The Crystal Structure of the Molecular Addition Compound Xenon Difluoride-Xenon Tetrafluoride

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The crystal structure of the molecular addition compound xenon difluoride–xenon tetrafluoride was solved by a combination of heavy-atom and direct methods using three-dimensional X-ray diffraction data. Structural parameters including anisotropic thermal motion were refined by the method of least squares. The existence in the crystal of discrete XeF_2 and XeF_4 molecules, with linear and square-planar configurations respectively, was established and a description of their thermal motions obtained. The short intermolecular distances in $XeF_2.XeF_4$ are similar to those in the crystals of the two components and suggest that there is electrostatic attraction between the molecules.

Introduction

The discovery that xenon reacts with fluorine to form simple compounds (Weeks, Chernick & Matheson, 1962; Smith, 1963; Claassen, Selig & Malm, 1962) and the need for information about the nature of the chemical bonding involved led to the rapid determination of the crystal structures of XeF_2 and XeF_4 by X-ray (Ibers & Hamilton, 1963; Hamilton & Ibers, 1963; Siegel & Gebert, 1963; Templeton, Zalkin, Forrester & Williamson, 1963a, b) and neutron diffraction (Levy & Agron, 1963a, b; Burns, Agron & Levy, 1963a, b). A third crystalline phase was found in mixtures of these two compounds and was reported erroneously by Burns (1963) to be a 'high-density form of XeF_4'. Crystal-structure analysis of this phase showed it to be $XeF_2.XeF_4$, and preliminary reports were given by Burns, Ellison & Levy (1963a, b). The present paper presents the details of this structure determination and a discussion of the thermal motion and the intermolecular contacts.

Experimental

Crystals of $XeF_2.XeF_4$ were prepared by sealing into a small glass tube a mixture of XeF_2 and XeF_4. Since all three phases have vapor pressures of a few millimetres at room temperature, specimens for X-ray diffraction study were grown by slight cooling of a spot on the tube wall.

Precession photographs were used, with film-shrinkage corrections, to establish the unit-cell dimensions and probable space group. The crystals are monoclinic, $P2_1/c$, with $a=6.64$, $b=7.33$, $c=6.40$ Å, each ± 0.01 Å and $\beta=92° 40 \pm 5'$. There are four xenon atoms per unit cell, and the X-ray density is 4.02 g.cm^{-3}.

Three-dimensional intensity data were obtained by the 2θ-scan technique employing a single-crystal orienter, Mo $K\alpha$ X-rays, and a scintillation-counter detector. The reflections fall into two groups (*vide infra*). Reflections having unmixed indices were measured out to $\theta=35°$, where the intensities were still detectable but quite weak; but reflections with mixed indices were measured only to $\theta=20°$, where intensities were unobservable above background. Within these ranges 366 intensities with unmixed indices and 209 with mixed indices were measured; of these, 482 had detectable intensity. The diffracting crystal grew larger during the data collection because of deposition of material from elsewhere in the tube, but frequent measurement of a reference reflection provided a means of normalization. From an approximate determination of the shape of the crystal an absorption correction was calculated for each reflection with the FORTRAN program of Wehe, Busing & Levy (1962). The absorption correction, A^*, ranged from 3.02 to 3.50. Lorentz-polarization corrections were applied, and the intensities were reduced to squared structure factors.

Structure determination and refinement

A survey of the structure amplitudes showed, in addition to the systematic absences of space group $P2_1/c$, that $F(hkl)$ is large for h, k, l unmixed (all odd or all even) and generally small for h, k, l mixed, indicating that the xenon atoms are in a face-centered array. The two chemically different kinds of xenon atoms must therefore occupy positions (*International Tables for X-ray Crystallography*, 1952) $2(a)$ and $2(d)$ of space group $P2_1/c$. However, the non-equivalence of the xenon atoms was not established until the structure was elucidated since the formula was initially thought to be XeF_4; so the other possibility for face-centered xenon atoms in $4(e)$ with $x=z=\frac{1}{4}$,

$y = 0$ was tried, but finally discarded. With the xenon atoms in positions $2(a)$ and $2(d)$, the signs of all structure factors with unmixed indices are positive. An electron-density map was computed† using only these terms. In this map, because of the omission of the mixed-index terms, the peaks attributable to fluorine atoms were repeated by a face-centering operation and had one-fourth the density of true fluorine peaks. Consequently, an assignment of fluorine sites was not readily achieved. A second Fourier summation was then made in which ten mixed-index reflections were also included with signs assigned as follows: two signs were chosen arbitrarily, three were deduced from these by Sayre's squaring method (1952), and five more were found by the same method to depend on the choice of one sign. The two choices of this sign were tried, and one of the maps obtained had the true fluorine peaks enhanced at the expense of the others, so that a suitable structure could be postulated. In this structure one pair of centrosymmetrically equivalent fluorine atoms is bonded to a xenon atom in one twofold equipoint and two pairs of fluorine atoms are bonded to a xenon atom in the other. The fluorine atoms are thus in three sets of equipoints of type $4(e)$.

This model was refined by an iterative least-squares program on the IBM 7090 (Busing, Martin & Levy, 1962). The variables included the individual anisotropic temperature parameters for all atoms, the positional parameters for the fluorine atoms, and one overall scale factor. As the refinement proceeded it became apparent that the thirty-five reflections of greatest intensity were affected by extinction; these were omitted from subsequent refinement cycles. Atomic scattering factors for neutral fluorine atoms (*International Tables for X-ray Crystallography*, 1962) and for neutral xenon atoms (Watson & Freeman, 1963), the latter corrected for anomalous dispersion (Dauben & Templeton, 1955), were used. The observations, F^2, were weighted as the inverse of their

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† For this and later Fourier summations a modified version of the FORDAP code by Zalkin (1962) was used.

variances, $\sigma^2(F^2)$, which were estimated from the expression:

$$\sigma^2(F^2) = s(A^*/Lp)^2[N + 2B + (0.04N)^2],$$

in which N is the net count in a peak, B is the background count, A^* is the absorption correction, s is the scale factor and Lp is the Lorentz-polarization correction. The applicability of this expression to counter-measured data has been discussed by Peterson & Levy (1957).

The refined parameters and their standard deviations are listed in Table 1. The discrepancy index $R = \Sigma ||F(\text{obs})| - |F(\text{calc})||/\Sigma|F(\text{obs})|$ had the value 0.048 for all 540 extinction-free reflections. For 441 reflections with $F^2(\text{obs}) > \sigma$, the value was 0.031; within this group, 331 with unmixed indices had $R = 0.022$, and 110 with mixed indices had $R = 0.102$. The standard deviation of an observation of unit weight:

$$\{\Sigma_i w_i[F_i^2(\text{obs}) - F_i^2(\text{calc})]^2/(m-n)\}^{\frac{1}{2}}$$

where w_i is the weight of an observation, m is the number of extinction-free observations, and n is the number of adjustable parameters, was 1.57 at the end of the refinement. Based on these two criteria, the agreement between model and data is considered quite satisfactory. Table 2 presents observed and calculated values of the squared structure amplitudes and the calculated signs.

After the refinement was completed, a three-dimensional electron-density map was computed using the observed structure amplitudes, except that the calculated values were substituted for those affected by extinction. In this map the maxima corresponding to xenon atoms were very large, and the series termination ripples around them caused appreciable distortion of the fluorine peaks. However, a difference map for which the xenon-atom contributions were subtracted from the total electron density showed the fluorine atoms without distortion. Sections of the three-dimensional map which pass closest to atomic centers are superimposed to produce Fig. 1. Only

Table 1. *Final parameters* and their standard deviations*

	Xe(1)		Xe(2)		F(1)		F(2)		F(3)	
	Parameter	σ	Parameter	σ	Parameter	σ	Parameter	σ	Parameter	σ
x	(0.0)	—	(0.5)	—	0.1681	0.0009	0.5053	0.0011	0.2400	0.0010
y	(0.0)	—	(0.0)	—	−0.1875	0.0010	0.0783	0.0013	0.1087	0.0010
z	(0.0)	—	(0.5)	—	0.1524	0.0011	0.2114	0.0009	0.5163	0.0013
β_{11}	0.0177	0.0003	0.0166	0.0003	0.025	0.002	0.045	0.003	0.020	0.002
β_{22}	0.0121	0.0002	0.0115	0.0002	0.021	0.002	0.036	0.003	0.021	0.002
β_{33}	0.0208	0.0003	0.0168	0.0003	0.030	0.002	0.021	0.002	0.069	0.004
β_{12}	−0.0005	0.0003	0.0008	0.0003	0.004	0.002	−0.019	0.002	0.003	0.002
β_{13}	−0.0012	0.0002	−0.0009	0.0002	−0.004	0.002	−0.006	0.002	0.004	0.002
β_{23}	0.0017	0.0003	−0.0002	0.0003	0.004	0.002	0.008	0.002	−0.003	0.003

* The numbers in parentheses were not varied in the least-squares refinement. The β's are the coefficients in the anisotropic temperature factor expression:

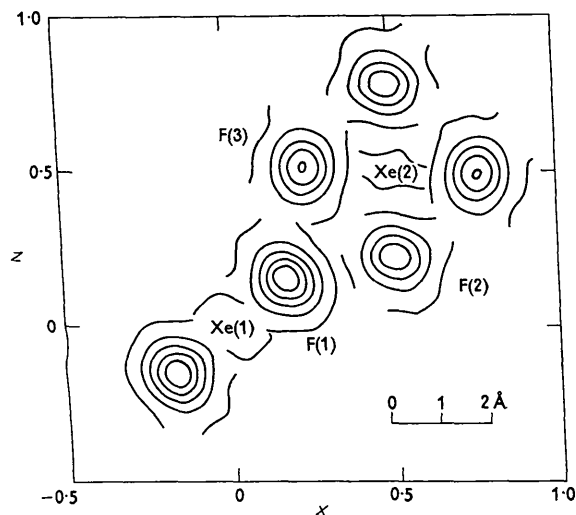$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

Table 2. *Observed and calculated values of the squared structure factors*

OBS is $0 \cdot 1F^2$(obs) and CAL is $0 \cdot 1F^2$(calc) on an absolute scale.
S is the sign of F(calc). Values of OBS preceded by E were affected by extinction

Column group 1

H	K	L	OBS	CAL	S
2	0	0	E1245	2411	+
3	0	0	164	171	-
4	0	0	E1179	1660	+
5	0	0	0	0	+
6	0	0	382	446	+
8	0	0	108	129	+
10	0	0	19	20	+
1	1	0	1	3	+
2	1	0	53	37	+
3	1	0	15	14	+
4	1	0	8	7	-
5	1	0	11	15	-
6	1	0	0	0	-
0	2	0	E1586	3233	+
1	2	0	57	51	-
2	2	0	E1436	2701	+
3	2	0	0	1	+
4	2	0	E1095	1275	+
5	2	0	0	2	-
6	2	0	342	325	+
8	2	0	99	108	+
10	2	0	18	20	+
1	3	0	69	58	-
2	3	0	9	9	-
3	3	0	20	18	+
4	3	0	5	2	+
5	3	0	0	0	-
0	4	0	E921	1150	+
1	4	0	0	1	+
2	4	0	E1179	1447	+
3	4	0	0	1	+
4	4	0	492	496	+
5	4	0	0	0	-
6	4	0	248	262	+
8	4	0	59	58	+
10	4	0	15	15	+
1	5	0	0	0	+
2	5	0	3	2	-
3	5	0	0	1	+
4	5	0	0	0	-
0	6	0	591	640	+
1	6	0	0	2	+
2	6	0	485	524	+
3	6	0	0	0	-
4	6	0	259	256	+
6	6	0	125	137	+
8	6	0	32	31	+
0	8	0	210	235	+
2	8	0	200	203	+
4	8	0	135	135	+
6	8	0	41	41	+
0	10	0	82	85	+
2	10	0	60	59	+
4	10	0	41	40	+
-1	-11	1	37	38	+
-3	-11	1	24	26	+
-1	-9	1	123	130	+
-3	-9	1	100	96	+
-5	-9	1	47	44	+
-1	-7	1	376	375	+
-3	-7	1	259	267	+
-5	-7	1	140	140	+
-7	-7	1	46	41	+
-1	-6	1	3	2	-
-2	-6	1	2	2	+
-3	-6	1	6	5	+
-1	-5	1	E1071	1170	+
-2	-5	1	5	3	-
-3	-5	1	536	528	+
-4	-5	1	0	0	-
-5	-5	1	291	275	+
-7	-5	1	97	93	+
-9	-5	1	24	23	+
-1	-4	1	2	3	-
-2	-4	1	0	0	+
-3	-4	1	27	26	-
-4	-4	1	5	2	+
-5	-4	1	0	1	+
-1	-3	1	E1132	1460	+
-2	-3	1	13	11	-
-3	-3	1	E1166	1231	+
-4	-3	1	18	19	+
-5	-3	1	504	500	+
-7	-3	1	137	132	+
-9	-3	1	38	38	+
-1	-2	1	5	4	+
-2	-2	1	144	115	+
-3	-2	1	30	28	-
-4	-2	1	0	1	+
-5	-2	1	0	0	-
-6	-2	1	0	1	+
-1	-1	1	E1289	3292	+
-2	-1	1	95	76	-
-3	-1	1	E1286	1589	+
-4	-1	1	14	14	-
-5	-1	1	612	574	+
-6	-1	1	0	2	+
-7	-1	1	224	219	+
-9	-1	1	49	41	+
-1	1	1	1	10	-
1	1	1	E1562	2959	+
2	1	1	12	12	+
3	1	1	E1118	1640	+
4	1	1	7	6	-
5	1	1	691	714	+
6	1	1	0	1	+
7	1	1	208	211	+
9	1	1	47	46	+
1	2	1	351	324	+
2	2	1	25	20	-
3	2	1	27	21	-
4	2	1	22	20	-
5	2	1	13	11	+
0	3	1	0	0	-
1	3	1	E1225	2222	+

Column group 2

H	K	L	OBS	CAL	S
2	3	1	7	3	+
3	3	1	E1207	1385	+
4	3	1	1	1	-
5	3	1	430	452	+
7	3	1	165	178	+
9	3	1	40	40	+
0	4	1	47	50	-
1	4	1	0	0	+
2	4	1	0	8	+
3	4	1	15	10	+
4	4	1	3	5	+
0	5	1	0	2	+
1	5	1	15	17	+
2	5	1	821	907	+
3	5	1	27	33	-
4	5	1	562	583	+
5	5	1	1	2	+
6	5	1	326	341	+
7	5	1	90	90	+
9	5	1	29	24	+
0	6	1	3	0	+
1	6	1	0	0	-
2	6	1	0	0	+
3	6	1	0	0	+
1	7	1	375	391	+
3	7	1	266	272	+
5	7	1	130	128	+
7	7	1	42	42	+
1	9	1	135	137	+
3	9	1	89	89	+
5	9	1	45	42	+
1	11	1	34	36	+
3	11	1	27	26	-
-2	-10	2	54	52	+
-4	-10	2	34	31	+
-2	-8	2	144	154	+
-4	-8	2	117	110	+
-6	-8	2	41	38	+
-1	-6	2	0	1	-
-2	-6	2	529	561	+
-4	-6	2	230	235	+
-6	-6	2	107	108	+
-8	-6	2	32	29	+
-1	-5	2	1	1	+
-2	-5	2	0	1	+
-3	-5	2	0	2	-
-4	-5	2	0	0	+
-1	-4	2	6	6	-
-2	-4	2	E1067	1221	+
-3	-4	2	0	1	-
-4	-4	2	489	475	+
-6	-4	2	214	215	+
-8	-4	2	53	48	+
-1	-3	2	19	16	-
-2	-3	2	0	0	+
-3	-3	2	0	1	+
-4	-3	2	4	2	+
-5	-3	2	0	1	-
-1	-2	2	E1083	1181	+
-2	-2	2	0	1	-
-3	-2	2	873	869	+
-4	-2	2	0	2	+
-5	-2	2	280	283	+
-6	-2	2	77	73	+
-8	-2	2	17	16	+
-10	-1	2	114	103	-
-1	-1	2	0	1	+
-2	-1	2	45	39	+
-3	-1	2	15	11	+
-4	-1	2	0	3	-
-5	-1	2	0	2	-
-1	0	2	219	173	-
-2	0	2	E1289	1672	+
-3	0	2	7	6	+
-4	0	2	865	881	+
-5	0	2	0	0	-
-6	0	2	264	252	+
-10	0	2	15	15	+
1	0	2	2	3	-
2	0	2	E721	896	+
3	0	2	31	31	+
4	0	2	E1007	1237	+
5	0	2	6	7	+
6	0	2	249	258	+
8	0	2	93	97	+
10	0	2	21	20	+
0	1	2	27	19	+
1	1	2	2	1	-
2	1	2	44	33	-
3	1	2	2	1	+
5	1	2	1	1	+
0	2	2	E1546	2168	+
2	2	2	53	48	+
2	2	2	E1173	1597	+
0	2	2	0	0	+
3	2	2	679	672	+
5	2	2	0	0	-
2	2	2	272	289	+
4	2	2	84	88	+

Column group 3

H	K	L	OBS	CAL	S
8	4	2	52	51	+
0	5	2	5	4	-
1	5	2	0	1	+
2	5	2	0	0	+
3	5	2	0	0	+
0	6	2	492	531	+
1	6	2	4	6	-
2	6	2	473	497	+
4	6	2	296	282	+
6	6	2	105	109	+
8	6	2	32	30	+
0	8	2	222	234	+
2	8	2	182	188	+
4	8	2	96	100	+
6	8	2	49	43	+
0	10	2	64	65	+
2	10	2	50	49	+
4	10	2	40	36	+
-1	-11	3	22	25	+
-1	-9	3	87	84	+
-3	-9	3	57	58	+
-5	-9	3	28	28	+
-1	-7	3	250	240	+
-3	-7	3	156	156	+
-5	-7	3	90	78	+
-7	-7	3	33	26	+
-1	-6	3	2	2	-
-1	-5	3	594	577	+
-3	-5	3	0	0	-
-5	-5	3	380	401	+
-7	-5	3	179	172	+
-9	-5	3	55	52	+
-1	-4	3	17	16	+
-2	-4	3	27	27	+
-3	-4	3	4	4	+
-4	-4	3	0	0	+
-5	-4	3	0	2	-
-1	-3	3	E1204	1273	+
-2	-3	3	21	23	-
-3	-3	3	678	630	+
-4	-3	3	0	1	-
-5	-3	3	355	358	+
-7	-3	3	105	105	+
-1	-2	3	23	23	-
-2	-2	3	11	11	+
-3	-2	3	6	7	-
-4	-2	3	0	0	+
-5	-2	3	0	0	-
-1	-1	3	E1414	1786	+
-2	-1	3	2	0	-
-3	-1	3	E1255	1284	+
-4	-1	3	11	11	-
-5	-1	3	409	396	+
-7	-1	3	127	144	+
-9	-1	3	29	28	+
-1	0	3	100	89	-
-2	0	3	E1288	1872	+
-3	0	3	0	0	-
-4	0	3	E1040	1220	+
-5	0	3	7	5	-
-7	0	3	425	456	+
-9	0	3	151	153	+
-1	1	3	36	36	+
-2	1	3	21	22	+
-3	1	3	10	9	-
-1	2	3	0	1	-
-2	2	3	23	20	-
-3	2	3	7	7	+
-5	2	3	2	1	+
-7	2	3	13	12	+
-1	3	3	E1101	1319	+
-2	3	3	0	7	-
-3	3	3	624	612	+
-4	3	3	1	1	-
-5	3	3	332	342	+
-7	3	3	120	120	+
-1	4	3	0	0	-
-2	4	3	0	0	+
-3	4	3	12	12	+
-5	4	3	1	3	-
-7	4	3	0	0	-
-9	4	3	13	11	+
0	5	3	482	489	+
1	5	3	0	0	-
3	5	3	451	443	+
5	5	3	184	184	+
7	5	3	60	58	+
9	5	3	19	18	+
0	6	3	0	4	-
1	6	3	264	256	+
3	6	3	170	176	+
5	6	3	88	84	+
7	6	3	36	33	+
9	6	3	89	89	+
1	8	3	60	60	+
3	8	3	33	34	+
5	8	3	25	25	+
1	11	4	27	30	+
-2	-10	4	18	19	+
-4	-10	4	93	91	+
-2	-8	4	54	52	+
-4	-8	4	23	22	+
-6	-8	4	223	222	+
-2	-6	4	119	136	+
-4	-6	4	47	48	+
-6	-6	4	15	15	+
-8	-6	4	0	4	+
-1	-5	4	0	0	+
-2	-5	4	493	477	+
-3	-5	4	0	0	+
-4	-4	4	220	221	+
-6	-4	4	103	105	+

Column group 4

H	K	L	OBS	CAL	S
-8	-4	4	27	25	+
-1	-3	4	4	5	+
-2	-3	4	3	1	-
-3	-3	4	9	10	+
-4	-3	4	0	0	+
-1	-2	4	770	770	+
-2	-2	4	5	5	-
-4	-2	4	384	362	+
-6	-2	4	147	153	+
-2	-1	4	40	40	+
-4	-1	4	0	0	-
-6	-1	4	18	16	-
-8	-1	4	0	0	+
-1	0	4	32	31	-
-2	0	4	882	867	+
-3	0	4	1	1	-
-4	0	4	573	600	+
-5	0	4	0	0	-
-6	0	4	144	145	+
-8	0	4	46	48	+
-10	0	4	9	10	+
0	0	4	E1028	1243	+
2	0	4	E1009	1169	+
3	0	4	3	0	-
4	0	4	511	578	+
6	0	4	170	176	+
8	0	4	66	66	+
0	1	4	3	2	-
1	1	4	34	36	-
2	1	4	0	0	+
3	1	4	2	1	+
4	1	4	5	5	+
0	2	4	E993	1155	+
2	2	4	707	731	+
3	2	4	8	9	-
4	2	4	477	471	+
6	2	4	180	196	+
8	2	4	48	47	+
0	3	4	0	3	+
1	3	4	10	7	-
2	3	4	5	5	+
3	3	4	0	1	-
0	4	4	483	510	+
1	4	4	1	0	-
2	4	4	508	511	+
3	4	4	0	0	-
4	4	4	265	274	+
6	4	4	118	121	+
8	4	4	33	33	+
0	5	4	0	1	+
1	5	4	0	0	-
0	6	4	242	249	+
2	6	4	269	263	+
4	6	4	135	137	+
6	6	4	59	57	+
8	6	4	19	19	+
0	8	4	128	127	+
2	8	4	84	84	+
4	8	4	68	59	+
6	8	4	27	26	+
0	10	4	37	35	+
2	10	4	32	32	+
4	10	4	40	41	+

Column group 5

H	K	L	OBS	CAL	S
-1	-9	5	31	29	+
-1	-7	5	124	129	+
-3	-7	5	82	79	+
-5	-7	5	25	38	+
-7	-7	5	15	13	+
-1	-5	5	246	250	+
-3	-5	5	167	173	+
-5	-5	5	88	91	+
-7	-5	5	28	25	+
-1	-4	5	0	0	-
-3	-4	5	0	0	+
-5	-4	5	2	3	-
-1	-3	5	483	455	+
-3	-3	5	0	0	+
-5	-3	5	356	350	+
-7	-3	5	154	159	+
-9	-3	5	60	54	+
-1	-1	5	589	555	+
-3	-1	5	357	349	+
-5	-1	5	171	179	+
-7	-1	5	67	68	+
-9	-1	5	18	17	+
-1	1	5	7	6	-
-3	1	5	0	1	+
-5	1	5	0	0	-
-1	3	5	380	381	+
-3	3	5	314	320	+
-5	3	5	170	175	+
-7	3	5	55	49	+
-1	5	5	0	0	+
-3	5	5	1	1	-
-5	5	5	295	296	+
-7	5	5	201	202	+

Column group 6

H	K	L	OBS	CAL	S
1	7	5	122	122	+
3	7	5	89	83	+
5	7	5	46	46	+
1	9	5	39	41	+
3	9	5	37	32	+
-2	-8	6	38	35	+
-4	-8	6	23	20	+
-2	-6	6	86	85	+
-4	-6	6	50	48	+
-6	-6	6	25	20	+
-2	-4	6	178	179	+
-4	-4	6	98	100	+
-6	-4	6	34	38	+
-8	-4	6	11	11	-
-2	-2	6	271	274	+
-4	-2	6	137	142	+
-6	-2	6	57	51	+
-8	-2	6	17	16	+
-1	-1	6	0	0	+
-2	-1	6	0	1	-
-2	0	6	247	245	+
-4	0	6	148	159	+
-6	0	6	57	63	+
-8	0	6	16	16	+
0	0	6	362	405	+
2	0	6	268	285	+
4	0	6	158	161	+
6	0	6	82	78	+
8	0	6	21	23	+
0	1	6	2	3	-
0	2	6	297	293	+
2	2	6	254	257	+
4	2	6	163	173	+
6	2	6	60	59	+
8	2	6	20	20	+
0	4	6	205	208	+
2	4	6	196	193	+
4	4	6	99	103	+
6	4	6	48	44	+
0	6	6	116	117	+
2	6	6	95	91	+
4	6	6	54	53	+
6	6	6	29	27	+
0	8	6	40	40	+
2	8	6	42	38	+
4	8	6	28	26	+
-1	-7	7	76	73	+
-3	-7	7	41	42	+
-5	-7	7	24	23	+
-1	-5	7	124	123	+
-3	-5	7	89	92	+
-5	-5	7	42	38	+
-7	-5	7	14	13	+
-1	-3	7	199	192	+
-3	-3	7	116	122	+
-5	-3	7	52	52	+
-7	-3	7	19	18	+
-1	-1	7	197	202	+
-3	-1	7	132	143	+
-5	-1	7	68	71	+
-7	-1	7	25	25	+
-1	1	7	136	139	+
-3	1	7	103	106	+
-5	1	7	44	45	+
-1	3	7	69	72	+
-3	3	7	58	49	+
-5	3	7	33	30	+
-7	3	7	35	34	+
-1	5	7	29	27	+
-3	5	7	23	24	+
-5	5	7	12	13	+
-1	7	7	42	39	+
-3	7	7	22	22	+
-1	-5	9	12	12	+
-3	-5	9	25	27	+
-1	-3	9	18	18	+
-3	-3	9	28	31	+
-1	-1	9	24	22	+
-3	-1	9	12	10	+
-1	1	9	31	30	+
-3	1	9	23	20	+
-1	3	9	19	18	+
-2	-2	10	15	12	+
-2	0	10	13	14	+
0	0	10	21	17	+
2	0	10	14	16	+
0	2	10	13	16	+

Fig. 1. Sections of the three-dimensional electron-density map with the xenon-atom contributions subtracted. Contours are at 2·0 e.Å⁻³.

that part of the unit cell required to show one of each kind of molecule is presented.

Results and discussion

Interatomic distances and angles and their standard deviations were calculated from the refined parameters, the variance–covariance matrix, and the unit-cell dimensions. The Busing & Levy (1959) Function and Error computer program was used to obtain these and other functions of the parameters.

Because the xenon atoms lie at centers of symmetry, the XeF_2 and XeF_4 molecules in $XeF_2.XeF_4$ are required to be linear and planar, respectively. Further description of the molecules requires consideration of the effect of thermal motion. Since the thermal amplitudes of Xe and F atoms are unequal, the Xe–F distances appear foreshortened (Cruickshank, 1956). As the structure consists of discrete molecules with heavy atoms at the centers of mass, it is plausible that the fluorine atoms 'ride' on the xenon atoms. Based on this model, corrected bond distances were calculated (Busing & Levy, 1964). For XeF_2 the corrected bond length, Xe(1)–F(1) is 2·010 ($\sigma = 0.006$) Å and the two corrected bond lengths for XeF_4 are Xe(2)–F(2) = 1·972 ($\sigma = 0.007$) Å and Xe(2)–F(3) = 1·945 ($\sigma = 0.007$) Å. The F(2)–Xe(2)–F(3) angle in the XeF_4 molecule is 89·1 ($\sigma = 0.4$)°. The sigmas are least-squares measures of precision. We estimate the corresponding measures of accuracy to be about twice as large; hence the XeF_4 molecule does not deviate significantly from a square-planar configuration. In crystals of XeF_2 itself the Xe–F bond length is 2·00 Å (Levy & Agron, 1963a, b), while in crystalline XeF_4, the Xe–F bond lengths are all 1·95 Å and the F–Xe–F angle is 90·0° (Burns, Agron & Levy, 1963a,b).

The individual intramolecular configurations are thus retained in the addition compound with little if any change.

The thermal motion of the XeF_2 moiety is described by giving, in Table 3, the root-mean-square displacements of its atoms along and perpendicular to its molecular axis. Also in Table 3 are the root-mean-square components of thermal displacement of the atoms of the XeF_4 moiety; these are referred to a right-handed Cartesian system defined by the direction of the normal to the molecular plane and the direction of the Xe(2)–F(2) bond. The third axis is nearly collinear with the Xe(2)–F(3) bond direction. The large fluorine motions perpendicular to the bonds suggest rigid-body librations of these molecules. Assuming this type of motion, an approximate calculation yields for the XeF_4 molecule two out-of-plane librations of about 5° r.m.s. amplitude and an in-plane libration with about 9° r.m.s. amplitude. The XeF_2 molecule can be similarly described as having two librations about axes perpendicular to the molecule with r.m.s. amplitudes of about 4°, or as precessing with a half angle of about 7°. Similar motions were deduced to occur in crystals of the component compounds, except that the in-plane libration of XeF_4 is approximately 5°.

Table 3. *Root-mean-square thermal displacements* (Å)

XeF_2

	Parallel to molecular axis	Perpendicular to molecular axis*
Xe(1)	0·182	0·287
F(1)	0·198	0·371

XeF_4

	Along plane normal	Along axis Xe(2)–F(2)	Along axis near Xe(2)–F(3)
Xe(2)	0·182	0·188	0·187
F(2)	0·260	0·192	0·372
F(3)	0·254	0·374	0·203

* $\sqrt{(\overline{\mu^2} - \overline{\mu_a^2})}$, where $\overline{\mu^2}$ is the mean square radial displacement and $\overline{\mu_a^2}$ is the mean square component along the molecular axis.

Table 4 lists the interatomic distances in a manner which emphasizes the kind and number of neighbors possessed by each atom in the asymmetric unit, out to an arbitrary limit of 3·70 Å. Fig. 2, a perspective drawing of one unit cell with a set of non-related interatomic distances indicated, is useful in identifying the atom pairs listed in Table 4.

Intermolecular F · · · F contacts have a range of values increasing from 2·87 Å; these are normal for molecular crystals containing fluorine atoms. However, in $XeF_2.XeF_4$, as in crystals of XeF_2 and XeF_4, there are several intermolecular contacts between xenon and fluorine atoms which are interestingly short. In addition to the bonded fluorine atoms, the divalent xenon atom has two fluorine-atom neighbors at

Table 4. *Interatomic distances**

Number and kind of atoms at distance d from

Xe(1)	Xe(2)	F(1)	F(2)	F(3)	d (Å)	σ
—	2F(3)	—	—	1Xe(2)	1·909†	0·007
—	2F(2)	—	1Xe(2)	—	1·936†	0·006
2F(1)	—	1Xe(1)	—	—	1·996†	0·006
—	—	—	1F(3)	1F(2)	2·698†	0·011
—	—	—	1F(3)	1F(2)	2·739†	0·011
—	—	1F(2)	1F(1)	—	2·869	0·010
—	—	—	1F(2)	—	2·938	0·013
—	—	1F(2)	1F(1)	—	2·979	0·011
—	—	—	1F(3)	1F(2)	3·118	0·012
—	—	1F(3)	—	1F(1)	3·204	0·011
—	—	1F(3)	—	1F(1)	3·235	0·009
—	—	1F(3)	—	1F(1)	3·249	0·009
2F(3)	—	—	—	1Xe(1)	3·280	0·008
—	—	2F(1)	—	—	3·328	0·006
—	—	1F(2)	1F(1)	—	3·352	0·010
—	2F(1)	1Xe(2)	—	—	3·353	0·007
—	2F(1)	1Xe(2)	—	—	3·355	0·007
—	2F(2)	—	1Xe(2)	—	3·374	0·010
2F(1)	—	1Xe(1)	—	—	3·416	0·008
—	—	—	—	1F(3)	3·561	0·015
—	—	1F(3)	—	1F(1)	3·565	0·012
2F(2)	—	—	1Xe(1)	—	3·605	0·007
2F(3)	—	—	—	1Xe(1)	3·635	0·010
2F(2)	—	—	1Xe(1)	—	3·656	0·009
2F(3)	—	—	—	1Xe(1)	3·688	0·007
—	—	—	2F(2)	—	3·699	0·005

* Not corrected for thermal motion.   † Intramolecular.
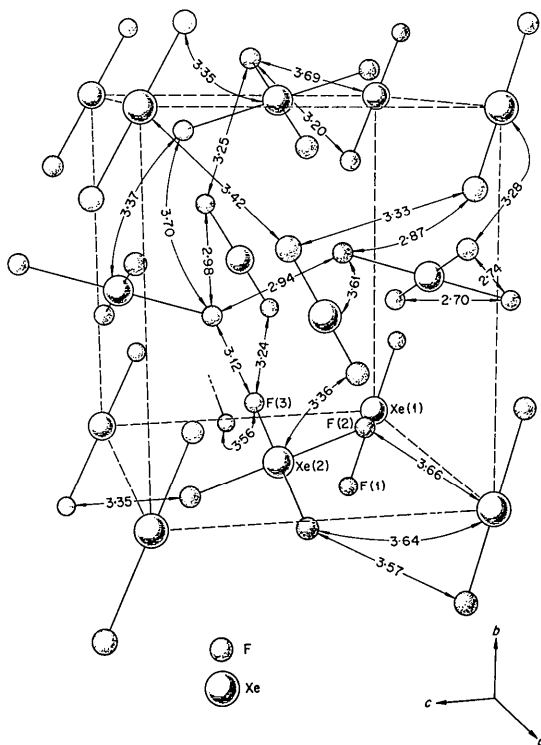
Fig. 2. A perspective drawing of the unit cell of $XeF_2.XeF_4$ for use with Table 4 in identifying the interatomic distances.

3·28 Å, two at 3·42 Å, and a group of eight in the range 3·61–3·69 Å. The tetravalent xenon atom has

six fluorine atoms at 3·35 to 3·37 Å, and the four intramolecular fluorine atoms fill the remaining space around it. For comparison, each xenon atom in crystalline XeF_2 has eight non-bonded fluorine-atom neighbors at 3·41 Å, while in XeF_4 crystals there are two such contacts at 3·22 Å and two at 3·25 Å. A van der Waals contact distance of about 3·6 Å between these atoms is obtained by summing half the interatomic distance in crystalline xenon and the van der Waals radius of the fluorine atom. The shorter values observed in the xenon fluoride crystals probably imply additional electrostatic attraction between molecules arising from electron migration from xenon to fluorine atoms within each molecule. We have calculated Xe · · · F distances from crystal radii R_z for atoms bearing charge ze, derived according to the formula (Pauling, 1960)

$$R_z = R_1 |z|^{-2/(n-1)}$$

in which R_1 is Pauling's univalent radius, and n is the Born exponent (7 for F^- and 12 for Xe^0). In using this theory, which can apply only approximately in this case, we visualize the electron configuration of both atoms in the contact region as being similar to that in the normal noble-gas atom or ion; that is, we neglect the dependence of R_1 itself on the magnitude of the charge migration. We calculate Xe · · · F distances of 3·45 and 3·23 Å for Xe(II) and Xe(IV), respectively, for a charge transfer of 0·6e to each fluorine atom. If the dependence of R_1 on net charge

were considered, distances in this range would be calculated with a somewhat smaller charge migration.

Other evidence for the charge migration has been cited: theoretical treatments of the Xe–F bond have indicated a charge transfer of about $0.5e$ per fluorine atom (Lohr & Lipscomb, 1963; Rundle, 1963; Pitzer, 1963; Jortner, Rice & Wilson, 1963; Pimentel & Spratley, 1963), and experiments on heats of sublimation (Jortner, Wilson & Rice, 1963) and nuclear magnetic resonance studies (Lazdins, Kern & Karplus, 1963) have been explained by the assumption of a charge transfer of about 0.5–$0.6e$ per fluorine atom.

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