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LETTERS TO THE EDITOR

A Powder Neutron Diffraction Investigation of the Solid Phases of IF_7

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The solid-state phases formed by IF_7 have been investigated by powder neutron diffraction. These measurements demonstrate that there are only three solid phases for this material at ambient pressure. An apparent transition at around 180 K reported in earlier NMR studies is due to the presence of an SiF_4 impurity whose melting point is close to this temperature. The structure of the intermediate phase II has been refined as a disordered model in space group *Abam*. Although the neutron diffraction study is more sensitive to the fluorine atom distribution than earlier X-ray diffraction studies, the high degree of thermal motion in this phase prohibits a definitive assessment of the molecular geometry of IF_7. This must await the solution of the structure of phase III, which has been indexed as primitive orthorhombic, with a = 8.506 Å, b = 8.821 Å, and c = 6.001 Å. The space group is a subgroup of *Abam*.

Introduction

The solid phases formed by IF_7 have been investigated with powder neutron diffraction. IF_7 is one of only two stable heptacoordinated AB_7 compounds, the other being ReF_7. Interest in the solid phases stems not only from a desire to characterize the behavior of these unique compounds, but also as a route for determining whether in the molecular structures the fluorine atoms adopt an ideal or distorted pentagonal bipyramidal arrangement. Since IF_7 undergoes several solid-state phase transitions, single crystals of the lowest-temperature ordered phase have been impossible to grow. Although we have not yet been able to solve the crystal structure of the lowest-temperature phase, our powder diffraction study gives new insight into the solid-state behavior of IF_7.

Burbank and Bensey (*1*) reported that solid IF_7 is body-centered cubic (phase I) between the melting point (278 K) and 153 K, where it undergoes a transition to phase II which has an A-centered orthorhombic cell. In the early sixties, based on the interpretation of a single-crystal X-ray diffraction study, the molecular geometry of IF_7 in this phase was a subject of debate between

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Burbank and Donohue (*1–6*). The former proposed that the molecular structure was distorted from D_{5h} symmetry with two longer, neighboring I–F bonds, whereas the latter argued that the experimental data available were not adequate to demonstrate that the symmetry was different from D_{5h}. There had also been earlier doubt concerning the symmetry of the crystal structure hinging on whether the molecules adopt a disordered arrangement in the space group *Abam* or an ordered one in the noncentrosymmetric subgroup *Aba*2.

Weulersse *et al.* (*7*) investigated the behavior of IF_7 between the melting point and 56 K with ^{19}F and ^{127}I NMR and NQR. In addition to the I–II cubic-to-orthorhombic transition, they reported evidence for two further solid-state transitions: a cubic-to-cubic transition at 180 K plus a transition from phase II to the lowest-temperature phase at 96 K.

The use of neutrons has a number of advantage for the investigation of the solid-state phases of IF_7. Owing to its low absorption for neutrons, a bulk sample can be easily handled in a silica-glass ampoule. In addition, the fluorine atom has a similar scattering power to iodine (*8*) (b_F = 5.654 fm versus b_I = 5.28 fm), in contrast to earlier X-ray studies where iodine is by far the dominant scatterer. Finally, with powder diffraction there are fewer problems associated with the breakup of single crystals in passing through the various phase transitions.

Experimental Procedure

IF_7 (about 25 g) was supplied by Speciality Chemical Services (SPECS), The Hague, The Netherlands, in a silica-glass ampoule which was loaded into a standard Institut Laue–Langevin (ILL) liquid-helium-cooled orange cryostat (*9*). Diffraction patterns with λ = 2.52 Å were collected on the high-flux diffractometer D1B equipped with a 400-wire position-sensitive detector covering the 2θ-range 5° to 85° with data recorded every 2 min (Fig. 1). The sample temperature was scanned repeatedly between 1.5 and 270 K. High-resolution diffraction patterns of the various phases of IF_7 were measured on the powder diffractometers D1A (with λ = 2.99 and 1.909 Å)

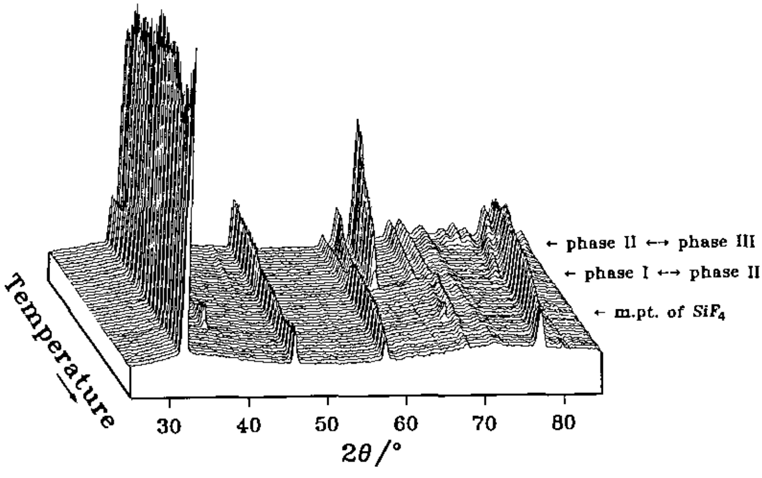

FIG. 1. The evolution of the diffraction pattern of IF_7 on cooling, taken on D1B with λ = 2.52 Å.

and D2B (with λ = 1.594 Å) using a step size of 0.05°.

Results

To ascertain the phase-change behavior, the multidetector powder diffractometer D1B has been used to study the evolution of the diffraction pattern with temperature (Fig. 1). At first glance, the four phases detected by Weulersse *et al.* (*7*) seem to be present: at high temperature, the body-centered cubic phase I is followed by the appearance of a few additional peaks at 180 K, where a small discontinuity in the fluorine longitudinal relaxation time was observed. At about 150 K the A-centered orthorhombic phase II appears, and below 100 K the growth of further peaks is evident.

The reflections appearing at 180 K cannot be indexed in conjunction with the ones arising from the other phases. They can, however, be indexed with the I-centered cubic cell of SiF_4 (*10*) which melts at 183 K or sublimes at 177.5 K (*11, 12*). Weulersse *et al.* used pyrex tubes and we used silica-glass ampoules as sample containers. Catalytic amounts of water promote chain reactions such as

$$2IF_7 + 2H_2O \rightarrow 2IOF_5 + 4HF$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O,$$

resulting in the conversion of SiO_2 from the sample holder to SiF_4. Refinements of the structure of the orthorhombic phase II at 120 K from the data collected on D2B (see below) confirmed the presence of this impurity by including SiF_4 (≈0.7% by weight) as a second phase. Thus at ambient pressure IF_7 has only three solid-state phases.

The structure of phase II at 120 K was refined from D2B data using the Rietveld (*13*) program PROFIL (*14*) with SiF_4 included as a second phase. Several different models were investigated for this phase which was refined in terms of (a) an ordered IF_7 molecule, space group *Aba*2; (b) an IF_7 molecule having orientational disorder, space group *Abam*, and with unconstrained thermal parameters for all atoms; and (c) as for the latter, but with thermal parameters constrained by TLS to a rigid-molecule description.

The best fit to the data is the unconstrained disordered model (b) and is shown in Fig. 2. Final parameters are given in Table I. From the plot of the thermal ellipsoids, Fig. 3, it can be seen that the IF_7 molecule is disordered; the equatorial fluorine atoms form a toroidal distribution and perform large-amplitude librations. The large atomic-displacement parameters and the poorer fit to the data with the TLS constraint is indicative of large vibrational motion leading to jump rotations and intramolecular exchange of the fluorine atoms consistent with the NMR and NQR results. Large vibrational amplitudes of the fluorine atoms have been observed in salts of IF_6^-

TABLE I

FINAL PARAMETERS FOR THE REFINEMENT OF THE STRUCTURE OF PHASE II OF IF_7 FROM NEUTRON DIFFRACTION DATA COLLECTED ON D2B AT 120 K WITH λ = 1.594 Å

Atom	Site symmetry	*X*	*Y*	*Z*	*B*(iso)	*N*
I	4*a* ..2/*m*	0	0	0	1.93(5)	4
F(1)	8*d* ..2	0	0	0.279(2)	0	4
F(2)	16*g* 1	0.069(1)	0.086(1)	−0.260(1)	0	8
F(3)	16*g* 1	0.1129(6)	0.1550(6)	0.074(2)	0	8
F(4)	8*f* ..*m*	0.1660(3)	−0.1167(3)	0	0	8

Atom	*B*[1,1]	*B*[2,2]	*B*[3,3]	*B*[1,2]	*B*[2,3]	*B*[3,1]
F(1)	26(2)	8(1)	1.7(3)	−0.9(9)	0	0
F(2)	17(1)	9.8(9)	7.8(6)	8.7(8)	5.9(6)	7.1(8)
F(3)	5.4(2)	4.7(2)	18(2)	−2.9(1)	−5.2(5)	−0.9(4)
F(4)	3.3(1)	4.5(1)	7.5(2)	1.9(1)	0	0

Note. Space group *Abam* (No. 64), a = 8.6745(4) Å, b = 8.8320(4) Å, c = 6.1433(3) Å. $Z = 4$, ρ_{calc} = 3.667 g cm^{-3}, R_{wp} = 7.2%, R_{exp} = 2.60%, $R_I(IF_7)$ = 6.6%, $R_I(SiF_4)$ = 8.5%.

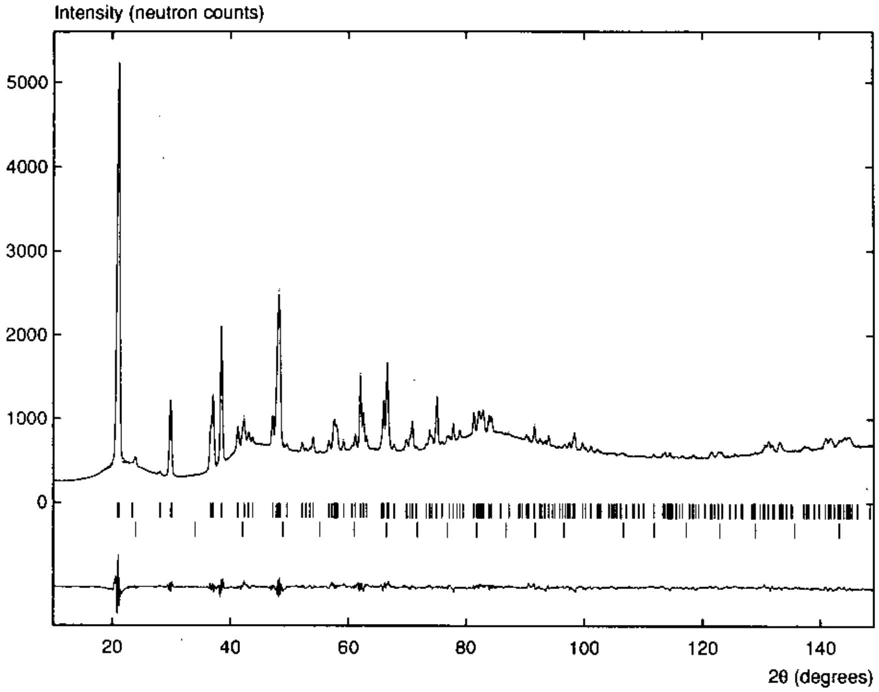

FIG. 2. Observed, calculated, and difference profiles for IF_7 phase II at 120 K measured on D2B with $\lambda = 1.594$ Å.

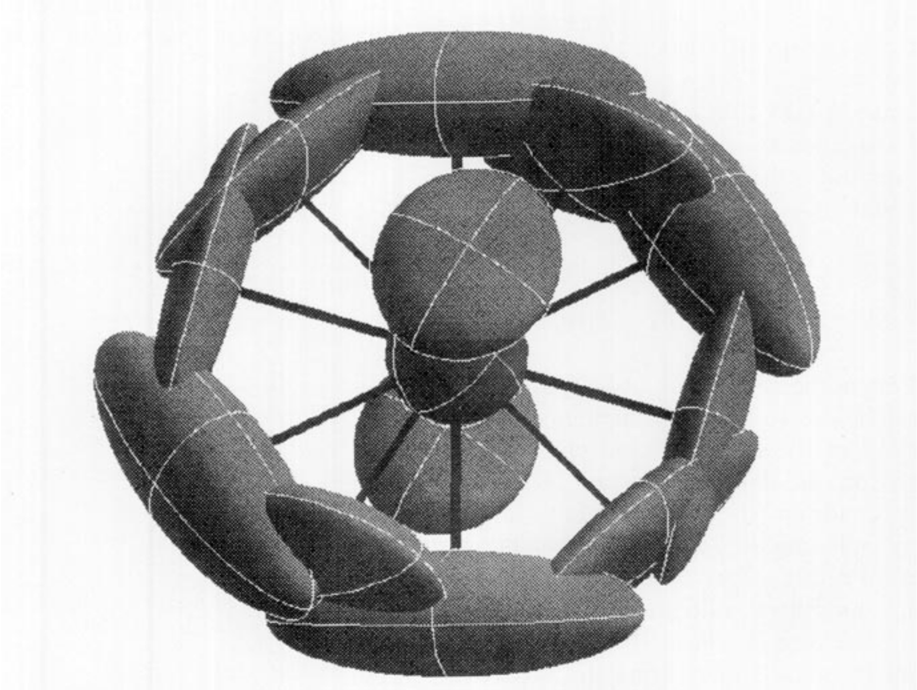

FIG. 3. Ellipsoids of 50% probability showing the disorder and the large-amplitude librations of the IF_7 molecule in phase II (*17*). The equatorial fluorine atoms form a torroidal distribution of scattering density perpendicular to the *ab*-plane containing the two axial (F(4)) fluorine atoms.

and IF_8^- (*15*). The average I–F bond length corrected for librational motion is 1.858 Å, in good agreement with the value of 1.837(2) Å determined by gas-phase electron diffraction (*16*). The molecule appears distorted from D_{5h} symmetry. However, despite the higher sensitivity available using neutrons in the determination of the fluorine scattering density, we do not feel that the distortion from D_{5h} symmetry is proven by this study. With such large-scale molecular motion, an accurate description of the thermal parameters is hard to achieve, and this difficulty can easily be translated into errors in the positional parameters. The definitive solution must await the determination of the structure of phase III.

We have made a significant step toward achieving this goal. From data collected on the powder neutron diffractometer D1A ($\lambda = 2.99$ Å) at 1.5 K, the lowest-temperature phase of IF_7 has been indexed as primitive orthorhombic with $a = 8.506$ Å, $b = 8.821$ Å, and $c = 6.001$ Å. The anisotropic contraction of the unit cell and the decrease in symmetry are consistent with orientational ordering of the IF_7 molecules at the transition. The space group is undoubtedly a subgroup of *Abam*, but a solution has so far proven elusive. Complementary information from other techniques, such as molecular mechanics simulations or spectroscopic studies, may be beneficial in arriving at a solution.

References

1. R. D. Burbank and F. N. Bensey, *J. Chem. Phys.* **27,** 981 (1957).
2. J. Donohue, *J. Chem. Phys.* **30,** 1618 (1959).
3. R. D. Burbank, *J. Chem. Phys.* **30,** 1619 (1959).
4. L. L. Lohr and W. N. Lipscomb, *J. Chem. Phys.* **36,** 2225 (1962).
5. R. D. Burbank, *Acta Crystallogr.* **15,** 1207 (1962).
6. J. Donhue, *Acta Crystallogr.* **18,** 1018 (1965).
7. J. M. Weulersse, J. Virlet, and P. Rigny, *Mol. Phys.* **38,** 923 (1979).
8. L. Koester and H. Rauch, IAEA Report No. 2517/RB, International Atomic Energy Agency, Vienna (1983).
9. P. Suttling, "Sample Environment Equipment," ILL report, Grenoble, France (1992).
10. M. Atoji and W. N. Lipscomb, *Acta Crystallogr.* **7,** 597 (1954).
11. M. Windholz (Ed.), "The Merck Index," p. 1100, Merck and Co., Inc., Rahway, New Jersey (1976).
12. K. H. Hellewege and A. M. Hellwege (Eds.), "Landolt–Börnstein Numerical Data and Functional Relationships in Science and Technology," New Series, Group III, "Crystals and Solid-State Physics," Vol. 7, Part a, p. 48, Springer-Verlag, Berlin (1973).
13. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969).
14. J. K. Cockcroft, PROFIL, A Rietveld refinement program with chemical constraints, Institut Laue–Langevin, Grenoble, France (1990).
15. A. R. Mahjoub and K. Seppelt, *Angew. Chem. Int. Ed. Engl.* **30,** 323 (1991); **30,** 876 (1991).
16. W. J. Adams, H. Bradford Thompson, and L. S. Bartell, *J. Chem. Phys.* **53,** 4040 (1970).
17. Plot prepared using the program CERIUS from Molecular Simulations, Cambridge CB4 4WS, U.K.