

## Rutile-Type Compounds.

VI. Refinement of  $\text{VF}_2$  and Computer Simulation of  $\text{V}:\text{MgF}_2$ 

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**Abstract**

Single-crystal X-ray diffraction data of rutile-type  $\text{VF}_2$ ,  $M_r = 88.94$ , have been refined in the space group  $P4_2/m2_1/n2/m$  to  $R = 0.035$  ( $237F_{\text{obs}}$ ). Result:  $x = 0.3055$  (3),  $(\text{V}-\text{F})_1 = 2.092$  (1),  $(\text{V}-\text{F})_2 = 2.073$  (1) Å and with  $a = 4.7977$  (8),  $c = 3.2469$  (10) Å ( $\frac{c}{a} = 0.67678$ ),  $V = 74.74$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 3.951$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ Å}) = 5.98$  mm<sup>-1</sup>. The radius of  $\text{V}^{2+}$  in octahedral coordination is 0.786 Å. The  $\text{VF}_6$  octahedron is axially compressed. The difference between equatorial and axial octahedral bond lengths (0.019 Å) is of the same magnitude as in other rutile-type fluorides in which the cations have no degeneracies in their electron configurations. Computer simulation of  $\text{V}:\text{MgF}_2$  (1:127) predicts that the coordination octahedron around  $\text{V}^{2+}$  is reduced in size by about 0.25% compared with its dimensions in  $\text{VF}_2$ . The  $\text{VF}_6$  octahedra in  $\text{V}:\text{MgF}_2$  are effectively in a high-pressure environment due to the constraining size of neighboring  $\text{MgF}_6$  octahedra. The anisotropy of the thermal motion of fluorine in  $\text{VF}_2$  is similar to the anisotropy of the anions observed in nine other rutile-type compounds. In all these cases, the thermal motion of the anions points in the direction in which they would have to move in order to change from the less dense eleven-coordinated tetragonal close packing (packing density 0.72) to the denser twelve-coordinated hexagonal close packing (density 0.74).

**Introduction**

The most common formal oxidation states of vanadium are +5 and +4, although it can occur in all states from +5 to -1. Compounds in which it has a formal valence of +3 or +2 are rare, but a few have been characterized crystallographically (Shafer, 1969; Williamson & Boo, 1977; Montgomery, Chastain, Natt, Witkowska & Lingafelter, 1967). One of these is vanadium difluoride, which crystallizes in the rutile-type structure and has been studied mostly for its antiferromagnetic properties (Stout & Boo, 1966; Stout & Lau, 1967; Lau, Stout, Koehler & Child, 1969).

The rutile-type structure is a relatively simple structure composed of edge-sharing coordination oc-

tahedra forming chains parallel to [001]. Chains are cross-linked by shared corners so that each chain is connected to four neighboring chains. Within space group  $P4_2/m2_1/n2/m$ , the bond lengths of the coordination octahedron can be distorted in two different ways. Either the apical cation to anion distance may be shorter (axially compressed) or longer (axially elongated) than the four equatorial cation-anion distances. This distortion is related to the ratio of  $\frac{c}{a}$  of the cell constants and to the value of  $x$  of the anion, the only parameter of positional freedom allowable in this arrangement. Baur (1976) has illustrated in a  $\frac{c}{a}$  vs  $x$  positional-parameter plot that most oxides tend to have axially elongated distortions of the octahedra whereas the fluorides tend to be octahedrally compressed. Simple Born-model-type calculations predict that, if bonding is electrostatic in nature, octahedral compression is the rule. Hence, the fluorides conform better to the ionic description given by the Born model than do the oxides. Two fluorides,  $\text{VF}_2$  and  $\text{PdF}_2$ , appear to contradict these trends as they apparently have axially elongated octahedra (Bartlett & Maitland, 1958; Baur, 1976). However, the standard deviation associated with the  $x$  parameter in both structures is large enough to make any conclusions regarding the nature of the distortion at best tentative.

Because of its high efficiency as an oscillator, a  $\text{V}:\text{MgF}_2$  laser (with up to 1 wt%  $\text{VF}_2$ ) is being considered for use as a fusion driver (Dickson, 1980; Moulton & Mooradian, 1980). By studying the end members of the series, it is possible to predict details of local environment in the structure of the solid solution. The host material,  $\text{MgF}_2$ , has been recently well characterized crystallographically (Vidal-Valat, Vidal, Zeyen & Kurki-Suonio, 1979). Since synthetic single crystals of  $\text{VF}_2$  are now available (Boo, 1975), a single-crystal X-ray study was undertaken. These experimental studies of  $\text{VF}_2$  and  $\text{MgF}_2$  form the basis of a computer simulation of  $\text{V}:\text{MgF}_2$ .

**Experimental**

The preparation of  $\text{VF}_2$  single crystals has been described by Stout & Boo (1966) and by Shafer (1969).

Table 1. *R* values and final parameters

V is located in 2(a), F in 4(f). The value  $x_{\text{exp}}$  is experimentally determined, while  $x_m$  is calculated, assuming that all six octahedral bonds are of equal length, that is  $x_m = \frac{1}{4} + (c^2/8a^2)$ . The temperature factor is  $\exp \{-[\beta_{11}(h^2 + k^2) + \beta_{33}l^2 + 2\beta_{12}hk]\}$ .

$R = \frac{\sum  F_o  -  F_c }{\sum  F_o }$	0.035	$\beta_{11}$ , V	0.0036 (1)
$R_w = \frac{[\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}}{\sum w(F_o - F_c)^2 / \sum wF_o^2}^{1/2}$	0.037	$\beta_{33}$ , V	0.0123 (4)
$x_{\text{exp}}$	0.3055 (3)	$\beta_{12}$ , V	-0.0003 (2)
$x_m$	0.3072	$\beta_{11}$ , F	0.0094 (3)
		$\beta_{33}$ , F	0.0232 (11)
		$\beta_{12}$ , F	-0.0049 (5)

The crystals used for this study were kindly furnished by W. O. J. Boo. These crystals are deep blue, rod shaped, with irregular U-shaped cross-section, up to 4 mm long and not wider than 0.5 mm. Since they are too fragile to be ground into a sphere, an irregular fragment of approximate dimensions 0.4 × 0.3 × 0.2 mm and with a U-shaped cross-section, was used for data collection. Three-dimensional X-ray intensities were collected in the range of  $\sin \theta/\lambda$  from 0.42 to 1.168 Å<sup>-1</sup> in one octant of reciprocal space on a computer-controlled four-circle diffractometer using graphite-crystal-monochromatized Mo  $K\alpha$  ( $\lambda = 0.71069$  Å) radiation. The diffractometer was controlled by Lenhert's (1975) disk-oriented diffractometer control system. Empirical absorption correction factors were obtained by rotating several selected reflections around the diffraction vector and by measuring their intensities at 10° intervals (John McAlister in the manual to Lenhert, 1975). For further details of data collection and for a list of computer programs used in this work, see Baur & Khan (1970). The 581 measured  $I_{hkl}$  were corrected for the usual factors and averaged over symmetrically equivalent reflexions, resulting in 304 unique structure factors of which 67 were considered to be of zero intensity since they were smaller than three times their standard deviations. Atomic scattering factors for V<sup>2+</sup> and F from *International Tables for X-ray Crystallography* (1974) were employed in the refinement. The data were affected by extinction, since refinement of Zachariasen's (1963) extinction parameter ( $C = 0.41 \times 10^{-5}$ ) reduced the *R* value significantly. Final parameters and *R* values are reported in Table 1.\*

## Discussion

### Bond distances

The mean distance V<sup>[6]</sup>-F<sup>[3]</sup> in VF<sub>2</sub> is 2.084 Å (Table 2), where the superscripts in brackets indicate

\* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36293 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the coordination numbers of the atoms. A radius of 0.784 Å for V<sup>[6]</sup> is calculated by assuming the radius of 1.300 Å for F in three-coordination (Shannon & Prewitt, 1969). The value of the radius given by Shannon (1976) for V<sup>2+</sup> cannot be used as a check on our value since it was derived from preliminary information from the present refinement. In perovskite-type KVF<sub>3</sub> and RbVF<sub>3</sub> (Williamson & Boo, 1977) the V<sup>[6]</sup>-F<sup>[6]</sup> distances are 2.066 and 2.091 Å respectively. These values may not be strictly comparable with the one obtained from VF<sub>2</sub> because of a possible bond-shortening effect observed in highly symmetric structures such as the perovskite- or the sodium-chloride-type structures (Shannon & Prewitt, 1969). In V(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Montgomery *et al.*, 1967) the mean distance V<sup>[6]</sup>-O<sup>[3]</sup> is 2.148 Å. Since O<sup>[3]</sup> is assigned a radius of 1.360 Å, the value for the radius of V<sup>2+</sup> from this compound is 0.788 Å. For these two structures, the average V<sup>2+</sup> radius for six-coordination therefore is 0.786 Å, in agreement with Shannon's (1976) value of 0.79 Å.

The experimentally determined positional parameter,  $x_{\text{exp}}$ , of the F ion is less than the calculated value (see Table 1). Consistent with this value are the bond lengths which show the octahedra to be axially compressed by 0.019 Å as determined by the difference of the apical bonds from the equatorial ones. This result contrasts with the previous, but less accurate, determination and is now in agreement with the observed trend for all other fluorides (with the possible exception of PdF<sub>2</sub>).

For transition-metal compounds that are both chemically and structurally simple, crystal-field theory may be applied to explain geometric distortions. Baur (1976) considered the difference between the apical and equatorial bond lengths ('bond-delta') as a measure of octahedral coordination distortion. The cations in the compounds VF<sub>2</sub>(*d*<sup>3</sup>), MnF<sub>2</sub>(*d*<sup>5</sup>), NiF<sub>2</sub>(*d*<sup>8</sup>) and ZnF<sub>2</sub>(*d*<sup>10</sup>) have no degeneracies (Dunitz & Orgel,

Table 2. Bond lengths and angles for VF<sub>2</sub>, for V in V:MgF<sub>2</sub> and for MgF<sub>2</sub>

The geometry of the environment of V in V:MgF<sub>2</sub> is derived from a computer simulation: the geometry of MgF<sub>2</sub> is calculated with  $x_{\text{exp}} = 0.3030$ . The value of (M-F)<sub>m</sub> is calculated with  $x_m$  as parameter.

	VF <sub>2</sub>	V in V:MgF <sub>2</sub>	MgF <sub>2</sub>
(M-F) <sub>1</sub> , equatorial (4×)	2.092 (1) Å	2.087 Å	1.997 (1) Å
(M-F) <sub>2</sub> , apical (2×)	2.073 (1)	2.068	1.980 (1)
(M-F) <sub>m</sub> (6×)	2.084	2.079	1.990
(F-F) <sub>1</sub> (8×)	2.945 (2)	2.938	2.812 (1)
(F-F) <sub>2</sub> (2×)	2.639 (2)	2.653	2.575 (1)
(F-F) <sub>3</sub> = (M-M) <sub>1</sub> = <i>c</i> (2×)	3.247 (1)	3.100	3.052 (1)
(M-M) <sub>2</sub> (8×)	3.761 (1)	{3.659 3.638}	3.606 (1)
(F-M-F) (2×)	78.21 (5)°	78.91°	80.31 (1)°

1960) in their electron configurations. Their bond deltas are small indicating slight octahedral compression as would be predicted with simple Born-model-type calculations. Generally, the bond-delta values are greater for the other fluorides due to incomplete  $e_g$  or  $t_{2g}$  orbitals [ $\text{FeF}_2(d^6)$ ] and Jahn–Teller effects [ $\text{CrF}_2(d^4)$  or  $\text{CuF}_2(d^9)$ ], see Baur (1976) for a discussion].

#### Computer simulation of V:MgF<sub>2</sub> structure

Computer simulation of crystal structures is a powerful method for simulating structural details when either material or diffraction data are not accessible [for details and a review, see Baur (1977)]. Recently, this approach has been used by Dollase (1980) to study the atomic displacements in several cubic host structures upon isovalent substitution by cations larger than the cations of the host. Such simulations are made in periodic supercells of the host structure in order to avoid boundary conditions due to finite size of the modeled structure. Usually it is sufficient to choose supercells that are  $3 \times 3 \times 3$  or  $4 \times 4 \times 4$  times the size of the original cell. In addition to other results, Dollase determined that deviations from the ideal structure are approximately inversely proportional to the square of the distance to the substituent, and that the size of the coordination polyhedron around the substituted atom was reduced compared to its normal, unrestrained size.

Magnesium difluoride doped with about 1 wt% VF<sub>2</sub> was simulated by substituting one V<sup>2+</sup> ion into the origin of a  $4 \times 4 \times 4$  supercell of MgF<sub>2</sub> in space group *Cmmm*. In order to make the supercell more easily comparable to the subcell a primitive setting of *Cmmm* was used (*P2/m12/m*) with the coordinates of the general equivalent position  $\pm(x, y, z; x, y, \bar{z}; y, x, z; y, x, \bar{z})$ . Each subcell contains two Mg atoms and, therefore, the supercell contains one V and 127 Mg ions. The input into the simulation (Villiger, 1969) consisted of the dimensions of the VF<sub>6</sub> coordination octahedron as observed in VF<sub>2</sub> and the dimensions of 32 different MgF<sub>6</sub> octahedra as observed in MgF<sub>2</sub> [with  $x_{\text{exp}} = 0.3030$  of the F atom, which is the average of the values observed by Baur & Khan (1971) and by Vidal-Valat *et al.* (1979)]. In addition, the Mg–Mg distances, parallel to [001] and across the short F–F edge, and the appropriate Mg–V distances were used as observations. The weights given to the observations were  $w = 1.0$  for M–F,  $w = 0.14$  for F–F and  $w = 0.07$  for M–M, in accord with empirically derived values (Baur, 1977; Dollase, 1980). The total number of observations was 370 and the number of refined variables was 165 (163 positional parameters of 33 M atoms and 50 F atoms and two cell constants). The r.m.s. magnitude of the atomic shifts due to the substitution was 0.019 Å, the largest ones of course were close to the position of the V<sup>2+</sup> atom. The unit-cell parameters for this simulated V:MgF<sub>2</sub> are  $a =$

4.6236 Å and  $c = 3.0545$  Å; they are within 0.001 Å of the values expected if Vegard's law were strictly to apply, that is, if linearity of cell constants obtained between MgF<sub>2</sub> and VF<sub>2</sub>. The dimensions of the VF<sub>6</sub> environment in V:MgF<sub>2</sub> are listed in Table 2. The coordination octahedron is reduced in size by about 0.25%. The apparent reason for this is that the VF<sub>6</sub> octahedra are surrounded by the smaller MgF<sub>6</sub> octahedra. Therefore, the VF<sub>6</sub> octahedra in V:MgF<sub>2</sub> are effectively in a high-pressure environment caused by the smaller surrounding octahedra.

How reliable is such a simulation? Dollase's (1980) simulation of K-doped NaCl agrees with calculations based on energy minimizations using atomic interaction potentials (Hardy, 1962) and with experimentally derived estimates of atomic displacements using quadrupolar broadening of <sup>23</sup>Na NMR spectra (Fukai, 1963). More specifically, however, we can compare an experimentally determined superstructure of rutile with its simulated structure. Although a  $4 \times 4 \times 4$  superstructure has not yet been determined, several trirutiles ( $1 \times 1 \times 3$  structures) have been refined, among them Cr<sub>2</sub><sup>3+</sup>Te<sup>6+</sup>O<sub>6</sub> (Kunnmann, LaPlaca, Corliss, Hastings & Banks, 1968). This structure was simulated assuming a mean Cr–O distance of 1.975 Å and a mean Te–O of 1.92 Å (both based on radii given by Shannon, 1976). Furthermore, it was assumed that the coordination octahedra around Cr<sup>3+</sup> and Te<sup>6+</sup> are distorted in the same fashion as the MnO<sub>6</sub> octahedron in MnO<sub>2</sub> (Baur, 1976). The resulting simulated structure reproduced within 0.01 Å the positions and bond distances observed experimentally by Kunnmann *et al.* (1968). Whereas this does not prove that the simulated V:MgF<sub>2</sub> structure is correct in its details, it nevertheless shows that some rutile superstructures can be simulated well. The stimulated emission of V<sup>2+</sup> in MgF<sub>2</sub> has been measured by Johnson & Guggenheim (1967). Theoretical model calculations of this emission should not assume the geometry of VF<sub>6</sub> which it has in VF<sub>2</sub> itself, but instead, the simulated environment deduced here for VF<sub>6</sub> in V:MgF<sub>2</sub>.

#### Thermal vibration of anions

Vidal-Valat *et al.* (1979, 1980) have determined the anisotropy of the thermal ellipsoids in MgF<sub>2</sub> by single-crystal neutron diffraction. Their results have been discussed by Pauling (1980), who points out that the F atoms are vibrating mainly perpendicular to the plane formed by the three strong Mg–F bonds. For several rutile-type structures the anisotropic thermal parameters have been determined (see Table 3) in the last few years. The  $U_{11}$  ( $=U_{22}$ ) and  $U_{33}$  are the mean-square amplitudes of vibration in the main crystallographic directions as calculated by us from the  $\beta$  parameters supplied in the original papers. The anisotropy parameters  $\Delta_1 U$  and  $\Delta_2 U$  are as defined by

Vidal-Valat *et al.* (1979), the prolateness of the thermal motion ( $\Delta_1 U = U_{33} - U_{\text{mean}}$ ) and the non-axiality of the thermal ellipsoid ( $\Delta_2 U = -U_{12}$ ). These parameters indicate the shape and the orientation of the thermal ellipsoids. Vidal-Valat *et al.* used  $\Delta_1 U$  and  $\Delta_2 U$  because these parameters were more independent from the particular extinction model assumed in the refinement of the diffraction data of  $\text{MgF}_2$  than  $U_{\text{mean}}$ . Similarly, they can be used to compare the anisotropy observed for the ten compounds listed in Table 3. The negative values of  $\Delta_1 U$  indicate prolateness of the thermal motion of the F or O atoms with respect to the long axis of its thermal ellipsoid normal to the plane of its three strong bonds to the cation. The only exception to that occurs in  $\text{VF}_2$ , but it is not significant in terms of the probable error in  $\Delta_1 U$ . Even in  $\text{VF}_2$ , the longest principal mean-square amplitude is normal to this plane; and the shortest is parallel to the shortest F–V bond. The positive value means only that the medium principal amplitude is closer in its value to the longer axis than to the shorter axis. This is shown by the positive value of  $\Delta_2 U$  which indicates the large anisotropy of motion in the (001) plane at right angles to the plane containing  $\text{FV}_3$ . The only precise work on a rutile-type structure which does not show this anisotropy is the  $\text{MgF}_2$  refinement by Göttlicher & Niederauer (1970), where both the Mg and the F atoms appear to be isotropic. This is clearly in contrast to the refinement of  $\text{MgF}_2$  by Vidal-Valat *et al.* (1979). It appears that there are systematic errors in the data of Göttlicher & Niederauer's work. The results of their work and the refinement of their data by Baur (1976) should therefore be disregarded, even though the parameter  $x$  of the F atom resulting from the refinement is very close to the values obtained from other refinements (Baur & Khan, 1971; Vidal-Valat *et al.*, 1979).

The anisotropic motion of the anion in all these rutile-type compounds points in the direction in which

the anion moves permanently when the rutile-type proper deforms into the orthorhombic  $\text{CaCl}_2$  form (a distorted rutile type). This is also the vibration direction of the Raman-active  $B_{1g}$  mode in the rutile-type structure. Nagel & O'Keeffe (1971) therefore proposed that rutile-type  $\text{TiO}_2$  has a high-pressure polymorph of the  $\text{CaCl}_2$  type. This has not been borne out (Mammone, Sharma & Nicol, 1980). However, Jorgensen, Worlton & Jamieson (1979) have determined the structure of  $\text{NiF}_2$  by powder neutron diffraction at pressures ranging from 0.12 to 3.42 GPa, that is below and above its pressure-induced transition (at 1.83 GPa) from the tetragonal to the orthorhombically deformed rutile type. Thus, for  $\text{NiF}_2$  the suggestion of Nagel & O'Keeffe (1971) is confirmed. The details of the high-pressure structure determination show also that the transition involves clearly a shift of the fluorine positions in  $\text{NiF}_2$  from the eleven-coordinated tetragonal close-packing arrangement (Baur, 1981) in the low-pressure form to the twelve-coordinated hexagonal close packing in the high-pressure form. Therefore, it can be said that the anisotropy of the thermal motion of the anions in the tetragonal rutile-type structures (Table 3) points in the direction in which the anions have to move in order to change from the less dense tetragonal close packing (packing density 0.719) to the denser hexagonal close packing (density 0.740).

There is a large spread in the mean value of  $U$  ranging from 0.0029  $\text{\AA}^2$  for  $\text{SiO}_2$  to 0.0115  $\text{\AA}^2$  for  $\text{VF}_2$ . However, little may be concluded from these differences, because  $U_{\text{mean}}$  depends on the model used for the refinement. Also, the thermal parameters absorb those systematic experimental errors that are smooth functions of  $\sin \theta/\lambda$ .

We thank W. O. J. Boo for the crystals of  $\text{VF}_2$  and the Computer Center of the University of Illinois at Chicago for computer time.

Table 3. Mean-square amplitudes ( $\text{\AA}^2$ ) of atoms in rutile-type crystals (all values multiplied by  $10^4$ )

	Anions				Cations				References
	$U_{11}$	$U_{33}$	$\Delta_1 U$	$\Delta_2 U$	$U_{11}$	$U_{33}$	$\Delta_1 U$	$\Delta_2 U$	
$\text{SiO}_2$	32 (1)	23 (1)	-6 (2)	6 (1)	20 (1)	15 (1)	-3 (2)	-1 (1)	<i>a</i>
$\text{TiO}_2$	50 (2)	36 (2)	-9 (4)	14 (1)	64 (1)	40 (2)	-8 (3)	11 (3)	<i>b</i>
$\text{VO}_2$	86 (2)	62 (4)	-16 (6)	12 (2)	111 (2)	96 (3)	-5 (5)	-7 (1)	<i>c</i>
$\text{CrO}_2$	68 (4)	55 (6)	-9 (10)	7 (4)	55 (2)	42 (3)	-4 (5)	-2 (1)	<i>d</i>
$\text{MnO}_2$	62 (1)	41 (1)	-14 (2)	15 (1)	37 (1)	32 (1)	-3 (2)	-1 (1)	<i>e</i>
$\text{GeO}_2$	37 (1)	23 (2)	-9 (3)	9 (1)	21 (1)	12 (1)	-6 (2)	0 (1)	<i>f</i>
$\text{PbO}_2$	121 (6)	46 (1)	-50 (7)	43 (6)	68 (5)	29 (1)	-26 (6)	-3 (5)	<i>g</i>
$\text{MgF}_2$	87 (2)	62 (2)	-17 (4)	34 (2)	53 (3)	36 (3)	-6 (4)	4 (2)	<i>h</i>
$\text{VF}_2$	110 (3)	124 (6)	9 (9)	39 (4)	42 (1)	66 (2)	16 (3)	2 (2)	<i>i</i>
$\text{NiF}_2$	110 (10)	60 (20)	-33 (30)	150 (20)	30 (10)	10 (10)	-13 (20)	50 (10)	<i>j</i>

(*a*) Sinclair & Ringwood (1978); (*b*) Abrahams & Bernstein (1971); (*c*) McWhan, Marezio, Remeika & Dernier (1974); (*d*) Porta, Marezio, Remeika & Dernier (1972); (*e*) Baur (1976); (*f*) Baur & Khan (1971); (*g*) D'Antonio & Santoro (1980); (*h*) Vidal-Valat *et al.* (1979); (*i*) this work; (*j*) Jorgensen *et al.* (1979).

## References

- ABRAHAMS, S. C. & BERNSTEIN, J. L. (1971). *J. Chem. Phys.* **55**, 3206–3211.
- BARTLETT, N. & MAITLAND, R. (1958). *Acta Cryst.* **11**, 747–748.
- BAUR, W. H. (1976). *Acta Cryst.* **B32**, 2200–2204.
- BAUR, W. H. (1977). *Phys. Chem. Miner.* **2**, 3–20.
- BAUR, W. H. (1981). *Mater. Res. Bull.* **16**, 339–345.
- BAUR, W. H. & KHAN, A. A. (1970). *Acta Cryst.* **B26**, 1584–1596.
- BAUR, W. H. & KHAN, A. A. (1971). *Acta Cryst.* **B27**, 2133–2139.
- BOO, W. O. J. (1975). Abstracts. Am. Chem. Soc. 169th Meeting, FLU015.
- D'ANTONIO, P. & SANTORO, A. (1980). *Acta Cryst.* **B36**, 2394–2397.
- DICKSON, D. (1980). *Nature (London)*, **288**, 204–205.
- DOLLASE, W. A. (1980). *Phys. Chem. Miner.* **6**, 295–304.
- DUNITZ, J. D. & ORGEL, L. E. (1960). *Adv. Inorg. Chem. Radiochem.* **2**, 1–60.
- FUKAI, Y. (1963). *J. Phys. Soc. Jpn*, **18**, 1580–1589.
- GÖTTLICHER, S. & NIEDERAUER, K. (1970). *Z. Angew. Phys.* **29**, 16–21.
- HARDY, J. R. (1962). *Phys. Chem. Solids*, **23**, 113–116.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, L. F. & GUGGENHEIM, H. J. (1967). *J. Appl. Phys.* **38**, 4837–4839.
- JORGENSEN, J. D., WORLTON, T. G. & JAMIESON, J. C. (1979). *High Pressure Science and Technology*, edited by K. D. TIMMERHAUS & M. S. BARBER, pp. 152–160. New York: Plenum.
- KUNNMANN, W., LAPLACA, S., CORLISS, L. M., HASTINGS, J. M. & BANKS, E. (1968). *J. Phys. Chem. Solids*, **29**, 1359–1364.
- LAU, H. Y., STOUT, J. W., KOEHLER, W. C. & CHILD, H. R. (1969). *J. Appl. Phys.* **40**, 1136.
- LENHERT, P. G. (1975). *J. Appl. Cryst.* **8**, 568–570.
- MCWHAN, D. B., MAREZIO, M., REMEIKA, J. P. & DERNIER, P. D. (1974). *Phys. Rev. B*, **10**, 490–495.
- MAMMONE, J. F., SHARMA, S. K. & NICOL, M. (1980). *Solid State Commun.* **34**, 799–802.
- MONTGOMERY, H., CHASTAIN, R. V., NATT, J. J., WITKOWSKA, A. M. & LINGAFELTER, E. C. (1967). *Acta Cryst.* **22**, 775–780.
- MOULTON, P. F. & MOORADIAN, A. (1980). *J. Opt. Soc. Am.* **70**, 635.
- NAGEL, L. & O'KEEFFE, M. (1971). *Mater. Res. Bull.* **6**, 1317–1320.
- PAULING, L. (1980). *Acta Cryst.* **B36**, 761–762.
- PORTA, P., MAREZIO, M., REMEIKA, J. P. & DERNIER, P. D. (1972). *Mater. Res. Bull.* **7**, 157–162, 355–356.
- SHAFFER, M. W. (1969). *Mater. Res. Bull.* **4**, 905–912.
- SHANNON, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–945.
- SINCLAIR, W. & RINGWOOD, A. E. (1978). *Nature (London)*, **272**, 714–715.
- STOUT, J. W. & BOO, W. O. J. (1966). *J. Appl. Phys.* **37**, 966.
- STOUT, J. W. & LAU, H. Y. (1967). *J. Appl. Phys.* **38**, 1472.
- VIDAL-VALAT, G., VIDAL, J.-P., ZEYEN, C. M. E. & KURKI-SUONIO, K. (1979). *Acta Cryst.* **B35**, 1584–1590.
- VIDAL-VALAT, G., VIDAL, J.-P., ZEYEN, C. M. E. & KURKI-SUONIO, K. (1980). *Acta Cryst.* **B36**, 2857.
- VILLIGER, H. (1969). *DLS manual*. Zürich: ETH.
- WILLIAMSON, R. F. & BOO, W. O. J. (1977). *Inorg. Chem.* **16**, 646–648.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

*Acta Cryst.* (1982). **B38**, 355–358

## Structure du Décachlorure de Tricadmium et de Dicalcium Octadécahydraté, 2[Ca(H<sub>2</sub>O)<sub>8</sub>].[Cd<sub>3</sub>Cl<sub>10</sub>]<sub>∞</sub>.2H<sub>2</sub>O\*

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### Abstract

2[Ca(H<sub>2</sub>O)<sub>8</sub>].[Cd<sub>3</sub>Cl<sub>10</sub>]<sub>∞</sub>.2H<sub>2</sub>O crystallizes in space group  $P\bar{1}$ . The unit-cell dimensions are  $a = 12.792$  (2),  $b = 6.573$  (1),  $c = 11.989$  (2) Å,  $\alpha = 106.54$  (2),  $\beta =$

\* Nom de IUPAC: poly-Tétra- $\mu$ -chloro-di- $\mu_3$ -chloro-tétrachloro-tricadmiate(II) d'octaquaocalcium(II) dihydraté.

120.46 (1),  $\gamma = 91.97$  (1)°;  $V = 813.3$  Å<sup>3</sup>;  $Z = 1$ ;  $d_m = 2.23 \pm 0.01$ ,  $d_c = 2.24$  Mg m<sup>-3</sup>;  $\mu_{Mo K\alpha} = 2.96$  mm<sup>-1</sup>. The structure was refined by least-squares calculations to a final  $R = 0.034$  ( $R_w = 0.031$ ) for 6616 independent reflections. Cd atoms are octahedrally coordinated to six Cl atoms and the Ca atom is surrounded by eight O atoms of water molecules located on the Archimedean antiprism tops. The