Lawrence Berkeley National Laboratory
Recent Work

Title
A DETERMINATION OF THE CRYSTAL STRUCTURE OF XENON TETRAFLUORIDE

Permalink
https://escholarship.org/uc/item/63s2q4n5

Authors
Templeton, David H.
Zalkin, Allan
Forrester, J.D.
et al.

Publication Date
1963-04-01

University of California

Ernest O. Lawrence
Radiation Laboratory

A DETERMINATION OF THE CRYSTAL
STRUCTURE OF XENON TETRAFLUORIDE

DISCLAIMER

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

A DETERMINATION OF THE CRYSTAL STRUCTURE
OF XENON TETRAFLUORIDE*

David H. Templeton, Allan Zalkin, J. D. Forrester
and Stanley M. Williamson

April 1963

A Determination of the Crystal Structure of Xenon Tetrafluoride[*]

David H. Templeton, Allan Zalkin, J. D. Forrester and Stanley M. Williamson

Department of Chemistry and Lawrence Radiation Laboratory

University of California, Berkeley, California

April, 1963

The crystal and molecular structure of XeF_4 has been determined

by single-crystal x-ray diffraction techniques. The intensities

of Mo $K\alpha$ x-rays diffracted by the crystal were measured with

a scintillation counter. The monoclinic unit cell dimensions

are a = 5.050 Å, b = 5.922 Å, c = 5.771 Å (each ± 0.003 Å),

and β = 99.6° ± 0.1°. The space group is $P2_1/n$ with two

molecules per unit cell. The xenon atoms occupy the corners

and body centers so that the molecular packing is pseudo

body-centered cubic. The molecule has a square planar configuration.

The Xe-F bond distance is 1.93 ± 0.02 Å, after a correction

of +0.02 Å for thermal vibration effects; the F-Xe-F bond

angle is a right angle (90.4 ± 0.9°) within the accuracy of

the determination.

INTRODUCTION

This paper is an extended and slightly modified version of our

earlier report[1] which described our determination of the crystal and

(1) D. H. Templeton, A. Zalkin, J. D. Forrester and S. M. Williamson,

J. Am. Chem. Soc. 85, 242 (1963).

molecular structure of XeF_4.

The earliest x-ray study of this compound was by Siegel and Gebert[2] who determined the cell dimensions and space group. The atomic coordinates were determined simultaneously by Ibers and Hamilton[3] and ourselves[1] by x-ray diffraction. Ibers and Hamilton used photographic data from precession films, while we used stationary scintillation counter data. This work was soon followed by a neutron-diffaction study by Burns, Agron and Levy[4] which gives somewhat higher precision for the fluorine coordinates than is feasible with the x-ray data.

EXPERIMENTAL

Xenon tetrafluoride was prepared by heating the elements to 300° in a flow system.[1] Subsequently a slightly modified procedure was adopted. A 4 to 1 molar ratio mixture of F_2 and Xe was mixed well in a half liter copper chamber which contained baffles with twice as much helium, which acted as a carrier gas. The gas mixture then flowed through a copper U-trap at -120° into a 12 in. length of 3/4 in. nickel tubing. The nickel and copper were joined by a silver-soldered connection. The last six inches of the reactor tube was heated to 350° by an electric furnace. The reactor ended with 4 in. of 1/2 in. copper tubing so that there was a thermal gradient before the copper-to-glass seal. A glass U-trap was then either sealed to the glass of the copper-to-glass seal or connected through an ungreased ground joint. The joint was used if the XeF_4 sample was to be transferred to other containers in a dry-box and the seal was used if the trap were equipped with

(2) S. Siegel and E. Gebert, J. Am. Chem. Soc. 85, 240 (1963).

(3) J. A. Ibers and W. C. Hamilton, Science 139, 106 (1963).

(4) J. H. Burns, P. A. Agron, and H. A. Levy, Science

a break-seal so that the sample could be transferred into a vacuum system. The trap was cooled with solid CO_2 and the other end went by tubing directly to a hood. The glass from the copper-to-glass seal to the $CO_2(s)$ level was maintained at about 75° by means of a heating tape to prevent condensation upstream from the trap. Good conversion of the Xe to XeF_4 was attained with a flow rate such that the residence time in the reactor was one minute. The apparatus is very similar in design to that of Holloway and Peacock[5] except that our apparatus had only one trap. This procedure yielded the material described by Gunn and Williamson[6] for which the chemical analysis was close to theoretical for XeF_4. Our x-ray studies of material prepared in this way detected crystals only of the structure described here, except when samples had been exposed to water.

In some of our earlier work we attempted quick transfers of the material in damp air into capillaries, but the resulting samples survived only long enough for a few preliminary x-ray patterns. It was only when the capillaries were loaded by sublimation under vacuum that we obtained stable specimens. The capillaries were thin-walled vitreous silica of 0.5 mm diameter. During the investigation of the final crystal, it is estimated to have undergone about 10 hours of irradiation with no evidence of decomposition, and in fact the crystal continued to grow at the expense of other crystals in the capillary. A few weeks after the experiment, the crystal disappeared by sublimation to regrow in another location in the capillary. Four months later it was still there. Photographs of the crystal taken the day following

(5) J. H. Holloway and R. D. Peacock, Proc. Chem. Soc. 1962, 389.

(6) S. R. Gunn and S. M. Williamson, Science 140, 177 (1963).

the intensity measurements are shown in Fig. 1. The crystal diameter ranged from 0.13 to 0.24 mm in various directions. Eleven faces of the pseudo-cubic dodecahedron were developed; the twelfth surface was attached to the curved surface of the capillary.

Molybdenum Kα x-rays were produced with a General Electric XRD-5 unit operated at 25 ma. and 40 kvp. A 0.001 in. Zr foil was used to filter the diffracted radiation just before it entered the scintillation counter. The range of intensities measured was from 1 to 14,000 counts per second. The counter was checked and found to be linear over this range.

The cell dimensions were measured with a take-off angle of 2° using the resolved $K\alpha_1$ peaks of Mo ($\lambda = 0.70926$ Å). The crystal was set on the goniostat with the a^* axis perpendicular to the phi circle; this axis coincides very roughly with the axis of the capillary.

The intensities were measured using the stationary technique and counting each reflection for 20 seconds, with a take-off angle of 4°. A fixed-time count is appropriate for approximately equal weighting of the data in the least-squares analysis. The background, plotted as a function of the diffraction angle 2θ, was ordinarily applied to the data; in a case where the reflection was a multiple of a strong reflection, the background was checked near the reflection. All of the 293 independent independent reflections up to a 2θ angle of 50° ($\sin\theta/\lambda \sim 0.59$) were measured; 35 of these were below the detection limit and were recorded as zero. The crystal grew about 30 percent during the measurements (two days), and the data were normalized by repeated measurement of a few standard reflections. The data were corrected for the Lorentz-polarization factor using the formula: $I_{cor} = I \sin2\theta/(1+\cos^2 2\theta)$.

The least-squares program of Gantzel, Sparks and Trueblood[7] was used on an IBM7090; this program minimizes the function $\sum ||F_o|-|F_c||^2 / \sum |F_o|^2$ where F_o and F_c are the observed and calculated structure factors. The weighting factors were all unity. The program utilizes a full-matrix calculation for the parameter shifts. Our results are stated in terms of temperature factors of the form $\exp(-\beta_{11}h^2 -2\beta_{12}hk -...)$, although the program actually uses $\exp(-B_{11}h^2 -B_{12}hk -...)$.

Scattering factors for the neutral Xe and F atoms were obtained from Tables 3.3.1B and 3.3.1A respectively as given in the International Tables.[8] Due to an oversight the Xe scattering factors were not corrected for the dispersion correction $\Delta f'$ which is approximately -0.5 electrons.

STRUCTURE DETERMINATION

Reflections are strong when $h+k+l$ is even and weak when it is odd, showing that the Xe atoms are at 0,0,0 and 1/2,1/2,1/2. Trial coordinates for fluorine atoms were estimated by some simple calculations which in principle were equivalent to making projections of the fluorine electron density down the $\underline{a}$ and $\underline{c}$ axes with use of only a few terms in which the effect of the fluorine atoms was large. The electron densities were not actually calculated, but were roughly approximated graphically. For example, reflections 060 and 110 were judged to be stronger than average, while 031 and 200 were weaker than average. In these cases the phases are fixed by xenon. Reflections 012, 014, and 520 were judged to be strong among reflections depending only on fluorine. In these cases phases

(7) P. Gantzel, R. Sparks and K. Trueblood, private communication (1961).

(8) International Tables for X-ray Crystallography, Vol. 3, Kynoch Press, Birmingham, England (1962).

were chosen in all permutations. These calculations resulted in six coordinates for the two fluorine atoms which in five cases were within 0.05 of the final values. For F(2) the trial value of y was 0.18, in error by 0.15. Refinement by least squares quickly corrected this error.

Eight cycles of least squares refinement using isotropic temperature factors brought the unreliability factor $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ to 0.11. Four cycles using anisotropic temperature factors then diminished R to 0.089. Two obvious blunders in data taking were corrected by remeasurement of their intensities, and three more cycles of least squares brought R to 0.076.

Some of the low-angle data appeared to suffer from extinction and/or absorption, so the 7 reflections with $\sin\theta/\lambda$ less than 0.17 were deleted from the refinement. A final set of refinements of 5 cycles reduced R to our final value of 0.059 for 286 data. The results in Table 1 and Table 2 are from this last calculation. Table 1 lists the final parameters. Table 2 lists the observed and calculated structure factors; those marked with an asterisk were deleted from the final refinement.

Some additional calculations were performed with the 96 non-zero, odd $h+k+\ell$ data. These reflections are the result of fluorine atoms exclusively. A refinement with isotropic temperature factors resulted in coordinates for fluorine atoms which were the same as those in Table 1 within 0.005 or less. The corresponding R was 0.18.

The data were not corrected for absorption. The dimensions of the crystal correspond to μR of about 0.9. In the approximation of spherical shape, absorption would be almost perfectly compensated by systematic errors in the thermal parameters. We estimate that to compensate for the absorption error the temperature parameters of each atom in Table 1

should be increased by the following amounts:

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
0.0007	0.0005	0.0005	0.0000	0.0001	0.0000

DISCUSSION

The space group symmetry requires the molecule to be planar, and within the accuracy of the determination it is square planar. Fig. 2 shows the molecular packing, and Fig. 3 the molecular dimensions before correction for thermal motion. If the fluorine atoms are assumed to ride on the xenon atoms, the Xe-F bond distances should be increased by 0.02 Å to the value 1.93 Å.

In Table 3 are listed interatomic distances, without correction for thermal motion. Each xenon has four fluorine neighbors in other molecules at an average distance of 3.25 Å. Each fluorine atom has 8 fluorine neighbors in other molecules at an average distance of 3.13 Å or 3.15 Å, as well as one xenon neighbor in another molecule. The average intermolecular F-F distance infers a van der Waals radius of 1.57 Å, which is considerably larger than the accepted value of 1.35 Å,[9] perhaps because of the considerable thermal motion of the molecules. Using the smaller value for fluorine, one gets an upper limit of 1.9 Å for the van der Waals radius of xenon in this tetravalent state.

We have three independent sets of results for the structure of this crystal: the neutron diffraction study of Burns, Agron and Levy,[4,10] the photographic x-ray study of Hamilton and Ibers,[3,11] and our own counter x-ray study. There is no significant disagreement with respect to

(9) L. Pauling, "The Nature of the Chemical Bond", 3rd Ed., Cornell

University Press, Ithaca, N. Y. (1960).

(10) J. H. Burns, P. A. Agron and H. A. Levy, private communication.

(11) J. A. Ibers and W. C. Hamilton, private communication.

the geometry of the structure; the three sets of coordinates agree in each case within two standard deviations or less. The thermal parameters of the fluorine atoms are in similar agreement. The agreement between the sets of thermal parameters for xenon is as good as for fluorine on an absolute scale, but is poorer than the ostensible precision of the measurements. Systematic errors which are a function of θ (for example, absorption) will have equal effect on thermal parameters of heavy and light atoms. We attribute the disagreement to systematic errors which have an effect on the thermal parameters at a level of the order of 0.3 in terms of the equivalent isotropic B value, but we have not identified the precise nature of these errors. We are not surprised that such errors are present; rather, we did not expect them to be so small.

Table 1. Crystal structure data for XeF_4

$a = 5.050 \pm 0.003$ Å $Z = 2$

$b = 5.922 \pm 0.003$ Å   Space group $P2_1/n$ (C_{2h}^5)

$c = 5.771 \pm 0.003$ Å   Molecular weight $= 207.30$

$\beta = 99.6 \pm 0.1°$ X-ray density $= 4.04$ g/ml

$V = 170.2$ Å^3

Atomic positions:

Xe: 0, 0, 0; 1/2, 1/2, 1/2.

F: $\pm(x, y, z;$ $1/2 - x, 1/2 + y, 1/2 - z)$,

F(1): $x = 0.260 \pm 0.003$ F(2): $x = 0.229 \pm 0.003$

$y = 0.146 \pm 0.002$ $y = 0.033 \pm 0.002$

$z = -0.153 \pm 0.002$ $z = 0.297 \pm 0.002$

Anisotropic temperature parameters:

	Xe	F(1)	F(2)
β_{11}	0.0208 ± 0.0007	0.044 ± 0.006	0.044 ± 0.006
β_{22}	0.0097 ± 0.0005	0.025 ± 0.004	0.021 ± 0.004
β_{33}	0.0120 ± 0.0005	0.031 ± 0.004	0.029 ± 0.005
β_{12}	0.0012 ± 0.0004	-0.006 ± 0.004	0.000 ± 0.004
β_{13}	0.0070 ± 0.0008	0.023 ± 0.005	0.002 ± 0.004
β_{23}	0.0000 ± 0.0006	0.004 ± 0.004	0.000 ± 0.004

(each multiplied by 10).

Table 2: Observed and calculated structure factors. An asterisk indicates a reflection given zero weight.

```
H,K= 0, 0      L FOBS FCAL     -4   44  -40    H,K= 2, 2     -1   71  -69    -4    0   15    -4   26   30
L FOBS FCAL   -5  557  568     -3  524  481    L FOBS FCAL    0  309  321    -3  458  436    -3  486  488
2  550  567   -3  611  605     -2   33   38    -6  344  367    1   33   42    -2   24  -29    -2   50  -49
4  556  545   -1  758  565*    -1  758  740    -5   63  -64    2  310  323    -1  382  367    -1  384  364
6  417  405    1  758  637*     0   20  -38    -4  534  499                    0    0    1     0    0   -8
               3  782  792      1  430  427    -3   30   26    H,K= 3, 0       1  467  472     1  315  344
H,K= 0, 1      5  381  353      2   38   46    -2  814  759    L FOBS FCAL     2   30  -40     2    0    3
L FOBS FCAL                     3  467  468    -1  129   89    -5  377  390    3  290  296     3  289  287
1  641  973*   H,K= 1, 1        4   33  -38     0  599  599    -3  626  621
2  245  202    L FOBS FCAL      5  320  323     1   48  -42    -1  712  683    H,K= 3, 5       H,K= 4, 4
3  692  724   -6  344  363                      2  650  677     1  681  620    L FOBS FCAL     L FOBS FCAL
4   85  -70   -5   12    5      h,K= 1, 5        3   68  -58     3  353  335    -3   51   57    -4  304  345
5  393  401   -4  771  740      L FOBS FCAL      4  362  355     5  309  296    -2  404  396    -3   23   -6
6    0   -7   -3  141  105     -4  398  377      5   20   25                    -1   53  -56    -2  379  385
              -2  615  551     -3  103  -53                     H,K= 3, 1       0  353  354    -1   21   24
H,K= 0, 2     -1  140  -98*    -2  463  444     H,K= 2, 3      L FOBS FCAL      1   42  -32     0  335  340
L FOBS FCAL    0  734  958*    -1   57   58     L FOBS FCAL    -6  355  384     2  284  309     1   52  -50
0  730 1052*   1  145 -115*     0  504  457     -6   18   10   -5    0    2                     2  237  259
1  124   95    2  807  943      1   46   43     -5  460  449   -4  404  402    H,K= 3, 6
2  571  616    3   88   65      2  439  435     -4   76  -71   -3   97  -83    L FOBS FCAL     H,K= 4, 5
3   74   66    4  415  404      3   72  -68     -3  428  394   -2  819  776    -1  316  326    L FOBS FCAL
4  577  585    5    0   10      4  292  311     -2   78   75   -1   31   28     0    0   -4    -2   15   -7
5   50  -53    6  356  339                      -1  767  742    0  609  582                    -1  298  308
6  333  341                     H,K= 1, 6        0    0  -13    1   62   54    H,K= 4, 0       0    0    4
              H,K= 1, 2        L FOBS FCAL       1  626  644    2  423  428    L FOBS FCAL
H,K= 0, 3     L FOBS FCAL      -3  335  330      2   59  -55    3   21  -28    -4  374  392    H,K= 5, 0
L FOBS FCAL   -6   46  -41     -2   14   10      3  350  361    4  406  370    -2  411  417    L FOBS FCAL
1  541  586   -5  447  438     -1  398  383      4   21   25    5    0   -9     0  672  610    -3  345  375
2   99   95   -4   64   56      0   23  -23      5  318  313                    2  329  314    -1  344  347
3  690  724   -3  663  608      1  376  387                    H,K= 3, 2       4  263  261     1  281  294
4   61  -61   -2  175  130      2   14   23     H,K= 2, 4      L FOBS FCAL
5  328  354   -1  933 1047      3  314  327     L FOBS FCAL    -6   35   41    H,K= 4, 1       H,K= 5, 1
6    0   14    0  366 -324                      -5   29   20   -5  430  444    L FOBS FCAL     L FOBS FCAL
               1  499  543      H,K= 2, 0       -4  410  389   -4   47  -55    -5  333  375    -4  352  395
H,K= 0, 4      2  110   95     L FOBS FCAL       -3    0   -6   -3  588  543    -4   50   48    -3   29   31
L FOBS FCAL    3  642  650     -6  305  335     -2  554  509   -2  118  -92    -3  483  468    -2  314  318
0  610  598    4   28   31     -4  635  650     -1  126 -102   -1  525  487    -2   81  -75    -1   13  -10
1  140 -130    5  391  380     -2  912  977      0  542  540    0  155  135    -1  489  451     0  328  353
2  498  528    6   18  -20      0  417  364      1   87   83    1  604  629     0    0   -9     1   22  -23
3    0   21                     2  810  813      2  473  479    2   40  -46     1  431  460     2  262  272
4  450  463    H,K= 1, 3        4  472  428      3   24  -32    3  346  341     2   28   26
5   14   13    L FOBS FCAL      6  245  253      4  288  285    4    0  -13     3  326  306    H,K= 5, 2
              -6  287  300                                     H,K= 3, 3       4    0  -11    L FOBS FCAL
H,K= 0, 5     -5    0   13      H,K= 2, 1       H,K= 2, 5      L FOBS FCAL                     -4    0   15
L FOBS FCAL   -4  557  506     L FOBS FCAL      L FOBS FCAL    -5   17   -8    H,K= 4, 2       -3  319  353
1  473  478   -3   17  -11     -6    0  -13     -4    0   -7   -4  451  448    L FOBS FCAL     -2   31   25
2   15  -24   -2  746  703     -5  527  515     -3  350  373   -3    0   -9    -5   29   36    -1  374  370
3  431  440   -1   19   10     -4  103  -84     -2   26  -26   -2  528  490    -4  400  422     0   51  -48
4    0  -10    0  690  733     -3  688  646     -1  479  456   -1   39  -38    -3    0   -9     1  222  258
               1   21  -25     -2  212  163      0   32  -30    0  485  469    -2  460  441     2    0    4
H,K= 0, 6      2  541  548     -1  874  831      1  422  421    1    0   16    -1   67  -57
L FOBS FCAL    3    0  -12      0   13    4      2    0   13    2  431  446     0  476  469    H,K= 5, 3
0  460  456    4  409  413      1  609  649      3  300  312    3    0   -4     1    0   -1    L FOBS FCAL
1   66  -73    5   22   18      2  133 -107                    4  309  298     2  291  305    -3    0   -9
2  339  356                     3  517  506     H,K= 2, 6                      3    0   18    -2  314  333
3    0   19    H,K= 1, 4        4   27   29     L FOBS FCAL    H,K= 3, 4      H,K= 4, 3       -1   27    5
              L FOBS FCAL       5  406  373     -3    0    6    L FOBS FCAL    L FOBS FCAL     0  291  315
H,K= 1, 0     -5  336  333                      -2  373  368                                  1    0  -22
```

Table 3: Distances in XeF$_4$. The asterisked values are inter-

molecular distances.

Xe	-	2 F$_1$	1.91 $\pm$ .02 Å *
		2 F$_2$	1.91 $\pm$ .02 Å *
		2 F$_2$	3.22 $\pm$ .02 Å
		2 F$_1$	3.27 $\pm$ .02 Å
F$_1$	-	Xe	1.91 $\pm$ .02 Å *
		F$_2$	2.71 $\pm$ .03 Å *
		F$_2$	2.69 $\pm$ .03 Å *
		F$_2$	3.03 $\pm$ .03 Å
		F$_2$	3.08 $\pm$ .03 Å
		F$_2$	3.09 $\pm$ .03 Å
		2 F$_1$	3.16 $\pm$ .02 Å
		F$_2$	3.22 $\pm$ .03 Å
		F$_1$	3.24 $\pm$ .04 Å
		F$_2$	3.26 $\pm$ .03 Å
		Xe	3.27 $\pm$ .02 Å
F$_2$	-	Xe	1.91 $\pm$ .02 Å *
		F$_1$	2.71 $\pm$ .03 Å *
		F$_1$	2.69 $\pm$ .03 Å *
		2 F$_2$	3.02 $\pm$ .01 Å
		F$_1$	3.03 $\pm$ .03 Å
		F$_1$	3.08 $\pm$ .03 Å
		F$_1$	3.09 $\pm$ .03 Å
		F$_1$	3.22 $\pm$ .03 Å
		F$_1$	3.26 $\pm$ .03 Å
		F$_2$	3.32 $\pm$ .04 Å
		Xe	3.22 $\pm$ .02 Å

Figure 1: Two views of the crystal of XeF_4 used in this structure determination. The two views are approximately 75° rotation apart from each other. The a axis is approximately parallel to the long edge of the crystal.
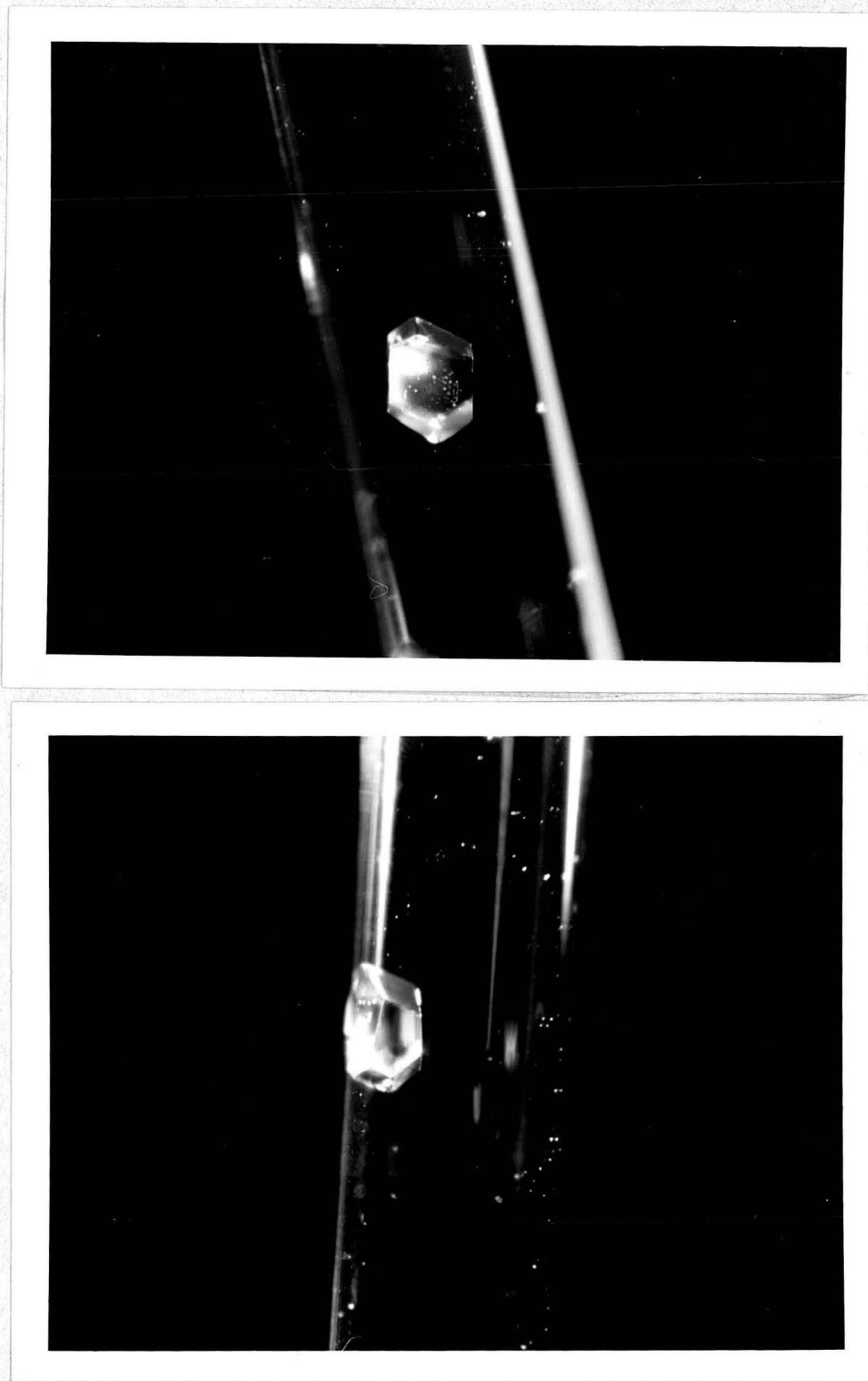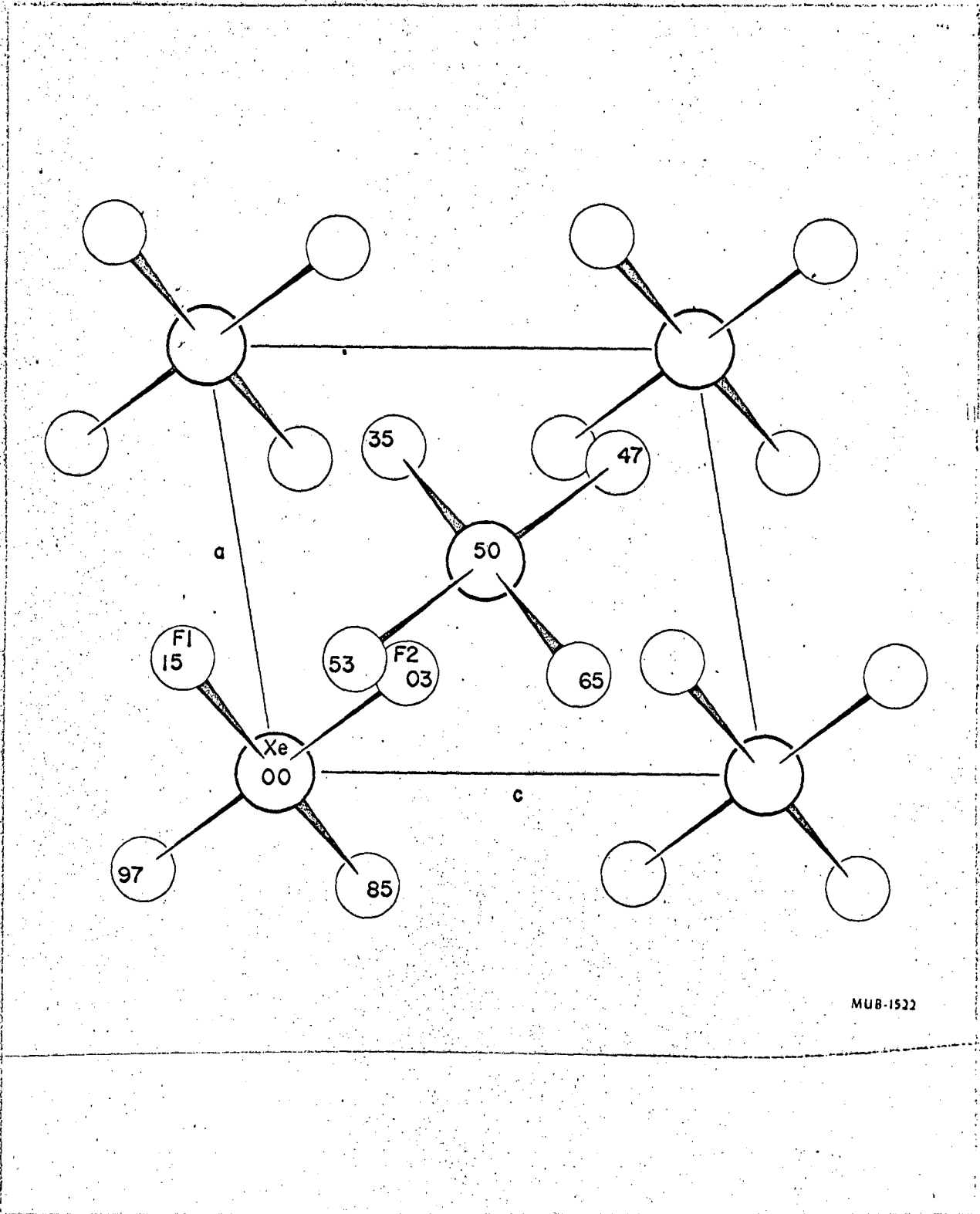
Figure 2: Molecular packing in XeF_4 as seen in projection down the b axis. The numbers on some of the atoms are b coordinates (x100).

MUB-1522

Figure 3: Molecular dimensions in XeF$_4$. Distances have not been

corrected for thermal vibrations in this figure.

XeF4

MUB-1521