

TABLE II,1  
Elements with the Cubic Close-Packed Structure (II,a)

Element	Name	Cell edge, $a_0$ , A.
Ac	Actinium	5.311
Ag	Silver	4.0862
Al	Aluminum	4.04958 (25°C.)
Am	Americium	4.894 (see II,b2)
Ar	Argon	5.256 (4.2°K.)
Au	Gold	4.07825 (25°C.)
Ca	Calcium	5.576
Ce	Cerium	5.1612
Co	Cobalt	3.548
Cr	Chromium	3.68
Cu	Copper	3.61496 (18°C.)
Fe	Iron	3.5910 (22°C.)
Ir	Iridium	3.8394 (26°C.)
Kr	Krypton	5.721 (58°K.)
La	Lanthanum	5.296
Li	Lithium	4.404 (4.379) (-195°C.)
Mo	Molybdenum	4.16
Ne	Neon	4.429 (4.2°K.)
		4.471 for Ne <sup>20</sup>
		4.455 for Ne <sup>22</sup>
Ni	Nickel	3.52387 (25°C.)
Pb	Lead	4.9505
Pd	Palladium	3.8898 (25°C.)
Pr	Praseodymium	5.161
Pt	Platinum	3.9231 (25°C.)
Pu	Plutonium	4.6370 (320°C.)
Rh	Rhodium	3.8031 (25°C.)
Sc	Scandium	4.541
Sr	Strontium	6.0847 (25°C.)
Th	Thorium	5.0843 (25°C.)
Xe	Xenon	6.197 (58°K.)
Yb	Ytterbium	5.4862

In almost all hexagonal close-packed metals the axial ratio is slightly under 1.633, lying between 1.63 and ca. 1.57. That is, atoms in the same basal plane are usually a little farther apart than those immediately above and below. With beryllium as the only apparent exception, the axial ratios of

TABLE II,2  
Elements with the Hexagonal Close-Packed Structure (II,b1)

Element	Name	$a_0$ , A.	$c_0$ , A.
Be	Beryllium	2.2866	3.5833 (ca. 22°C.)
$\beta$ -Ca	Calcium	3.98	6.52 (450°C.)
Cd	Cadmium	2.97887	5.61765 (26°C.)
Ce	Cerium	3.65	5.96
$\alpha$ -Co	Cobalt	2.5071	4.0686 (20°C.)
Cr	Chromium	2.722	4.427
Dy	Dysprosium	3.584	5.668 (49°K.)
		3.5903	5.6475 (ca. 20°C.)
Er	Erbium	3.550	5.590 (43°K.)
		3.5588	5.5874 (ca. 20°C.)
Gd	Gadolinium	3.629	5.796 (106°K.)
		3.6360	5.7826 (ca. 20°C.)
He	Helium	3.57	5.83 (-271°C.)
Hf	Hafnium	3.1967	5.0578 (26°C.)
Ho	Holmium	3.5773	5.6158 (ca. 20°C.)
La	Lanthanum	3.75	6.07 (see II,b2)
Li	Lithium	3.111	5.093 (78°K.)
Lu	Lutetium	3.5031	5.5509 (ca. 20°C.)
Mg	Magnesium	3.20927	5.21033 (25°C.)
Na	Sodium	3.767	6.154 (5°K.)
Nd	Neodymium	3.657	5.902 (see II,b2)
Ni	Nickel	2.65	4.33
Os	Osmium	2.7352	4.3190 (20°C.)
Pr	Praseodymium	3.669	5.920 (see II,b2)
Re	Rhenium	2.7608	4.4582 (25°C.)
Ru	Ruthenium	2.70889	4.28168 (20°C.)
Sc	Scandium	3.3090	5.2733 (ca. 20°C.)
$\beta$ -Sr	Strontium	4.32	7.06 (248°C.)
Tb	Terbium	3.6010	5.6936 (ca. 20°C.)
Ti	Titanium	2.950	4.686 (25°C.)
Tl	Thallium	3.456	5.525
		3.438	5.478 (5°K.)
Tm	Thulium	3.5375	5.5546 (ca. 20°C.)
Y	Yttrium	3.6474	5.7306 (ca. 20°C.)
Zn	Zinc	2.6648	4.9467 (25°C.)
$\alpha$ -Zr	Zirconium	3.232	5.147 (25°C.)

TABLE II,3  
Elements with the Cubic Body-Centered Structure (II,c)

Element	Name	$a_0$ , A.
Ba	Barium	5.025 (26°C.) 5.000 (5°K.)
$\gamma$ -Ca	Calcium	4.38 (ca. 500°C.)
Cr	Chromium	2.8839 (25°C.)
Cs	Cesium	6.045 (5°K.) 6.067 (78°K.)
Eu	Europium	4.606 4.551 (5°K.)
$\alpha$ -Fe	Iron	2.8635 (25°C.)
$\beta$ -Fe	Iron	2.91 (800°C.)
$\delta$ -Fe	Iron	2.94 (1425°C.)
K	Potassium	5.225 (5°K.) 5.247 (78°K.)
Li	Lithium	3.5093 (20°C.) 3.491 (78°K.)
Li <sup>6</sup>	Lithium	3.5107 (20°C.)
Li <sup>7</sup>	Lithium	3.5092 (20°C.)
Mo	Molybdenum	3.1473 (25°C.)
Na	Sodium	4.2906 (20°C.) 4.225 (5°K.)
Nb	Niobium	3.3004 (18°C.)
$\gamma$ -Np	Neptunium	3.52 (ca. 600°C.)
$\epsilon$ -Pu	Plutonium	3.638 (500°C.)
Rb	Rubidium	5.585 (5°K.) 5.605 (78°K.)
$\gamma$ -Sr	Strontium	4.85 (614°C.)
Ta	Tantalum	3.3058 (25°C.)
Th	Thorium	4.11 (1450°C.)
$\beta$ -Ti	Titanium	3.3065 (900°C.)
Tl	Thallium	3.882
$\gamma$ -U	Uranium	3.474
V	Vanadium	3.0240 (25°C.)
W	Tungsten	3.16469 (25°C.)
Zr	Zirconium	3.62 (850°C.)

II,d. *Hydrogen* (and its isotopes) is the only element belonging to the first three vertical columns of the periodic table whose crystalline structure is completely in doubt. Diffraction data exist, however, and according to

these the structures of hydrogen, deuterium, and tritium are not necessarily alike.

Hydrogen is reported to be dimorphous with the two modifications having the cell dimensions:

Tetragonal H<sub>2</sub>:  $a_0 = 4.42$  A.;  $c_0 = 3.75$  A.

Hexagonal H<sub>2</sub>:  $a_0 = 3.75$  A.;  $c_0 = 6.49$  A.

The atomic positions have yet to be established.

Deuterium and tritium have been described as tetragonal with similar cells which, however, are unlike those of the tetragonal form of hydrogen:

Tetragonal D<sub>2</sub>:  $a_0 = 3.35$  A.;  $c_0 = 5.86$  A.

Tetragonal T<sub>2</sub>:  $a_0 = 3.3$  A.;  $c_0 = 5.78$  A.

Obviously much more work is required.

II,e1. *Mercury*, Hg, remains the only other element belonging to columns I and II whose atomic arrangement is not described by one of the simple structures already listed. The usual,  $\alpha$ , form of solidified mercury is hexagonal, like that of its analogs, zinc and cadmium, but its atomic grouping is different. Its unit containing but one atom (at the origin) is a rhombohedron with

$a_0 = 2.9863$  A.,  $\alpha = 70^\circ 44.6'$  at  $5^\circ$  K.

and

$a_0 = 2.9925$  A.,  $\alpha = 70^\circ 44.6'$  at  $78^\circ$  K.

The corresponding triatomic hexagonal cells are

$a_0' = 3.457$  A.,  $c_0' = 6.663$  A. at  $5^\circ$  K.

and

$a_0' = 3.464$  A.,  $c_0' = 6.677$  A. at  $78^\circ$  K.

A cell of this shape expresses a cubic close-packing deformed by compression along a body diagonal. The larger four-atomic pseudocell diagonal to it that shows this relation to structure II,a has  $a_0' = 4.581$  A. and an axial angle of  $98^\circ 13'$ .

The zinc and cadmium distortions of the hexagonal close-packing make atoms in adjacent planes farther apart than those in the same plane; the compressive distortion in mercury, on the other hand, brings atoms in neighboring layers especially close together. The mercury-mercury separa-

C. Nitrides, phosphides and other fifth column binary compounds with trivalent metals, chiefly rare earths.

D. Carbides of various metals.  
The lengths of edge of the unit cells of these substances are listed in Table III, 1.

TABLE III, 1  
Crystals with the NaCl Arrangement (III, a1)

Crystal	$a_0$ , A.
AgBr	5.7745
AgCl	5.547
AgF	4.92
AmO	5.05
BaO	5.523
BaNH	5.84
BaS	6.3875 (21°C.)
BaSe	6.600
BaTe	6.986
BiSe	5.99
BiTe	6.47
CaO	4.8105
CaNH	5.006
CaS	5.6903 (21°C.)
CaSe	5.91
CaTe	6.345
CdO	4.6953 (27°C.)
CeAs	6.060
CeBi	6.487
CeN	5.011
CeP	5.897
CeS	5.778
CeSb	6.399
CeSe	5.982
CeTe	6.346
CoO	4.2667 (22°C.)
CrN	4.140
CrCl	7.02 (450°C.)
CsF	6.008
CsH	6.376
DyAs	5.780
DyN	4.905
DySb	6.153

(continued)

TABLE III, 1 (continued)

Crystal	$a_0$ , A.
DyTe	6.092
ErAs	5.732
ErN	4.839
ErSb	6.106
ErTe	6.063
EuN	5.014
EuS	5.957
EuO	5.1439
EuSe	6.191
EuTe	6.584
FeO	4.2774 (on Fe <sub>3</sub> O <sub>4</sub> surface)
FeO	4.3108 (on Fe boundary)
GdAs	5.854
GdN	4.999
GdSb	6.217
GdSe	5.771
HfC	4.4578
HoAs	5.771
HoBi	6.228
HoN	4.874
HoP	5.626
HoS	5.465
HoSb	6.130
HoSe	5.680
HoTe	6.049
KBr	6.6000 (25°C.)
KCN <sup>a</sup>	6.527 (25°C.)
KCl	6.29294 (25°C.)
KF	5.347
KH	5.700
KI	7.06555 (25°C.)
KOH	5.78 (130°C.)
KSH	6.60 (170°C.)
KSeH	6.92 (180°C.)
LaAs	6.125
LaBi	6.565
LaN	5.301
LaP	6.013
LaS	5.842
LaSb	6.475

(continued)

TABLE III,1 (continued)

Crystal	$a_0, \text{Å}$
LaSe	6.060
LaTe	6.409
LiBr	5.5013 (26°C.)
LiCl	5.12954
LiD	4.065
LiF	4.0173
Li <sup>6</sup> F	4.0271
LiF	4.0263
LiH	4.085
LiI	6.000
LuN	4.766
MgO	4.2112 (21°C.)
MgS	5.2023 (21°C.)
MgSe	5.451
MnO	4.4448 (26°C.)
MnS	5.2236 (26°C.)
MnSe	5.448
NH <sub>4</sub> Br	6.90 (250°C.)
NH <sub>4</sub> Cl	6.52 (250°C.)
NH <sub>4</sub> I	7.2613 (26°C.)
NaBr	5.97324 (26°C.)
NaCN	5.893
NaCl	5.62779 (18°C.)
	5.63978 (18°C.)
	5.64056 (26°C.)
NaF	4.620
NaH	4.880
NaI	6.4728 (26°C.)
NaSH	6.06 (150°C.)
NaSeH	6.30 (150°C.)
NbC	4.4691 (20°C.)
NbC <sub>0.7</sub>	4.432
NbN <sub>0.98</sub>	4.702 (25°C.)
NbO	4.2097
NdAs	5.958
NdBi	6.424
NdN	5.151
NdP	5.826
NdS	5.681

(continued)

TABLE III,1 (continued)

Crystal	$a_0, \text{Å}$
NdSb	6.309
NdSe	5.879
NdTe	6.249
NiO	4.1684
NpN	4.897
NpO	5.01
PaO	4.961
PbS	5.9362 (26°C.)
PbSe	6.1243 (26°C.)
PbTe	6.454
PdH <sup>b</sup>	4.02
PrAs	5.997
PrBi	6.448
PrN	5.155
PrP	5.860
PrS	5.727
PrSb	6.353
PrSe	5.952
PrTe	6.309
PuAs	5.855
PuB	4.92
PuC	4.920
PuN	4.905
PuO	4.959
PuP	5.644
PuS	5.536
PuTe	6.183
RbBr	6.854
RbCN	6.82
RbCl	6.5810 (27°C.)
RbF	5.64
RbH	6.037
RbI	7.342 (27°C.)
RbNH <sub>2</sub>	6.395 (50°C.)
RbSH	6.93 (200°C.)
RbSeH	7.21 (180°C.)
ScAs	5.487
ScN	4.44
ScSb	5.859

(continued)

TABLE III,1 (continued)

Crystal	$a_0$ , Å.
TmN	4.809
TmSb	6.083
TmTe	6.042
UAs	5.766
UBi	6.364
UC	4.9591 (24°C.)
UN	4.884
UO	4.92
UP	5.589
US	5.484
USb	6.191
USE	5.750
UTe	6.163
VC	4.182
VC <sub>0.76</sub>	4.136
VN	4.128
VO <sup>c</sup>	4.062 (800°C.)
YAs	5.786
YN	4.877 (23°C.)
YSb <sub>1.10</sub>	5.658
YTe	6.095
YbAs	5.698
YbN	4.7852
YbO	4.86
YbSb	5.922
YbSe	5.867
YbTe	6.353
ZrB	4.65
ZrC	4.6828 (23°C.)
ZrN	4.61
ZrO	4.62
ZrP	5.27
ZrS	5.250

<sup>a</sup> Recent neutron diffraction data on KCN support the idea that the CN radicals are freely rotating.

<sup>b</sup> The beta phase of the Pd-H system has, by neutron diffraction, an incomplete NaCl structure with up to 70% of the H, or D, positions filled.

<sup>c</sup>  $a_0$  varies with composition between TiO<sub>0.86</sub> and TiO<sub>1.294</sub> and between VO<sub>0.75</sub> and VO<sub>1.25</sub>.

TABLE III,1 (continued)

Crystal	$a_0$ , Å.
SmAs	5.921
SmBi	6.362
SmN	5.0481
SmO	4.9883
SmP	5.760
SmS	5.970
SmSb	6.271
SmSe	6.200
SmTe	6.594
SnAs	5.681
SnSb	6.130
SnSe	6.020
SnTe	6.313
SrNH	5.45
SrO	5.1602 (25°C.)
SrS	6.0198 (20°C.)
SrSe	6.23
SrTe	6.47
TaC	4.4540 (23°C.)
TaO	4.422-4.439
TbAs	5.827
TbBi	6.280
TbN	4.933
TbP	5.688
TbS	5.516
TbSb	6.181
TbSe	5.741
TbTe	6.102
ThAs	5.972
ThC	5.338
ThP	5.818
ThS	5.682
ThSb	6.318
ThSe	5.875
TiC	4.3186
TiN	4.235
TiO <sup>c</sup>	4.1766 (25°C.)
TmAs	5.711

(continued)

TABLE III,3  
 Crystals with the CsCl Arrangement (III,b1)

Crystal	$a_0$ , A.
Salt-like	
CsBr	4.286
CsCl	4.123 (25°C.)
CsCN	4.25
CsI	4.5667 (20°C.)
CsNH <sub>2</sub> (high)	4.063 (50°C.)
CsSH	4.30
CsSeH	4.437
ND <sub>4</sub> Br	4.034 (-30°C.)
ND <sub>4</sub> Cl	3.8682 (18°C.)
NH <sub>4</sub> Br	3.8190 (-185°C.)
NH <sub>4</sub> Cl	4.0594 (26°C.)
	3.8756 (26°C.)
	3.8684 (18°C.)
	3.8200 (-185°C.)
NH <sub>4</sub> I	4.37 (-17°C.)
RbCl	3.74 (190°C.)
TbTe	3.827
TlBr	3.97
TlCl	3.8340
TlCN	3.82
TlI	4.198
Some intermetallic examples	
AgCd	3.33
AgCe	3.731
AgLa	3.760
AgMg	3.28
AgZn	3.156

(continued)

In crystals of the ammonium halides which have this structure the hydrogen atoms presumably are in (4c) of  $T_d^1$  ( $P\bar{4}3m$ ):



if they are in positions dictated by symmetry. X-ray diffraction did not settle this but it can be established through electron or neutron diffraction. From a recent study at -40°C. and at room temperature using electrons it has been decided that in NH<sub>4</sub>Cl,  $u = 0.153$ , corresponding to N-H = 1.03 Å.; in another investigation  $u$  was found to be 0.146, leading to N-H = 0.98 Å.

TABLE III,3 (continued)

Crystal	$a_0$ , A.
AlNd	3.73
AlNi	2.881
AuCd	3.34 (400°C.)
AuMg	3.259
AuZn	3.19
BeCo	2.606
BeCu	2.698
BePd	2.813
CaTi	3.847
CdCe	3.86
CdLa	3.90
CdPr	3.82
CuPd	2.988
CuZn	2.945
LiAg	3.168
LiHg	3.287
LiTi	3.424
MgCe	3.898
MgHg	3.44
MgLa	3.965
MgPr	3.88
MgSr	3.900
MgTi	3.628
SrTi	4.024
TlBi	3.98
TlSb (excess Tl)	3.84
ZnCe	3.70
ZnLa	3.75
ZnPr	3.67

The eightfold coordination that characterizes this CsCl arrangement is, as stated above, encountered in compounds having especially large cations. The radius ratio of the ions involved conforms to the  $r(R)/r(X) \geq 0.73$  that must prevail if ions of opposite signs are to make contact.

Under high pressures, crystals with the NaCl arrangement are known to transform to the CsCl structure. Thus at 7500 kg./cm.<sup>2</sup> and room temperature, RbCl is CsCl-like with  $a_0 = 3.82$  Å. Similarly, at 11,000 atmospheres and 25°C., RbI is CsCl-like with  $a_0 = 4.29$  Å.

TABLE III,4  
 Crystals with the ZnS Arrangement (III,c1)

Crystal	$a_0$ , A.
AgI	6.473
AlAs	5.62
AlP	5.451
AlSb	6.1347 (26°C.)
BAAs	4.777
BN	3.615 (25°C.)
BP	4.538
BeS	4.85
BeSe	5.07
BeTe	5.54
CdS	5.818
CdTe <sup>a</sup>	6.480
CuBr	5.6905 (26°C.)
CuCl	5.4057
CuF	4.255
CuI	6.0427
GaAs <sup>b</sup>	5.6537
GaP	5.4505
GaSb	6.118
HgS	5.8517 (26°C.)
HgSe	6.084
HgTe	6.429
InAs	6.036
InP	5.8687
InSb	6.4782 (25°C.)
MnS (red)	5.600
MnSe	5.82
SiC	4.348
ZnS <sup>c</sup>	5.4093 (26°C.)
ZnSe <sup>b</sup>	5.6676
ZnTe	6.089
Ga <sub>2</sub> S <sub>3</sub>	5.171
Ga <sub>2</sub> Se <sub>3</sub>	5.441
Ga <sub>2</sub> Te <sub>3</sub>	5.899
In <sub>2</sub> Te <sub>3</sub>	6.158
Sm <sub>2</sub> O	5.3761
ZnSnAs <sub>2</sub> <sup>d</sup>	5.851

<sup>a</sup> There is also said to be a multiple layering of this CdTe structure to give a hexagonal cell with  $a_0 = 4.60$  A.,  $c_0 = 45.1$  A.

<sup>b</sup> GaAs and ZnSe form a continuous series of solid solutions.

<sup>c</sup> If 1% ZnO present, 5.4065 A.

<sup>d</sup> Zn and Sn statistically distributed.

2. Halides, oxides, nitrides, etc. of transitional and less electropositive metals. With many it cannot be inferred that ionization is sufficiently complete to give meaning to a calculated radius ratio. An additivity of interatomic distances has, however, been observed and this is usually expressed through the use of nonionic, "tetrahedral radii." In many of the compounds and structures for which such radii are approximately valid there are X-X as well as R-X close contacts and it is these that give the basis for the atomic radii chosen.

III,c2. The atoms in the two-molecule hexagonal unit of the *zincite*, ZnO, arrangement are in the positions:

$$R: 000; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}$$

$$X: 00u; \frac{1}{3}, \frac{2}{3}, u + \frac{1}{2}$$

which are derived from two sets of special positions of  $C_{6v}^4$  ( $C6mc$ ):

$$(2b) \frac{1}{3}, \frac{2}{3}, v; \frac{2}{3}, \frac{1}{3}, v + \frac{1}{2}$$

by a change of origin to the point  $\frac{2}{3}, \frac{1}{3}, 0$ . The axial ratios of crystals with this structure have always been close to  $c/a = 1.63$  and the parameter  $u$  to 0.375. Under these circumstances (Fig. III,13), each atom has about it a tetrahedron of atoms of the opposite sort just as in the cubic ZnS arrangement.

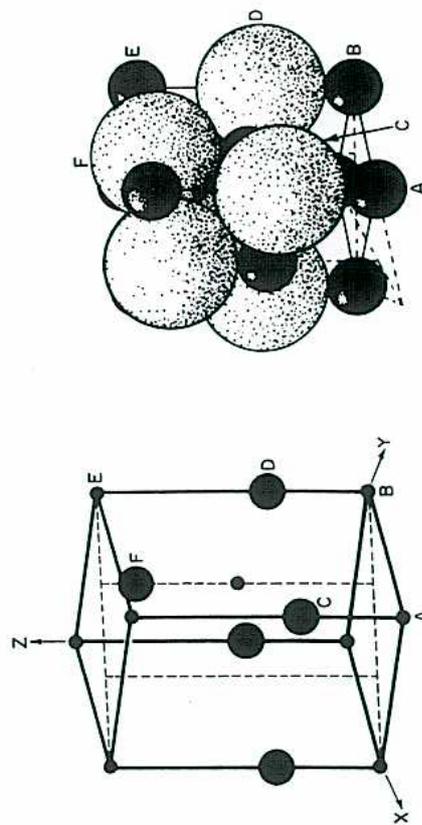


Fig. III,13a (left). A drawing that shows the positions of the atoms in the hexagonal unit cell of ZnO. The zinc atoms are represented by the small black circles.

Fig. III,13b (right). A perspective drawing showing how atoms of ZnO would pack together if they were ions. The small black spheres are zinc. Letters in this drawing refer to atoms similarly designated in Figure III,13a.

TABLE III,5  
Crystals with the ZnO Arrangement (III,c2)

Crystal	$a_0$ , A.	$c_0$ , A.	Remarks
AgI	4.580	7.494	A long range, somewhat disordered structure
Al <sub>2</sub> CO	3.17	5.06	
AlN	3.111	4.978	$u = 0.385$
BeO	2.698	4.380	$u = 0.378$
CdS	4.1348	6.7490	
CdSe	4.30	7.02	
CuBr	4.06	6.66	391–470°C.
CuCl	3.91	6.42	410°C.
CuH	2.893	4.614	
CuI	4.31	7.09	402–440°C.
GaN	3.180	5.166	
InN	3.533	5.693	
MgTe	4.52	7.33	
MnS (pink)	3.976	6.432	
MnSe	4.12	6.72	
MnTe	4.087	6.701	
NH <sub>4</sub> F	4.39	7.02	$u = 0.365$
NbN	3.017	5.580	
SiC	3.076	5.048	
TaN	3.05	4.94	
ZnO	3.24950	5.2069	$u = 0.345$
ZnS	3.811	6.234	
ZnSe	3.98	6.53	
ZnTe	4.27	6.99	

These structures can be conveniently (Table III,5), though rather artificially, considered as composed of ZnO<sub>4</sub> or OZn<sub>4</sub> tetrahedra. In zincite the tetrahedra are stacked in a hexagonal close-packed array with the tetrahedral edges of alternate layers rotated through 180° about the  $c_0$  axis; in zinc sulfide they are parallel to one another in layers repeated according to the demands of a cubic close-packing. Such a way of looking at these structures suggests the possibility of mixed packings similar to those described in the previous chapter for graphite and for metallic cobalt. The modifications of SiC about to be described are such mixed tetrahedral arrangements.

No clear distinction can be drawn between the types of compounds which crystallize with the ZnO and ZnS structures. The two arrangements are so much alike in their spatial distributions that one would not expect im-

portant energy differences between them. It is therefore not surprising to find that a number of compounds appear with both structures.

**III,c3.** *Silicon carbide*, SiC, occurs in several modifications which, in spite of a formal complexity, are similar in basic principle and closely related to one another and to the tetrahedral structures just described. One form is cubic with the ZnS arrangement (III,c1), the others are either rhombohedral or hexagonal. Their close relationship to one another is best expressed in terms of hexagonal units and pseudocells; when this is done they prove to have the same value of  $a_0$  and a value of  $c_0$  which is ca. 2.51 A. times the number of molecules in the hexagonal cell (Table III,6).

TABLE III,6  
Cell Dimensions of SiC

Modification	True unit			Hexagonal cell		
	$a_0$ , A.	$\alpha$	$M$	$a_0'$ , A.	$c_0'$ , A.	$M'$
$\beta$	4.439	—	4	3.073	7.57	3
2H	—	—	—	3.076	5.048	2
4H-III	—	—	—	3.073	10.053	4
6H-II	—	—	—	3.073	15.08	6
8H	—	—	—	3.079	20.1470	8
10H	—	—	—	3.079	25.183	10
19H	—	—	—	3.079	47.849	19
27H	—	—	—	3.079	67.996	27
15R-I	12.69	13°55'	5	3.073	37.70	15
21R-IV	17.68	9°58'	7	3.073	52.78	21
27R	22.735	7°46'	9	3.079	67.996	27
33R-VI	27.70	6°21.5'	11	3.073	82.94	33
51R(1)-V	42.763	4°7'	17	3.073	129.03	51
51R(2)	42.849	4°7'	17	3.079	128.437	51
75R	62.984	2°48'	25	3.079	188.878	75
84R	70.537	2°30'	28	3.079	211.543	84
87R-VII	72.907	2°25'	29	3.073	218.657	87
141R	118.359	1°30'	47	3.079	355.04	141
174R	—	—	58	3.079	436.7	174
393R	329.87	0°32'	131	3.079	989.60	393
Related forms of ZnS						
4H-III	—	—	—	3.806	12.44	4
6H-II	—	—	—	3.813	18.69	6
8H	—	—	—	3.82	24.96	8
10H	—	—	—	3.824	31.20	10
15R-I	—	—	5	3.822	46.79	15

TABLE III,7  
Crystals with the NiAs Arrangement (III,d1)

Crystal	$a_0$ , Å.	$c_0$ , Å.	Remarks
AuSn	4.314	5.512	
CoS	3.367	5.160	
CoSb	3.866	5.188	
CoSe	3.6294	5.3006	
CoTe	3.886	5.360	
CrS	3.448	5.754	53 at.-% S
CrSb	4.108	5.440	
CrSe	3.684	6.019	
CrTe	3.981	6.211	
CuSn	4.190	5.086	
FeS	3.438	5.880	
FeS <sub>2</sub>	3.43	5.68	
FeSb	4.06	5.13	
FeSb <sub>2</sub>	4.11	5.17	ca. Fe <sub>3</sub> Sb <sub>2</sub>
FeSe	3.637	5.958	
FeSe <sub>2</sub>	3.51	5.55	
Fe <sub>2</sub> Sn	4.230	5.208	$x > 1$
FeSb <sub>2</sub>	4.233	5.213	$x > 1$
FeTe	3.800	5.651	
IrSb	3.978	5.521	$u = \text{ca. } 1/4$
IrTe	3.930	5.386	
MnAs	3.710	5.691	20°C.
MnBi	4.30	6.12	
MnSb	4.120	5.784	
Mn <sub>2</sub> Sb	4.13	5.74	ca. Mn <sub>3</sub> Sb <sub>2</sub>
MnTe	4.1429	6.7031	20°C.
$\delta'$ -NbN	2.968	5.549	Anti-NiAs
NbS	3.32	6.46	Excess S
NiAs	3.602	5.009	
NiS	3.4392	5.3484	Stable above 485°C. Excess S reduces cell dimensions
NiSb	3.94	5.14	
NiSe	3.6613	5.3562	Can accept up to 20% excess Se
NiSn	4.048	5.123	42 at.-% Sn
NiTe	3.957	5.354	
PdSb	4.070	5.582	
PdSn	4.378	5.627	36-42 at.-% Sn
PdTe	4.1521	5.6719	
PbB	3.358	4.058	Anti-NiAs

(continued)

The large differences in composition shown by so many of these crystals have given rise to difficult problems. Such variations could be due to additional atoms occupying holes in the normal structure (excess structures) or to vacancies in the normal atomic positions (deficit structures). It should be possible to distinguish between these two types of grouping, since one should be more, the other less, dense than the perfect 1:1 compound. Application of this criterion has indicated that in general they are of the deficit type. Further evidence of this is provided by the observation, for example, that FeS<sub>1.2</sub> and FeSe<sub>1.2</sub> have unit cells smaller than those of FeS and FeSe. Apparently, metallic deficits when they occur do not exceed ca. 10%, but deficits in the metalloid atoms run much higher in such materials as Fe<sub>1.5</sub>Sb and Mn<sub>1.5</sub>Sb. With metalloid-deficient substances, cell dimensions vary little with the composition.

A complete understanding of NiAs-like crystals is made still harder by the "superlattice" that is often associated with them. The apparent cell dimensions of the superlattice structures may be very great, thus indicating an unusually complicated atomic arrangement. Only gradually can we expect to acquire an adequate knowledge of these complications and the reasons for them.

TABLE III,7 (continued)

Crystal	$a_0$ , Å.	$c_0$ , Å.	Remarks
PtBi	4.315	5.490	
PtSb	4.130	5.472	
PtSn	4.103	5.428	Anti-NiAs
RhB <sub>1.1</sub>	3.309	4.224	Accepts large amounts of excess
RhBi	4.094	5.663	Bi with little cell change
RhSn	4.340	5.555	40 at.-% Sn
RhTe	3.99	5.66	
ScTe	4.122	6.735	
TiS <sup>a</sup> (low)	3.30	6.44	
TiS <sup>a</sup>	3.559	6.220	
TiTe <sup>a</sup>	3.834	6.390	Form continuous solid solutions with diselenide and ditelluride
VP	3.18	6.22	
VS	3.360	5.813	
VSe	3.580	5.977	
VTe	3.942	6.126	53 at.-% Te
ZrTe	3.953	6.647	Forms continuous solid solutions with ZrTe <sub>3</sub> from ZrTe <sub>0.5</sub> → ZrTe <sub>2.0</sub>

<sup>a</sup> Also reported to have larger cells due to regular stacking disorders or to deficit structures.

In cooperative each metal atom has about it four metalloid atoms at the corners of a square and each sulfur is surrounded by a tetrahedron of metal atoms (Fig. III,25). This structure, too, can be considered as a distorted cubic close-packing of the metal atoms, but in this case the metalloid atoms are in interstices different from those occupied in PbO.

Two oxides of the platinum metals have also been given this structure. They are:

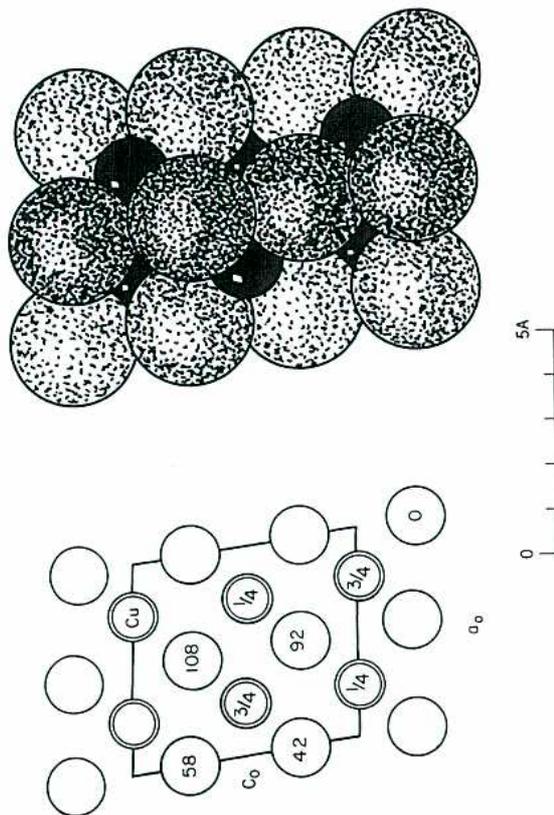
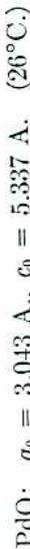


Fig. III,26a (left). The monoclinic structure of CuO projected along its  $b_0$  axis. Origin in lower left.

Fig. III,26b (right). A packing drawing of the CuO arrangement viewed along the  $b_0$  axis. The dotted oxygen atoms have their ionic size.

**III,e5.** *Cupric oxide*, CuO, as the mineral *tenorite* has been given a structure different from the preceding, but one in which there is the same kind of square coordination around the metal atom. It is monoclinic with a tetramolecular cell of the dimensions:

$$a_0 = 4.653 \text{ \AA.}; b_0 = 3.410 \text{ \AA.}; c_0 = 5.108 \text{ \AA.}; \beta = 99^\circ 29'$$

The proposed atomic arrangement based on  $C_{2h}^6$  ( $C2/c$ ) has its atoms in the

following positions:



If  $u = -0.584$ , rather than the usually stated 0.584, each atom of copper in the resulting arrangement (Fig. III,26) is surrounded by an approximate square of oxygens, with Cu-O = ca. 1.88 Å. and 1.96 Å. Each oxygen has about it a distorted tetrahedron of copper atoms.

**III,e6.** *Silver monoxide*, AgO, as investigated with x rays, was described as having the same structure as CuO though with a cell of the somewhat different shape:

$$a_0 = 5.852 \text{ \AA.}; b_0 = 3.478 \text{ \AA.}; c_0 = 5.495 \text{ \AA.}; \beta = 107^\circ 30'$$

A recent neutron diffraction study in giving more weight to the contributions of oxygen shows that the correct space group is  $C_{2h}^5$  ( $P2_1/c$ ) rather than  $C_{2h}^6$ . As in the earlier work, the metal atoms are face-centered (origin shifted by  $\frac{1}{4}, \frac{1}{4}, 0$ ); the oxygens are in general positions:

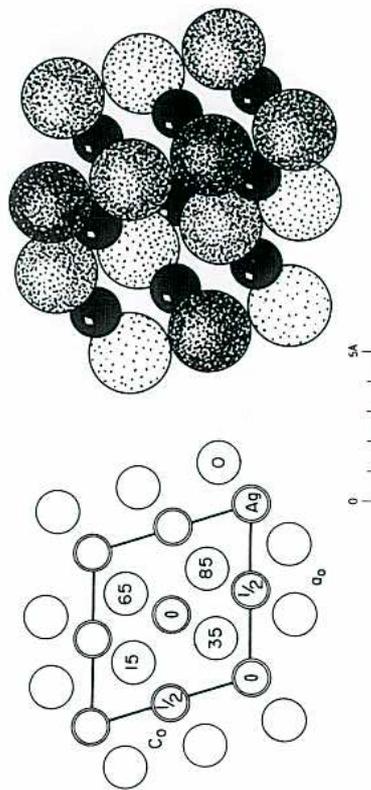
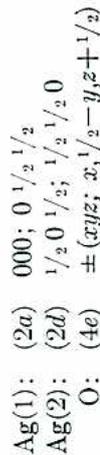


Fig. III,27a (left). The monoclinic AgO arrangement projected along its  $b_0$  axis. The difference between this and the CuO structure becomes evident by comparing Figures 26 and 27. Origin in lower left.

Fig. III,27b (right). A packing drawing of the structure of AgO seen along its  $b_0$  axis. The dotted oxygen circles have been given their ionic size.

TABLE IV,3  
Crystals with the Tetragonal SnO<sub>2</sub> Structure (IV,b1)

Crystal	a <sub>0</sub> , A.	c <sub>0</sub> , A.	u
CoF <sub>2</sub>	4.6951	3.1796	0.306
FeF <sub>2</sub>	4.6966	3.3091	0.300
MgF <sub>2</sub>	4.623	3.052 (27°C.)	0.303
MnF <sub>2</sub>	4.8734	3.3099	0.305
NiF <sub>2</sub>	4.6506	3.0836	0.302
PdF <sub>2</sub>	4.931	3.367	—
ZnF <sub>2</sub>	4.7034	3.1335 (25°C.)	0.303
CrO <sub>2</sub>	4.41	2.91	—
(Cr <sub>0.19</sub> , Mo <sub>0.81</sub> )O <sub>2</sub>	4.760	2.848	—
(Cr <sub>0.33</sub> , Mo <sub>0.67</sub> )O <sub>2</sub>	4.696	2.886	—
CrO <sub>2.14</sub>	4.423	2.917	—
GeO <sub>2</sub>	4.395	2.859	0.307
IrO <sub>2</sub>	4.49	3.14	—
β-MnO <sub>2</sub>	4.396	2.871	0.302
MoO <sub>2</sub>	4.86	2.79	—
NbO <sub>2</sub>	4.77	2.96	—
OsO <sub>2</sub>	4.51	3.19	—
PbO <sub>2</sub>	4.946	3.379	—
RuO <sub>2</sub>	4.51	3.11	—
SnO <sub>2</sub>	4.73727	3.186383 (20–23°C.)	0.307
TaO <sub>2</sub>	4.709	3.065	—
TeO <sub>2</sub>	4.79	3.77	—
TiO <sub>2</sub> (rutile)	4.59373	2.95812 (25°C.)	0.3053
WO <sub>2</sub>	4.86	2.77	—

valent ions. The symmetry is tetragonal with a flat unit containing two molecules. Atoms are in the following special positions of D<sub>4h</sub><sup>14</sup> (P4<sub>2</sub>/mmm):

$$R: (2a) \quad 000; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$$

$$X: (4f) \quad \pm(xu0; u+\frac{1}{2}, \frac{1}{2}-u, \frac{1}{2})$$

As can be seen from Table IV,3, all the crystals with this structure (Fig. IV,8) have about the same axial ratio. Wherever determined, the parameter  $u$  has been not far from 0.30. The six X atoms about each R atom are of two sorts and the octahedron is not exactly regular, four being at a slightly different distance from the other two. In general, these observed R-X separations do not differ by more than about 0.10 Å. and they agree well with the sums of the ionic radii. This structure brings anions close together, however, and in fact it makes one anion-anion contact considerably less than

Though these dimensions are close to what would be expected from a PbFCl arrangement, and the space group is the same as for PbFCl (D<sub>4h</sub><sup>7</sup>—P4/mmm), a different structure (Fig. IV,7) has been assigned. As with PbFCl, fluorine atoms are in

$$(2a) \quad 000; \frac{1}{2}, \frac{1}{2}, 0$$

and the metal atoms are in

$$(2c) \quad 0 \frac{1}{2} u; \frac{1}{2}, 0 \bar{u}$$

But the value of  $u$  is somewhat different, 0.778, and the oxygen atoms are in

$$(2b) \quad 00 \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$$

rather than in another set of (2c).

This structure, like the rhombohedral EuOF of IV,a5, is a small distortion of the cubic CaF<sub>2</sub> arrangement. Thus the axial ratio for gamma-LaOF is 1.430 instead of 1.414, and  $u = 0.778$  instead of 0.75.

### Octahedrally Coordinated Compounds

IV,b1. The most common structure with an octahedral coordination is that typified by *cassiterite*, SnO<sub>2</sub>. It is possessed by the dioxides of a number of quadrivalent metals and by fluorides of metals having especially small di-

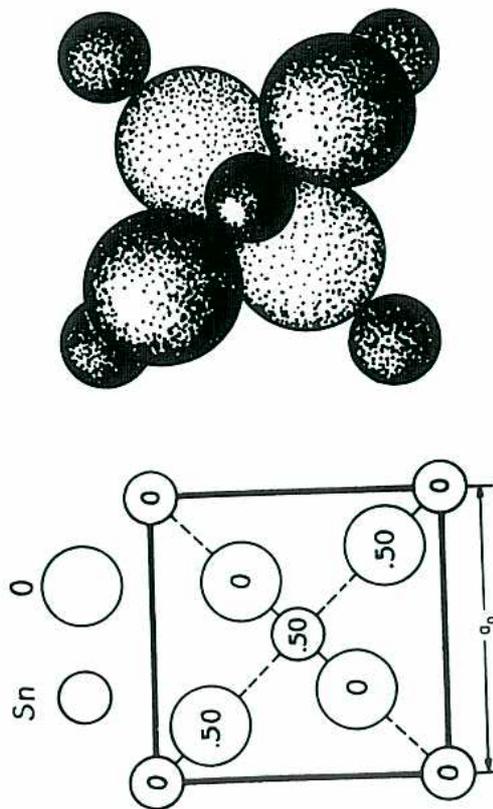


Fig. IV,8a (left). The atomic arrangement in the tetragonal unit of SnO<sub>2</sub> projected on the basal,  $c$ , face. The small circles represent tin atoms.

Fig. IV,8b (right). A drawing to show the way the atoms of SnO<sub>2</sub> pack together if they are given their expected ionic sizes. The large spheres are the oxygen ions.

TABLE IV,4  
Crystals RMX<sub>4</sub> with the Simple Tetragonal SnO<sub>2</sub> Arrangement (IV,b1)

Crystal	a <sub>0</sub> , A.	c <sub>0</sub> , A.
AlSbO <sub>4</sub>	4.510	2.961
CrNbO <sub>4</sub>	4.635	3.005
CrSbO <sub>4</sub>	4.577	3.042
CrTaO <sub>4</sub>	4.626	3.009
FeNbO <sub>4</sub>	4.68	3.05
FeSbO <sub>4</sub>	4.623	3.011
FeTaO <sub>4</sub>	4.672	3.042
GaSbO <sub>4</sub>	4.59	3.03
RhNbO <sub>4</sub>	4.686	3.014
RhSbO <sub>4</sub>	4.601	3.100
RhTaO <sub>4</sub>	4.684	3.020
RhVO <sub>4</sub>	4.607	2.923

the ionic radial sum. Thus in the typical case of SnO<sub>2</sub>, one O-O = 2.54 Å., whereas the other close approaches of oxygen atoms are 2.90 Å., which is near the uncorrected ionic radial sum.

A number of compounds of the type RMX<sub>4</sub> have substantially this atomic arrangement. Their cell dimensions are listed in Table IV,4. It has been said that their R and M atoms should be considered as statistically distributed among the positions of (2a) with the oxygen atoms in (4f). In the case of AlSbO<sub>4</sub>, u(O) was assigned the value 0.305.

**IV,b2.** A structure which is only a slight distortion of the cassiterite grouping has been given the orthorhombic crystals of anhydrous calcium chloride, CaCl<sub>2</sub>. The bromide, CaBr<sub>2</sub>, has the same arrangement. Their bimolecular cells have the dimensions:

$$\text{CaCl}_2: a_0 = 6.24 \text{ \AA.}; b_0 = 6.43 \text{ \AA.}; c_0 = 4.20 \text{ \AA.}$$

$$\text{CaBr}_2: a_0 = 6.55 \text{ \AA.}; b_0 = 6.88 \text{ \AA.}; c_0 = 4.34 \text{ \AA.}$$

Atoms are in the following positions of  $V_h^{12}$  ( $Pnmm$ ):

$$\begin{aligned} \text{Ca: } & (2a) \quad 000; \quad \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \\ \text{Cl (or Br): } & (4g) \quad \pm(w0; u+\frac{1}{2}, \frac{1}{2}-v, \frac{1}{2}) \end{aligned}$$

For CaCl<sub>2</sub>,  $u = 0.275$ ,  $v = 0.325$ . The bromine parameters have not been determined in CaBr<sub>2</sub>. The nearest approach of the calcium and chlorine atoms, 2.70-2.76 Å., and of the chlorine atoms to one another, 3.60 Å., are in accord with the idea of ions.

This structure (Fig. IV,9) would be exactly the SnO<sub>2</sub> arrangement if  $a_0 = b_0$  and  $u = v$ . The distortion it expresses corresponds to a small displacement of the halogen atoms from positions in the more symmetrical structure.

Another compound has now been found with this structure. *Chromous chloride*, CrCl<sub>2</sub>, has a unit of the dimensions:

$$a_0 = 5.974 \text{ \AA.}; b_0 = 6.624 \text{ \AA.}; c_0 = 3.488 \text{ \AA.}$$

The parameters are:  $u = 0.278$ ,  $v = 0.362$ . These give rise to the significant interatomic distances Cr-4Cl = 2.37 Å., Cr-2Cl = 2.91 Å.

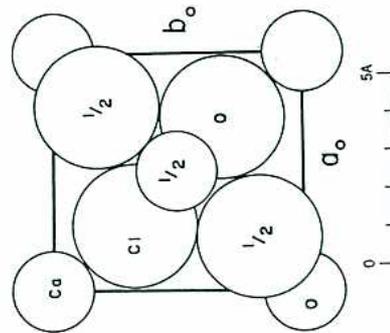


Fig. IV,9. A projection along the  $c_0$  axis of the orthorhombic structure of CaCl<sub>2</sub>. Comparison with Figure IV,8a brings out the close similarity to the SnO<sub>2</sub> arrangement. Origin in lower right.

**IV,b3.** Titanium dioxide, TiO<sub>2</sub>, has two modifications in addition to the cassiterite form that occurs naturally as the mineral rutile. The simpler, found as the mineral *anatase*, is tetragonal with the elongated cell:

$$a_0 = 3.785 \text{ \AA.}, \quad c_0 = 9.514 \text{ \AA.}$$

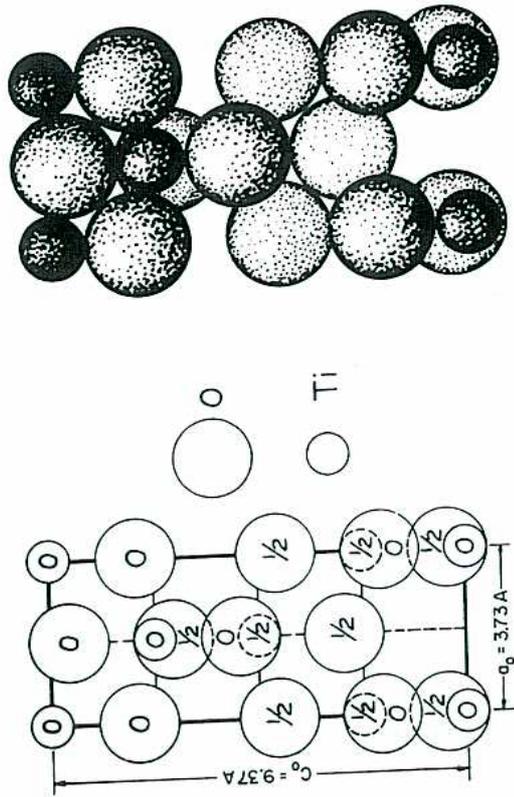
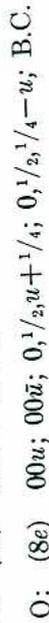


Fig. IV, 10a (left). The positions of atoms in the tetragonal unit of anatase,  $\text{TiO}_2$ , projected on an  $a$  face. Large circles are the oxygen atoms.

Fig. IV, 10b (right). A packing drawing, with atoms having their ionic sizes, corresponding to the projection of anatase shown in Figure IV, 10a.

Atoms of its four molecules are in the following special positions of  $D_{4h}^{19}$  ( $I4/amd$ ):



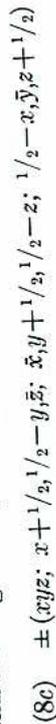
with  $u = 0.2066$ .

In this arrangement (Fig. IV, 10) the distances between a titanium atom and its six octahedrally coordinated oxygen neighbors are nearly equal (1.91–1.95 Å.) to one another and to those in rutile, but the oxygen octahedron is not regular. In rutile there is one, in anatase there are two especially short oxygen-to-oxygen separations (2.43 Å.).

**IV, b4.** The third form of  $\text{TiO}_2$ , the orthorhombic mineral *brookite*, has a more complicated crystal structure. Its eight-molecule unit has the edge lengths:

$$a_0 = 9.184 \text{ \AA.}; b_0 = 5.447 \text{ \AA.}; c_0 = 5.145 \text{ \AA.}$$

All atoms are in general positions of  $V_h^{15}$  ( $Pbca$ ):



with the recently determined values:

Atom	$x$	$y$	$z$
Ti	0.1290	0.0972	-0.1371
O(1)	0.0101	0.1486	0.1824
O(2)	0.2304	0.1130	-0.4629

These are more accurate than but not very different from the original values established many years ago.

Interatomic distances of this structure (Fig. IV, 11) are similar to those in the other modifications, the six oxygen atoms about each titanium atom being at distances which range from ca. 1.87 Å. to ca. 2.04 Å. In brookite too there is close anion-anion contact, the oxygen-oxygen separations varying upwards from 2.49 Å.

The mineral *telurite*,  $\text{TeO}_2$ , is the only other substance known to have this structure. If its axes are taken so as to give a unit with the dimensions:

$$a_0 = 11.75 \text{ \AA.}; b_0 = 5.50 \text{ \AA.}; c_0 = 5.59 \text{ \AA.}$$

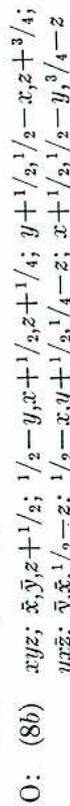
all atoms will be in positions (8c) listed above. The determined parameters referred to these axes are:

Atom	$x$	$y$	$z$
Te	0.118	0.027	-0.116
O(1)	-0.022	0.240	0.235
O(2)	0.174	0.164	-0.465

**IV, b5.** Besides the previously investigated rutile-like and brookite-like structures for *tellurium dioxide*,  $\text{TeO}_2$ , another tetragonal form has now been described. It is not, as might have been expected, like anatase but has a differently shaped tetramolecular cell with the dimensions:

$$a_0 = 4.805 \text{ \AA.}, \quad c_0 = 7.609 \text{ \AA.}$$

Atoms have been found to be in the following positions of  $D_4^4$  ( $P4_12_12$ ) (or in the corresponding positions of the enantiomorphous  $D_4^8$ ):



with  $u = 0.030$ ,  $x = 0.177$ ,  $y = 0.227$ , and  $z = 0.217$ .

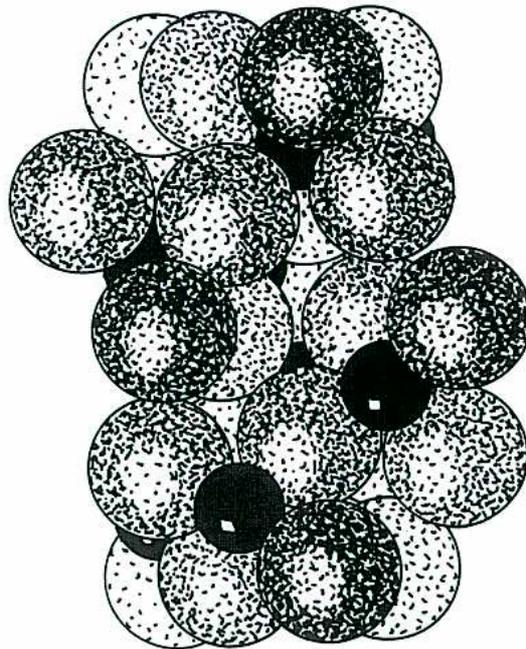
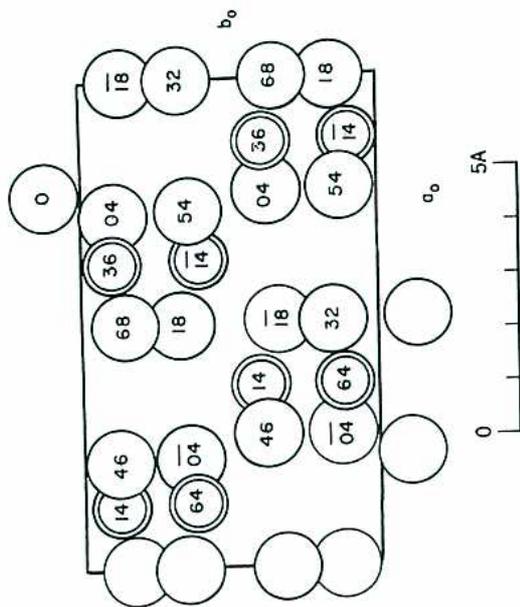


Fig. IV,11a (top). The orthorhombic structure of brookite,  $\text{TiO}_2$ , projected along its  $c_0$  axis. The titanium atoms are doubly ringed. Origin in lower right.

Fig. IV,11b (bottom). A packing drawing of the brookite,  $\text{TiO}_2$ , arrangement viewed along its  $c_0$  axis. The titanium atoms are black.

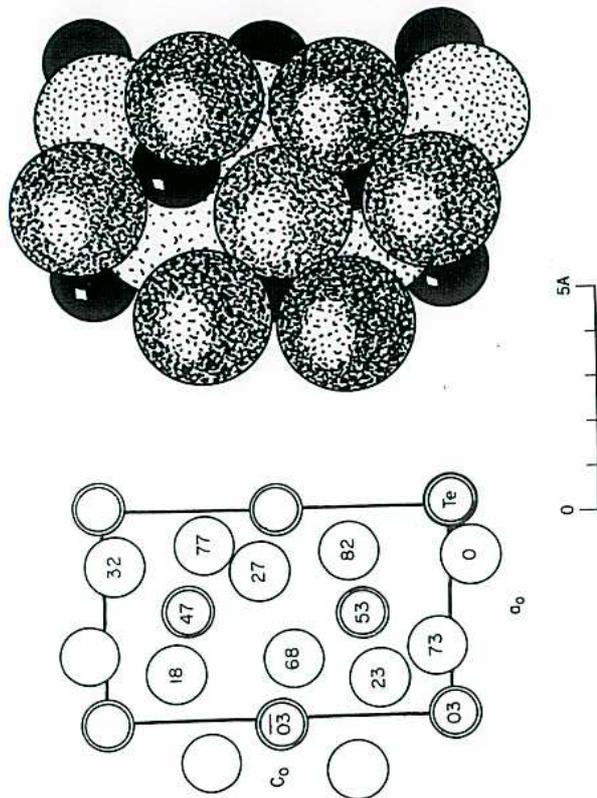


Fig. IV,12a (left). The tetragonal  $\text{TeO}_2$  structure projected along its  $b_0$  axis. Origin in lower left.

Fig. IV,12b (right). A packing drawing of the  $\text{TeO}_2$  structure viewed along its  $b_0$  axis. The tellurium atoms are black.

The resulting arrangement, as shown in Figure IV,12, can be thought of as a distortion of the rutile structure doubled in the  $c_0$  direction. In the deformed octahedron of oxygen atoms enveloping a tellurium atom there are four  $\text{Te-O} = 2.03$  Å. and two  $\text{Te-O} = 2.67$  Å.

It is stated that synthetically prepared  $\text{TeO}_2$  has invariably had this structure.

IV,b6. It has recently been shown that the rutile-like form of vanadium dioxide,  $\text{VO}_2$ , is a different distortion of this higher symmetry arrangement (IV,b1). The true symmetry for  $\text{VO}_2$  is monoclinic and there are four molecules in a cell of the dimensions:

$$a_0 = 5.743 \text{ Å.}; b_0 = 4.517 \text{ Å.}; c_0 = 5.375 \text{ Å.}; \beta = 122^\circ 36'$$

All atoms are in the general positions of  $C_{2h}^5$  ( $P2_1/c$ ):

$$(4e) \quad \pm(xyz; x, 1/2 - y, z + 1/2)$$

with the following parameters:

Atom	$x$	$y$	$z$
V	0.242	0.975	0.025
O(1)	0.10	0.21	0.20
O(2)	0.39	0.69	0.29

The originally proposed tetragonal cell had the dimensions:  $a_0' = 4.54$  Å.,  $c_0' = 2.88$  Å. The edges of the correct monoclinic cell are connected with this pseudo-cell by the following vector relations:

$$a_0 = 2c_0'; \quad b_0 = a_0'; \quad c_0 = a_0' - c_0'$$

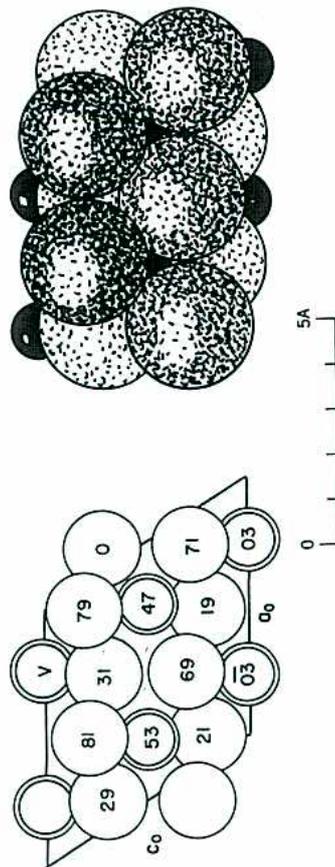


Fig. IV, 13a (left). The monoclinic  $\text{VO}_2$  arrangement projected along its  $b_0$  axis. Origin in lower left.

Fig. IV, 13b (right). A packing-drawing of the  $\text{VO}_2$  structure viewed along its  $b_0$  axis. The vanadium atoms are black.

In this monoclinic structure (Fig. IV, 13), metallic atoms have very nearly the same octahedral coordination of oxygen atoms that prevails in  $\text{SnO}_2$  with V-O between 1.76 and 2.05 Å. The O-O separations within an oxygen octahedron lie between 2.50 and 2.90 Å.

The naturally occurring paramontroseite (IV, d1) is a different form of  $\text{VO}_2$ .

The structure described a number of years ago for *molybdenum dioxide*,  $\text{MoO}_2$ , is very near to that of  $\text{VO}_2$ . Though the space group was reported as  $C_{2v}^2$  (P2), it is now pointed out that the  $\text{VO}_2$  arrangement based on  $C_{2v}^2$  fits

the data equally well. Parameters thus applicable to  $\text{MoO}_2$  are about the same as those for  $\text{VO}_2$ :

Atom	$x$	$y$	$z$
Mo	0.232	0.000	0.017
O(1)	0.11	0.21	0.24
O(2)	0.39	0.70	0.30

The only important difference from the  $\text{VO}_2$  structure is a small displacement of the metal atoms from the centers of their octahedra. This brings the molybdenum atoms rather close together with Mo-Mo = 2.48 Å. Within an octahedron Mo-O varies between 1.9 and 2.1 Å.

The cell dimensions of  $\text{MoO}_2$  and of other compounds with this arrangement are:

$\text{MoO}_2$ :  $a_0 = 5.584$  Å.;  $b_0 = 4.842$  Å.;  $c_0 = 5.608$  Å.;  $\beta = 120^\circ 59'$

$\text{WO}_2$ :  $a_0 = 5.565$  Å.;  $b_0 = 4.892$  Å.;  $c_0 = 5.650$  Å.;  $\beta = 120^\circ 42'$

$\text{ReO}_2$ :  $a_0 = 5.562$  Å.;  $b_0 = 4.838$  Å.;  $c_0 = 5.561$  Å.;  $\beta = 120^\circ 52'$

$\text{TcO}_2$ :  $a_0 = 5.53$  Å.;  $b_0 = 4.79$  Å.;  $c_0 = 5.53$  Å.;  $\beta = 120^\circ$

The relation to rutile is brought out by the fact that, described in terms of a pseudocell having the axial orientation of  $\text{VO}_2$ , the rutile axes would be:

$a_0' = 5.918$  Å.;  $b_0' = 4.593$  Å.;  $c_0' = 5.464$  Å.;  $\beta = 122^\circ 48'$

IV, b7. The alpha form of *lead dioxide*,  $\text{PbO}_2$ , produced by electrolysis of neutral solutions, has been assigned the tetramolecular orthorhombic cell:

$a_0 = 4.947$  Å.;  $b_0 = 5.951$  Å.;  $c_0 = 5.497$  Å.

Atoms have been placed in the following positions of  $V_h^{14}$  ( $Pbcn$ ):

Pb: (4c)  $\pm(0 \ u \ 1/4; \ 1/2, u \pm 1/2, 1/4)$ ,

O: (8d)  $\pm(xy, z; \ 1/2 - x, 1/2 - y, z \pm 1/2; \ x \pm 1/2, 1/2 - y, \bar{z}; \ \bar{x}, y, 1/2 - z)$

with  $u = 0.178$ ,  $x = 0.276$ ,  $y = 0.410$ , and  $z = 0.425$ .

In this structure (Fig. IV, 14), Pb-O = 2.16-2.22 Å. It is an arrangement that closely resembles that of columbite,  $\text{Nb}_2(\text{V}, \text{Mn})\text{O}_6$  (Chapter IX) with lead atoms replacing all metallic atoms in the mineral.