

sumed to be the structure of Na₃AlF₆ when it becomes cubic at 540°C. In the structure of K₂NaAlF₆, which is cubic at all temperatures studied, K atoms occupy the sites within the cube and Na atoms the sites on the edges.

The deviations from the ideal cryolite structure are greater in α -Li₃AlF₆ than in Na₃AlF₆, but the similarity can still be recognized by reference to Fig. 3. The octahedra are in a pseudo face-centered cubic array, but the Li atoms are displaced from the center of the edges and the center of the cell. The 'cube' of eight Li atoms within the cell is also quite distorted.

It is unlikely that Li₃AlF₆ exists at any temperature in the idealized cryolite structure in which two thirds of the Li atoms would have 12-fold coordination; but this would not preclude there being a cubic structure of this type which had these Li atoms in a disordered arrangement within the space surrounded by 12 F atoms. The cubic cell assigned by Garton & Wanklyn (1965) to γ -Li₃AlF₆ does not have the proper dimensions indicative of a cryolite structure; in fact, the assignment of cubic symmetry to this phase is questionable as described earlier. On the other hand, δ - or

ϵ -Li₃AlF₆ may be cubic; data are not available for their powder patterns.

References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, a Fortran Crystallographic Least-Squares Program*, ORNL TM-305: Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- GARTON, G. & WANKLYN, B. M. (1965). *J. Inorg. Nucl. Chem.* **27**, 2466.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*, ORNL-3794, Revised: Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- NÁRAY-SZABÓ, S. & SASVÁRI, K. (1938). *Z. Kristallogr.* **99**, 27.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd edition, p. 561. Ithaca: Cornell Univ. Press.
- STEWART, E. G. & ROOKSBY, H. P. (1953). *Acta Cryst.* **6**, 49.
- WINKLER, H. G. F. (1952). *Heidelberg. Beitr. Min.* **3**, 297; *Structure Reports*, **16**, 174.
- WINKLER, H. G. F. (1954). *Acta Cryst.* **7**, 33.

Acta Cryst. (1968). **B24**, 230

The Crystal Structure of Na₇Zr₆F₃₁*

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The structure of Na₇Zr₆F₃₁ was determined by single-crystal X-ray and neutron diffraction methods. Zirconium atomic positions were deduced from an X-ray Patterson map, and the remaining atomic sites from electron-density maps. Refinement including anisotropic thermal parameters was carried out by the method of least squares. The neutron scattering amplitude of Zr was determined to be $0.69 \pm 0.01 \times 10^{-12}$ cm. The rhombohedral unit cell, with $a = 8.5689$ Å, $\alpha = 107^\circ 21'$, contains one formula weight of Na₇Zr₆F₃₁. Six Na atoms, six Zr atoms, and five sets of six F atoms occupy general sixfold positions of $R\bar{3}$, while one Na atom is in a onefold special position and one F atom is statistically distributed over a twofold site. Each Zr atom is bonded to eight F atoms arranged as a square antiprism. Six antiprisms share corners to enclose a cuboctahedral cavity which is occupied by one disordered F atom. This structural feature accounts for the unusual stoichiometry of the compound. The Na atoms are located outside the triangular faces of the cuboctahedron. One edge of each antiprism is shared with an antiprism of a different octahedral group of antiprisms, bridging all groups together.

Introduction

The study of this crystal structure was undertaken primarily because of the curious stoichiometry of the compound. There are a large number of compounds which have this formula type and which, from their X-ray powder patterns, appear to be isostructural. In

fact, although the stoichiometry was checked by chemical analysis in some instances, the formula has been assigned to many of these compounds only on the basis of similarity of their powder patterns to those of the well-established 7:6 compounds. Six of these double fluorides were reported by Zachariasen (1948) to have 1:1 composition. Subsequent phase diagram studies by Barton, Friedman, Grimes, Insley, Moore & Thoma (1958) and Barton, Grimes, Insley, Moore & Thoma (1958) showed that they actually have 7:6 ratios, and

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these workers as well as many others have appreciably extended the list; see Table 1 for the presently known examples.

Table 1. *Compounds with 7:6 stoichiometry*

Formula	Reference	Formula	Reference
7NaF.6ZrF ₄	(1)	7KF.6NpF ₄	(7)
7NaF.6PrF ₄	(2)	7KF.6PuF ₄	(4, 7)
7NaF.6PaF ₄	(3)	7KF.6AmF ₄	(10)
7NaF.6UF ₄	(4, 5)		
7NaF.6NpF ₄	(6, 7)	7NH ₄ F.6UF ₄	(11)
7NaF.6PuF ₄	(4, 6, 7)	7NH ₄ F.6PuF ₄	(11)
7NaF.6AmF ₄	(6)	7RbF.6ThF ₄	(8)
7NaF.6CmF ₄	(6)	7RbF.6PaF ₄	(3, 12)
		7RbF.6UF ₄	(11)
7KF.6ThF ₄	(4, 8)	7RbF.6NpF ₄	(7)
7KF.6PaF ₄	(3)	7RbF.6PuF ₄	(4, 7)
7KF.6UF ₄	(4, 9)		

- (1) Barton, Grimes, Insley, Moore & Thoma (1958).
- (2) Asprey & Keenan (1961).
- (3) Asprey, Kruse & Penneman (1967).
- (4) Zachariasen (1948).
- (5) Barton, Friedman, Grimes, Insley, Moore & Thoma (1958).
- (6) Keenan (1966).
- (7) Keller & Schmutz (1966).
- (8) Thoma & Carlton (1961).
- (9) Thoma, Insley, Landau, Friedman & Grimes (1958).
- (10) Asprey (1954).
- (11) Benz, Douglass, Kruse & Penneman (1963).
- (12) Asprey, Kruse & Penneman (1965).

Previous work on this structure type was the determination of the space-group symmetry, $R\bar{3}$, by Zachariasen (1948, 1951) and his suggestion of possible sites for Na and U atoms in 'NaUF₅'. After the stoichiometry was shown to be 7:6, Agron & Ellison (1959) made further structural proposals to take this into account. Neither of these reports suggested any F positions or presented any data, so a complete structure determination was required. The results to be given here show that these earlier suggestions were correct only in certain qualitative aspects.

Our structure determination was also expected to yield further knowledge of the type of coordination achieved by zirconium in complex fluorides. Only a few such compounds have been studied in sufficient detail for comparison with bonding theory.

Experimental procedure

A single-crystal specimen, crystallized from a melt of composition 53% NaF-47% ZrF₄, as previously reported by Agron & Ellison (1959), was ground to a sphere with 0.1 mm radius. Intensity measurements were made with the computer-controlled four-circle diffractometer described by Busing, Ellison, Levy, King & Roseberry (1967). Ni-filtered Cu $K\alpha$ X-rays were employed and θ - 2θ scans were made in the region $2\theta > 30^\circ$, in which the peak did not overlap the Ni absorption edge. At lower 2θ angles an ω -scan technique was used, with the counter aperture restricted to exclude the nickel edge. All independent reflections were

recorded to the limit of the instrument and totalled 725.

As the structure refinement proceeded it was observed that some weak reflections were being observed to be too strong relative to their calculated values. This excess intensity was discovered in most cases to be due to multiple reflection (Renninger, 1937; Burbank, 1965), ascertained by setting the crystal in reflecting position and rotating about the normal to the plane in question, a so-called ψ -(azimuthal) scan. Such a mode of operation involves simultaneous adjustment of χ , ϕ and ω angles of the diffractometer (Busing & Levy, 1967). Typically, a ψ -scan of about 10° revealed the presence of one to five Renninger reflections; a setting of ψ between these peaks was chosen for repetition of the 2θ -scan in each case. About thirty weak reflections were remeasured in this way. Of course many other (stronger) reflections may have had undetected contributions from multiple reflection, but of a less significant fraction of the intensity. Indeed it appears that all crystal structure determinations may have some error, usually undetected, from this source.

The crystal was also affected by secondary extinction; a correction was made with the technique proposed by Zachariasen (1963) for a spherical crystal. A multiplicative correction factor for F_o^2 was derived and applied to all reflections. Its maximum value was 1.99 and was less than 1.06 for reflections weaker than the 100 strongest.

An absorption correction was applied to all reflections with the use of the values for a sphere given in *International Tables for X-ray Crystallography* (1959). For $\mu R = 2.98$, $A^*(\theta = 0^\circ) = 37.5$ and $A^*(\theta = 80^\circ) = 8.3$. Because of the large change in A^* over the range of data, it was estimated that nonsphericity of the specimen could contribute 5-10% systematic error in the intensity, at the extremes. After being corrected for these effects, the intensities were multiplied by Lorentz-polarization factors to convert them to squared structure factors.

Two-theta values for the α_1 components ($\lambda = 1.54051 \text{ \AA}$) of twelve high-angle reflections were used to refine the unit-cell dimensions by the method of least squares. The values obtained were $a = 8.56885 \pm 0.00005 \text{ \AA}$ and $\alpha = 107^\circ 21' \pm 1'$, (the indicated errors are least-squares standard deviations) which agree reasonably well with the values which Agron & Ellison (1959) obtained from powder data. The corresponding hexagonal cell has $a = 13.807 \text{ \AA}$, $c = 9.429 \text{ \AA}$. The only systematic absences are those of rhombohedral centering, in agreement with the previously assigned space group $R\bar{3}$.

In order to distinguish between a fluoride and a sodium ion, in one instance, a limited amount of neutron-diffraction data was collected. Some 252 independent reflections from a single crystal weighing 50 mg were measured with the Oak Ridge automatic neutron diffractometer (Busing, Smith, Peterson & Levy, 1964). All reflections with $\sin \theta/\lambda < 0.47$ were included; the neutron wavelength was 1.078 \AA . For the collection of data and the reduction to structure factors

and their standard errors, the procedures described by Brown & Levy (1964) were followed.

Structure determination and refinement

The asymmetric unit contains one Zr atom in a general hexagonal site 18(*f*); its coordinates were obtained from a three-dimensional map made with the X-ray data. Calculated phases based on Zr atoms alone were used with the observed amplitudes to prepare a three-dimensional electron density map. From it were determined the positions of five independent F atoms and one Na atom, all in sites 18(*f*), and one Na atom in site 3(*b*). A difference Fourier electron-density map (Fig. 1) then showed two peaks at 0, 0, $\pm z$ ($z \approx 0.05$) from which it was concluded that the remaining F atom occupies this site, 6(*c*), in statistical disorder. An electron count over the two peaks supported this conclusion. It was noted, however, that an interchange of the Na atom at 3(*b*) with the F atom at 6(*c*) would also be consistent with the electron density maps because the two ions have nearly identical scattering factors. Neutron diffraction measurements were used to resolve this question in favor of the F atom at site 6(*c*), as will be discussed later.

The positional parameters and anisotropic thermal parameters of the nine independent atoms of the structure were refined by the least-squares method employing the full-matrix program of Busing, Martin & Levy (1962) and the X-ray data. The final values of these parameters and their standard deviations are given in Table 2 and the structure factors in Table 3. Atomic scattering factors for Na⁺, F⁻ and Zr⁴⁺ were taken from *International Tables for X-ray Crystallography* (1962); both real and imaginary components of anomalous dispersion were included for Zr and are respectively -0.6 and 2.4 electrons. The function minimized was

$$\sum w(s^2 F_c^2 - F_o^2)^2,$$

where F_o and F_c are observed and calculated structure factors, s is a scale factor, and $w = 1/\sigma^2$. The following empirical relation was used to represent the variance:

$$\sigma^2(F_c^2) = \{T + k^2B + [0.05(T - kB)]^2 + 0.01E^2\} \cdot [c/A(Lp)]^2.$$

In this equation $c/A(Lp)$ is a factor to convert counts to squared structure factors (Lp = Lorentz-polarization, A = absorption factor), T = total counts, kB = normalized background counts, and E = extinction correction in counts. The $0.05(T - kB)$ is added to account for the presence of systematic errors such as arise from absorption, beam fluctuations, or other, unknown sources; this is roughly the amount of variation observed among equivalent reflections.

Refinement cycles were continued until the parameter shifts were all appreciably less than the estimated standard deviations. The agreement index $R = \sum ||F_o| - |sF_c|| / \sum |F_o|$, reached a value of 0.027 for all reflections. The standard deviation of an observation of unit weight,

$$\sigma_1 = \{ \sum w[F_o^2 - s^2 F_c^2]^2 / (m - n) \}^{1/2},$$

was 1.38. In this expression w is the weight of an observation, m is the number of observations (725), and n is the number of adjustable parameters (70). These

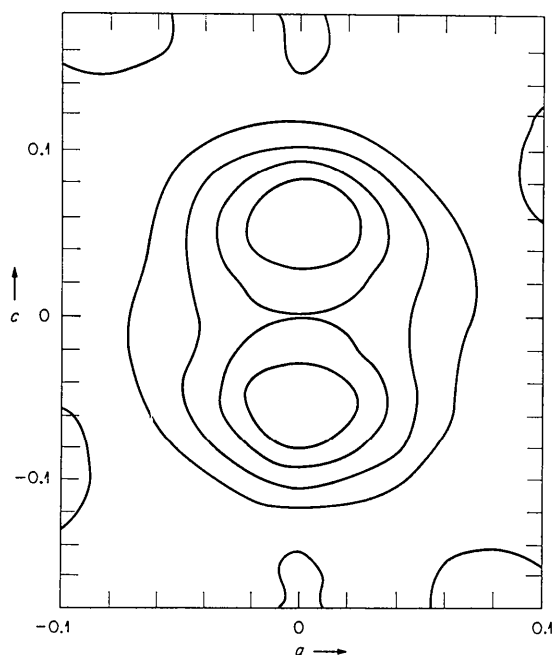


Fig. 1. Partial-difference electron-density map in the region near the origin, showing the disordered F atom peaks.

Table 2. Structural parameters* and standard errors for Na₇Zr₆F₃₁ obtained from refinement to the X-ray data

	<i>x</i>	<i>y</i>	<i>z</i>	10 ⁴ β ₁₁	10 ⁴ β ₂₂	10 ⁴ β ₃₃	10 ⁴ β ₁₂	10 ⁴ β ₁₃	10 ⁴ β ₂₃
Na(1)	0.0792 (2)	0.3040 (2)	0.4926 (2)	31 (1)	39 (2)	49 (3)	19 (1)	-5 (1)	-1 (1)
Na(2)	0	0	$\frac{1}{2}$	39 (2)	39†	57 (5)	20†	0	0
Zr	0.18955 (3)	0.05153 (2)	0.17903 (3)	16 (1)	12 (1)	18 (1)	7 (1)	2 (1)	1 (1)
F(1)	0.3558 (2)	0.1114 (2)	0.0917 (2)	19 (2)	20 (2)	32 (3)	10 (1)	4 (2)	-5 (1)
F(2)	0.1835 (2)	0.0554 (2)	0.3944 (3)	32 (2)	23 (2)	25 (3)	13 (1)	-1 (1)	-2 (1)
F(3)	0.2735 (2)	0.3706 (2)	0.4243 (3)	27 (2)	17 (2)	33 (3)	8 (1)	-7 (2)	-4 (1)
F(4)	0.2088 (2)	0.1585 (2)	0.0017 (2)	38 (2)	34 (2)	27 (2)	24 (2)	-1 (2)	7 (2)
F(5)	0.2432 (2)	0.5417 (2)	0.4416 (3)	28 (2)	43 (2)	76 (3)	27 (1)	15 (2)	19 (2)
F(6)	0	0	0.0526 (5)	189 (12)	189†	126 (18)	95†	0	0

* Hexagonal coordinates for all atoms in positions 18(*f*) of space group $R\bar{3}$, except Na(2) and F(6) which are in 3(*b*) and 6(*c*), respectively.

† Constrained by symmetry.

Table 3. Observed and calculated structure factors and standard errors

The column headings have the following meaning: H is the Miller index h, OBS and CAL are the observed and calculated structure factors (x 10), S is the calculated sign, and ERR is the standard error computed as 10σ(F2)/2|F0|. The observed structure factor and its error have been placed on the absolute scale with the least-squares scale factor.

Table with multiple columns for Miller indices (H, K, L), observed structure factors (OBS), calculated structure factors (CAL), signs (S), and standard errors (ERR). The table contains a large grid of data points for various Miller indices.

two criteria indicate a satisfactory agreement between model and data.

The question of whether F and Na occupy sites 6(c) and 3(b) or *vice versa* was examined by a least-squares refinement of the model having these atoms interchanged, using the X-ray data. The agreement reached is indicated by $\sigma_1 = 1.44$. The significance of the difference was evaluated by application of the statistical theory of linear hypotheses (Hamilton, 1965). The ratio, \mathcal{R} , of the weighted R indices for the two refinements is 1.063. Taking the hypothesis to be tested, that the interchanged model is correct, to be of dimension 1, we compared $\mathcal{R}_{1,655,0.005} = 1.006$ with 1.063. This indicated that the hypothesis can be rejected at a confidence level much higher than 99.5%. We were skeptical of this result for two reasons: (1) both the hypothesis and the least-squares fit are non-linear (in particular, the proper dimensionality of the hypothesis is uncertain), and (2) non-random errors in the observations might be present. Therefore, the neutron diffraction measurements were made; similar refinements of both models using 252 observations and 69 parameters yielded $\sigma_1 = 1.64$ for F in 6(c) versus 2.84 for Na in 6(c). The ratio $\mathcal{R} = 1.732$ is to be compared to $\mathcal{R}_{1,183,0.005} = 1.022$, leaving no reasonable doubt that the model with F in 6(c) is correct.

In the refinement with neutron-diffraction data, scattering amplitudes for sodium and fluorine were taken from the compilation by Bacon (1955). They are 0.351×10^{-12} cm and 0.55×10^{-12} cm, respectively. The scattering amplitude for zirconium was varied in the refinement, and much better agreement was obtained than when the literature value of 0.62×10^{-12} cm (Bacon, 1955) was used. The refined value is $0.69 \pm 0.01 \times 10^{-12}$ cm. Other than this, all the structural parameters adjusted were the same ones as in the X-ray refinement.

Of the 22 pairs of atomic coordinate values obtained from refinements of the X-ray and neutron data, 16 differed by less than one σ , and the largest difference was 3 times the combined σ 's. Thermal parameters obtained were generally lower in the neutron-diffraction analysis.

After the refinement was completed in the centrosymmetric space group, consideration was given to the hypothesis that the structure actually may be acentric. The possibility was considered that displacement of the F(6) atom be not random, but ordered, to produce a polar structure, with perhaps slight deviations of the other atoms from centrosymmetry.

Two such models were tested by least-squares adjustment: in one the thermal parameters of atoms related by approximate centrosymmetry were constrained to be equal, and in the other all structural parameters were varied. The constrained acentric model yielded better agreement than the centric disordered one; the improvement, as measured by the weighted R index ratio, was judged by Hamilton's (1965) criterion to be significant at the 99.5% confidence level. The resulting

structure, aside from the absence of disorder, is a minor distortion of the centric structure. In the unconstrained model, the improvement over the constrained one was also significant at the 99.5% confidence level, but some of the temperature factors were not positive definite. Furthermore, the structure factors calculated from the acentric models differ from those of the centric model mostly in the weakest reflections, which are generally larger in the acentric case; hence the agreement is sensitive to systematic errors of the sort which might enhance weak reflections. Consequently, both improvements were viewed with reservation, and we concluded that diffraction data alone do not distinguish definitely between the ordered and disordered models. For the present we choose to describe the structure as disordered. Most of the description to follow could however apply equally well to the ordered model.

Discussion of the structure

The basic structural unit in this crystal is an approximately square antiprism formed by eight F atoms around a Zr atom as illustrated in Fig. 2. This and other structural drawings were produced by a computer program written by Johnson (1965). Six of these antiprisms share corners to form the octahedral array shown in Fig. 3, right, which encloses a cavity containing one additional F atom. The twelve F atoms at the shared corners form a tetrakaidecahedron having six square and eight triangular faces, an approximately regular cuboctahedron shown in Fig. 3, left. Each square face belongs to one of the antiprisms; each triangular face

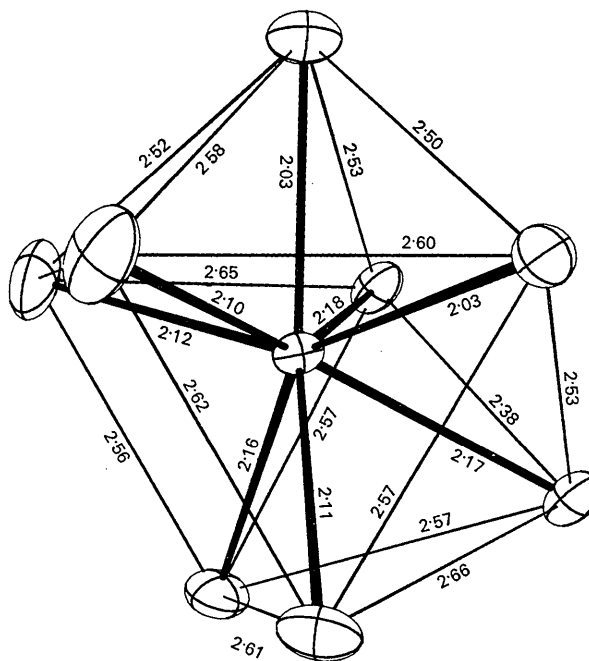


Fig. 2. A ZrF_8 antiprism showing interatomic distances. Atoms are represented by their thermal ellipsoids.

is bounded by an edge of each of three antiprisms. Exterior to each triangular face of the cuboctahedron is situated one Na atom; six of these are equivalent, in general positions, and two others occupy the sites $0, 0, \pm \frac{1}{2}$. Each octahedral array is linked to six others by the sharing of external edges of antiprisms. Fig. 4 shows, in stereographic form, parts of two octahedral arrays linked through the shared edge of two antiprisms. All other antiprisms are linked to other octahedral arrays by identical means.

A list of significant interatomic distances and their standard errors, calculated with the Busing, Martin & Levy (1964) computer program, is presented in Table 4. The atoms to which these distances refer are shown, in part, by Fig. 2, in which interatomic distances are given for one antiprism.

Table 4. *Interatomic distances and standard deviations*

From atom in x, y, z of Table 2	to atom	in position*	distance (σ)	
Zr	F(3)	6, 1, $-b$	2.031 (2) Å	
	F(2)	1	2.034 (3)	
	F(5)	6, 1, $-b$	2.098 (2)	
	F(4)	5	2.112 (2)	
	F(5)	4, 1	2.119 (2)	
	F(4)	1	2.158 (2)	
	F(1)	1	2.176 (2)	
	F(1)	4, 2	2.179 (2)	
	Na(1)	F(2)	6, 0, $+c$	2.342 (3)
		F(3)	4, 1	2.371 (3)
F(2)		2	2.386 (3)	
F(3)		6, 0, $+c$	2.387 (3)	
F(3)		1	2.448 (3)	
F(1)		3, 1	2.508 (3)	
F(1)		1, 2, $-a$	2.512 (3)	
F(5)		1	2.949 (3)	
F(4)		3, 1	3.034 (3)	
F(4)		4, 1	3.035 (3)	
Na(2)	F(2)	1	2.461 (2)	
	F(2)	2	2.461 (2)	
	F(2)	3	2.461 (2)	
	F(2)	4, 0, $+c$	2.461 (2)	
	F(2)	5, 0, $+c$	2.461 (2)	
	F(2)	6, 0, $+c$	2.461 (2)	
	F(5)	4, 1	3.016 (2)	
	F(5)	5, 1, $-a-b$	3.016 (2)	
	F(5)	6, 1, $-b$	3.016 (2)	
	F(5)	1, 2, $-a-b$	3.016 (2)	
F(1)	F(5)	2, 2	3.016 (2)	
	F(5)	3, 2, $-a$	3.016 (2)	
	F(1)	4, 2	2.380 (4)	
	F(2)	4, 2	2.532 (3)	
	F(3)	6, 1, $-b$	2.537 (3)	
	F(4)	1	2.566 (3)	
	F(4)	4, 2	2.577 (3)	
	F(5)	1, 1, $-b-c$	2.650 (3)	
F(2)	F(4)	5	2.664 (3)	
	F(3)	4, 2	2.916 (3)	
	F(3)	6, 1, $-b$	2.504 (3)	
	F(5)	4, 1	2.524 (3)	
	F(1)	4, 2	2.532 (3)	
F(5)	F(5)	6, 1, $-b$	2.584 (3)	
	F(3)	5, 0, $+c$	2.905 (3)	

Table 4 (cont.)

From atom in x, y, z of Table 2	to atom	in position*	distance (σ)
F(2)	F(2)	5, 0, $+c$	3.005 (4) Å
	F(2)	6, 0, $+c$	3.005 (4)
F(3)	F(4)	3, 1	2.570 (3)
	F(5)	1	2.602 (3)
F(4)	F(5)	4, 1	2.564 (3)
	F(4)	5	2.606 (2)
	F(4)	6	2.606 (2)
	F(5)	2, 2, $-c$	2.618 (3)
	F(6)	1	2.650 (4)
F(5)	F(6)	4	2.656 (4)
	F(6)	4, 1	2.241 (11)
	F(5)	2, 0, $+a+b$	2.671 (4)
F(5)	F(5)	3, 0, $+b$	2.671 (4)

* The symbols designating the equivalent position have the following meanings:

First symbol: point group operations	1	x, y, z of Table 2
	2	$-y, x-y, z$
	3	$y-x, -x, z$
	4	$-x, -y, -z$
	5	$y, y-x, -z$
	6	$x-y, x, -z$
Second symbol: rhombohedral centering	0	0, 0, 0
	1	$\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$
	2	$\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$
Third symbol: hexagonal cell translations	$\pm a, \pm b, \pm c.$	

The stereochemistry of eight-coordination has been discussed in papers by Clark, Kepert, Nyholm & Lewis (1963), Hoard & Silverton (1963), and Kepert (1965). The latter two papers are concerned with the calculation of most favorable polyhedra for eight-coordination. Both conclude that for eight equivalent monodentate ligands, the repulsion between ligands is the shape-determining factor, and that the square antiprism and the dodecahedron are equally favored as the most probable configurations. Examples of crystals in which fluorine coordinates zirconium with dodecahedral configuration are K_2ZrF_6 (Bode & Teufer, 1956) and $Li_6BeF_4ZrF_8$ (Sears & Burns, 1964); with antiprismatic configuration are ZrF_4 (Burbank & Bensey, 1956); $Cu_2ZrF_8 \cdot 12H_2O$ (Fischer, Elchinger & Weiss, 1967), and the present case. For both types of polyhedron, the most favorable shape was calculated to be a slight distortion from one in which all edge lengths are equal: in the antiprism, the ratio of a triangle edge to a square edge was predicted to be 1.057. Since in the crystals the polyhedra are not isolated, the distortions brought about by crystal lattice requirements tend to obscure these small variations. In the case of $Na_7Zr_6F_{31}$, the largest external influence on a particular antiprism is, no doubt, the presence of the neighboring antiprism linked by a shared edge. This causes a shortening of the F-F distance within that edge (2.38 Å, compared with 2.58 Å for the average of the others) and a stretching of the Zr-F bonds to the shared edge F atoms (2.18 Å, compared with 2.09 Å for the average of the others). This distortion alone

affects the lengths of several edges of the antiprism; hence any distortion due to internal repulsions in the antiprism is masked.

Each Na(1) atom is coordinated by ten F atoms of six antiprisms; three antiprisms share faces and three share edges with the polyhedron around the Na(1) atom. Five of these antiprisms are joined together by sharing edges or corners with one another, and the sixth one is linked to the others only through the Na atom.

The Na(2) atom can be considered to be the 'extra' Na; it fits into a cavity with point symmetry $\bar{3}$, made by six antiprisms; this cavity is similar to the one occupied by the 'extra' F atom. Three of the antiprisms belong to one octahedral array and three to another. The F neighbors of Na(2) thus comprise a trigonally compressed octahedron with Na-F distances of 2.46 Å and a concentric trigonally elongated octahedron with Na-F distances of 3.02 Å.

The 'extra' F atom, F(6), is displaced from the center of the cuboctahedron by 0.50 Å along the trigonal axis of the crystal. In this position F(6) has three F neighbors at the very short distance of 2.24 Å. The corresponding distance from the unique site in the center of the cuboctahedron has the normal value of 2.62 Å. The actual and hypothetical environments for F(6) are compared in the following table:

Displaced		Centered	
3F	2.24 Å	6F	2.62 Å
3F	2.65	6F	2.60
3F	2.66		
3F	3.03		
3Zr	2.63	6Zr	2.89
3Zr	3.20		

A calculation of the electrostatic energy, including the Born repulsive interaction, showed the displaced-atom model to have a lower potential energy than the

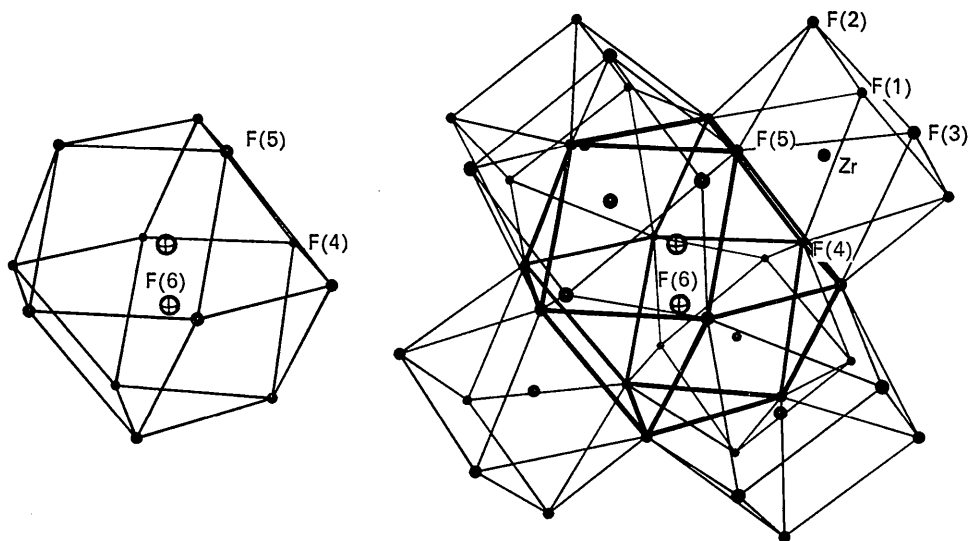


Fig. 3. A portion of the $\text{Na}_7\text{Zr}_6\text{F}_{31}$ structure showing how six antiprisms (right) share corners to form a cuboctahedral cavity (left) in which the disordered atom F(6) is situated. Both sites for F(6) are shown, although only one is occupied in each cavity.

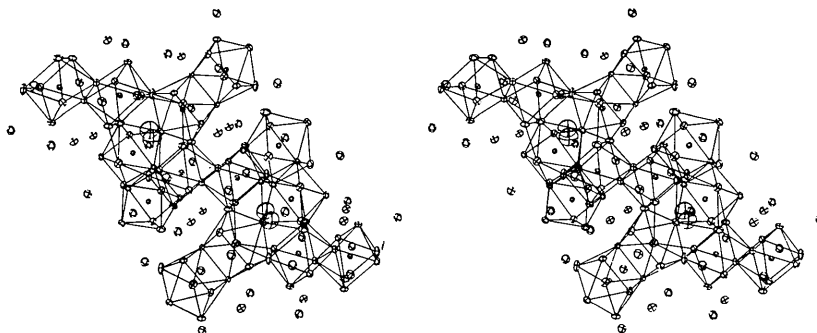


Fig. 4. A stereoscopic drawing of parts of two cuboctahedral groups of antiprisms. This Figure shows how these groups are linked together and how each triangular face of the cuboctahedra is capped by a sodium atom. There are centers of inversion at the midpoints between pairs of disordered sites (large ellipsoids), and the parts of the structure missing from the figure may be filled in by inversion through these points. Sodium atoms are shown as ellipsoids with no connecting lines to them.

centered-atom model by a few kcal.mole⁻¹, in spite of the close F-F contact. The method given by Pauling (1960) was used for the calculation; point charges were assumed and only the F(6) atom, its surrounding cuboctahedron of F atoms, and the next nearest neighbors, 6 Zr atoms, were included. Thus the calculated stability of the displaced-atom model is consistent with the observed position for the F(6) atoms. If the structure is in fact disordered in short range, this stability is enhanced by an entropy contribution.

Thermal motions of the atoms are represented by 50% probability ellipsoids in Figs. 2 and 4. The anisotropy of motion seems plausible for all atoms: the Zr atom has its greatest movement along the unique axis of its antiprism, while each F atom has much less freedom in directions along a Zr-F bond than perpendicular to it. Atom F(5) shows an unusually large thermal displacement along the line toward atom F(6) with which it makes a very short contact (2.24 Å). This may actually represent a correlated motion (or disorder) in which atom F(5) moves away from the site of atom F(6) when that site is occupied, thereby maintaining the F-F contact at a greater distance than indicated by the centers of the ellipsoids. This consideration would suggest that if the ordered model is correct, the F(6)-F(5) contact should be relieved by appropriate displacements of the pair of atoms corresponding to F(5). The refined acentric models however did not show such an effect.

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References

- AGRON, P. A. & ELLISON, R. D. (1959). *J. Phys. Chem.* **63**, 2076.
- ASPREY, L. B. (1954). *J. Amer. Chem. Soc.* **76**, 2019.
- ASPREY, L. B. & KEENAN, T. K. (1961). *J. Inorg. Nucl. Chem.* **16**, 260.
- ASPREY, L. B., KRUSE, F. H. & PENNEMAN, R. A. (1965). *J. Amer. Chem. Soc.* **87**, 3518.
- ASPREY, L. B., KRUSE, F. H. & PENNEMAN, R. A. (1967). *Inorg. Chem.* **6**, 544.
- BACON, G. E. (1955). *Neutron Diffraction*. Oxford: Clarendon Press.
- BARTON, C. J., FRIEDMAN, H. A., GRIMES, W. R., INSLEY, H., MOORE, R. E. & THOMA, R. E. (1958). *J. Amer. Ceram. Soc.* **41**, 63.
- BARTON, C. J., GRIMES, W. R., INSLEY, H., MOORE, R. E. & THOMA, R. E. (1958). *J. Phys. Chem.* **62**, 665.
- BENZ, R., DOUGLASS, R. M., KRUSE, F. H. & PENNEMAN, R. A. (1963). *Inorg. Chem.* **2**, 799.
- BODE, H. & TEUFER, G. (1956). *Acta Cryst.* **9**, 929.
- BROWN, G. M. & LEVY, H. A. (1964). *J. Phys.* **25**, 497.
- BURBANK, R. D. (1965). *Acta Cryst.* **19**, 957.
- BURBANK, R. D. & BENSEY, F. N. (1956). *The Crystal Structure of Zirconium Tetrafluoride*. K-1280, Oak Ridge, Tennessee.
- BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBERRY, R. T. (1967). *The Oak Ridge Computer-Controlled X-ray Diffractometer*, ORNL-4143. Oak Ridge National Laboratory, Tennessee.
- BUSING, W. R. & LEVY, H. A. (1967). *Acta Cryst.* **22**, 457.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *A Fortran Crystallographic Least-Squares Program*, ORNL-TM-305, Oak Ridge, Tennessee.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *A Fortran Crystallographic Function and Error Program*, ORNL-TM-306, Oak Ridge, Tennessee.
- BUSING, W. R., SMITH, H. G., PETERSON, S. W. & LEVY, H. A. (1964). *J. Phys.* **25**, 495.
- CLARK, R. J. H., KEPERT, D. L., NYHOLM, R. S. & LEWIS, J. (1963). *Nature, Lond.* **199**, 559.
- FISHER, J., ELCHINGER, R. & WEISS, R. (1967). *Chem. Comm.* no. 7, p. 329.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
- HOARD, J. L. & SILVERTON, J. V. (1963). *Inorg. Chem.* **2**, 235. *International Tables for X-ray Crystallography* (1959). Vol. II. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*. ORNL-3794, Oak Ridge, Tennessee.
- KEENAN, T. K. (1966). *Inorg. Nucl. Chem. Letters*, **2**, 211.
- KELLER, C. & SCHMUTZ, H. (1966). *Inorg. Nucl. Chem. Letters*, **2**, 355.
- KEPERT, D. L. (1965). *J. Chem. Soc.* p. 4736.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd edition, p. 507. Ithaca: Cornell Univ. Press.
- RENNINGER, M. (1937). *Z. Physik*, **106**, 141.
- SEARS, D. R. & BURNS, J. H. (1964). *J. Chem. Phys.* **41**, 3478.
- THOMA, R. E. & CARLTON, T. S. (1961). *J. Inorg. Nucl. Chem.* **17**, 88.
- THOMA, R. E., INSLEY, H., LANDAU, B. S., FRIEDMAN, H. A. & GRIMES, W. R. (1958). *J. Amer. Ceram. Soc.* **41**, 538.
- ZACHARIASEN, W. H. (1948). *J. Amer. Chem. Soc.* **70**, 2147.
- ZACHARIASEN, W. H. (1951). *The Chemistry of Uranium* (Edited by KATZ, J. J. & RABINOWITZ, E.) p. 380. New York: McGraw-Hill.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.