530 v_4 380 A_u 95.400 v_4 397 B_u 129.310396sh395m v_4 398 A_g 00.62395m v_2 400 B_u 0.620 v_2 v_4 404 A_g 00.36 v_2 v_2 405 A_u 0.240 v_2 v_4 408 B_g 00.50407s v_2 409 A_u 2.090413sh v_4 448 B_g 00.55425sh v_1 541 A_g 013.80 v_1 v_1 541 B_g 00559s559s v_3 574 A_u 762.850 v_3 v_3 578 B_u 657.320580m v_3 597 A_u 21.770601m v_3	341	B	0	0.08	,			ν_5
380 A_u 95.40 0 y_4 397 B_u 129.31 0 $396h$ $395m$ y_4 398 A_g 0 0.62 $395m$ y_2 400 B_u 0.62 0 y_4 404 A_g 0 0.36 y_2 405 A_u 0.24 0 y_2 408 B_g 0 0.50 $407s$ y_2 409 A_u 2.09 0 $413sh$ y_4 448 B_g 0 0.05 $425sh$ y_2 541 A_g 0 0 $559s$ y_1 541 B_g 0 0 $559s$ y_3 574 A_u 762.85 0 y_3 578 B_u 657.32 0 $580m$ y_3 597 A_u 21.77 0 $601m$ y_3	379	B	108.53	0				ν_A
397 B_u 129.31 0 $396h$ $395m$ y_4 398 A_g 0 0.62 $395m$ v_2 400 B_u 0.62 0 y_4 404 A_g 0 0.36 v_2 405 A_u 0.24 0 v_4 408 B_g 0 0.50 $407s$ v_2 409 A_u 2.09 0 $413sh$ v_4 448 B_g 0 0.055 $425sh$ v_2 541 A_g 0 13.80 v_1 541 B_g 0 0 $559s$ $559s$ B_u 562.08 0 $559s$ $559s$ v_3 574 A_u 762.85 0 v_3 578 B_u 657.32 0 $580m$ v_3 597 A_u 21.77 0 $601m$ v_3 $596sh$ v_3 v_3 v_3	380	Au	95.40	0				ν_4
398 A_g 00.62395m p_2 400 B_u 0.620 p_4 404 A_g 0 p_2 405 A_u 0.240 p_4 408 B_g 00.50407s p_2 409 A_u 2.090413sh p_4 448 B_g 00.05425sh p_2 541 A_g 0 p_2 p_1 541 B_g 00 p_2 541 A_g 0 p_2 p_1 541 B_g p_1 p_2 p_1 543 B_u 562.08 p_2 p_3 574 A_u 762.85 p_2 p_3 578 B_u 657.32 p_2 p_3 597 A_u 21.77 p_1 605 B_u 336.80 p_2 p_3	397	B	129.31	0	396sh		395m	ν_A
400 B_u 0.620 r_d 404 A_g 00.36 r_2 405 A_u 0.240 r_2 408 B_g 00.50407s r_2 409 A_u 2.090413sh r_4 448 B_g 00.05425sh r_2 541 A_g 00554s r_1 565 B_u 562.080559s559s r_3 574 A_u 762.850 r_3 r_3 578 B_u 657.320580m r_3 597 A_u 21.770601m r_3	398	A	0	0.62		395m		ν_2
404 A_g 00.36 y_2 405 A_u 0.240 y_4 408 B_g 00.50 $407s$ y_2 409 A_u 2.090 $413sh$ y_4 448 B_g 00.05 $42ssh$ y_2 541 A_g 00 $554s$ y_1 541 B_g 00 $559s$ y_3 574 A_u 762.850 y_3 578 B_u 657.320 $580m$ y_3 597 A_u 21.770601m y_3 605 B_u 336.80 0 $59csh$ y_3	400	B	0.62	0				ν_A
405 A_u^3 0.24 0 r_4 408 B_g 0 0.50 $407s$ r_2 409 A_u 2.09 0 $413sh$ r_4 448 B_g 0 0.05 $42sh$ r_2 541 A_g 0 13.80 r_1 541 B_g 0 0 $559s$ r_3 565 B_u 562.08 0 $559s$ $559s$ r_3 574 A_u 762.85 0 r_3 r_3 578 B_u 657.32 0 $580m$ r_3 597 A_u 21.77 0 $601m$ r_3 597 B_u 336.80 0 $596sh$ r_3	404	A _o	0	0.36				ν_2
408 B_g 00.50407s p_2 409 A_u 2.090413sh p_4 448 B_g 00.05425sh p_2 541 A_g 013.80 p_1 541 B_g 00554s p_1 565 B_u 562.080559s559s p_3 574 A_u 762.850 p_3 p_3 578 B_u 657.320580m p_3 597 A_u 21.770601m p_3 605 B_u 336.800596sh p_3	405	Å	0.24	0				ν_A
409 A_u^5 2.09 0 $413sh$ μ_4^7 448 B_g 0 0.05 $42sh$ ν_2 541 A_g 0 13.80 ν_1 541 B_g 0 0 $554s$ ν_1 565 B_u 562.08 0 $559s$ $559s$ ν_3 574 A_u 762.85 0 ν_3 ν_3 578 B_u 657.32 0 $580m$ ν_3 597 A_u 21.77 0 $601m$ ν_3 605 B_u 336.80 0 $596sh$ ν_3	408	Ba	0	0.50	407s			ν_2
448 B_g 00.05425sh v_2 541 A_g 013.80 v_1 541 B_g 00554s v_1 565 B_u 562.080559s v_3 574 A_u 762.850 v_3 578 B_u 657.320580m v_3 597 A_u 21.770601m v_3 605 B_u 336.800596sh v_3	409	A	2.09	0			413sh	ν_A
541 A_g^s 0 13.80 v_1 541 B_g 0 0 $554s$ v_1 565 B_u 562.08 0 $559s$ $559s$ v_3 574 A_u $762.85s$ 0 v_3 v_3 578 B_u 657.32 0 $s80m$ v_3 597 A_u 21.77 0 $601m$ v_3 605 B_u 336.80 0 $596sh$ v_3	448	B _o	0	0.05	425sh			ν_2
541 B_g 00 $554s$ v_1 565 B_u 562.08 0 $559s$ $559s$ v_3 574 A_u 762.85 0 v_3 578 B_u 657.32 0 $s80m$ v_3 597 A_u 21.77 0 $601m$ v_3 605 B_u 336.80 0 $596sh$ v_3	541	A	0	13.80				ν_1
565 B_u 562.08 0 $559s$ $559s$ v_3 574 A_u 762.85 0 v_3 578 B_u 657.32 0 $580m$ v_3 597 A_u 21.77 0 $601m$ v_3 605 B_u 336.80 0 $596sh$ v_3	541	Ba	0	0		554s		ν_1
574 A_u 762.85 0 v_3 578 B_u 657.32 0 $580m$ v_3 597 A_u 21.77 0 $601m$ v_3 605 B_u 336.80 0 $596h$ v_3	565	Bu	562.08	0	559s		559s	ν_3
578 B_u 657.32 0 $580m$ v_3 597 A_u 21.77 0 $601m$ v_3 605 B_u 336.80 0 $596sh$ v_2	574	A	762.85	0				ν_3
597 A_u 21.77 0 601m v_3 605 B_u 336.80 0 596sh v_a	578	Bu	657.32	0	580m			ν_3
605 B. 336.80 0 596sh y ₂	597	Au	21.77	0	601m			ν_3
	605	B	336.80	0			596sh	ν_3
619 A ₁₁ 21.74 0 608 sh v_3	619	A	21.74	0			608sh	ν_3

 a^{a} s = strong, m = medium, w = weak, br = broad, sh = shoulder. b^{b} Lib = libration of $[AlF_{6}]^{3-}$ ion, AlF6 = translation of $[AlF_{6}]^{3-}$ ion, Na1 trans = translational mode of Na1, Na2 trans = translational mode of Na2.

Materials and methods

Cryolite, Na₃[AlF₆], (>99%) was purchased from Sigma-Aldrich (Gillingham, Dorset, UK) and used as received.

INS spectra were recorded at 5 K using the VISION³⁰ spectrometer at the Spallation Neutron Source (SNS) (Oak Ridge, Tennessee, USA). An empty aluminium sample can has been subtracted from the measured INS data. Infrared spectra (50–4000 cm⁻¹, 4 cm⁻¹ resolution, 64 scans) were recorded at room temperature with a Bruker Vertex 70 Fourier transform infrared spectrometer using a Bruker Platinum single reflection attenuated total internal reflection accessory. The FT-Raman spectrum was recorded at room temperature a from the sample inside a quartz cuvette with a Bruker MultiRam spectrometer using 1064 nm excitation (500 mW laser power and 1024 scans at

4 cm⁻¹ resolution). Variable temperature (13–300 K) Raman spectra were recorded with a modified Renishaw InVia spectrometer using 785 nm excitation.³⁹

Dispersion corrected periodic density functional theory (DFT-D) calculations were carried out with CASTEP (version 17.21).⁴⁰ On-the-fly generated norm conserving pseudopotentials with a plane-wave cut-off of 870 eV were used with the PBE⁴¹ functional with the Tkatchenko–Scheffler (TS) dispersion correction scheme⁴² within the generalized gradient approximation (GGA). Brillouin zone sampling of electronic states was performed on a $10 \times 8 \times 9$ Monkhorst–Pack grid (180 *k*-points). The starting structure was that determined here at 5 K. The equilibrium structure, an essential prerequisite for lattice dynamics calculations, was obtained by BFGS geometry optimization after which the residual forces were converged to

|0.00097| eV Å⁻¹. A second calculation that optimised both the lattice parameters and the geometry resulted in a 5.9% increase in the volume of the unit cell. Phonon frequencies were obtained by diagonalization of the dynamical matrix, computed using density-functional perturbation theory,⁴³ to compute the dielectric response and the Born effective charges, and, from these, the mode oscillator strength tensor and infrared absorptivity were calculated. Raman intensities were calculated by a finite displacement method.⁴⁴ In addition to the calculation of transition energies at zero wavevector, phonon dispersion was also calculated along high symmetry directions throughout the Brillouin zone. For this purpose, dynamical matrices were computed on a regular grid of wavevectors throughout the Brillouin zone, and Fourier interpolation was used to extend the computed grid to the desired fine set of points along the highsymmetry paths.⁴⁵ The atomic displacements in each mode, that are part of the CASTEP output, enable visualization of the modes in Materials Studio⁴⁶ to aid assignments and are also all that is required to generate the INS spectrum using the program ACLIMAX (version 6.0.0 LE).47 It is emphasised that, for the calculated spectra and dispersion curves shown, the transition energies have not been scaled.

Conclusions

In this work we have shown that the structure of cryolite is the same at 5 K as previously determined at room temperature.^{25–27} We have used a combination of vibrational spectroscopies to observe all of the modes for the first time, including those that are infrared and Raman forbidden under octahedral symmetry.

This work also allows some assignments to be made for elpasolite²⁰ and Cs₂Na[AlF₆].²¹ For the former, the Raman bands at 561, 330 and 138 cm⁻¹ are v_1 , v_5 and the librational mode, the infrared bands at 590, 401 and 238 cm⁻¹ are v_3 , v_4 and a Na⁺ translation. For Cs₂Na[AlF₆] the Raman bands at 520 and 364 cm⁻¹ are v_1 and v_2 , those at 316, 310 and 307 cm⁻¹ are from v_5 .

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

The authors gratefully acknowledge the invaluable assistance of Professor Kenneth Shankland (University of Reading) with the analysis of the diffraction data. This research benefited from the use of the VISION beamline at the Spallation Neutron Source, Oak Ridge National Laboratory (ORNL), which is supported by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy (DOE). Computing resources (time on the SCARF computer cluster for the CASTEP calculations) was provided by STFC's e-Science facility. This research has been performed with the aid of facilities at the Research Complex at Harwell, including the FT-Raman spectrometer. The authors would like to thank the Research Complex for access and support to these facilities and equipment.

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