The Order–Disorder Transition of Stage-1 Graphite Fluoroarsenate Intercalation Compound: the Structure of $C_{16}AsF_6$ below 170 K

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Guinier–Simon X-ray diffraction data for the stage-1 graphite fluoroarsenate intercalation compound, $C_{16}AsF_6$, indicate that it undergoes an order–disorder transition at *ca.* 170 K and has the F-ligands of AsF_6^- anions nestled in adjacent three-fold sets of carbon-atom hexagons of the enclosing graphite layers with three-dimensional (3-D) ordering of the anions in the low-temperature phase.

Significant differences have been observed between the room temperature Debye–Scherrer (DS) powder diffraction pattern for the stage-1 graphite–AsF_5 intercalation compound, C_8AsF_5[1,2] (*c*-axis repeat distance, $I_c \simeq 8.0$ Å) and that for the stage-1 compound, $C_{\sim 14}AsF_6$ (graphite hexafluoroarsenate).[3–5] The typical diffraction patterns are shown in Fig. 1. The former is made by the reaction of graphite with AsF_5 and the latter with AsF_5–F_2 or O_2AsF_6. The latter is characterized by the very small I_c ($\simeq$7.6 Å) and the unusual features, *i.e.* the appearance of a low angle halo [halo A in pattern (*b*) in Fig. 1] and two peaks (B and C), and the absence of (100) and (10*l*) reflections. These features suggested[3–5] that the F-ligands of AsF_6^- are nestled in contiguous three-fold sets of C-atom hexagons of the graphite. A model has been proposed[3,4] in which staggered C-layers are randomly stacked (*e.g.* A|B-|A|C|B|..., where | denotes intercalate layer) with short-range ordering or domain structure of nestled AsF_6^- anions within each gallery. All the unusual features of the pattern for the $C_{\sim 14}AsF_6$ sample with $I_c \simeq 7.6$ Å are explained by the nestling of AsF_6^-. Ideally, the most dense arrangement of AsF_6^- has the composition $C_{14}AsF_6$ (see Fig. 2). However, the large anisotropic thermal parameters (U_{11}) for As and F atoms (0.25 and 0.50 Å^2, respectively) needed for the simulation had made the nestling of AsF_6^- less convincing. In order to obtain more definite evidence for the nestling, Guinier–Simon X-ray diffraction photographs[6] were obtained for the stage-1 graphite fluoroarsenate intercalation compound, C_xAsF_6, in the temperature ranges of 300–390 K[4] and 290–80 K. We report here the results of the 290–80 K photograph.

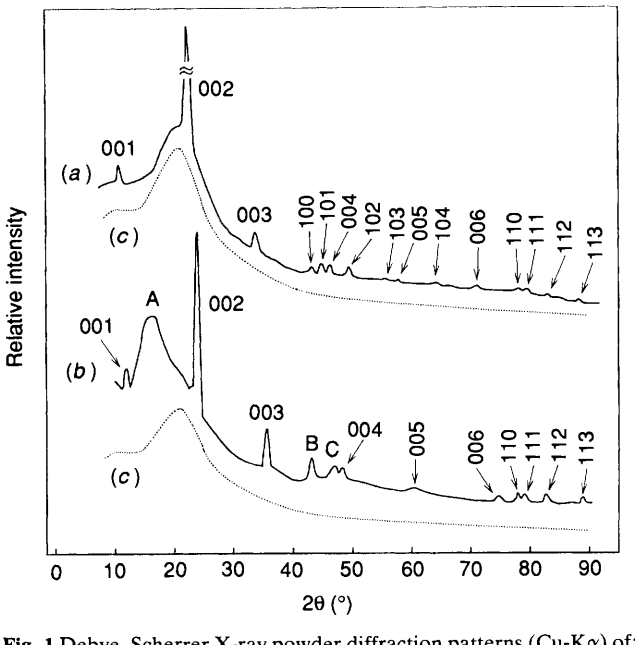

Fig. 1 Debye–Scherrer X-ray powder diffraction patterns (Cu-Kα) of: (*a*) C_8AsF_5 (I_c = 8.0 Å), (*b*) $C_{14}AsF_6$ (I_c = 7.6 Å) and (*c*) quartz capillary background

The Guinier–Simon photograph was obtained for a sample with the nominal composition of $C_{18.9}AsF_6$ (see below) using Cu-$K\alpha_1$ radiation in the temperature range of 290–80 K. The sample was prepared by the reaction of graphite powder (Union Carbide SP-1) with AsF_5 and F_2. The reaction was run for 6 h at room temperature and the composition was determined by gravimetry assuming the formula C_xAsF_6. Previous studies[3,4] had demonstrated that, if the I_c-distances of samples prepared in this way were less than *ca.* 7.6 Å, their compositions were $C_{\sim 14}AsF_{6.0}$. In the present work some loss of graphite and/or product from the reaction cell was observed during the manipulation. Therefore, the composition of the sample should be C_xAsF_6 ($14 \leqslant x \leqslant 18.9$). The diffraction

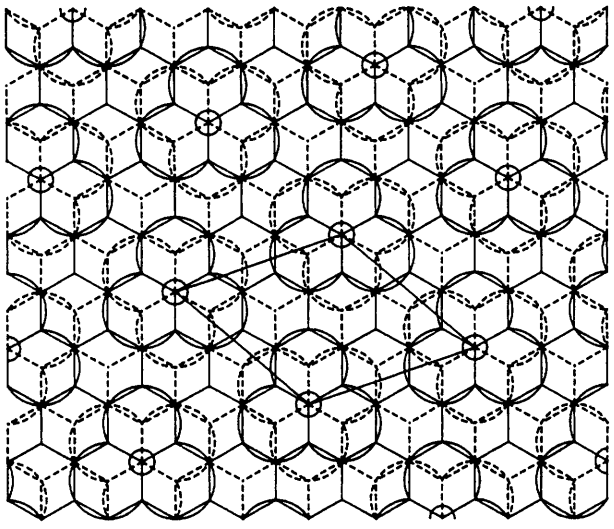

Fig. 2 In-plane structure of $C_{14}AsF_6$

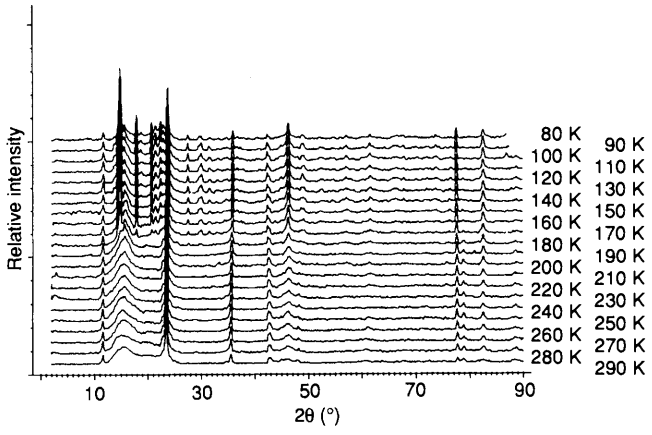

Fig. 3 Temperature dependence of X-ray powder diffraction pattern of C_xAsF_6 ($14 < x < 18.9$) between 80–290 K

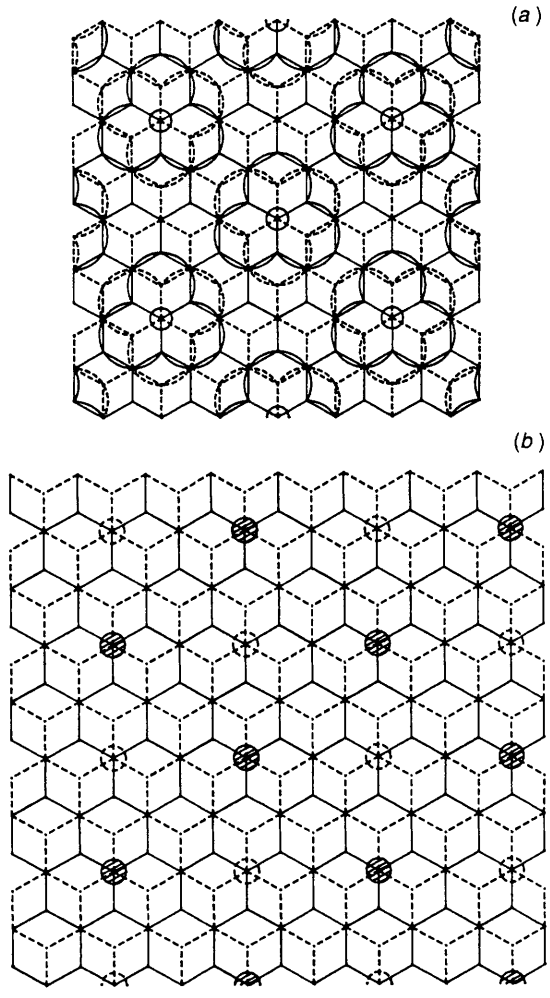

Fig. 4 Structure of $C_{16}AsF_6$: (*a*) in-plane structure of $C_{16}AsF_6$ (nestling of AsF_6^- is shown) and (*b*) positions of As-atoms (open and hatched circles belong to different galleries)

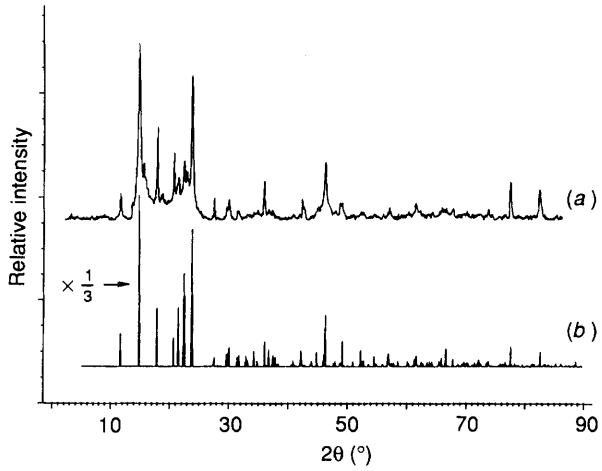

Fig. 5 (*a*) Observed and (*b*) calculated X-ray diffraction patterns for $C_{16}AsF_6$ at 90 K

patterns read by an image scanner[7] at intervals of 10 K are shown in Fig. 3.

As the temperature is lowered, super-lattice reflections appear, indicating an order–disorder transition in the AsF_6^- arrangement and, consequently, in the carbon layer stacking sequence at *ca.* 170 K. The reflection pattern at lower temperature has been satisfactorily simulated by a nestled $C_{16}AsF_6$ model. The in-plane arrangement of AsF_6^- for the model is shown in Fig. 4(*a*). The pseudo-face-centred orthorhombic arangement of AsF_6^- requires the carbon-layer stacking sequence to be A|B|A|B|, [see Fig. 4(*b*)]. The space group is *C*2/*m*, and the lattice constants† are $a = 4 \times a$(graphite) = 9.8 Å, $b = 2\sqrt{3} \times a_g = 8.5$ Å, $c = 2 \times I_c = 14.9$ Å and $\beta = 90°$ at 90 K. The observed and calculated diffraction patterns at 90 K are shown Fig. 5. The fit is satisfactory, although there are some discrepancies: (*i*) some of the observed lower angle reflections do not appear in the simulated pattern, (*ii*) the relative intensities of some of the reflections are reversed, (*iii*) in the simulated pattern most of the super-lattice reflections are much stronger than the others, and (*iv*) in the observed pattern the graphite (100) reflection is shifted towards a higher angle. These discrepancies indicate that even at 90 K there exist some disorders in the 3-D arrangement of AsF_6^- and in the carbon layer stacking sequence.[3,4] However, the pattern on the whole is simulated well by the $C_{16}AsF_6$ model.

The nestling of AsF_6^- is geometrically justified as follows. The As–F distance in the AsF_6^- ion is *ca.* $\sqrt{3}$ Å.[8,9] Then, assuming that the ion is a regular octahedron with d(As–F) = $\sqrt{3}$ Å. the neighbouring F–F distance is $\sqrt{6}$ Å, which is essentially the same as the lattice constant, a, of graphite. In

† In taking the Guinier–Simon photographs no internal standard was used to aid precise lattice constant determination. The second decimal digits in Å were rounded.

the present model, the F-atoms are placed at the centre of the carbon hexagons in the *ab*-projection and 1.0 Å above and below the central As-atom along the *c*-axis direction. The thermal parameters were not used, *i.e.* they were set equal to zero.

Some comments need to refer to the composition of the sample. Although the ideal composition of the ordered structure is $C_{16}AsF_6$,‡ the disordered phase need not have the exact composition $C_{16}AsF_6$ to produce the observed diffraction pattern.§ It is reasonable to assume that, as the temperature is lowered, the ordered phase $C_{16}AsF_6$ 'crystallizes out' in the bulk of the sample leaving the rest of the sample having a composition different from $C_{16}AsF_6$, thus, allowing the overall composition to be different from $C_{16}AsF_6$. This is probably one of the reasons why some disorders persist even in the low-temperature phase.

‡ Not only the composition but also the formulation, $C_{16}^{+}AsF_6^{-}$, warrant some comments. Chemical analyses done on the vacuum stable samples made by the reaction of graphite with AsF_5, AsF_5–F_2, or O_2AsF_6 have shown that their compositions are $C_xAsF_{6.0}$ with x varying between 13–20 (refs. 3 and 4). Therefore, although the physical ionic salt limit (charge transfer limit) in graphite–fluoroarsenate can be C_{20}^{+} (J. W. Milliken and J. E. Fischer, *J. Chem. Phys.*, 1983, **78**, 5800), the chemical formulation, $C_{16}^{+}AsF_6^{-}$, should be valid. The present structural study also supports this.

§ When the compositions of samples are C_xAsF_y ($x < 14$, $5 \leq y \leq 6$), then the I_c-distances are *ca.* 8.0 Å, and their diffraction patterns look essentially the same [see Fig. 1(*a*)].

Apparently, strong Coulombic interaction among AsF_6^{-} ions controls the structure of $C_{16}AsF_6$, which was expected but not clearly observed in $C_{8n}AsF_5$.[10] This interaction probably renders the $C_{14}AsF_6$ structure,[3,4] which has the most dense arrangement of nestled AsF_6^{-} ions, unstable, since a torque is exerted on each AsF_6^{-} by the electric field produced by the other AsF_6^{-} ions in the same gallery (see Fig. 2).

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References

1 E. R. Falardeau, G. M. T. Foley, C. Zeller and F. L. Vogel, *J. Chem. Soc., Chem. Commun.*, 1977, 389.
2 E. R. Falardeau, L. R. Hanlon and T. E. Thompson, *Inorg. Chem.*, 1978, **17**, 301.
3 F. Okino, PhD Thesis, 1984, University of California, Berkeley, California.
4 F. Okino and N. Bartlett, *J. Chem. Soc., Dalton Trans.*, in the press.
5 N. Bartlett, F. Okino, T. E. Mallouk, R. Hagiwara, M. Lerner, G. L. Rosenthal and K. Kourtakis, *Advances in Chemistry No. 226*, 1990, 392.
6 A. Simon, *J. Appl. Crystallogr.*, 1971, **4**, 138.
7 F. Okino, *Tanso* (Jpn., *Carbon*), 1991, 166.
8 N. Bartlett, B. G. DeBoer, F. J. Hollander, F. O. Sladky, D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 1974, **13**, 780.
9 J. A. Ibers, *J. Acta Crystallogr.*, 1956, **9**, 967.
10 D. Vaknin and J. E. Fischer, *Synth. Met.*, 1988, **23**, 101.