

# Synthesis and Raman Spectra of $[\text{Nd}(\text{XeF}_2)_n](\text{AsF}_6)_3$ ( $n = 3, 2.5$ ) and Crystal Structure of $[\text{Nd}(\text{XeF}_2)_{2.5}](\text{AsF}_6)_3$

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IN HONOR OF PROFESSOR PAUL HAGENMULLER ON THE OCCASION OF HIS 80TH BIRTHDAY

The reaction between  $\text{Nd}(\text{AsF}_6)_{3(\text{solv})}$  and excess of  $\text{XeF}_{2(\text{solv})}$  in anhydrous HF (aHF) yields compounds of the type  $[\text{Nd}(\text{XeF}_2)_n](\text{AsF}_6)_3$  ( $n = 3, 2.5$ ). The first compound is very soluble in aHF while the latter crystallizes from the saturated solution in aHF. Pink needles  $[\text{Nd}(\text{XeF}_2)_{2.5}](\text{AsF}_6)_3$  crystallize in the space group  $C2/m$  with  $a = 3463.7(8)$  pm,  $b = 586.3(2)$  pm,  $c = 1010.7(2)$  pm,  $\beta = 103.53(2)^\circ$ ,  $V = 1.9955(9)$  nm<sup>3</sup>,  $Z = 4$ ,  $R_1 = 0.0379$ ,  $wR_2 = 0.0910$ , 5341 reflections collected, 2318 independent reflections. The Nd center is coordinated by a tricapped trigonal prism of nine fluorine atoms. The rectangular faces are capped by three coordinated  $\text{XeF}_2$  molecules. The regular trigonal prisms are formed by six different edge-bridging  $\text{AsF}_6$  octahedra, connecting the Nd centers to infinite chains. Two of such chains are interconnected by one of the  $\text{XeF}_2$  molecules forming a double chain. © 2001 Elsevier Science

**Key Words:**  $\text{XeF}_2$  as ligand; synthesis; crystal structure; Raman spectrum;  $\text{Nd}(\text{AsF}_6)_3$ .

## 1. INTRODUCTION

Lanthanoid trifluorides ( $\text{LnF}_3$ ) dissolve at room temperature in anhydrous hydrogen fluoride (aHF) acidified with  $\text{AsF}_5$ , yielding stable solutions of  $\text{Ln}(\text{AsF}_6)_3$  (1). The lanthanoid metal centers in  $\text{Ln}(\text{AsF}_6)_3$  are almost “naked” and interact with various, even weak, ligands ( $L$ ) to form complex compounds of the type  $[\text{Ln}(L)_n](\text{AsF}_6)_3$  ( $L = \text{SO}_2$  (2),  $\text{CH}_3\text{CN}$  (3),  $\text{HF}$  (4),  $\text{AsF}_3$  (5),  $\text{NSF}_3$ , and  $\text{OPF}_3$  (6)). Recently we briefly reported that even  $\text{XeF}_2$  can be introduced as a ligand in the reactions of  $\text{Ln}(\text{AsF}_6)_3$  dissolved in aHF. During this study  $[\text{La}(\text{XeF}_2)_{2.5}](\text{AsF}_6)_3$  was isolated and its crystal structure determined (5).

In the present paper with the synthesis and Raman spectra of  $[\text{Nd}(\text{XeF}_2)_n](\text{AsF}_6)_3$  ( $n = 3, 2.5$ ) and the crystal structure of  $[\text{Nd}(\text{XeF}_2)_{2.5}](\text{AsF}_6)_3$ , a detailed report on the

chemistry of this new class of compounds is given for the first time. While a large number of Xe(II) compounds with binary metal and nonmetal fluorides is known (7),  $[\text{Nd}(\text{XeF}_2)_{2.5}](\text{AsF}_6)_3$  represents the first fully described Xe(II) compound in the lanthanoid series and only the second example where  $\text{XeF}_2$  is acting as a ligand toward a metal ion (8).

## 2. EXPERIMENTAL SECTION

### 2.1. Apparatus, Techniques, and Reagents

A nickel vacuum line and Teflon vacuum system were used as previously described (9). Nonvolatile materials, which were very sensitive to traces of moisture, were handled in the dry argon atmosphere of a glove box with a maximum content of 0.1 ppm of water vapor (Mbraun, Garchig, Germany). PFA reaction vessels equipped with Teflon valves and Teflon-covered stirring bars were used for the syntheses. T-shaped PFA reaction vessels constructed from a large PFA tube (16 mm i.d.) and a smaller PFA tube (4 mm i.d.) jointed at a right angle and equipped with Teflon valves were used for crystallization.  $\text{NdF}_3$  was used as purchased (Johnson Matthey, Alfa Products, 99.9%), and aHF (Praxair, 99.9%) was treated with  $\text{K}_2\text{NiF}_6$  for several days prior to use.  $\text{AsF}_5$  was prepared by high-pressure fluorination of  $\text{As}_2\text{O}_3$ , a procedure previously described for  $\text{PF}_5$  (10).  $\text{XeF}_2$  was prepared by the photochemical reaction between Xe and  $\text{F}_2$  at room temperature (11).

### 2.2. X-Ray Crystallography

Crystal data were collected on a Siemens P4 diffractometer (details:  $\omega$ - $2\theta$  scans; refinement based on  $F^2$ ;  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \{\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]\}^{1/2}$ ). An absorption correction using the program DIFABS (12) was applied. Further details on the data collection and the basic crystallographic data are given in Table 1. Programs SHELX-97 (13) and DIAMOND (14) were used.

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**TABLE 1**  
**Crystal Data and Structure Refinement for  $[\text{Nd}(\text{XeF}_2)_{2.5}](\text{AsF}_6)_3$**

Empirical formula	$\text{As}_3\text{F}_{23}\text{NdXe}_{2.50}$
Formula weight	1134.25
Temperature	173(2) K
Wavelength	71.073 pm
Crystal system	Monoclinic
Space group	$C2/m$
Unit cell dimensions	$a = 3463.7(8)$ pm $b = 586.3(2)$ pm $c = 1010.7(2)$ pm $\beta = 103.53(2)^\circ$
Volume	$1.9955(9)$ nm <sup>3</sup>
Z	4
Density (calculated)	$3.775$ Mg/m <sup>3</sup>
Absorption coefficient	$11.905$ mm <sup>-1</sup>
$F(000)$	2004
Crystal size	$0.50 \times 0.30 \times 0.20$ mm <sup>3</sup>
Theta range for data collection	$2.63^\circ$ to $27.51^\circ$
Index ranges	$-44 \leq h \leq 44$ , $-1 \leq k \leq 7$ , $-12 \leq l \leq 12$
Reflections collected	5341
Independent reflections	2318 [ $R(\text{int}) = 0.0397$ ]
Completeness to theta = $27.51^\circ$	91.7%
Max. and min. transmission	0.1993 and 0.0660
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2318/0/162
Goodness-of-fit on $F^2$	1.099
Final R indices [ $I > 2\sigma(I)$ ] <sup>a,b</sup>	$R_1 = 0.0379$ , $wR_2 = 0.0910$
R indices (all data) <sup>a,b</sup>	$R_1 = 0.0486$ , $wR_2 = 0.0957$
Extinction coefficient	0.00016(6)
Largest diff. peak and hole	1.755 and $-2.269$ e Å <sup>-3</sup>

Note.  $w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 14.2171P]$ ;  $P = [2F_o^2 + \text{Max}(F_o^2, 0)]/3$ .

<sup>a</sup>  $R_1 = \sum \|F_o\| - |F_c| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ .

### 2.3. Raman Spectroscopy

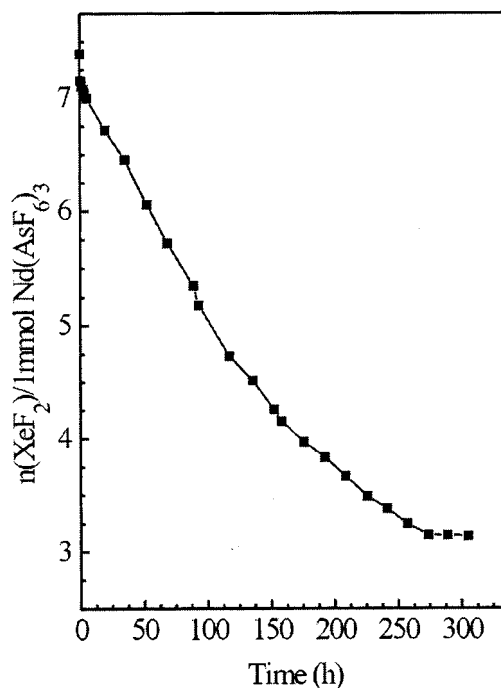
Raman spectra of powdered samples and crystals were measured in sealed quartz capillaries on a Renishaw Raman Imaging Microscope System 1000, with the existing line at 632.8 nm of a He-Ne laser.

### 2.4. Chemical Analysis

Free and total fluoride ion contents were determined with an ion selective electrode (15, 16). Nd was determined by complexometric titration (17), arsenic by the ICP method (18).

### 2.5. Synthesis of $[\text{Nd}(\text{XeF}_2)_3](\text{AsF}_6)_3$

$\text{NdF}_3$  (1.44 mmol) was weighted into a PFA vessel in a glove box. The aHF was added by condensation at 77 K. The suspension of  $\text{NdF}_3$  in aHF was allowed to warm to room temperature. Small portions of  $\text{AsF}_5$  gas, monitored



**FIG. 1.** Weight-loss versus time of pumping curve in the course of the synthesis of  $[\text{Nd}(\text{XeF}_2)_3](\text{AsF}_6)_3$ .

by pressure–volume measurements and by weight, were added to the suspension of  $\text{NdF}_3$  in aHF until the molar ratio of 1:3 was reached (total amount 4.35 mmol). The reaction was carried out at room temperature for 24 h until all  $\text{NdF}_3$  dissolved to give a clear pink solution of  $\text{Nd}(\text{AsF}_6)_3$ . An excess of  $\text{XeF}_2$  (10.14 mmol) was then added by sublimation from 295 K to the solution of  $\text{Nd}(\text{AsF}_6)_3$  kept at 77 K. The reaction was carried out for 48 h at room temperature. The solution remained clear and no precipitate was observed. Anhydrous HF and the excess of  $\text{XeF}_2$  were pumped off. The weight-loss versus time of pumping curve was recorded (Fig. 1). At the end of pumping a pink solid with the composition  $[\text{Nd}(\text{XeF}_2)_n](\text{AsF}_6)_3$  with  $n = 3.14$  determined by mass balance was obtained. Chemical analysis of the bulk of the sample gave a molar ratio Nd:As:F<sub>1</sub> close to 1:3:24. Anal. Calcd. for  $[\text{Nd}(\text{XeF}_2)_3](\text{AsF}_6)_3$ : F(total), 37.4; F(free), 9.4; As, 18.5; Nd, 11.8. Found: F(total), 37.0; F(free), 8.4; As, 21.1; Nd, 11.8.

### 2.6. Preparation of Single Crystals

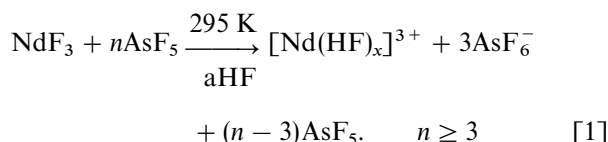
A small portion of  $[\text{Nd}(\text{XeF}_2)_3](\text{AsF}_6)_3$  (approx. 400 mg) was transferred into the T-shaped PFA reaction vessel. After addition of 4–5 ml of aHF a clear pink solution was obtained. This solution was decanted into the narrower arm of the reaction vessel, which was left at room temperature while the wider arm was cooled with running water. By this method a small temperature gradient of 6 K was achieved.

The crystallization proceeded for several days. Pink needles were obtained in the narrower tube of the reaction vessel after all of the aHF was removed. Crystals were immersed in Kel-F oil in the glove box, selected under the microscope, and transferred into the cold nitrogen stream of the diffractometer.

### 3. RESULTS AND DISCUSSION

#### 3.1. Synthesis of [Nd(XeF<sub>2</sub>)<sub>3</sub>](AsF<sub>6</sub>)<sub>3</sub>

A solution of Nd(AsF<sub>6</sub>)<sub>3</sub> in aHF was prepared by the reaction of NdF<sub>3</sub> with AsF<sub>5</sub>:



Nd(AsF<sub>6</sub>)<sub>3</sub> is stable in neutral or AsF<sub>5</sub>-acidified aHF. When aHF and excess of AsF<sub>5</sub> are removed under vacuum Nd(AsF<sub>6</sub>)<sub>3</sub> starts losing AsF<sub>5</sub> to give the pink solid NdF(AsF<sub>6</sub>)<sub>2</sub> as the stable final product. If this solid is dissolved again in aHF the compound partly solvolyses, yielding some NdF<sub>3</sub>, which precipitates while the remaining Nd is present in solution as Nd(AsF<sub>6</sub>)<sub>3</sub> (1). Pure Nd-XeF<sub>2</sub> complexes can be prepared only if no excess of AsF<sub>5</sub> is present. XeF<sub>2</sub> is a fluorobase which will neutralize all excess AsF<sub>5</sub> from the preparation of Nd(AsF<sub>6</sub>)<sub>3</sub> to give the very soluble Xe<sub>2</sub>F<sub>3</sub>AsF<sub>6</sub> salt as an impurity, which cannot be separated from the main product. Therefore Nd(AsF<sub>6</sub>)<sub>3</sub> should be prepared with the exact stoichiometric amount of the acid AsF<sub>5</sub>. To a solution of pure Nd(AsF<sub>6</sub>)<sub>3</sub> in neutral aHF an excess of XeF<sub>2</sub> is added, yielding [Nd(XeF<sub>2</sub>)<sub>n</sub>](AsF<sub>6</sub>)<sub>3</sub>; excess XeF<sub>2</sub> is removed under vacuum. For the final product which has no vapor pressure at room temperature and which is stable in a dynamic vacuum *n* equals 3. The weight loss versus time of pumping curve is shown on Fig. 1.

The reaction between Nd(AsF<sub>6</sub>)<sub>3</sub> and XeF<sub>2</sub> dissolved in aHF was also monitored by recording Raman spectra of the solution and of the solid product. It is interesting that even at a molar ratio XeF<sub>2</sub>/NdF<sub>3</sub> = 7 no free XeF<sub>2</sub> was observed in the aHF solution. This could mean that *n* could be 6 or even higher but compounds of the type [Nd(XeF<sub>2</sub>)<sub>6</sub>](AsF<sub>6</sub>)<sub>3</sub> are not stable at room temperature under dynamic vacuum. They lose XeF<sub>2</sub> during pumping at room temperature until the composition [Nd(XeF<sub>2</sub>)<sub>3</sub>](AsF<sub>6</sub>)<sub>3</sub> is reached.

When [Nd(XeF<sub>2</sub>)<sub>3</sub>](AsF<sub>6</sub>)<sub>3</sub> is dissolved in neutral aHF in order to grow single crystals, only [Nd(XeF<sub>2</sub>)<sub>2.5</sub>](AsF<sub>6</sub>)<sub>3</sub> crystallizes from the saturated solution, suggesting that it is less soluble than [Nd(XeF<sub>2</sub>)<sub>3</sub>](AsF<sub>6</sub>)<sub>3</sub>. The high solubility of [Nd(XeF<sub>2</sub>)<sub>3</sub>](AsF<sub>6</sub>)<sub>3</sub> in aHF is probably due to the solvated [Nd(XeF<sub>2</sub>)<sub>3</sub>]<sup>3+</sup> complex cation. The solvent molecules interact via strong hydrogen bonding to the terminal

fluorines of the XeF<sub>2</sub> ligands. During evaporation of the solvent the concentration of the solvated [Nd(XeF<sub>2</sub>)<sub>3</sub>]<sup>3+</sup> cations increases and leads to the interaction between solvated cations, yielding a less soluble compound with a polymeric double-chain structure which precipitates out of solution. During the formation of the double chain one XeF<sub>2</sub> molecule is liberated per two connected cations. This XeF<sub>2</sub> is probably not free but it is coordinated in still dissolved [Nd(XeF<sub>2</sub>)<sub>3</sub>]<sup>3+</sup> cations increasing a number of XeF<sub>2</sub> ligands around the Nd center. The compounds [Nd(XeF<sub>2</sub>)<sub>n</sub>](AsF<sub>6</sub>)<sub>3</sub> (*n* = 3, 2.5) can be kept indefinitely in evacuated quartz or PFA reaction vessels or in a dry argon or nitrogen atmosphere but they decompose immediately on contact with traces of moisture.

#### 3.2. Crystal Structure of [Nd(XeF<sub>2</sub>)<sub>2.5</sub>](AsF<sub>6</sub>)<sub>3</sub>

Atomic coordinates, equivalent isotropic displacement parameters, and selected bond distances and angles are given in Tables 2 and 3. The Nd atoms are coordinated by nine fluorine atoms in the form of a tricapped trigonal prism (Fig. 2). The regular trigonal prisms are formed by the fluorine atoms of six different edge-bridging AsF<sub>6</sub> octahedra, connecting the Nd centers to infinite chains. The

**TABLE 2**  
Atomic Coordinates and Equivalent Isotropic Displacement Parameters (pm<sup>2</sup> × 10<sup>-1</sup>) for [Nd(XeF<sub>2</sub>)<sub>2.5</sub>](AsF<sub>6</sub>)<sub>3</sub>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Nd(1)	0.38358(1)	0.0000	0.20558(5)	14(1)
F(1)	0.4456(2)	0.0000	0.3793(7)	29(2)
Xe(1)	0.5000	0.0000	0.5000	17(1)
F(2)	0.3231(2)	0.0000	0.2675(7)	33(2)
Xe(2)	0.27696(2)	0.0000	0.36704(7)	25(1)
F(3)	0.2344(2)	0.0000	0.4616(9)	54(3)
F(4)	0.3900(2)	0.0000	-0.0158(6)	36(2)
Xe(3)	0.41143(2)	0.0000	-0.19101(6)	23(1)
F(5)	0.4298(2)	0.0000	-0.3560(7)	39(2)
F(6)	0.3421(1)	0.2959(10)	0.0834(5)	33(1)
As(1)	0.32270(3)	0.5000	-0.04342(11)	25(1)
F(7)	0.3683(2)	0.5000	-0.0840(7)	40(2)
F(8)	0.3062(2)	0.2900(12)	-0.1571(6)	55(2)
F(9)	0.2808(2)	0.5000	0.0136(10)	52(2)
F(10)	0.3854(1)	0.2927(10)	0.3760(5)	31(1)
As(2)	0.36896(3)	0.5000	0.47701(10)	18(1)
F(11)	0.3245(2)	0.5000	0.3608(6)	26(2)
F(12)	0.4148(2)	0.5000	0.5814(6)	30(2)
F(13)	0.3533(1)	0.2882(10)	0.5659(5)	35(1)
F(14)	0.4288(1)	0.2965(10)	0.1692(5)	38(1)
As(3)	0.46660(3)	0.5000	0.18039(10)	17(1)
F(15)	0.4718(2)	0.5000	0.3511(6)	31(2)
F(16)	0.4565(2)	0.5000	0.0092(6)	31(2)
F(17)	0.5002(2)	0.2873(11)	0.1941(6)	45(2)

Note. *U*(eq) is defined as one third of the trace of the orthogonalized *U*<sup>*ij*</sup> tensor.

**TABLE 3**  
**Selected Bond Length (pm) and Angles (°)**  
**for [Nd(XeF<sub>2</sub>)<sub>2.5</sub>](AsF<sub>6</sub>)<sub>3</sub>**

Nd-F			
Nd(1)-F(4)	230.0(6)		
Nd(1)-F(2)	232.1(6)		
Nd(1)-F(6)	240.2(5)		
Nd(1)-F(10)	242.1(5)		
Nd(1)-F(14)	242.4(5)		
Nd(1)-F(1)	243.5(6)		
Xe-F			
F(1)-Xe(1)	199.1(6)	F(1)-Xe(1)-F(1)#2	180.0(2)
F(2)-Xe(2)	207.9(6)	Xe(2)-F(2)-Nd(1)	167.2(4)
Xe(2)-F(3)	193.6(6)	F(3)-Xe(2)-F(2)	179.4(3)
F(4)-Xe(3)	207.3(6)	Xe(3)-F(4)-Nd(1)	165.1(4)
Xe(3)-F(5)	191.8(6)	F(5)-Xe(3)-F(4)	178.5(3)
AsF <sub>6</sub> octahedra			
F(6)-As(1)	176.7(5)	As(1)-F(6)-Nd(1)	160.4(3)
As(1)-F(7)	172.3(8)	F(7)-As(1)-F(6)	87.6(2)
As(1)-F(8)	169.0(6)	F(8)-As(1)-F(6)	90.6(3)
As(1)-F(9)	168.3(8)	F(9)-As(1)-F(7)	173.9(4)
F(10)-As(2)	176.6(5)	As(2)-F(10)-Nd(1)	160.2(3)
As(2)-F(11)	170.4(6)	F(11)-As(2)-F(10)	87.9(2)
As(2)-F(12)	168.8(6)	F(12)-As(2)-F(10)	88.7(2)
As(2)-F(13)	169.5(5)	F(13)-As(2)-F(10)	89.4(3)
F(14)-As(3)	175.7(5)	As(3)-F(14)-Nd(1)	167.4(3)
As(3)-F(15)	169.2(6)	F(15)-As(3)-F(14)	88.0(2)
As(3)-F(16)	168.3(6)	F(16)-As(3)-F(14)	87.8(2)
As(3)-F(17)	169.0(6)	F(17)-As(3)-F(14)	89.6(3)

Note. Symmetry transformations used to generate equivalent atoms: #1,  $x, -y, z$ ; #2,  $-x+1, -y, -z+1$ ; #3,  $x, -y+1, z$ .

rectangular faces of the trigonal prisms are occupied by three fluorine atoms from three XeF<sub>2</sub> molecules. Two of these coordinated XeF<sub>2</sub> are terminal ligands, the third bridges two Nd centers under formation of a double chain. Arrangements of the chains in the structure are presented in Fig. 3. Due to the special crystallographic position of the bridging XeF<sub>2</sub>, there is only one independent Xe-F distance (Xe(1)-F(1) 199.1(6) pm), which is not significantly different from the Xe-F distance in XeF<sub>2</sub> itself (200 pm) (19). As a result of the interaction with the highly acidic Nd centers, the two terminal XeF<sub>2</sub> molecules are strongly distorted, the Xe-F bonds to the bridging fluorines are stretched to 207.3(6)-207.9(6) pm, while the terminal Xe-F distances shrink to 191.8(6)-193.6(6) pm, respectively. For the Xe-F<sup>+</sup> cation a distance less than 190 pm is expected (20). These data suggest that the neodymium compound should be considered as a XeF<sub>2</sub> complex rather than a fluorine bridges Xe-F<sup>+</sup> salt.

The Nd-F distances to the Fs of the AsF<sub>6</sub> forming the corners of the trigonal prism are in the range from 240.2(5) to 242.4(5) pm while the Nd-F distances to the Fs of XeF<sub>2</sub> which are capping the trigonal prism are in the range from 230.0(6) to 243.5(6) pm. La-F distances in the isotypic com-

pound are in the range from 235.7(7) to 248.9(7) pm (H. Borrmann and M. Tramšek, private communication, 1997). The shortest Nd-F distances are in the case of both terminal XeF<sub>2</sub> molecules being 230.0(6) pm for Xe(3) and 232.1(6) pm for Xe(2). The longest Nd-F distance of 243.5(6) pm is in the case of bridging XeF<sub>2</sub>. In the compound Nd<sub>2</sub>F(AuF<sub>4</sub>)<sub>5</sub>, where CN is also nine, the Nd-F distances are from 226.0 to 255.0 pm (21). It is known that Nd-F distances are slightly shorter (22) than La-F distances which is in accordance with the smaller radius of neodymium ( $r_{\text{CN}9} = 130.3$  pm) in comparison with the radius of lanthanum ( $r_{\text{CN}9} = 135.6$  pm). The shortest La-F bonds in LaF<sub>3</sub> (CN = 9) are in the range from 242 to 248 pm (23).

The As-F distances for the terminal fluorines are in the range from 168.3(8) to 172.3(8) pm, while these distances for the bridging fluorine atoms are in the range from 175.7(5) to 176.7(5) pm (Table 3).

The closest interactions between negatively charged fluorine atoms from XeF<sub>2</sub> and AsF<sub>6</sub><sup>-</sup> of one double chain and positively charged Xe atoms of the other double chains are in the range from 326.0 to 374.5 pm. The F(Xe)-Xe distances are shorter than the F(AsF<sub>6</sub>)-Xe distances as consequence of the higher charge at F in XeF<sub>2</sub> being approximately -0.5 (24) in comparison to the charge at F in AsF<sub>6</sub><sup>-</sup> being much less. In crystalline XeF<sub>2</sub> each atom is surrounded by eight fluorine atoms from neighboring XeF<sub>2</sub> molecules at the distance of 342 pm (25).

### 3.3. Raman Spectra of [Nd(XeF<sub>2</sub>)<sub>n</sub>](AsF<sub>6</sub>)<sub>3</sub>

Raman spectra of the powder of [Nd(XeF<sub>2</sub>)<sub>3</sub>](AsF<sub>6</sub>)<sub>3</sub> and of the crystals of [Nd(XeF<sub>2</sub>)<sub>2.5</sub>](AsF<sub>6</sub>)<sub>3</sub> are given in Table 4 and Fig. 4. The high polarizability of xenon usually results in the Raman active modes of xenon fluorides and their complexes having intense Xe-F stretching modes. Modes involving As-F and Nd-F vibrations are ordinarily far less intense. The intense bands in the Raman spectra of the 1:3 compound (Fig. 4a) at 568 cm<sup>-1</sup> and for the 1:2.5 compound at 584 and 575 cm<sup>-1</sup> (Fig. 4b) can therefore be confidently attributed to Xe-F stretching modes. The latter splitting could be a consequence of the inequivalence of the two XeF<sub>2</sub> molecules coordinated singly to the Nd<sup>3+</sup>, or to some intermolecular coupling, as in some XeF<sub>2</sub>-MF<sub>5</sub> adducts (26).

The totally symmetric ( $a_{1g}$ ) stretching mode for XeF<sub>2</sub> (27) and symmetrical XeF<sub>2</sub> in complexes such as XeF<sub>2</sub> · 2XeF<sub>5</sub>AsF<sub>6</sub> (20) is at or near 497 cm<sup>-1</sup>. When XeF<sub>2</sub> is distorted (and on the ionization pathway toward Xe-F<sup>+</sup> and F<sup>-</sup>) as in the XeF<sub>2</sub> · XeF<sub>5</sub>AsF<sub>6</sub> (20), this band is replaced by two. The band at higher frequency is labeled as the short-bond Xe-F stretch ( $\nu$  (Xe-F)), and that at lower frequency as the long-bond Xe-F stretch ( $\nu$  (Xe...F)). It has previously been concluded that the stretching frequency for (Xe-F)<sup>+</sup> should be at or higher than 600 cm<sup>-1</sup> (28).

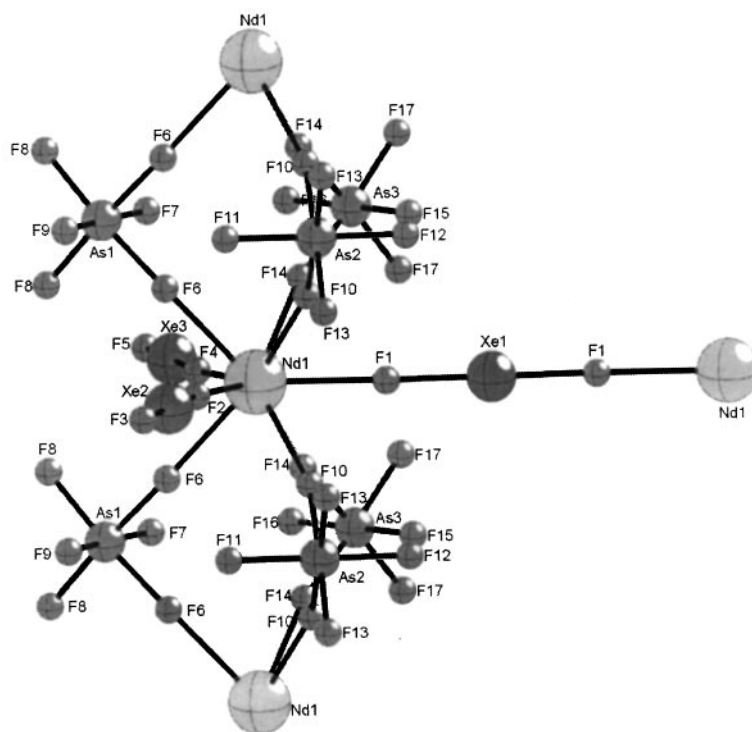


FIG. 2. Coordination of Nd center in  $[\text{Nd}(\text{XeF}_2)_{2.5}](\text{AsF}_6)_3$ .

From the structure of the 1:2.5 compound the  $\text{XeF}_2$  molecules that are uniquely bound to  $\text{Nd}^{3+}$  are seen to be distorted and on the ionization pathway. However, the

F ligand facing the  $\text{Nd}^{3+}$  is far from being  $\text{F}^-$ . The Raman spectra clearly show that the short-bonded Xe–F component in both complexes is far from  $(\text{Xe–F})^+$ . The slightly

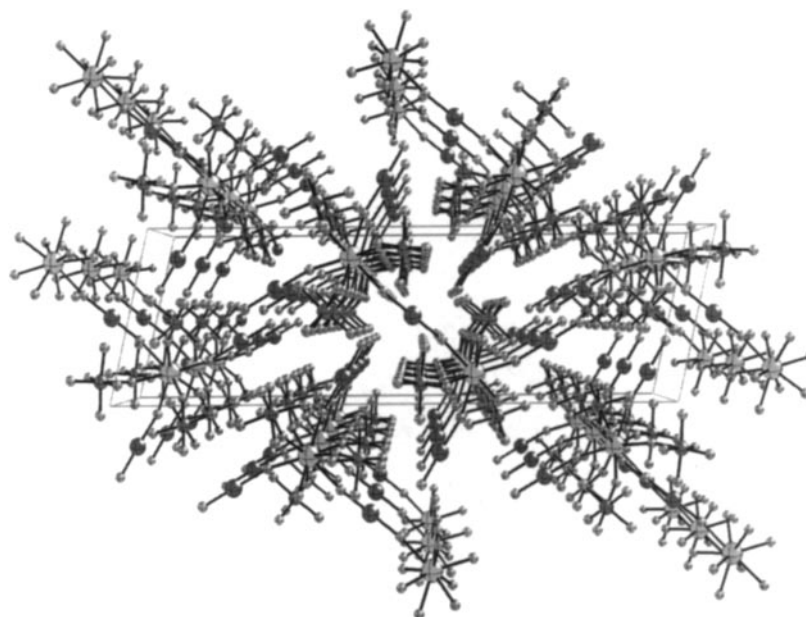


FIG. 3. Arrangement of double chains in the structure of  $[\text{Nd}(\text{XeF}_2)_{2.5}](\text{AsF}_6)_3$ .

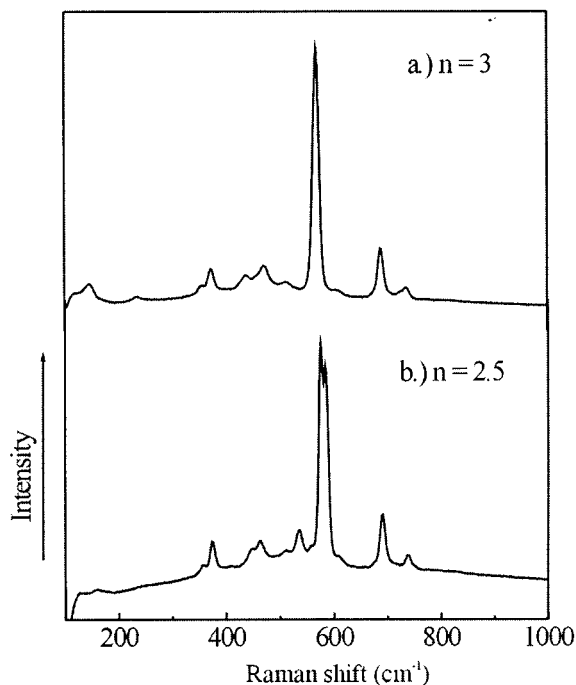
**TABLE 4**  
**Vibrational Frequencies for Raman Spectra of [Nd(XeF<sub>2</sub>)<sub>3</sub>](AsF<sub>6</sub>)<sub>3</sub> and Crystals of [Nd(XeF<sub>2</sub>)<sub>2.5</sub>](AsF<sub>6</sub>)<sub>3</sub> (in cm<sup>-1</sup>)<sup>a</sup>**

[Nd(XeF <sub>2</sub> ) <sub>3</sub> ](AsF <sub>6</sub> ) <sub>3</sub>	[Nd(XeF <sub>2</sub> ) <sub>2.5</sub> ](AsF <sub>6</sub> ) <sub>3</sub>	Assignment
736(0.4)	737(0.6)	$\nu$ (As-F)
689(1.9)	690(2.4)	$\nu$ (As-F)
606(0.1)	608(0.4)	$\nu$ (As-F)
	584(8.9)	$\nu$ (Xe-F)
	575(10)	$\nu$ (Xe-F)
568(10)		$\nu$ (Xe-F)
	555(0.8)	
	534(1.5)	$\nu$ (XeF <sub>2</sub> )
512(0.2)	509(0.5)	$\nu$ (Nd-F)
472(0.8)		$\nu$ (Nd-F)
	461(1.0)	$\nu$ (Xe...F)
437(0.5)		$\nu$ (Xe...F)
	446(0.7)	$\nu$ (Xe...F)
	411(0.2)	$\nu$ (Xe...F)
374(1.0)	374(1.5)	$\nu$ (As-F)
356(0.4)	356(0.4)	$\nu$ (As-F)
236(0.2)		
	159(0.5)	Lattice modes
145(0.9)		Lattice modes
120(0.6)	126(0.7)	Lattice modes

<sup>a</sup> Intensities are in parentheses.

higher value (Xe-F short) in the 1:2.5 compound may mean that the ionization is a little greater in the unique XeF<sub>2</sub> ligands of that material.

The undistorted (bridging) XeF<sub>2</sub> in the 1:2.5 compound might have been expected to exhibit a symmetric XeF<sub>2</sub>



**FIG. 4.** Raman spectra of [Nd(XeF<sub>2</sub>)<sub>n</sub>](AsF<sub>6</sub>)<sub>3</sub>.

stretch at  $\sim 497$  cm<sup>-1</sup>, but, as may be seen from Fig. 4 and Table 4, the observed band at 534 cm<sup>-1</sup> is most likely to be associated with this vibration. The enhancement of this stretching frequency is probably associated with the high Coulomb field (between two Nd<sup>3+</sup>) that this semiionic molecule is in.

The assignment of the Nd-F vibrations is difficult on the basis of comparison. It is possible that the band at 472 cm<sup>-1</sup> can be assigned to the Nd-F vibration although the symmetry and the environment are in our case different than in the case of NdF<sub>3</sub>. Raman active lattice modes in NdF<sub>3</sub> have been observed at 414 cm<sup>-1</sup> (29), although a recent study of molecular geometry and vibrational frequencies of LnF<sub>3</sub> presume that  $\nu_1$  for NdF<sub>3</sub> is at 556 cm<sup>-1</sup> (30). Stretching vibration  $\nu_1$  for a pyramidal structure of LnF<sub>3</sub> should have a reasonably high Raman intensity and in the case of PrF<sub>3</sub> band at 526 cm<sup>-1</sup> was observed (31).

The AsF<sub>6</sub><sup>-</sup> octahedra are deformed due to the formation of strong fluorine bridges between Nd atoms via *cis* fluorine atoms of AsF<sub>6</sub>. The O<sub>h</sub> symmetry is reduced and instead of three Raman active modes more bands could be assigned to AsF<sub>6</sub><sup>-</sup> anions. Some bands are split and some forbidden bands can appear.

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