Bravais' and Kossel-Stranski's Theories of Homopolar Crystals and their Application to Elements

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The two theories are shown to be in fair agreement for simple lattices. The results obtained by the author with the Kossel-Stranski theory differ from those reported by Stranski and co-workers. Both theories conform well with experimental data, as is shown for the crystal habit and structure of a number of common elements, including Cu, Ag, Au, Pb, Pt, Fe, W, V, C, Si, Be, Ti, Mg, Zn, Cd, Se, Te, Sn. In the case of Se and Te serious deviations from the Kossel-Stranski theory have been reported earlier due to inadequate theoretical predictions. The agreement between theory and experiment is best if the outer disturbances are small, as in sublimation, while deviations are found on metal crystals, electrodeposited from complex or molten salts. Electrodeposition as such is not a very disturbing factor.

It is of great interest to relate the habit, *i. e.* the external face development of a crystal to its internal structure. Two main such attempts have been made.

About 1850 Bravais suggested that the order of decreasing importance of the outer surfaces would be the same as the order of decreasing close-packing of the corresponding lattice planes¹. Hence, this idea has also been referred to as the "reticular density" theory². It has been elaborated in later years, mainly by mineralogists³⁻⁵.

The other theory was developed in 1928 by Kossel⁶ and has later been elaborated by Stranski and co-workers⁷⁻⁹. This theory considers the number of closest neighbors of a lone particle, settling on a face to begin a new layer. It may therefore be termed the "nearest neighbors" theory. It was reviewed by several authors^{2,10-12}.

BRAVAIS' OR RETICULAR DENSITY THEORY

The more closely packed with molecules a set of planes is, the wider is their spacing. It is easily shown that $D = \frac{n}{V} \cdot d$, where D = reticular density (number of molecules per unit area), d = interplanar spacing, V = volume of unit cell, n = number of molecules per unit cell.

The reticular density theory can be formulated in the following way: In close-packed planes the molecules form a dense aggregate and neutralise each other's bonds so that few free valencies are directed towards the outer space. Furthermore, a molecule trying to start a new such close-packed plane will be located relatively far from the molecules of the crystal and will form an excrescence on the surface of the latter. Hence, the new molecule will be but loosely bonded and the tendency for the formation of a seed will be low. On the other hand, a less densely packed plane will consist of molecules less tightly knitted together, which will therefore have more residual valencies pointing out from the crystal. Furthermore, a molecule trying to start a new plane will be close to the molecules of the outermost planes of the crystal and will not project very much above the surface of the crystal. Hence, it will have a greater tendency to stay and form a seed. It should be stressed that the reticular density theory does not take account merely of the outermost plane since a small spacing will mean that the lone molecule is close to the entire crystal.

According to the above, the smaller the reticular density and interplanar spacing of a surface is, the faster will it grow normally to itself. It is obvious, however, that the most rapidly growing surfaces will soon disappear from the crystal and in the final crystal only the surfaces of slowest perpendicular growth will persist. But these are the close-packed surfaces.

Burton and Cabrera¹³ and also Hartman and Perdok¹⁴ have divided the faces of a crystal into three different classes, viz. close-packed or flat faces, F-faces, containing 2 or more intersecting sets of parallel, close-packed atom chains; stepped or S-faces, containing one set of parallel, close-packed atom chains; and kinked or K-faces, containing no such chains. The directions of close-packed atom chains, called periodic bond chain vectors by Hartman and Perdok¹⁴, correspond to the preferred directions of growth and to important zone directions of the crystal.

It is interesting to note that the order of decreasing importance of the crystal faces according to the reticular density theory will be the same as the sequence in which the first order reflections appear on an X-ray powder recording, proceeding from small to large angles³. If the space lattice is known the order of decreasing spacings d can easily be calculated from formulas given in textbooks of X-ray crystallography. The calculation may be checked with the ASTM X-ray data cards.

KOSSEL-STRANSKI'S OR NEAREST NEIGHBORS' THEORY

According to the Kossel-Stranski theory the number of nearest, second-nearest and third-nearest neighbors (and so on) of a lattice particle, put together in an expression $n_1/n_2/n_3\dots$, are considered to be a measure of the bonding energy of the particle in question. Growth of the crystal will normally proceed by the addition of a molecule to an uncompleted lattice row. This process is called the *wiederholbarer Schritt* (the repeatable step) and the lattice site that the molecule then occupies is known as the *Halbkristall-Lage* (half-crystal position, growth position). The number of neighbors of a par-

ticle in the *Halbkristall-Lage* is exactly *half* of that of a particle in the interior of the crystal.

As far as the *wiederholbarer Schritt* is concerned, there is no difference between the various lattice planes of a crystal ^{4,6}. However, as one plane is completed a new one has to be started. A simplifying provision of the Kossel-Stranski theory is that all neighbors at a certain distance are equal. In reality, their bond energies are more or less utilized owing to their position. If this is disregarded it is easily demonstrated that a new layer of molecules will start from its middle and not from its edge, since the seed molecule will have more neighbors in the former case.

If a lone particle, settling on a face to begin an entirely new layer, has a great number of closest neighbors, it is obvious that this face will grow fast normally to itself, since new layers are easily nucleated.

If the corresponding neighbor numbers are recorded for the various lattice planes of a three-dimensional model, it is easy to arrange the faces in order of increasing normal growth velocity, *i. e.* in order of decreasing importance on the final crystal. The counting of the neighbors should be performed in a space lattice model of considerable size (20—30 unit cells).

In reality, the kinetics of crystal growth are more complicated than is provided in the Kossel-Stranski theory. Growth layers of visible thickness can be observed microscopically. They are easily studied in the electrodeposition of metals. They are about one micron thick and usually spread from a point in the interior of the crystal surface, though at high current densities from the edges. These thick growth layers are always to be found in the most close-packed surfaces. They are sometimes due to screw dislocations, a phenomenon that has played a great role in the literature on crystal growth lately ¹⁵.

CUBIC STRUCTURES

For cubic lattices the interplanar spacings d are calculated from the formula

$$d = a / \sqrt{h^2 + k^2 + l^2}$$

where a is the edge length of the unit cube and h, k, l the Miller indices of the surface. All sets of values h, k, l that are a multiple of 2, 3 or 4 of a former set should be excluded since they will correspond to higher order reflexions but not to physical lattice planes. For interlacing lattices certain other restrictions apply in addition. These are given in the table headings.

The reticular densities (number of atoms in the area a^2) are obtained from the relation $D = \frac{n}{V} \cdot d$ and are recorded in the second column in the tables. In the third column the number of nearest neighbors of a molecule starting a new plane is given. The last column, finally, gives the sequence according to column 3. In determining this order the following should be observed. Due to the rapid falling off of homopolar forces with distance, the expression $n_1/n_2/n_3$ may be considered as a kind of (decimal) fraction where one molecule in the first place corresponds to several in the second and so on. If, for instance, the

Table 1. Simple cubic lattice.

Restriction: h, k, l without common factor. $r_1 = a$; $r_2 = a/\sqrt{2}$; $r_3 = a/\sqrt{3}$.

Face hkl	Reticular density	Number of nearest neighbors	Sequence according to column 3
100	1	1/4/4	1 X
110	$1/\sqrt{2}$	2/5/2	2 X
111	$1/\sqrt{3}$	3/3/4	4 X
210	$1/\sqrt{5}$	2/6/4	3
211	$1/\sqrt{6}$	3/5/3	5 X
221	$1/\sqrt{9}$	3/5/4	6
310	$1/\sqrt{10}$	2/6/4	3

An X in the last column denotes the faces enumerated by Stranski and co-workers⁷.

Table 2. Face-centered cubic lattice (cubic close-packing).

Restriction: All h, k, l even or all odd. $r_1 = a/\sqrt{2} = 0.707 a$; $r_2 = a$; $r_3 = a\sqrt{3}/\sqrt{2} = 1.225 a$.

Face hkl	Reticular density	Number of nearest neighbors	Sequence according to column 3
111	$4/\sqrt{3}$	3/3/9	1 X
200 = 100	$4/\sqrt{4}$	4/1/12	2 X
220 = 110	$4/\sqrt{8}$	5/2/10	3 X
311	$4/\sqrt{11}$	5/3/10	4 X
331	$4/\sqrt{19}$	5/3/12	5
420 = 210	$4/\sqrt{20}$	6/2/10	6 X
422 = 211	$4/\sqrt{24}$	5/3/12	5
511	$4/\sqrt{27}$	5/3/12	5
531	$4/\sqrt{35}$	6/3/10	7 X
442 = 221	$4/\sqrt{36}$	5/3/12	5
620 = 310	$4/\sqrt{40}$	6/2/10	6

Table 3. Face-centered cubic elements.

Element	Mode of crystallization	Order of observed crystal faces compared to theories									
Cu	Sublimation ¹⁹	1	2	3							
		111, 100, 110									
		1 2 3									
	Solidification ^{19,23}	1 2 3									
		111, 100, 110									
	Electrodeposition	1 2 3									
		111, 100, 110, 211, 210, 311, 511									
	a) from simple salt solutions ^{19,20}	1 2 3 7 6 4 8									
		1 2 3 5 6 4 5									
	b) from complex halides ²¹	hk0, hkk, 111, 110									
Ag	Sublimation ¹⁹	100									
		100, 110, 111, 210, 310, 211, 311, 511, 531									
		1 2 3 10 6 6 5 4 5 7									
	Solidification ¹⁹	111, 100, 110									
		1 2 3									
	Electrodeposition	1 2 3									
		111, 100, 211, 110, 331, 751, 861									
	a) from simple salt solutions ^{19,22,23}	1 2 7 3 5 - -									
		1 2 5 3 5 - -									
	b) from ammoniacal solutions ²⁷	111, 100, 110, 720									
Au	Sublimation ¹⁹	111, 100									
		1 2 3									
		111, 100									
	Solidification ¹⁹	1 2 3									
		111, 100									
	a) Reduction with SO ₂ ¹⁹	100, 111									
		100, 111, 110, 210, 310, 410, 520, 740, 311									
	b) HCHO ¹⁹ , FeCl ₃ ¹⁹	100, 111, 110, hkk, hkl									
		100, 110, 210, 311, 321									
	Natural crystals ¹⁹	111, 100, 110, 210, 520, 310, 410, 311, 211									

Pb	Sublimation ¹⁰	$\begin{matrix} 1 & 2 \\ 111, & 100 \end{matrix}$
		$\begin{matrix} 1 & 2 \\ 1 & 2 \end{matrix}$
"	Solidification ¹⁰	$\begin{matrix} 1 & 2 \\ 111, & 100 \end{matrix}$
		$\begin{matrix} 1 & 2 \\ 1 & 2 \end{matrix}$
"	Electrodeposition from simple salt solutions ^{10,22}	$\begin{matrix} 1 & 2 & 3 & 4 \\ 111, & 100, & 110, & 311 \end{matrix}$
		$\begin{matrix} 1 & 2 & 3 & 4 \\ 1 & 2 & 3 & 4 \end{matrix}$
Pt	Gas phase reduction ¹⁰	$\begin{matrix} 1 & 2 & 3 \\ 111, & 100, & 110 \end{matrix}$
		$\begin{matrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{matrix}$
"	Solidification ¹⁰	$\begin{matrix} 1 & 2 \\ 111, & 100 \end{matrix}$
		$\begin{matrix} 1 & 2 \\ 1 & 2 \end{matrix}$
"	Natural crystals ¹⁰	$\begin{matrix} 2 & 1 & 3 & - & - & 6 & 11 \\ 100, & 111, & 110, & 320, & 530, & 210, & 310 \end{matrix}$
		$\begin{matrix} 2 & 1 & 3 & - & - & 6 & 6 \\ 2 & 1 & 3 & 2 & 2 & 6 & 6 \end{matrix}$
γ -Fe	Solidification of pig iron ¹⁰	$\begin{matrix} 1 & 3 & 2 \\ 111, & 110, & 100 \end{matrix}$
		$\begin{matrix} 1 & 3 & 2 \\ 1 & 3 & 2 \end{matrix}$
Ni	Electrodeposition from simple salts ²⁵	$\begin{matrix} 2 & 1 \\ 100, & 111 \end{matrix}$
		$\begin{matrix} 2 & 1 \\ 2 & 1 \end{matrix}$

bonding energy is proportional to r^{-6} , as is often assumed ¹⁶, and if $r_2 = r_1\sqrt{2}$, one molecule in the first place will correspond to 8 in the second. If r_2 is only 10 % longer than r_1 , the proportion will still be 1:1.8. Hence, we may safely adopt the following principle: The relative value of the expression $n_1/n_2/n_3$ is generally determined by n_1 . If two expressions have the same n_1 , their relative positions will be determined by n_2 . If both the n_1 's and n_2 's are equal, n_3 will decide and so on.

The discrepancies between the two theories will be obvious from the last column of the tables. An X in the last column denotes the faces enumerated by Stranski and co-workers ^{7,8}. They are usually, but not always, given by them in the same order as here. It should also be noted that there are several misprints in the tables in the paper by Stranski and Kaischew ⁷ that are cited uncorrected by later writers ^{10,12,17,18}. One curious feature in the paper mentioned is that the authors ⁷ arbitrarily leave out some important low-indexed surfaces, particularly those that give the same expression in column 3 of the tables. This omission does not seem justified since these surfaces, *e. g.* 331, 211, 310 and 511 in the face-centered cubic lattice, are often observed on crystals (Table 3).

According to Stranski, any molecule on the surface of the crystal must at least be as strongly bonded as in the *Halbkristall-Lage*. His method to derive the equilibrium form is therefore to start from an arbitrarily simple form and substitute surfaces for corners and edges until the above provision is fulfilled. It appears that this method is arbitrary and is apt to exclude certain faces. Furthermore, the imagined removal of molecules from the corners and edges of the simple form has only to be carried so far that surfaces of the extension of a few tens of Ångström units are created. This does not necessarily imply that these surfaces will be detected by microscopic means on the final crystal. For instance, Stranski in a number of papers takes considerable pains to explain ¹⁶ why on body-centered cubic crystals the surface 211 appears but not the surface 111. It is now obvious from Table 4 that the former is theoretically

much more important than the latter and it will obviously be sufficient if 111 is present in submicroscopic extension.

In the first three lattices dealt with here, the spacing d assumes only one value for any sequence of parallel planes. This is not the case with the diamond cubic lattice (Fig. 1). An inspection of the space model will show that the 111 planes are spaced in a narrow-wide-narrow-wide sequence (Fig. 2). The identity spacing d obtained by X-ray analysis is $d = p + q$. This means that in determining the reticular density two narrow-spaced planes are considered to be one plane of double density. In applying the Kossel-Stranski theory, the molecule starting a new layer should be located at the distance q from the outer surface of the crystal (e. g. if the crystal surface is plane 2, the lone molecule will be in plane 3). The same condition is found with some other planes in

Table 4. Body-centered cubic lattice.

Restriction: $h + k + l = 2n$. $r_1 = a\sqrt{3}/2 = 0.866a$; $r_2 = a$; $r_3 = a\sqrt{2}$

Face hkl	Reticular density	Number of nearest neighbors	Sequence according to column 3
110	$2/\sqrt{2}$	2/2/5	1 X
200 = 100	$2/\sqrt{4}$	4/1/4	4 X
211	$2/\sqrt{6}$	3/3/5	2 X
310	$2/\sqrt{10}$	4/2/6	5
222 = 111	$2/\sqrt{12}$	4/3/3	6 X
321	$2/\sqrt{14}$	3/3/6	3
411	$2/\sqrt{18}$	4/3/6	7

Table 5. Diamond cubic lattice.

Restriction: $h^2 + k^2 + l^2 = 8n$ or $8n + 3$

$r_1 = a\sqrt{3}/4 = 0.433a$; $r_2 = a\sqrt{2}/2 = 0.707a$; $r_3 = a\sqrt{11}/4 = 0.829a$; $r_4 = a$

Face hkl	Reticular density	Number of nearest neighbors	Sequence according to column 3
111 D	$8/\sqrt{3}$	1/3/6/3	1 X
220 = 110	$8/\sqrt{8}$	1/5/5/2	2 X
311 D	$8/\sqrt{11}$	2/5/4/3	5 X
400 = 100	$8/\sqrt{16}$	2/4/6/1	4 X
331 D	$8/\sqrt{19}$	1/5/7/3	3
422 = 211	$8/\sqrt{24}$	2/5/4/3	5
511 D	$8/\sqrt{27}$	2/5/4/3	5
531 D	$8/\sqrt{35}$	2/6/5/3	7
620 = 310	$8/\sqrt{40}$	2/6/5/2	6 X

A "D" in the first column denotes a "double", non-coplanar face.

Table 6. *Body-centered cubic and diamond cubic elements.*

Element	Mode of crystallization	Order of observed crystal faces compared to theories											
Body-c.cubic													
W, Mo, Ta	Sublimation ¹⁸	1	2	3									
		110,	100,	211									
		1	4	2									
V	Reduction of V ₂ O ₅ with Na ¹⁹	1	2										
		110,	100										
		1	4										
α-Fe	Reduction of FeCl ₃ with H ₂ ¹⁹	2	1										
		100,	110,	hk0									
		4	1										
,	Electrodeposition from fused chlorides ²⁰	2											
		100											
		4											
Diamond cubic													
C (diamond)	Natural crystals ¹⁹	1	2	4	-	9	6	7	12				
		111,	110,	100,	210,	310,	211,	511,	321				
		1	2	4	-	6	5	5	-				
Si	Reduction of SiCl ₄ with Al ¹⁹	1	2										
		111,	110										
		1	2										

the lattices dealt with below. Such "double" planes are marked "D" in the first column in the tables.

In Tables 3 and 6, the two theories are tested on elements with cubic structures. Most of the experimental data have been taken from P. Groth, *Chemische Krystallographie* ¹⁹, which contains an abundance of material that does not seem to have been utilized in this connection earlier. The third column in the tables gives the observed crystal faces in order of decreasing importance. Above and below the index figures, the ordinal numbers of the various faces according to Bravais' and Kossel-Stranski's theories are given with small figures. These numbers show the correlation between the two theories and experimental results.

HEXAGONAL STRUCTURES

In hexagonal lattices, the spacings d are obtained from the formula

$$\frac{1}{d^2} = \frac{4}{3a^2} (h^2 + k^2 + hk) + \frac{l^2}{c^2}$$

The hexagonal lattice is indexed with only three indices here. The fourth index i often given is related to h and k by the equation $h + k + i = 0$. In the hexagonal and following lattices, interplanar spacings are used instead of reticular densities. They are expressed in relative measure or in Ångström units.

In the hexagonal close-packed lattice, c equals $a\sqrt{8/3} = 1.633 a$. Mg ($c = 1.627 a$), Be and Ti ($c = 1.590 a$) are close to the ideal value. In Cd ($c = 1.890 a$) and Zn ($c = 1.855 a$) the c -axis is relatively longer and the sequence of planes will be somewhat different. Earlier workers ^{11,28} treated Zn and Cd as ideally close-packed. It will be obvious from the tables, however, that the correlation with observation will be better if account is taken of the stretching of the c -axis.

Fig. 1. Diamond cubic lattice, unit cell, basal projection. The figures denote the position of atoms above the basal plane.

Fig. 2. Arrangement of the 111-planes of the diamond cubic lattice. $q = 3p$. $d = p + q$.

Fig. 3. Unit cell of Se and Te, basal projection. Position of atoms: $x00$, $0x\frac{1}{3}$, $xx\frac{1}{3}$.

Fig. 4. Unit cell of white tin. a) Unit cell seen from top. b) Unit cell seen from side.

The elements selenium and tellurium have a more complex hexagonal structure. A basal projection of their unit cell is shown in Fig. 3. The lattice is built up of chains of atoms which are arranged in a spiral around an immaterial axis. The chains are perpendicular to the plane of the figure. Some data of importance are collected in Table 10.

These elements are of particular interest since deviations from the Kossel-Stranski theory have been reported with them. Stranski and co-workers⁸ predicted the surfaces 101, 001, 102 and 100. Straumanis^{11,29,30} in experiments on sublimated crystals of Se and Te did not find 001 and 102. The absence of the basis, 001, was particularly conspicuous. However, it seems clear that 001 should indeed *not*, according to the Kossel-Stranski theory, belong to the most important surfaces of the crystals. Since the closest neighbor is

Table 7. Hexagonal close-packed lattice (Be, Ti, Mg).

Restriction: $l = 2n$, if $h-k = 0$ or 3 p.

$$r_1 = a; r_2 = a\sqrt{2}; r_3 = a\sqrt{8}/\sqrt{3} = 1.633 a.$$

Face <i>hkl</i>	Interplanar spacing <i>d</i>	Number of nearest neighbors	Sequence according to column 3
100 D	0.866 <i>a</i>	4/4/0	3 X
002 = 001	0.816 <i>a</i>	3/3/1	1 X
101 D	0.765 <i>a</i>	4/2/1	2 X
102 D	0.594 <i>a</i>	5/2/1	5 X
110	0.500 <i>a</i>	5/2/0	4 X
103 D	0.461 <i>a</i>	5/3/1	6
112	0.427 <i>a</i>	5/3/1	6

Table 8. Stretched hexagonal close-packed lattice (Zn, Cd).

$$c = 1.87 a; r_1 = a; r_2 = 1.10 a; r_3 = 1.49 a.$$

Face <i>hkl</i>	Interplanar spacing <i>d</i>	Number of nearest neighbors	Sequence according to column 3
002 = 001	0.935 <i>a</i>	0/3/3	1
100 D	0.865 <i>a</i>	2/2/4	3
101 D	0.786 <i>a</i>	2/2/2	2
102 D	0.636 <i>a</i>	2/3/2	4
103 D	0.506 <i>a</i>	2/3/3	5
110	0.500 <i>a</i>	3/2/2	6
112	0.441 <i>a</i>	3/2/3	7

Same result with six kinds of neighbors.

in the same chain the continuation of a chain is obviously more favored than the starting of a new chain. Since 001 consists of ends of chains it should grow fast and hence not appear in the final crystal. Actually, Straumanis²⁹ found the *c*-axis to be the preferred direction of growth and that needles along this axis often resulted. In the case of Se and Te, the *c*-axis is obviously the most important periodic bond chain vector in the sense of Hartman and Perdok¹⁴. On the other hand, the surfaces parallel to the chains, *i. e.* the prism faces, requiring nucleation of new chains for their normal growth, should grow slowly and thus be important surfaces in the final crystal. In fact, four out of five faces observed by Straumanis²⁹ on selenium were prism faces. Although the Kossel-Stranski theory cannot distinguish between the higher prism faces, Table 11 shows that it is in good agreement with the observed faces on selenium. The Bravais theory is somewhat less successful since it does not take full account of the favored length growth of the chains and thus gives the pyramid faces, 102, 111 *etc.* a too important position.

Table 9. Hexagonal close-packed elements.

Element	Mode of crystallization	Order of observed crystal faces compared to theories				
		2	1	5	3	4
Be	Reduction of BeCl ₂ with Na ¹⁹	001, 1	100, 3	110, 4	101, 2	102, 5
Ti	Electrodeposition from fused salts ²⁷	2	1			
		001, 1	100, 3			
Mg	Sublimation ^{11,19}	2	3	1		
		001, 1	101, 2	100, 3		
Zn	Sublimation ^{11,28}	1	3	6	2	4
		001, 1	101, 2	110, 6	100, 3	102, 4
Cd	Sublimation ^{11,28}	1	2	3	6	—
		001, 1	100, 2	101, 3	110, 6	111, —
Cd	Electrodeposition from simple salts ^{12,22}	1	2	3		
		001, 1	100, 3	101, 2		

Table 10. Lattice constants of selenium and tellurium.

	<i>a</i>	<i>c</i>	<i>x</i>	<i>r</i> ₁	<i>r</i> ₂	<i>r</i> ₃	<i>r</i> ₄
Se	4.36	4.95	0.217	2.32	3.46	3.67	4.36
Te	4.45	5.91	0.269	2.86	3.46	4.45	4.45

x is expressed as a fraction of *a*. Cf. Fig. 3. *r*₁ is the distance to the nearest atom in the same chain, *r*₂ to the nearest atoms in adjacent chains, *r*₃ is the distance to the nearest atoms in the same plane 001 and *r*₄ to the next nearest atom in the same chain. All distances in this and the following tables are expressed in Ångström units.

Table 11. Selenium lattice.

Restriction: 00*l* only with *l* = 3*n*.

Face <i>hkl</i>	Interplanar spacing <i>d</i>	Number of nearest neighbors	Sequence according to column 3
100	3.77	0/3/0/2	1 X
101 D	3.01	1/0/1/2	3 X
110	2.17	0/4/0/3	2
102 D	2.07	1/1/1/2	5 X
111 D	2.00	1/0/1/3	4
201 D	1.77	1/1/1/2	5
112 D	1.64	1/0/1/3	4
003 = 001	1.43	1/2/1/0	6 X
120		0/4/0/3	2
230		0/4/0/3	2

Observed surfaces on sublimated crystals^{11,29}:

1	2	3	8	—
100, 1	101, 3	110, 2	120, 2	230, 2

Table 12. Tellurium.

hkl	100	101	102	110	111	201
d	3.86	3.24	2.34	2.22	2.08	1.83
Mode of crystallization	Order of observed crystal faces compared to theories					
Sublimation ^{11,22}			¹ 100,	² 101,	⁴ 110,	¹² 114
Solidification ¹⁹			¹ 101	³	²	—
Decomposition of K_2Te ¹⁹			¹ 100,	⁴ 110,	⁵ 111,	⁶ 201
Natural crystals ¹⁹			¹ 100,	² 101,	⁴ 001	⁵
			¹	³	⁷	⁶

The data derived from Groth ¹⁹ were transformed from rhombohedral to hexagonal lattice.

Table 13. Tetragonal tin lattice.

Restriction: $h + k + l = 2n$; $2k + l = 2n + 1$ or $4n$

$r_1 = 3.02$; $r_2 = 3.17$; $r_3 = 3.75$; $r_4 = 4.41$

Face hkl	Interplanar spacing d	Number of nearest neighbors	Sequence according to column 3
200 = 100	2.91	1/0/1/4	1
101 D	2.79	1/1/2/2	2
220 = 110	2.05	2/0/2/2	5
211 D	2.01	2/1/1/2	7
301 D	1.65	1/1/2/4	4
112	1.48	1/1/2/3	3
420 = 210	1.30	2/0/2/4	6
332	1.03	2/1/1/4	

Same result with five kinds of neighbors.

Observed sequence: Solidification ¹⁹	¹ 100,	² 101,	³ 110,	⁶ 112		
	¹	²	⁵	³		
Electrodeposition from simple salts ^{19,22}	² 101,	¹ 100,	³ 112,	³ 332,	⁵ 110,	⁵ 301
	²	¹	³	—	⁵	⁴

In applying the Kossel-Stranski theory to the latter faces, one finds that they are spaced in a narrow-narrow-wide sequence. The lone atom considered should be across a wide spacing from the surface of the crystal since this will correspond to the bottle-neck in the growth process. Furthermore, different results may be obtained owing to the position of the surface in relation to the axis cross. The smallest value has been chosen, since this will correspond to the appearance of the surface on the final crystal. Often only every second of the pyramid faces are present on the crystals.

It has been assumed that the growth of Se and Te occurs by addition of atom by atom to the crystal. With some pyramid faces one would then find that as an atom is added to a chain it would have no nearest neighbor in the chain but just a hole below itself. Since this cannot be the case, one is led, on purely geometric grounds, to assume that the particles added are actually diatomic molecules. This is in accordance with the fact that selenium vapor consists of diatomic molecules.

Tellurium will obtain the same theoretical equilibrium form as selenium according to the Kossel-Stranski theory. Owing to other lattice dimensions the faces will appear in a somewhat different order according to Bravais as shown in Table 12. It is obvious that the agreement between theory and fact is good also for tellurium.

TETRAGONAL TIN STRUCTURE

White tin crystallizes in a tetragonal interlacing body-centered lattice, the unit cell of which is shown in Fig. 4 in basal and side projections. The spacings d are obtained from the formula

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

The tin lattice may be considered as a diamond cubic lattice, compressed in the c direction. It is obvious from Fig. 4 b that the plane 101 is of the same nature as the octahedral plane 111 in the diamond cubic lattice, having alternating narrow and wide spacings.

The experimental data derived from Groth¹⁹ (originally published by Miller in 1843) had to be recalculated by turning the axis cross 45° around the c -axis. While the two theories do not agree too well in the case of tin, experimental data correlate well with the nearest neighbors' theory.

ORTHORHOMBIC STRUCTURES

Sulfur and iodine crystallize in the orthorhombic system. Sulfur has a complicated face-centered unit cell with 128 atoms belonging to it. The space group restrictions are: All hkl even or all odd; $h + k = 4n$ in $hk0$ etc. Donnay and Harker³ maintain that sulfur crystallizes in accordance with the Bravais theory. According to Hartman and Perdok¹⁴ better results are obtained for sulfur with the reticular density theory, if the flat, stepped and kinked surfaces are considered separately. All the authors mentioned take account only of the appearance of the surfaces, not of their relative importance. The latter is given by Groth¹⁹. Correlation of his data with decreasing d -values, considering the above restrictions, shows the following:

Orthorhombic sulfur, natural crystals³⁴:

¹	³	⁴	²	¹⁴	⁷	⁶	⁵	¹¹	⁹	¹⁰	⁸
111,	113,	011,	001,	010,	110,	115,	101,	112,	133,	013,	131

Orthorhombic sulfur, sublimated:

²001, ¹⁰013, ⁴011, ¹⁴010, ⁷110, ¹111, ³113, ⁶115, ¹⁵117

Orthorhombic sulfur, solidified from melt: ¹111, ⁴011, ³113

Orthorhombic sulfur, crystallized from solutions:

¹111, ¹⁴010, ³113, ²001, ⁴011, ⁷110, ²²100

Iodine has a less complicated structure with 4 I_2 -groups in the unit cell and with the following space-group restrictions: $h + k = 2n$ in hkl ; $h = 2n$, $k = 2n$ in $hk0$; $h = 2n$, $l = 2n$ in $h0l$; $k = 2n$ in $0kl$. Iodine crystals, obtained in various ways, show the following surfaces in order of decreasing importance¹⁹

and with the correlations with decreasing d -values noted: ²111, ¹001, ³010, ³¹³, ³¹⁶, ¹¹⁰, ¹¹⁹. The last four faces will obtain ordinal numbers ranging between 10 and 20.

On the whole, these elements do not conform very well with the Bravais theory.

DISCUSSION OF RESULTS

It will be obvious from the tables that the two theories are in fair agreement for simple structures. They almost coincide for the face-centered cubic lattice and the stretched hexagonal close-packing (Zn, Cd). Kossel-Stranski's theory seems to correlate somewhat better with experimental results. However, it should be noted that this is fictitious to some extent, because this theory is less selective so that two or more planes will often obtain the same ordinal number. It is noteworthy that the agreement is best with metallic structures, although these, consisting of positive metal ions and a negative electron gas, are not strictly homopolar. With more complicated structures, such as those of sulfur and iodine, deviations from the Bravais theory are found, while the Kossel-Stranski treatment will be too intricate. In general, the Bravais theory is much easier to apply.

It is further obvious from the tables that the degree of correlation between theory and experiment is dependent on the conditions of the crystallization process. This is natural because both theories take account of only the lattice geometry and not the environment (diffusion, adsorption *etc.*). Since both theories are energetic they imply conditions close to equilibrium, *i. e.* a small supersaturation, supercooling or polarization and hence generally a slow crystallization process. As the influence of the environment becomes more pronounced the crystals conform less well with the theories. It is natural that the best agreement is found with sublimated crystals: Sublimation is a slow process, occurring at high temperature, favoring equilibrium, and no foreign molecules are present to disturb the crystallization. On the other hand, in deposition from solutions, as by reduction agents (natural crystals seem to belong to this group) and sometimes by electrolysis, great disturbances and

deviations from the theories occur. It seems that the outer disturbances increase, *i. e.* the conformity with the theories decreases, somewhat in the following order: sublimation, solidification of melt, electrolysis of solutions of simple salts, chemical reduction, electrolysis of molten salts, electrolysis of complex salt solutions.

Electrodeposition as such, *i. e.* the superposition of an electric field on the lattice forces does not seem to influence the crystallization considerably, as is sometimes assumed^{11,31}. If the electrocrystallization of metals is observed under the microscope it is often striking how little the direction of stream-lines means in comparison with the direction of preferred growth in the lattice. A crystal needle may grow not only at right angles to the general direction of the stream-lines but actually just opposite it, *i. e.* towards the *cathode*. The fact that electrocrystallization as such conforms so well with the theories of homopolar crystal growth supports the view that the particles that are built into the lattice on the cathode are neutral atoms, not ions¹².

The nature of the crystallizing particles seems to be of minor influence as long as the lattice is the same. For instance, Table 3 shows that, in general, Cu, Ag and Au develop the same surfaces, particularly on natural crystals³².

Acknowledgements. The author's thanks are due to Prof. G. Angel for his constant encouragement of the work, to the *State Council of Technical Research* for grants and to *P. Klason's stipendiary fund* for a fellowship.

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Received January 17, 1955.