Electron diffraction studies of supersonic jets. V. Low temperature crystalline forms of SF_6, SeF_6, and TeF_6

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(Received 31 May 1983; accepted 17 June 1983)

Condensation of SF_6, SeF_6, and TeF_6 in nozzle flows with inert carrier gases produces microcrystals of these materials. All form the higher temperature body-centered cubic structure at higher partial pressures of hexafluoride. At lower partial pressures and colder nucleation conditions a lower symmetry form of each has been produced. Electron diffraction powder patterns are consistent with the space group *Pnma* to which metal hexafluorides of UF_6 type belong. Low temperature phases of the present materials differ from those of the metal compounds, however, in being less dense than the cubic forms. Aspects of the gas dynamics affording a control over nucleated species are briefly discussed.

INTRODUCTION

Hexafluorides of group VI elements, like most metal hexafluorides, form plastic crystalline body-centered cubic structures.[1] Metal hexafluorides all have lower temperature ordered phases known to be orthorhombic.[2,3] A similar lower temperature phase of SeF_6 has been observed by x-ray diffraction,[1] and SF_6 and TeF_6 have been shown by nuclear magnetic resonance experiments to undergo transitions to a lower temperature, ordered phase. Little more is known about the resulting materials.[1,4] A Monte-Carlo calculation modeling the effect of cooling the body-centered cubic lattice of SF_6 led to a triclinic, but nearly orthorhombic ordered phase.[5] X-ray powder data indicates that orthorhombic SeF_6 has a lower density than the higher temperature cubic phase, in contrast to the metal hexafluorides. Cell constant ratios deviate from those of the metallic compounds as well.

In several prior homogeneous nucleation experiments,[6,7] SF_6 seeded into inert carrier gases has been found to crystallize in the cubic form. In one study, this phase was reported to have been observed by electron diffraction at temperatures apparently below the 95 K transition temperature.[8] No lower symmetry phase was noted. As part on our investigation of the sizes and temperatures of clusters formed in supersonic expansions of gas mixtures under various conditions, we also saw cubic crystallites of SF_6 with temperatures of about 130 K in expansions of 12% SF_6 in neon.[8] When we attempted to produce colder crystals, especially near or below the transition temperature, our electron diffraction patterns began to display extra lines characteristic of a lower temperature phase. This prompted our interest in the related compounds SeF_6 and TeF_6, for which we have found similar behavior. Results of these studies are described in the following section.

EXPERIMENTAL

The subject gases SF_6(99.99%, Air Products Ltd.), SeF_6, and TeF_6(99.8%, NOAH Chemical Division) were used as received and mixed with helium, neon, or argon (>99.95%, Air Products Ltd.) in mole fractions 0.01 to 0.12. Procedures and times for mixing assured a uniform composition. Representative expansion conditions are given in Table I. The focused 40 keV electron beam ($\lambda = 0.06$ Å) had a diameter of 0.03 mm at the photographic plate, ~216 mm from its intersection with the subject jet. Gas mixtures at room temperature were expanded through our glass nozzle No. 6, a conical Laval nozzle (Table II) with 0.128 mm throat, 30 mm length, and 1.9 mm exit at a distance of 12 mm from the electron beam. A single skimmer, described in Ref. 8, intercepts gases expanding off axis. We have

TABLE I. Expansion and electron diffraction exposure conditions for nonmetal hexafluoride–inert carrier mixtures. All runs were through the glass nozzle No. 6 and exposures taken with the r^4 sector using a beam current of 18 nA.

Subject	Mole fraction	Carrier	P_{total} (bar)	Exp. time (s)	Plate No.	Crystal types[a]
SF_6	0.06	Ne	4.8	0.5	58	c
SF_6	0.06	Ar	4.8	0.4	66	c
SF_6	0.03	Ar	4.8	0.4	68	$c+o$
SeF_6	0.06	Ne	3.4	0.5	88	c
SeF_6	0.06	Ar	4.8	0.4	79	$c+o$
TeF_6	0.09	Ne	7.1	0.3	974	$c+o$

[a] c—represents body-centered cubic; o—orthorhombic.

TABLE II. Coefficients in the polynomial equation describing the diameter of the glass No. 6 nozzle as a function of distance $D(x) = \sum d_n x^{n-1}$.

d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7
0.015 582	0.006 119	0.113 260	−0.136 983	0.060 884	0.007 573	−0.010 990	0.001 863

constructed a small rotating sector, designated the r^1 sector, the open portion of which has an angular opening nearly proportional to the sector radius. The effective range of this sector is $s = 0.8-4.0$ Å^{-1} (scattering angle 0.4°−2.2°). This provides well leveled data substantially inside the angular range of our r^2 sector ($s = 2.2-12$ Å^{-1}) and easily records the inner diffraction features of liquids and crystals. Electron diffraction patterns were recorded on Kodak 4×5 in. medium projector slide plates. Typical exposures were 1.0 s or less with a beam current of 18 nA.

Supersonic expansions produced narrow beams of randomly oriented crystallites or clusters by homogeneous nucleation. Diffraction patterns show Debye−Scherrer powder rings indexable by standard methods (Fig. 1). The camera height was established by recording neat
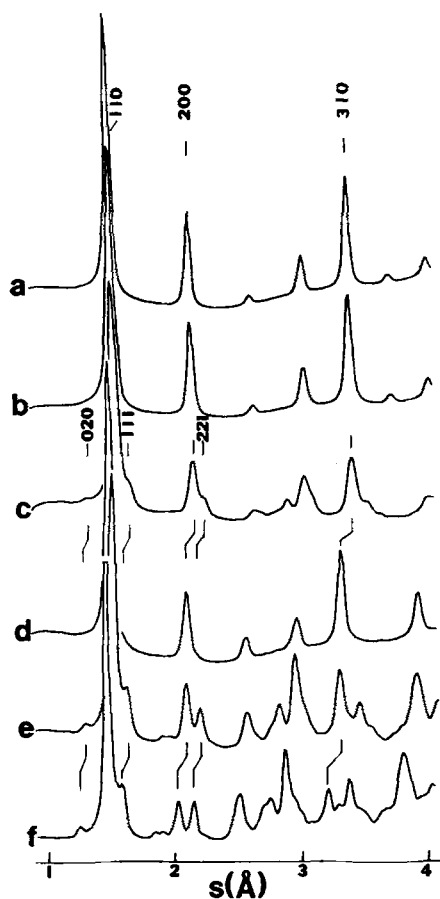

FIG. 1. Relative leveled intensities from electron diffraction plates recorded using the r^1 sector. Expansion conditions are given in Table I. (a) Plate 58, (b) Plate 66, (c) Plate 68, (d) plate 88, (e) plate 79, (f) plate 974. Reflection assignments above are above (a) for a body-centered cubic, above (c) for a primitive orthorhombic lattice.

CCl_4 gas diffraction patterns and standardizing against the 1.767 Å C−Cl length.[9] Average crystal size was estimated from the breadths of the diffraction rings[10] when the pattern was simple enough to permit such an analysis. Temperatures of the cubic phases of SF_6 and SeF_6 were inferred from the cubic cell constant and the linear coefficients of expansion for SF_6 (3.0×10^{-4}/deg[6]); SeF_6 (3.6×10^{-4}/deg[1]). Coefficients of expansion have not been measured for TeF_6.

RESULTS AND DISCUSSION

The subject gases SF_6, SeF_6, and TeF_6 readily condense while flowing through our glass Laval nozzle No. 6 in small mole fractions with inert carrier gases helium, neon, and argon. Electron diffraction patterns suggest particle sizes in the range 50–110 Å. Crystallites with these dimensions would contain 700–2500 molecules. Because very small clusters can show cell parameters shortened in comparison with the bulk values, temperatures of such clusters might be underestimated in some cases. Our crystallites are large enough to reduce this effect below our uncertainties. Our inferences of temperature are limited more by the lack of information about coefficients of thermal expansion. Nevertheless, the measured cell parameters are useful for comparisons of relative temperatures of the condensates.

One striking aspect of the nucleation experiments is the readily controllable production of more than one phase of the subject material. Under suitable conditions, both the higher temperature and little studied lower temperature phase of the group VI hexafluorides appear together in the nozzle effluent. These lower temperature forms can be indexed after the lower symmetry pattern of UF_6, which crystallizes in the orthorhombic system, space group Pnma[3].

Several general observations about the nucleation conditions deserve mention. For SF_6, only the cubic phase is seen when helium or neon carriers are used in the pressure range studied (Table I). Cell constants of the condensates for these runs are greater than or near the value 5.78(1) Å[11] corresponding to the phase transition ($T \sim 93$ K). Condensates of SF_6 in helium or neon produced in our nozzles have temperatures in the range 130–100 K. Argon carrier gas yields cubic SF_6 with cell constants just above the transition value in expansions at the higher mole fractions of SF_6. Decreasing the mole fraction delays condensation in the nozzle and results in smaller and colder crystallites. When cell parameters reach the transition value to within the (increasing) experimental uncertainties, diffraction patterns begin to show contamination by the lower symmetry phase. Additionally, in experiments with argon carrier gas at the lowest mole fractions of SF_6, argon

clusters are also produced. Although the diffraction lines of the argon clusters overlap the subject condensate features experiments with neat argon or argon with low mole fractions of certain other seeded materials produce similar but easily resolved diffraction rings. Argon clusters correspond to face-centered cubic crystallites 50 Å in diameter at temperatures below 70 K. Our experiments are consistent with earlier observations[6,12] and model calculations[7] on the effect of seeded mole fraction upon the apparent size of the subject crystallites; decreasing mole fraction tends to produce smaller crystallites. Effects of the molecular weight of the carrier gas on the crystal temperature have been less clear in prior studies with Laval nozzles. Mach numbers at the nozzle exit have been reported[7] to be higher with argon than helium, presumably because of the higher Reynolds number and, hence, lower friction. This implies lower exit temperatures. Temperatures of clusters during nucleation, growth, and subsequent lifetime cannot be directly correlated with exit temperature, however, among other reasons because of the substantial disparity between temperatures of crystallites and the gaseous medium around them (see below). Our experiments indicate that argon produces lower condensate temperatures and induces crystallization of the lower temperature phase more readily than do helium or neon. A contributing factor is undoubtedly the higher thermal accomodation coefficient[13] of argon whose mass more closely matches that of the hexafluorides studied.

In experiments with appreciable contributions from the low symmetry phase, we have yet to observe any significant decrease in the cell constant of the cubic phase below that of the 93 K transition temperature. In one previous study of SF_6 crystals generated in similar nucleation experiments, the cubic phase had been reported to have appreciably lower cell constants, suggesting that temperatures significantly lower than the transition value had been achieved.[8] No additional phase was mentioned. We note that the (111) orthorhombic feature occurs at a slightly higher scattering angle than the most prominent (110) cubic SF_6 line, and a cell constant deduced from the composite feature would be significantly shorter if the orthorhombic phase were present but overlooked. This and other features at higher angles make estimation of the cubic cell constant less precise even when orthorhombic lines are taken into account.

Coexisting multiple phases of the subject condensates may be envisioned to form by several routes: (a) Competitive nucleation in which metastable nuclei of each phase form and grow, (b) nucleation of different phases at different times as the temperature of the expansion decreases, (c) plating out of one phase on another, (d) incomplete phase transitions occurring after nucleation of one phase. Too little is known about the rate of solid-solid phase transitions under these conditions to warrant comment on (d). The considerable differences between the structures of the two phases implied by their crystal systems makes it difficult to understand why an epitaxial growth (c) would occur or why the observed roughly equal amounts of each phase would be likely to be produced by mechanism (a). Model competetive nu-

cleation calculations show that the subject gas tends overwhelmingly to condense in the favored form early in the flow. Very quickly the formation of new nuclei of both kinds is strongly inhibited by the heat of condensation released by the growing clusters but the existing clusters continue to grow. Further expansion may cool the flowing mixture until nucleation is reinitiated at a much lower temperature. While this is certainly the origin of the argon crystallites, most of the seeded vapor would already have condensed upon the existing nuclei. Perhaps the most plausible mechanism for the production of comparable amounts of the two phases is production of the lower temperature form under severe conditions. When the temperature rise of the system due to condensation has increased beyond the transition temperature, the existing crystallites may survive for the few microseconds involved and serve, in disordered outer layers, as nuclei for (nonepitaxial) growth of the higher temperature form. The simultaneous presence of cubic SF_6 near the transition temperature, the orthorhombic phase, and the much colder argon crystals in several of our jets suggests a large inhomogeneity in temperature between the gas, calculated to be below 40 K in these expansions at low subject mole fractions, and the condensate particles. Calculations of thermal relaxation of crystallites as small as those implied by the breadths of our diffraction rings indicate that crystallite temperatures would not lag far behind that of the carrier gas. To avoid postulating implausibly small thermal accomodation coefficients, it is simplest to infer much larger effective particle sizes or large skimmer effects. Ordinary Brownian motion is incapable of making the clusters collide frequently enough to aggregate. Perhaps, in these flows at high Reynolds number, turbulent mixing leads to agglomeration of the soft crystals, and thermal contact may be poor. For such polycrystalline particles, crystal size deduced from line breadths would represent the mean domain size. Light scattering experiments might reveal external sizes.

Results similar to those above for SF_6 are seen for SeF_6 and TeF_6 except that carrier clustering is absent in the runs with mole fractions down to 0.015 SeF_6 and 0.03 TeF_6. The lower symmetry phases of each, as indicated by their similar reflections and intensities, are probably isomorphous. In each case the calculated density is lower than that for the higher temperature cubic phase. This is in stark contrast to the metal hexafluorides. Moreover, the cell constant ratios are dissimilar. For nonmetallic hexafluorides, they are about 2.37 : 2.10 : 1 while for the metal compounds they are 1.90 : 1.73 : 1, and none of the observed phases are related to that predicted by the Monte Carlo calculation.[5] Knowledge of the structural features underlying these clear distinctions will have to await further study. Additional details concerning the characteristics of the crystallites and the conditions of their formation will be presented elsewhere.[14]

ACKNOWLEDGMENTS

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