CRYSTAL STRUCTURE TYPES

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INTRODUCTION

An enormous amount of information has been collected in recent years on the structure of crystals. Much of it is not in the domain of mineralogy, but a large part is becoming of ever increasing importance to this science. It is with this in mind that an attempt will be made to present a short review of some of the relations of structure types to one another.

V. M. Goldschmidt and his co-workers together with many others (see bibliography) have attempted to classify the known structures into definite types, and thus explain such properties as isomorphism, polymorphism, morphotropism, hardness, and optical properties.

ATOMIC ARRANGEMENTS AND TYPE STRUCTURES

The fundamental law governing the structure of crystals, according to V. M. Goldschmidt, may be expressed in the following words: *The structure of a crystal depends on the relative quantities, sizes, and deformability of its components.* The components may be atoms, ions and groups of atoms or ions.

Relative quantities, of course, are expressed in the chemical formula which tells us how many atoms of each element are contained in the molecule. The apparent radii of atoms and ions are now known at least approximately. We are not concerned in this study with the true radius of an atom or ion but with the effective radius, the radius of its sphere of influence, which it occupies in the structure of the crystal.

Deformability refers to the distortional or deforming behavior of atoms or ions towards their neighbors. This mutual influence on one anothers electromagnetic fields causes atoms or ions to behave like compressible spheres. It also causes a decrease in the size of the apparent radii of the atoms or ions. In some elements, especially those that resemble in structure the inert gases, as for example O and F, Na, Ca, and Sr, the deformability is small. Therefore, oxides and fluorides approach the ideal conditions of packing of spheres most closely. In many other elements including S, Te, Se, Br, I, Fe, and certain radicals like OH, the deformability is great enough to be a deciding factor in the production of structures containing them as well as in isomorphism, morphotropism and other physical properties.

For the present, let us imagine atoms or ions as incompressible spherical particles. *The electrostatic attraction causes each ion to be surrounded as closely as possible by ions of an opposite charge.* Definite geometrical arrangements are possible provided that the ions are all in contact. Figure 2 for example shows that a sphere A of a radius of 0.41 (the radius of $B=1.00$) can be placed between four spheres B, forming a square. A will touch each B sphere. Simple arrangements are:

Equilateral triangle	Fig. 1	Ratio A:B	=0.15
Square	Fig. 2	" "	0.41
Tetrahedron	Fig. 3	" "	0.22
Octahedron	Fig. 2	" "	0.41
Cube	Fig. 4	" "	0.73

The radii of the smaller circles A in the figures 1–4, as compared to the larger ones B, give us the ratios which indicate how large an ion or atom A can be accommodated between a set of ions or atoms B and just be in contact with each B atom. Investigations of a large number of crystal structures has shown that ratios which are relatively much below those given are rarely if ever encountered. On the other hand, there is no theoretical reason why the smaller atom A could not be considerably increased in size for contact with the B ions would be maintained during this increase. Whenever the ratio of the A to the B ions had become the reciprocal of the ratio given above, the upper limit of the ratio would be reached. Since we are dealing with geometrical lattices which are repeated an indefinite number of times in all directions we see that the A ions "enclose" the B ions, the latter having the same relative size to the A ions now as the A ions had to the B ions before.

It is obvious from this discussion that the *relative sizes of ions and not their absolute sizes are important* as was formerly thought. If, however, strongly deforming or deformable ions or atoms are in the structure, size of ions may become of secondary consideration.

A study of structure models Figs. 5–17 shows that the familiar type of chemical valence cannot be identified in crystals. Recourse must be had to the so-called valence coordinates as developed by Werner almost forty years ago. These coordinates are the shortest distances between the ions. They are shown in Figs. 5–17. No prediction as to the number of coordinates associated with an ion in a substance can be made with any degree of certainty. Regularities have been observed, however, according to which Goldschmidt (4, p. 23) has classified some structures into the following divisions:

Coordinate number 1.	Single molecules and lattices of them.
Coordinate number 2.	Double molecules and molecule chains and lattices.
Coordinate number 3.	Boron nitride and graphite structures. Each atom is bound to others by three bonds. Fig. 16.
Coordinate number 4.	Diamond, zincblende, wurtzite, and tetragonal "layer lattices." Four bonds for each atom or ion. Figs. 8, 9, 10.
Coordinate number 6.	Sodium chloride and nickel arsenide structure types. Six bonds for each atom or ion. Figs. 5 and 6.
Coordinate number 8.	Caesium chloride structure type. Eight bonds for each atom or ion. Fig. 7.

It will be noted that the structures enumerated (graphite and diamond excepted) are of the general formula $M\ R$ which, of course, is the reason why the M and R atoms or ions in the structures have an equal number of valence coordinates.

In compounds of the formula MR_2 or M_2R the following coordinate numbers have been observed:

2 and 1.	Single molecules and lattices of them.
4 and 2.	α- and β-quartz, β-cristobalite and cuprite structure types. Figs. 12, 14, 15. One atom or ion has two, and the oppositely charged 4 coordinates.
6 and 3.	Cadmium iodide, molybdenite, rutile, octahedrite structure types. Figs. 13, 17.
8 and 4.	Fluorite structure type. Fig. 11.

These types are not the only ones possible.

It is interesting to note in Table I the differences in chemical valence which may be found in the same type of structure. This, then, explains the apparent inconsistancy in isomorphous mixtures where a trivalent element may be replaced by a tetravalent one or by a bivalent element.

TABLE I

SUBSTANCES CRYSTALLIZING IN SOME OF THE STRUCTURE TYPES

NaCl		ZnS Zincblende	ZnS Wurtzite	Diamond	NiAs	CsCl	TiO_2 Rutile	CaF_2	Cu_2O	CdI	MoS_2
LiF	SrO	CuCl	NH_4F	C	FeS	CsCl	MgF_2	CaF_2	Ag_2O	CdI	MoS_2
LiCl	SrS	CuBr	BO	Si	FeSe	CsBr	MnF_2	SrF_2	Cu_2O	PbI	WS_2
LiBr	SrSe	CuI	MgTe	Ge	CoS	CsI	FeF_2	BaF_2		ZrS_2	
LiI	SrTe	AgI	ZnO	Sn (Gray)	CoSe	NH_4Cl	CoF_2	CdF_2		$ZrSe_2$	
NaF	BaO	BeS	ZnS		CoTe	NH_4Br	NiF_2	$\beta\text{-}PbF_2$		SnS_2	
NaCl	BaS	BeSe	CdS		NiS	NH_4I	ZnF_2	HgF_2		TiS_2	
NaBr	BaSe	BTe	CdSe		NiSe	TlCl	TiO_2	$SrCl_2$		$TiTe_2$	
NaI	BaTe	ZnS	AlN		NiTe	TlBr	VO_2	Li_2O		$Mg(OH)_2$	
KF	CdO	ZnSe			NiAs	TlI	MnO_2	Li_2S		$Ca(OH)_2$	
KCl	PbS	ZnTe			NiSb	CuZn	NbO_2	Na_2S			
KBr	PbSe	CdS			CrSb	AgZn	MoO_2	Cu_2S			
KI	PbTe	CdSe			CoSb	AuZn	RuO_2	Cu_2Se			
RbF	SnTe	CdTe				CuPd	SnO_2	ZrO_2			
RbCl	SnSb	HgS (Black)					TeO_2	CeO_2			
RbBr	MnO	HgSe					WO_2	PrO_2			
RbI	MnSe	HgTe					OsO_2	ThO_2			
CsF	MnS	AlP					IrO_2	UO_2			
NH_4I	FeO	AlAs					PbO_2	Mg_2Si			
AgF	CoO	AlSb						Mg_2Sn			
AgCl	NiO	GaP						Mg_2Pb			
AgBr	ScN	GaAs						K_2PtCl_6			
AgI	TiN	GaSb						$Ni(NH_3)_6Cl_2$			
MgO	VN	SiC									
MgS	ZrN	InSb									
MgSe	NbN										
CaO	TiC										
CaS	VC										
CaSe	ZrC										
CaTe	NbC										
	TaC										

That the radius of an element depends upon its electric charge has been pointed out by many investigators and was reviewed by E. T. Wherry in this journal.[1] The radius of the neutral atom then is quite different from that of the ion. For example, sulphur has a radius of about 1.03 Å when neutral, and about 1.8 Å when it has a negative charge of 2. In the positive state with a valence of 6, as for example in sulfate radicals, it shrinks to a radius of about 0.3 Å.

But even the radius of the same atom or ion in the same state with respect to its electric charge is not constant. The radius of a lattice particle depends partly upon the kind and number of neighbors it has as well as on the thermodynamic effects, such as pressure and temperature. Other things being equal, the greater the number of nearest neighbors the greater the apparent radius of the atom or ion. This is reasonable, for as may be seen in Figs. 3 and 4 there is more room between spheres arranged at the corners of a cube than spheres arranged at the corners of a tetrahedron. Also (and this is probably more important) the enclosed atom or ion is attracted by more electromagnetic fields in the one case than in the other, which tends to increase its radius.

Goldschmidt (4, p. 69) has published several instructive tables with reference to this matter. Assuming that the same compounds can occur in the different structure types (some of them occur in at least two or more) we find shrinkage of the apparent radii, that is, decreases in distances between neighboring atoms of opposite charge, as follows. The numbers following the types are the numbers of valence coordinates for each atom or ion.

Transition	from	CsCl	type	8:8,	to	NaCl	type	6:6,	shrinkage	3%
“	“	NaCl	“	6:6	“	ZnS	“	4:4	“	5–7%
“	“	NaCl	“	6:6	“	CaF_2	“	8:4	“	3%
“	“	CaF_2	“	8:4	“	TiO_2	“	6:3	“	3%
“	“	NaCl	“	6:6	“	TiO_2	“	6:3	“	6%
“	“	NaCl	“	6:6	“	SiO_2	“	4:2	“	6–10%

In some of these examples the shrinkage could be determined only indirectly for no direct comparisons of their structures are possible.

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[1] *Am. Mineral.*, Vol. 14, p. 54. I cannot agree with Dr. Wherry on his proposal to substitute the symbol "*am.*" for Å. Å has been adopted internationally. The word ångstrom is not much more difficult to pronounce than the word ampere.

MORPHOTROPISM AND POLYMORPHISM

It is practically impossible to give an adequate review in a short paper of the large amount of material which has been collected by Goldschmidt and others on isomorphism and morphotropism. A discussion of some of the more important points follows.

It was shown above that in the transition from certain types to others a reduction of more than 5% may take place in the distances between ions. These types in which the shrinkage is considerable are not directly "commensurable" or comparable. There are a number of reasons why it must be assumed that the particles in one are not in the same state (whether ionic or atomic) as in the other. Goldschmidt (4, p. 75) gives the example of the incommensurable NaCl and zincblende. There is every reason to believe that the NaCl structure is made up of ions while the particles in ZnS may be atoms or at least are closer to that state than to the ionic state. In other words, the particles as atoms in structures of the ZnS type (Table I) show greater resemblance to the atoms in diamond than to the ions in the NaCl structure. Therefore, when comparing the properties of one structure with those of another, as for example in isomorphism, consistent results will probably be obtained only if the two structures are commensurable, *i.e.*, their particles are in the same state or condition.

Morphotropism or morphotropic change is the change from one structure type to another type brought about in such a manner that by chemical substitution the limits of the ratio of the atomic radii in the structure are exceeded, which then results in the new type. A greater degree of deformability of the replacing substance may have the same effect. Such a change of type can also occur in crystal structures without chemical substitution by changing the thermodynamic conditions under which it is stable. This is called polymorphism.

A study of the ratios of the atomic radii in the various types shows the following limits (Table II).

Such structures as MoS_2, Fig. 17, and boron nitride, Fig. 16, are called "layer lattices" on account of the arrangements of the particles in distinct layers. They are due to great deformability of their atoms or ions. No limits for ratios of their radii can be given at present.

TABLE II

RATIO $A:B$

TYPE	APPROX. LOWER LIMIT	APPROX. UPPER LIMIT
NaCl	0.41	2.41
CsCl	0.73	1.37
NiAs	0.40	1.89
ZnS	0.22	4.45
CaF_2	0.73	4.45
TiO_2	0.41	0.73
SiO_2	0.22	0.41

It will be seen in Table II that the possible ranges of the radii for the types overlap in most cases. A selection then between these overlapping types, but within the limits given, is chiefly based on deformability of the particles as Goldschmidt has shown.

Several examples will be cited for illustrations. The rutile type has the valence coordinates 6 and 3 and a ratio $A:B$ between 0.41 and 0.73. If it is required to change to the quartz or cristobalite type with coordinates 4 and 2 and a ratio between 0.22 and 0.41, a smaller A particle or a larger B particle must be substituted in the rutile type. Of anions only F and O are available for those of higher atomic numbers are strongly deformable and their substitution might result in layer lattices or similar types. If we substitute, however, for Ti in rutile Si, we obtain a ratio of $Si:O=0.30$ and the mineral cristobalite or quartz results.

From CeO_2 which crystallizes with the fluorite type, the rutile type SnO_2 may be obtained by substitution of Sn for Ce. Sn is sufficiently small to come within the range of the rutile ratio 0.41 to 0.73.

The limits of the ratio of the CsCl type are well within the range of those of the NaCl type. To bring about a change from the NaCl type to the CsCl we substitute an ion of greater deformability. For example, by the substitution of Tl for Rb in RbCl, which belongs to the NaCl type and has the ratio 0.82, TlCl with the same ratio is obtained because Tl has the same radius as Rb. But TlCl is of the CsCl type.

STRUCTURES CONTAINING RADICALS

We have not thus far mentioned structures containing such radicals as CO_3, SO_4, NO_3, etc. The existance of such radicals seems to be almost entirely attributable to deformability of the ions concerned. The investigations by Fajan, Born, Heissenberg, Hund and others show that the following general statements are true.

(1) Deformability of an ion decreases with increasing positive valence and increases with increasing negative valence.

(2) Deformability decreases (valence being constant) with decreasing radius of the ions.

(3) The deforming influence of an ion increases with increasing positive or negative charge.

(4) The deforming influence of an ion increases (valence being constant) with decreasing radius of the ion.

This would make ions of C^{++++}, Si^{++++}, S^{+++}_{+++} (in the sulfate radical), Al^{+++}, N^{+++++}, highly deforming and O^{--}, and S^{--}, easily deformable ions. When these extremes meet, there result closely connected groups or radicals, usually with a strongly deforming ion in the center. That the bonds between the ions in the group are stronger than in the rest of the structure is also indicated by the fact that the distances between them may be smaller than would be expected from their normal behavior. For example, the distance $C-O$ in the CO_3 group of calcite is 1.25Å, though the radius of O alone is usually 1.32Å. In the SO_4 radical of $CaSO_4$, on the other hand, the distances between S^{+++}_{+++} and O^{--} are normal. The four O ions form a nearly regular tetrahedron about the S ion according to Wasatjerna.

There are also cases in which the radical has practically lost its identity due to the great deforming influence of the ions surrounding the radical. Such disruption is called counter-deformation (Kontra-polarisation) by Goldschmidt who also gives the following example (3, p. 67). In spinel $MgAl_2O_4$, the radical Al_2O_4 is no longer recognizable because of the strong counter deforming influence of the Mg ions. The O ions are now closer to the Mg ions than to the Al ions, though the radii of the ions would lead one to expect the reverse.

SUMMARY

An attempt has been made to present in a condensed form some of the recent investigations of crystal structure types especially those of Goldschmidt. Structure types and their valence coordinate bonds are discussed and illustrated. Morphotropism, polymorphism, the formation of radicals due to the deformability of ions and the effects of counter-deformability are explained with the aid of simple structure types.

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Figures*

* Most of the figures (1–4 excepted) with slight modifications are taken from P. P. Ewald and C. Hermann (2).

Fig. 1. Equilateral triangle of spheres showing size of sphere which may be placed inside. Limit of ratio of radii $A:B=0.15$.

Fig. 2. Square. Limit $A:B=0.41$. The same ratio holds for the octahedron which we obtain from Fig. 2 by placing a B sphere above and one below the A sphere.

Fig. 3. Tetrahedral arrangement. Limit $A:B=0.22$. The dotted circle represents two spheres one above, the other below, the plane of the paper.

Fig. 4. Cubic arrangement of spheres. Limit $A:B=0.73$. Two spheres placed above the dotted circles will close the cube.

Fig. 5. Sodium chloride, NaCl. The lines connecting the ions are valence coordinates. The cation as well as the anion has six bonds to its nearest neighbors of opposite charge, which we might imagine at the corners of an octahedron.

Fig. 6. Nickel arsenide, NiAs. (Niccolite). The hexagonal unit cells are outlined in dotted lines. Valence coordinates are shown in full lines. Each cation (Ni) is surrounded by six anions (As) which are at the corners of a slightly distorted octahedron. Each anion has six cations surrounding it. These we may imagine at the corners of a trigonal pyramid.

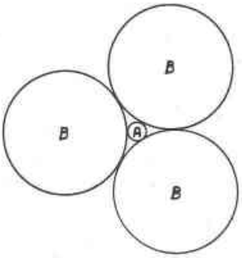

Fig. 1

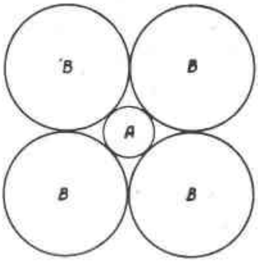

Fig. 2.

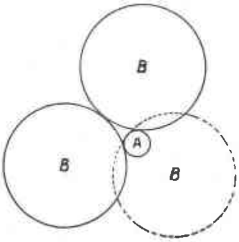

Fig. 3

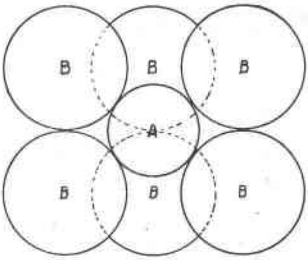

Fig. 4

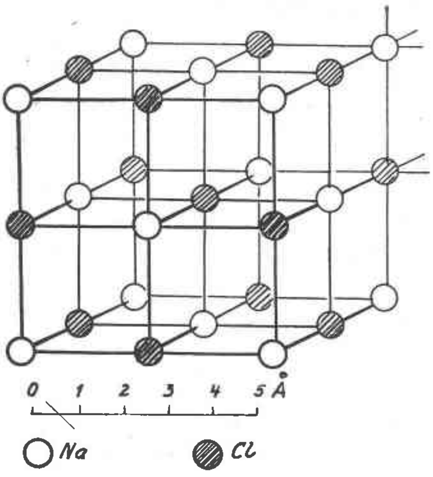

Fig. 5

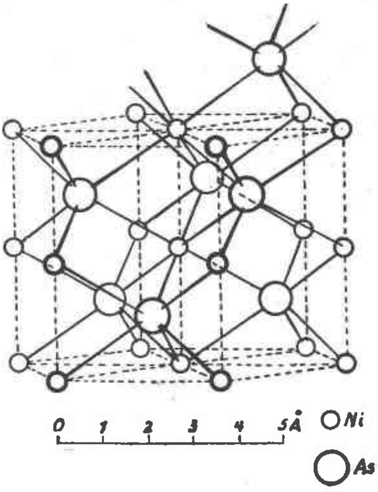

Fig. 6

Fig. 7. Caesium chloride, CsCl. The cubic unit cell is shown in dotted lines. Eight valence coordinates connect each ion with its neighbors of opposite charge.

Fig. 8. Zincblende, ZnS. The cubic unit cell is shown in dotted lines. The Zn atoms (or ions?) form a face-centered cube. The S atoms form a tetrahedron inside the cube in such a way that S atoms are placed in the centers of alternate octants. Each atom has four coordinates linking it to four atoms (or ions?) of opposite charge. These are at the corners of a tetrahedron. If we imagine all atoms to be alike in this structure we have the diamond structure type.

Fig. 9. Wurtzite, ZnS. The hexagonal unit cell (rhombic in cross-section) is dashed. The valence coordinates are very similar to zincblende, four from each atom at the center of a tetrahedron to four atoms at the corners.

Fig. 10. Chalcopyrite, $CuFeS_2$. This structure is very similar to zincblende. The only difference is that half of the Zn atoms are replaced by Cu and the other half by Fe.

Fig. 11. Fluorite CaF_2. The calcium ions form a face-centered cube (dotted unit cell). The fluorine ions form a smaller cube inside. Each calcium has eight coordinates to fluorine ions and each fluorine four coordinates to the corners of a tetrahedron of calcium.

Fig. 12. Cuprite Cu_2O. The O ions form a body-centered cube. The Cu ions form tetrahedrons around each O ion. The Cu ion has two coordinates, the O ion four.

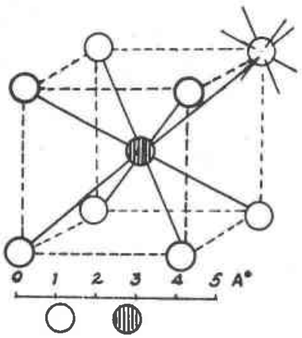

Fig. 7

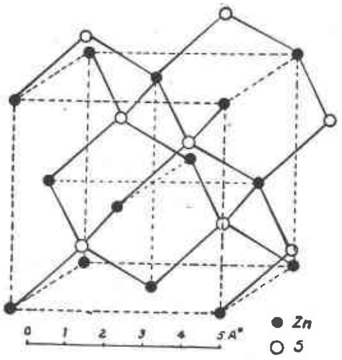

Fig. 8

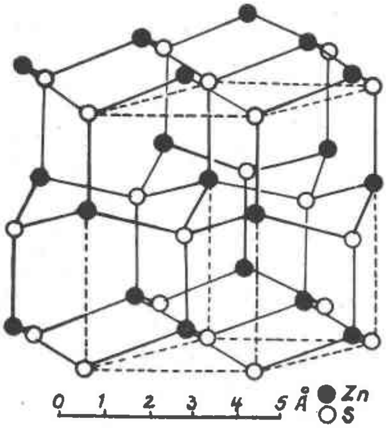

Fig. 9

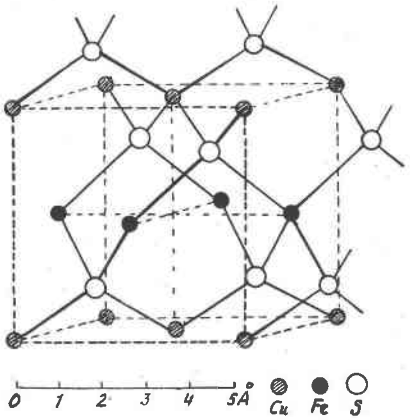

Fig. 10

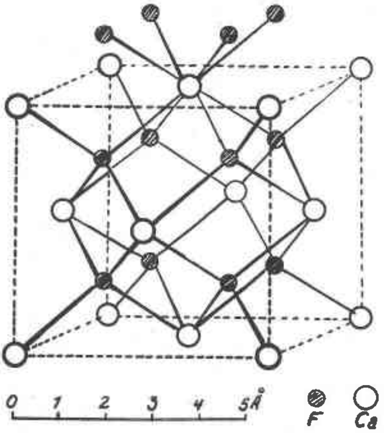

Fig. 11

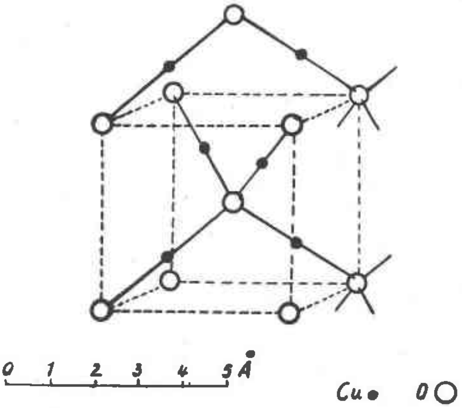

Fig. 12

Fig. 13. Rutile TiO_2. The unit body-centered tetragonal prism is dotted. Each T. ion has six coordinates to O ions which are at the corners of a slightly distorted octahedron. Each O ion has three coordinates.

Fig. 14. β-cristobalite, SiO_2. The cubic cell contains eight molecules of SiO_2 Each Si ion is surrounded by a tetrahedron of four O ions. Each O ion has two coordinates to the two Si ions between which it is placed.

Fig. 15. β-quartz, SiO_2. The hexagonal prism shown is three times the volume of the unit cell which is one of the rhombic prisms outlined. Each Si ion has four O ions at the corners of a distorted tetrahedron. Each O ion lies between two Si ions but not in a straight line with them.

Fig. 16. Boron nitride, BN. The hexagonal units are dotted. This is a "layer lattice." Each B ion has three coordinates to the N ions and each N ion three coordinates to the nearest B ions. Graphite has the same structure if we imagine all particles to be carbon.

Fig. 17. Molybdenite, MoS_2. A typical hexagonal "layer lattice." (Schichtengitter). The layers are outlined by stippled areas. On each side of a layer of Mo ions is a layer of S ions. Two S layers are in contact. The distance between these layers is greater than between the Mo-S layers. These two facts explain the easy basal cleavage of molybdenite. Cadmium iodide, CdI_2, has a similar structure.

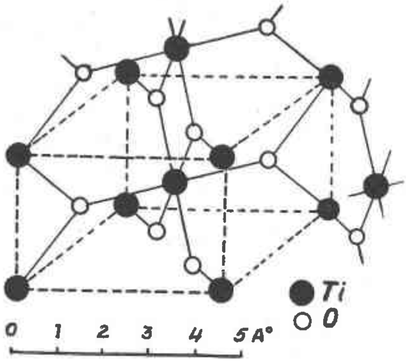

Fig. 13

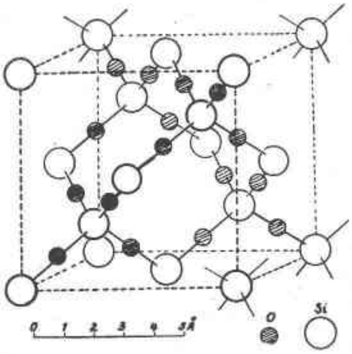

Fig. 14

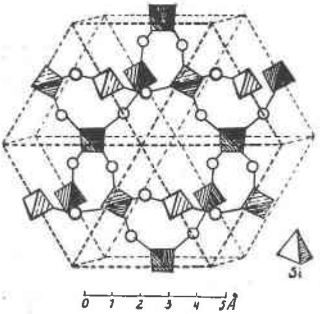

Fig. 15

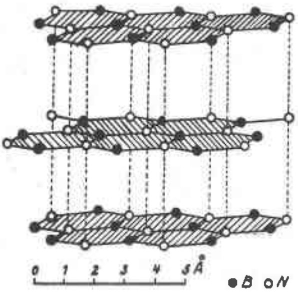

Fig. 16

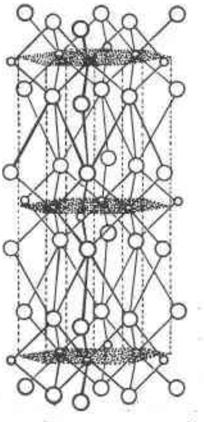

Fig. 17