

and NMR data. It should be mentioned that the viscosity of the microemulsions abruptly changes when water cylinders and lamellae are formed, and that the birefringent region is viscoelastic (13).

The chemical shift of water when it forms the continuous phase is the same as that of water when it is dispersed in spherical form. This result implies that the molecular environment of water in spherical droplets in microemulsions is the same as that of normal water and that the polar groups of surface-active molecules do not significantly alter the molecular environment. However, Cratin and Robertson (14) have reported that the chemical shift of solubilized water is different from that of emulsified water.

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References and Notes

1. J. H. Schulman, W. Stoeckenius, L. Prince, *J. Phys. Chem.* **63**, 1677 (1959).
2. W. Stoeckenius, J. H. Schulman, L. Prince, *Kolloid Z.* **169**, 170 (1960).
3. J. H. Schulman and D. P. Riley, *J. Colloid Sci.* **3**, 383 (1948).
4. J. H. Schulman and J. A. Friend, *ibid.* **4**, 497 (1949).
5. J. E. L. Bowcott and J. H. Schulman, *Z. Elektrochem.* **59**, 283 (1955).
6. C. E. Cooke and J. H. Schulman, in *Surface Chemistry* (Proceedings of the Second Scandinavian Symposium on Surface Activity, 1964) (Munksgaard, Copenhagen, 1965); J. E. L. Bowcott, thesis, Cambridge University, Cambridge, England (1957).
7. V. Luzzati and F. Husson, *J. Cell Biol.* **12**, 207 (1962); L. Mandell, K. Fontell, P. Ekwall, *Advan. Chem. Ser.* **63**, 89 (1967); P. Ekwall, L. Mandell, K. Fontell, *Acta Chem. Scand.* **22**, 373 (1968).
8. I. A. Zlochowar and J. H. Schulman, *J. Colloid Interface Sci.* **24**, 115 (1967).
9. T. F. Page, Jr., R. J. Jakobsen, E. R. Lippincott, *Science* **167**, 51 (1970); G. A. Petsko, *ibid.*, p. 171.
10. D. O. Shah, in preparation.
11. S. Ohki and O. Aono, *J. Colloid Interface Sci.* **32**, 270 (1970).
12. J. W. McBain and W. W. Lee, *Oil Soap Chicago* **20**, 17 (1943); K. D. Lawson and T. J. Flautt, *Mol. Crystallogr.* **1**, 241 (1966).
13. J. W. Falco and D. O. Shah, in preparation.
14. P. D. Cratin and B. K. Robertson, *J. Phys. Chem.* **69**, 1087 (1965).
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Xenon Hexafluoride: Structural Crystallography of Tetrameric Phases

Abstract. Three crystalline phases of xenon hexafluoride are based on tetrameric association of XeF_6^+ and F^- ions into eight-membered rings. Phase I (monoclinic, 8 XeF_6 units per cell) transforms at $\sim 10^\circ\text{C}$ to phase II (orthorhombic, 16 XeF_6 units per cell), which in turn transforms at $\sim -25^\circ\text{C}$ to phase III (monoclinic, 64 XeF_6 units per doubly primitive cell). The transformation from phase I to phase II requires gross reorientation of half of the tetramers in the structure. The transformation from phase II to phase III involves only an ordering of right-handed and left-handed configurations.

Recent developments are clarifying the complexities associated with XeF_6 in the solid state. Heat capacity measurements (1) indicated the existence of three phases, designated I, II, and III in order of decreasing temperature, with transitions at 19° and -19°C . A structure analysis (2) of the cubic phase (3) showed that it was an additional phase, designated IV, which is stable from the melting point to at least -180°C (4). Phase I is monoclinic (3), and phases II and III are now known to be orthorhombic and monoclinic, respectively (5). We here report structural relationships between phases I, II, and III inferred from x-ray crystallography.

Experimental details of the preparation of XeF_6 and the growth of single

crystals of phase II have been presented elsewhere (2, 4, 5). The most probable space group for phase II is $Pnma$ or $Pn2_1a$. To a moderate approximation the phase II cell constants bear a simple relation to the phase I cell constants: $a_{\text{II}} \cong 2a_{\text{I}}$, $b_{\text{II}} \cong b_{\text{I}}$, $c_{\text{II}} \cong c_{\text{I}}$. At -20°C the cell constants are $a_{\text{II}} = 17.01 \pm 0.04$ Å, $b_{\text{II}} = 12.04 \pm 0.03$ Å, $c_{\text{II}} = 8.57 \pm 0.02$ Å. The calculated density is 3.71 g cm^{-3} on the assumption of 16 XeF_6 units per unit cell. At -20°C with our x-ray cryostat XeF_6 has sufficient vapor pressure so that material transport between vapor and solid occurs continuously under the conditions of an x-ray experiment. Only a limited time is available for satisfactory x-ray measurements, and these consisted of Polaroid precession photo-

graphs of the $h0l$, $h1l$, $h2l$, and $0kl$ reflections out to $2\theta = 50^\circ$. We measured relative intensities of 216 reflections with the photometer, using the transmission mode on Polaroid prints. An additional 110 reflections were not measurable above background. The data contain serious limitations with respect to linearity. Corrections were made for Lorentz polarization effects.

The xenon atoms were placed in space group $Pnma$ by trial and error; this placement was followed by least-squares refinement with isotropic thermal parameters to yield an R factor (6) of 0.23 and a weighted R' factor of 0.26. A configuration of xenon atoms results which is compatible, within experimental error, with the 4 symmetry found for the tetrameric association of XeF_5^+ and F^- ions in phase IV (2) and for the xenon atoms in phase I (3). Least-squares refinement in space group $Pn2_1a$ leads to unrealistic Xe-Xe distances, and $Pnma$ is accepted as the most probable space group. This means that the tetramer is centered on a mirror plane as in phase IV and that the structure contains right-handed and left-handed configurations (7) distributed at random. The scattering model contains four tetramers of each configuration of weight $\frac{1}{2}$ which are superimposed.

No useful information concerning fluorine positions was obtained from difference syntheses. This is not unexpected in view of the limited quantity and quality of the available data. Fluorine positions were postulated from the tetrameric component of the phase IV structure (2). Least-squares refinement with a single thermal parameter for the fluorine atoms reduced R to 0.15 and R' to 0.18. This improvement suggests that the scattering model is largely correct in broad outline. However, the data are ill-conditioned for least-squares refinement, and no significant information about Xe-F distances was obtained. There are two F^- bridged Xe-Xe distances at $4.10(2)$ Å and two at $4.07(2)$ Å (estimated standard deviations are given in parentheses). There is one non-bridged Xe-Xe distance at $4.50(2)$ Å and one at $4.52(2)$ Å.

Figure 1A illustrates the Xe positions reported for phase I (3), and Fig. 1B shows the Xe positions of phase II. Half of the tetramers are in approximately the same orientation in either phase, whereas the other half are in grossly different orientations. Evidently a single crystal cannot maintain its integrity through either the transformation

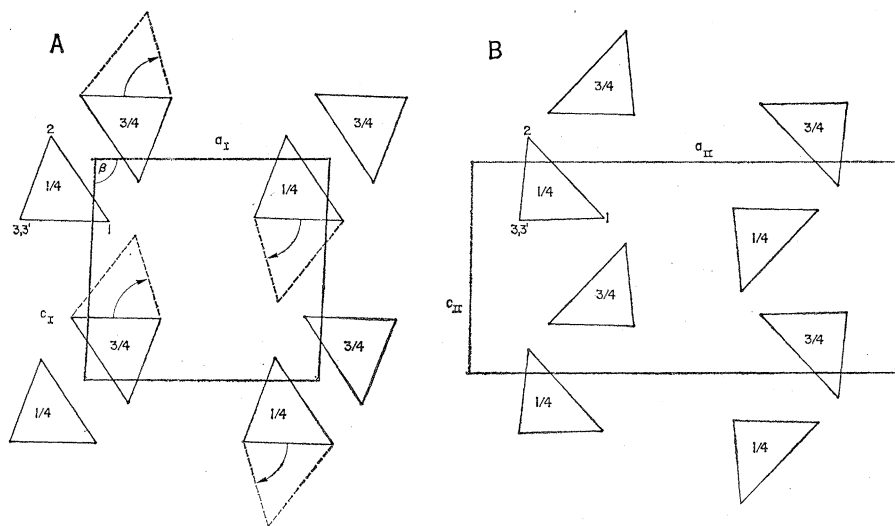


Fig. 1. (A) Unit cell of phase I of XeF_6 projected along the b_I axis. The tetrameric rings of XeF_5^+ and F^- are symbolized by tetrahedra of Xe atoms. The arrows indicate the gross rearrangement required to positions indicated by dotted lines for half of the tetramers in the transformation to phase II. (B) Unit cell of phase II projected along the b_{II} axis.

from phase I to phase II or the reverse transformation from phase II to phase I (3, 5) because of the violent disruption of the structure.

Superficial examination of a single crystal of phase II, cooled rapidly from -20°C to -100°C , indicates that its integrity is maintained in phase III. Careful study of phase III photographs, however, shows that all diffraction spots are slightly split and

can be accounted for by superposition of two monoclinic lattices, one right-handed and one left-handed, which are rotated relative to each other by an angle of $0^\circ 40'$ around a common a_{III} axis. The new structure is monoclinic with space group symmetry C_{2h}^{52} . If we choose an A -centered cell with a as the unique axis (8), the phase III cell constants bear a simple relation to the phase II cell constants: $a_{III} \cong a_{II}$,

$b_{III} \cong 2b_{II}$, $c_{III} \cong 2c_{II}$. At -146°C the cell constants are $a_{III} = 16.80 \pm 0.04$ Å, $b_{III} = 23.93 \pm 0.05$ Å, $c_{III} = 16.95 \pm 0.04$ Å, $\alpha_{III} = 90^\circ 40' \pm 10'$. The calculated density is 3.825 g cm^{-3} on the assumption of 64 XeF_6 units per unit cell. The phase III intensities may be described to an excellent approximation as consisting of the phase II intensities plus a superlattice of weak reflections which double the b and c axes. The strong reflections can be accounted for by the same array of Xe atoms as in phase II, whereas the superlattice reflections are accounted for by F atoms only. This is what would be expected if the right-handed and left-handed tetrameric configurations are no longer distributed at random but have been sorted into an orderly array. Figure 2A illustrates the Xe positions of phase II projected along the a_{II} axis, and Fig. 2B illustrates the doubled b_{III} and c_{III} axes arising from an ordered array in phase III. The asymmetric scattering unit in phase III comprises two tetramers of like-handed configuration. The eight Xe atoms of the unit are numbered in Fig. 2B.

A right-handed lattice, in which tetramers of similar orientation are grouped in planes parallel to (011) planes of the predecessor phase II lattice, is illustrated in Fig. 2B. Tetramers of similar orientation could equally well be grouped in planes parallel to (011) planes of the predecessor phase II lattice, thus giving rise to a left-handed lattice rotated by $0^\circ 40'$ around the a_{III} axis. The resulting crystals have a domain structure with variable amounts of each type of component present in different crystals. A considerable amount of strain must be locked into the domain structure. The transformation from phase III to phase II always yields microcrystals, no matter whether the heating is done slowly or rapidly. The transformation from phase II to phase III yields microcrystals on slow cooling and a pseudo single crystal on rapid cooling. The variable domain structure makes the superimposed superlattice reflections useless for analyzing F positions.

The present observations together with those on phase I (3, 9) are consistent with the following interpretation: Phase I contains tetrameric rings that are in some state of dynamic disorder. This disorder might consist of a coupled, hindered rotation of the XeF_5^+ ions around the Xe-F (axial) directions or of an inversion of the tetrameric rings from right-handed to left-handed

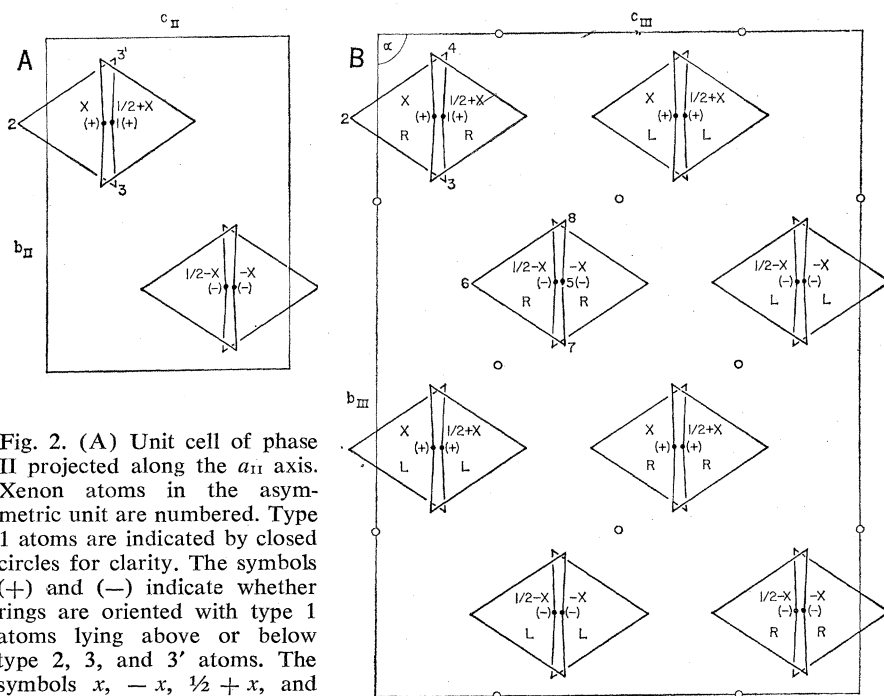


Fig. 2. (A) Unit cell of phase II projected along the a_{II} axis. Xenon atoms in the asymmetric unit are numbered. Type 1 atoms are indicated by closed circles for clarity. The symbols (+) and (-) indicate whether rings are oriented with type 1 atoms lying above or below type 2, 3, and $3'$ atoms. The symbols x , $-x$, $1/2 + x$, and $1/2 - x$ indicate the general symmetry component along the a_{II} axis. (B) Unit cell of phase III projected along the a_{III} axis. The symbols R and L indicate whether fluorine atoms are in right-handed or left-handed configurations. Open circles denote centers of symmetry.

orientations. Phase II contains tetrameric rings that do not invert but that are randomly distributed with respect to orientation in a static disorder. Phase III contains tetrameric rings that are in an orderly array with respect to orientation.

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References and Notes

1. F. Schreiner, D. W. Osborne, J. G. Malm, G. N. McDonald, *J. Chem. Phys.* **51**, 4838 (1969).
2. R. D. Burbank and G. R. Jones, *Science* **168**, 248 (1970).
3. P. A. Agron, C. K. Johnson, H. A. Levy, *Inorg. Nucl. Chem. Lett.* **1**, 145 (1965).
4. G. R. Jones, R. D. Burbank, W. E. Falconer, *J. Chem. Phys.* **52**, 6450 (1970).
5. ———, *ibid.* **53**, 1605 (1970).
6. The quantities R and R' are defined as follows:

$$R = \frac{\sum |F_o - F_c|}{\sum |F_o|}$$

$$R' = \frac{[\sum w(F_o - F_c)^2]^{\frac{1}{2}}}{(\sum w F_o^2)^{\frac{1}{2}}}$$
7. The use of the terms "right-handed" and "left-handed" needs qualification in point group 4. Two of the monomer components of a 4 tetramer must be right-handed and two left-handed, by definition of the symmetry operations. When a mirror plane operates on the tetramer, the right-handed and left-handed identities are interchanged. The transformed tetramer is not an enantiomorph of the original tetramer in the classical sense. It is formally equivalent to the original tetramer, being subjected to a compound rotation of 180° around an axis through the center of the tetramer and normal to the mirror plane combined with a rotation of 90° around the 4 axis. This qualification should be incorporated in the description of phase IV (2).
8. The complete Hermann-Mauguin space group symbol for this cell may be written as $A2_1/d''11$. The conventional symbol d for a diamond glide does not suffice in the monoclinic system. Here we use the symbol d'' for a "diamond glide of the second kind" with glide components of $b/4 - c/4$ ($0kl$ reflections extinguished unless $k - l = 4n$) and propose the symbol d' for a "diamond glide of the first kind" with glide components of $b/4 + c/4$ ($0kl$ reflections extinguished unless $k + l = 4n$).
9. The static disorder found in phase IV and proposed for phase II does not suffice to give good agreement between F_o and F_c for phase I (C. K. Johnson, personal communication).

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Opal Precipitation by Marine Gastropods (Mollusca)

Abstract. *The high silicon content of certain radular sites of the Patellacea (Mollusca, Gastropoda) is shown by infrared absorption spectrums to be fixed in the form of the mineral opal. Opal and goethite mineralize the cusps and bases of the teeth. The presence of opalized base plates only in the families Acmaeidae and Lepetidae appears to be of taxonomic significance. Minimum values of the volume of fixation and of the turnover rate of opal by the Patellacea are calculated to assess the role of this previously neglected taxon in biological fixation of silica in the oceans. The significance of these organisms points to the much needed study of the silica transport system in tissue-grade Metazoa.*

The fixation of silica by marine organisms, apparently in the form of opal ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), is generally identified with certain unicellular algae, heterotrophs, and Protozoa and with cellular-grade Metazoa. They include the diatoms, some dinoflagellates, the silicoflagellates, ebridians, most radiolarians, the Hyalispongia, many Demospongia, and the coralline sponges (1). Determinations of elements present in invertebrates of the tissue grade long ago established that high amounts of silicon are also present in radular teeth of a few gastropod species of the superfamily Patellacea (2, 3). It has been suggested that the silicon-bearing compound of such teeth is opal on the basis of its specific gravity and optical properties (2). The teeth are also reported to contain high amounts of iron (2, 3). Therefore, the possibility of an iron silicate mineral has been considered (4). Most investigators have favored the idea that the iron and silicon are

present in two separate minerals (2, 3). X-ray diffraction studies of mature teeth from four patellacean species have strengthened this concept, because goethite (αFeOOH) has been detected as the only crystalline compound (5). In the absence of the application of modern techniques, the mineralogic form of the silicon-containing compound has remained uncertain, consistently being referred to as the "silica" (2, 3).

Patellacea are found in all oceans. They are common on rocky shores in the intertidal zone where their populations may exceed 500 individuals per square meter. Smaller populations occur subtidally, mostly in mid- and high latitudes to depths of about 200 m. A few species of the family Lepetidae extend from shelf depths down to about 3600 m in the abyssal zone (6).

The compound reported to contain the high silicon concentrations in some species of these gastropods needs pre-

cise identification. One would like to know further whether all Patellacea precipitate a silicon-bearing compound. Currently there is disagreement on whether the low amounts of silicon in surface waters of the oceans is entirely or largely the result of biologic activity or largely due to inorganic processes (7). Petallacean gastropods, because they are common, should be included in reevaluating the total amounts of biologically fixed silicon and of the volume of siliceous hard parts transferred to oceanic sediments. The ability to metabolize silicon by a biochemical system of the tissue grade of Metazoa, such as the Patellacea, acquires greater significance in the light of the recent discovery that silicon may be important in the process of bone calcification in mammals (8).

In order to determine the mineralogy of the silicon-bearing compound of the Patellacea we initially studied samples of *Patella vulgata* from the family Patellidae and of *Lottia gigantea* from the family Acmaeidae (9). Radulae of adult individuals preserved in 75 percent alcohol were treated with Clorox to digest most of the organic fractions. The residue from the radulae of *P. vulgata* consisted of dark brown to brownish gray cusps and tooth bases; that of *L. gigantea* contained similarly colored cusps and tooth bases plus rectangular-shaped base plates which are embedded in pairs in the radular membrane underneath the tooth bases (Fig. 1). The rectangular base plates are colorless and translucent where they are thin, milky-white in thicker portions, and iridescent in reflected light. When the radulae are stripped of their teeth and viewed in transmitted light under the microscope, the base plates are seen to be confined to the anterior part of the radula and to decrease in size and thickness posteriorly. The brownish tooth cusps and tooth bases of both species have been shown through x-ray diffraction studies to contain goethite (5). To remove this mineral, the cusps and tooth bases of both species were boiled in a solution of 38 percent hydrochloric acid for 2 days at 60°C. Under these conditions, the tooth cusps and their bases remain firm, retained their original shape, and acquired a colorless, milky-white appearance similar to that of the rectangular base plates of *L. gigantea* when extracted solely with Clorox. The tooth cusps and their bases were reduced in size and marginally in thickness. The teeth acquired a por-