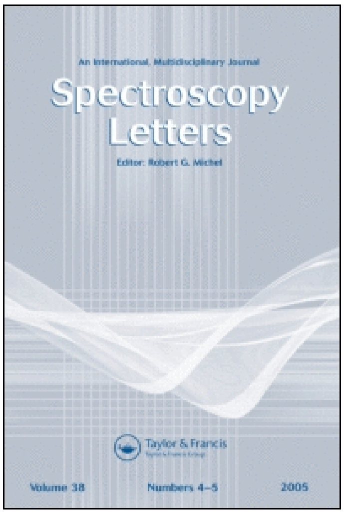

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A Refinement of the $InF_3.3H_2$ O Structure by the Use of NMR Data

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A REFINEMENT OF THE $InF_3.3H_2O$ STRUCTURE BY THE USE OF NMR DATA

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Bokij and Khodashova[I] derived from X-ray diffraction study and coordination considerations that $InF_3.3H_2O$ is pseudotetragonal with a=7.90, c=4.14 Å, z=2, space group PII2/n. In the $InF_3.3H_2O$ structure each indium atom is surrounded by six ligands (F and H_2O) to form nearly a regular octahedron. The adjacent octahedra have common apices forming infinite chains along the c-axis. Since the F and O scattering factors are much the same, the identification of F atoms and H_2O molecules was performed on the basis of coordination considerations. The bridges between In atoms were unambiguously identified as fluorine atoms (F_I). The four other ligands of each octahedron are two fluorine atoms (F_{II}) and two water molecules (H_2O_{II}) located in opposite apices of the equatorial plane of the octahedra (fluorines under fluorines in order to retain Z=2). The atoms which do not coordinate with indium atoms were estimated as oxygens of H_2O_I molecules due to their specific tetrahedral surrounding by F_{II} and H_2O_I of four neighbouring octahedra. In such a lamellar structure, the layers of H_2O_I and H_2O_{II} molecules interchange with the layers of F atoms. The existence of H_2O layers in the $InF_3.3H_2O$

structure, claimed by B. and K., is not in agreement with the fact that the crystals of this fluoride have needle-like habitus and do not exhibit excellent cleavage in the plane (110). In order to resolve this contradiction and find out the proton positions in the $InF_3.3H_2O$ structure, we have applied the NMR method.

The NMR spectra of ^{I}H and ^{19}F in polycrystalline $InF_3.3H_2O$ were recorded by JNM-3H-60 and JNM-4H-100 spectrometers with broad line attachments BL-2 in the fields 6.2, 9.2 and 23.4 kOe. All the spectra had no marked asymmetry, indicating the absence of a dispersion admixture and that of chemical shift anysotropy. The correctness of experimental second moments (S_2) was verified in comparison with the S_2 value for well studied fluoride CaF_2. The mean experimental second moments for $InF_3.3H_2O$ were: $S_2^F = 19.5$ and $S_2^H = 33.9$ Oe^2 (standard mean deviation ±3%) at -95°C and -130°C respectively.

Inasmuch as S_2^F was field independent, it was suggested that dipole-dipole interactions alone determined the second moments.

The experimental S_2^F were compared to those calculated by Van Vleck's[2] formula for the B. and K. model of the $InF_3.3H_2O$ structure. During these calculations the interactions F-F, F-H and F-In, as well as H-H, H-F and H-In, were taken into account, the protons being placed along the O-H...O and O-H...F bonds[I] with interproton distance in water molecules[3] of 1.60 Å. The calculated second moments were: $S_2^F = 11.9$ and $S_2^H = 41.0$ Oe^2. These do not agree with the experimental S_2. Thus the calculated S_2^F accounts only for about half of the experimental. The main reason for such a discrepancy is the appreciable disconnection of fluorines and water molecules in the B. and K. structure model. The disagreement will disappear if every other octahedron in this model is turned about the c-axis by 90°. In such a structure the H_2O layers are destroyed and F_{II}

atoms are no longer under each other, which likewise refers to H_2O_{II} molecules. Each F_{II} is placed under H_2O_{II} and vice versa (see figure). Near each F_{II} the new proton of H_2O_{II} appears at a short distance of 1.56 Å, increasing S_2^F by about 8 Oe^2.

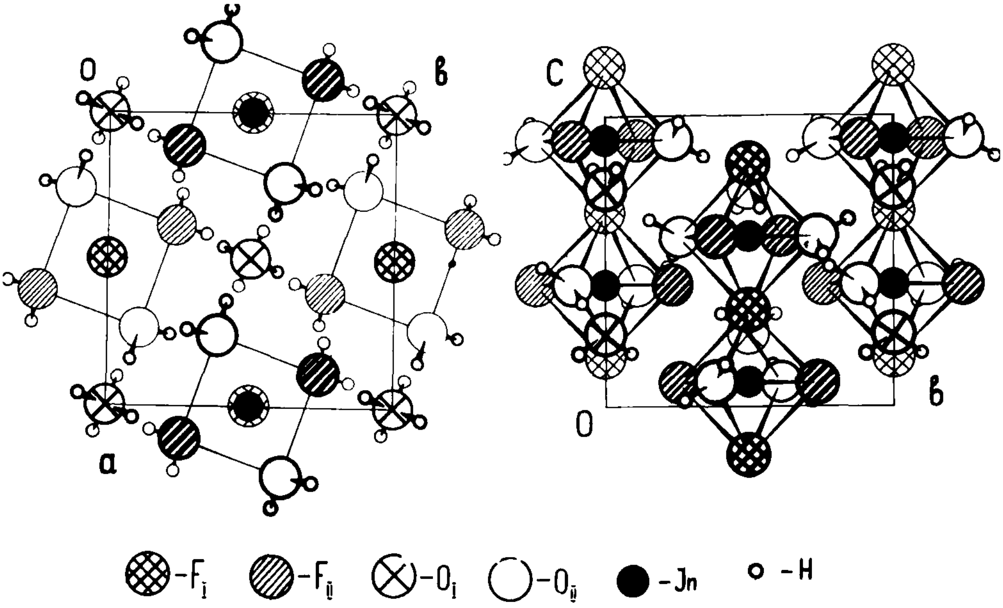

FIG. 1

Two projections of the refined $InF_3.3H_2O$ structure.

For such a structure the calculated second moments — $S_2^F = 20.1$ and $S_2^H = 35.4$ Oe^2 are in good agreement with the experimental. As can be seen, the proposed structure alteration is the only possible one compatible with the X-ray and NMR evidence.

This modified $InF_3.3H_2O$ structure is tetragonal, space group $P4_2/n$, with parameters c and Z twice as large as for the B. and K. model. The atomic coordinates, including protons, are listed in Table 1.

TABLE 1

Atomic coordinates in the $InF_3.3H_2O$ structure

Atom	Position	$\frac{x}{a}$	$\frac{y}{b}$	$\frac{z}{c}$
In	(e)	0	0.500	0.082
F_I	(e)	0	0.500	- 0.168
F_{II}	(g)	0.113	0.261	0.082
O_I	(f)	0	0	0.250
H_I	(g)	0.040	0.094	0.182
O_{II}	(g)	0.113	0.261	0.582
H_{II}	(g)	0.220	0.241	0.522
H_{III}	(g)	0.081	0.155	0.642

In the proposed structure the bond length $H_2O_I - F$ is 2.56 Å, and the $H_2O_{II} - H_2O_{II}$ distance is 3.58 Å, indicating the absence of hydrogen bonds between neighbouring H_2O_{II} molecules. The refinement of the $InF_3.3H_2O$ structure, made in this work, allowed for a satisfactory explanation of the needle-shaped form of the crystals studied.

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