The Infrared Transmission Spectrum of $KMnF_3$

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DEVIATION from the ideal cubic perovskite structure in the low-temperature modification of $KMnF_3$ is only sufficient to cause the i.r.-forbidden ν_4 (F_{2u}) mode to be observed. Force-constant data indicates that ν_4 occurs at higher frequencies than ν_2.

At temperatures above 184°K $KMnF_3$ adopts the ideal cubic perovskite structure of $SrTiO_3$[1] despite compression of the Mn^{2+} and F^- ions (Goldschmidt tolerance factor $=0{\cdot}88$). Group theoretical considerations predict that for compounds with the cubic perovskite structure there should be five triply degenerate modes of vibration ($4F_{1u} + F_{2u}$) of which one (F_{1u}) is an acoustic mode having zero energy at the centre of the Brillouin zone and hence does not contribute to the optical spectrum. Applying selection rules to the remaining modes, three are i.r. allowed while one (F_{2u}) is forbidden. The vibrational spectrum of $KMnF_3$ at temperatures above 184° K should therefore consist of three bands *only*.

The frequencies of the observed i.r. bands at various temperatures are given in Table 1. At 300° K all the frequencies were 15 cm.$^{-1}$ higher than those reported by Axe and Petit[2] but this is to be expected since these workers obtained their frequency values from a Kramers–Kronig analysis of reflectivity data. Only three bands were observed at 300° K and 188° K of which the two above 200 cm.$^{-1}$, ν_1 and ν_2, are assigned to internal modes of vibration of the MnF_6 octahedron while the band at 130 cm.$^{-1}$, ν_3, is a lattice mode. At 77° K ν_1 moves to higher frequencies, due to the decrease of the Mn–F bond distance associated with low-temperature contraction of the crystal lattice, and a new band appears at 265 cm.$^{-1}$ (also observed when the spectrum was recorded at 168° K but completely disappeared on warming the sample to 188° K).

TABLE 1

Vibrational frequencies (cm.$^{-1}$) for $KMnF_3$ *at various temperatures*

	300° K	188° K	168° K	77° K
ν_1	410	nr	nr	427
ν_2	212	212	208	208
ν_3	130	130	128	127
ν_4	ia	ia	263	265

nr, Not recorded.
ia, Inactive in i.r. spectrum.

It is known that at temperatures below 184° K $KMnF_3$ adopts an orthorhombic phase with the space group D_{2h}^{16}–*Pbnm* in which the MnF_6 octahedra are not distorted, but twist and tilt relative to each other.[3] A factor group analysis[4] based on this structure gives rise to the following external and internal i.r.-active representations

$$\Gamma \text{ (external)} = B_{1u} + 2B_{2u} + 2B_{3u}$$

$$\Gamma \text{ (internal)} = 6B_{1u} + 7B_{2u} + 7B_{3u}$$

indicating that twenty-five bands should be observed in the i.r. spectrum. This in no way correlates with our observed spectrum for the low-temperature modification of $KMnF_3$.

TABLE 2. *Calculated and observed frequencies (cm.$^{-1}$) for* KMF_3 (M = Mn, Ni, and Zn)

	$KMnF_3$		$KNiF_3$		$KNiF_3$[a]		$KZnF_3$		$KZnF_3$[a]	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
ν_1 (F_{1u})	411	410	448	447	455	446	423	424	435	430
ν_2 (F_{1u})	212	212	256	257	250	253	225	226	225	206
ν_3 (F_{1u})	132	130	155	155	144	153	143	144	134	142
ν_4 (F_{2u})	245	265[b]	294	ia	214	ia	258	ia	196	ia

[a] Calculated and observed frequencies from ref. 6. [b] Frequency from spectrum recorded at 77° K. ia, Inactive in i.r. spectrum.

We therefore suggest that since the displacements of the F and K atoms from cubic co-ordinates in the orthorhombic phase of $KMnF_3$ are extremely small (*ca.* 0·25 Å) and the MnF_6 octahedra are not distorted, the overall distortion from cubic crystal symmetry is insufficient to cause either interactions between the molecules in the unit cell or degeneracy splitting of the triply degenerate modes. However, the slight change in atomic co-ordinates will violate the *Oh* selection rules and the extra band at 265 cm.$^{-1}$ is therefore assigned to the i.r.-forbidden F_{2u} mode.

This assignment is supported by the calculated frequencies for the vibrational modes of cubic $KMnF_3$. The force constants were calculated by the method developed by Shimanouchi *et al.*,[5] with the potential function used by Nakagawa *et al.*[6] *K*, *H*, *F*, f_1 and f_2 are the M–F bond stretching, F–M–F angle bending, nearest non-bonded fluorine-atom repulsion, K · · · F interaction and K · · · M interaction constants respectively.

Symmetry co-ordinates approximating the normal co-ordinates obtained by Nakagawa *et al.*[6] for $KNiF_3$ were used. The variation of the force constants to obtain the best fit between the experimental and calculated frequencies was based on the additional constraints derived from the fact that the off-diagonal elements of the F-matrix, obtained with symmetry co-ordinates close to the normal co-ordinates, must be close to zero.

Using the above method, good agreement was obtained between the observed and calculated frequencies. However, the calculated (and observed) frequency for ν_4 was higher than that of ν_2 whereas Nakagawa *et al.*,[6] using a slightly different method of calculation, found the reverse to be true for the perovskite fluoride $KNiF_3$ and $KZnF_3$. The vibrational frequencies of $KNiF_3$ and $KZnF_3$ were, therefore, calculated using the method employed for $KMnF_3$ and an even closer agreement was thus obtained with the previously reported frequencies;[6] again the calculated frequencies for ν_4 in these compounds were found to be higher than those of ν_2.

The observed and calculated frequencies of the present study together with those reported for $KNiF_3$ and $KZnF_3$ by Nakagawa *et al.* are presented in Table 2.

The values of the force constants used in the present study are given in Table 3. It should be noted that the set of force constants given is not unique and an equally good agreement between the observed and calculated frequencies could be obtained using other force constants differing slightly from the set given. The differences are small, however, and the corresponding force constants in the different sets have the same order of magnitude.

TABLE 3. *Force constants in mdyne/Å for* KMF_3
(M = Mn, Ni, and Zn)

	$KNiF_3$	$KZnF_3$	$KMnF_3$
K (M–F)	0·739	0·697	0·627
H (F–M–F)	0·0755	0·054	0·0515
F (F · · · F)	0·077	0·055	0·053
f_1 (K · · · F)	0·138	0·119	0·097
f_2 (K · · · M)	0·01	0·02	0·01

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[1] K. Knox, *Acta Cryst.*, 1961, **14**, 583.

[2] J. D. Axe and G. D. Petit, *Phys. Rev.*, 1967, **157**, 435.

[3] O. Beckman and K. Knox, *Phys. Rev.*, 1961, **121**, 376.

[4] S. S. Mitra and P. J. Gielisse, *Progr. Infrared Spectroscopy*, 1964, **2**, 47. $KMnF_3$ with the space group D_{2h}^{16}–*Pbnm* contains a tetramolecular unit cell. The only element of symmetry containing invariant atoms apart from the identity *E* is the (*xy*) reflection plane. The representation from the factor group analysis for the Raman active modes is:

$$\Gamma = 7A_{1g} + 7A_{2g} + 5B_{2g} + 5B_{3g}$$

[5] T. Shimanouchi, M. Tsuboi, and T. Miyazawa, *J. Chem. Phys.*, 1961, **35**, 1597.

[6] I. Nakagawa, A. Tsuchida, and T. Shimanouchi, *J. Chem. Phys.*, 1967, **47**, 982.