Second Series *May, 1921* *Vol. XVII, No. 5*

THE

PHYSICAL REVIEW.

GRAPHICAL DETERMINATION OF HEXAGONAL AND TETRAGONAL CRYSTAL STRUCTURES FROM X-RAY DATA.

By Albert W. Hull and Wheeler P. Davey.

Synopsis.

Graphic Method for Interpreting X-Ray Patterns of Powders.—For each type of lattice the logarithms of the theoretical spacings of the different planes are plotted as functions of the axial ratio. Six such plots are reproduced, three for the hexagonal and three for the tetragonal system. By plotting the logarithms of the observed spacings on the edge of a strip of paper, this may be fitted by trial to the theoretical plot; the axial ratio and type of lattice being thus found in a few minutes.

Crystal Structure of Zn, Cd, In.—As examples three complete analyses are given. *Zinc* is shown to be a hexagonal close packed assemblage of prolate spheroids. The axial ratio is 1.860 and the side of the unit triangle 2.760 Å. *Cadmium* shows a structure like that of Zn, with axial ratio 1.89 and elementary triangle 2.980 Å. *Indium* shows a structure nearly like Al (cubic close-packed), viz., a tetragonal close packed arrangement of prolate spheroids, with axial ratio 1.06 and a unit square of 4.58 Å.

Introduction.

SUBSTANCES available for X-ray crystal analysis by the Bragg method fall into three classes:

A. Simple substances, *i.e.*, elements and simple compounds, regarding which no reliable crystallographic data exists;

B. Complex substances, *i.e.*, compounds containing three or more different kinds of atoms, with reliable crystallographic data;

C. Complex substances with no crystallographic data.

Substances of Class *B* are obtainable in large crystals, and hence are easy to investigate, and much useful information may be obtained. Their complete analysis, however, requires a better knowledge of the laws of X-ray scattering than we possess at present.

This knowledge may be most easily and reliably obtained from the study of Class *A* substances. There are a great many of these, and their

investigation in powder form is very easy, by the method previously described.[1]

In the X-ray powder photographs the patterns that represent cubic arrangements can be recognized at a glance, and their complete analysis requires only a few minutes. Anisometric crystals are almost as simple if correct crystallographic data are available. Without such data one must proceed either by systematic mathematical analysis,[2] or by a series of guesses. Either method is, in general, very laborious. The process of guessing becomes very easy, however, by the use of plots.

DESCRIPTION OF PLOTS.

The plots (Figs 6–11) show the spacings of all possible planes (within the range of the plot) as a function of axial ratio.[3]

The scale of abscissas is logarithmic, so that if the planer spacings are plotted on the same logarithmic scale (shown on the bottom of each plot) they may be compared directly with the observed values without regard to the absolute length of the unit axes.

Three plots are given for each system. The first represents a single lattice of right triangular prisms and tetragonal prisms respectively; the second, two intermeshed lattices; and the third, three intermeshed lattices for the hexagonal and four for the tetragonal system.

The single lattice is an aggregate of points whose cartesian coördinates are m, n, pc, where m, n, and p represent all possible integers, c is the axial ratio, and the unit of length is the side of the unit triangle or square respectively.

The two intermeshed lattices of triangular prisms have coördinates

$$m,\ n,\ pc,$$
$$m + 1/3;\ n + 2/3;\ (p + 1/2)c.$$

This is the arrangement which, when the axial ratio is 1.633, gives the closest possible packing of equal spheres. It is therefore designated as "hexagonal close packing," though it is obviously not the closest packed arrangement of spheres for all axial ratios.

The two intermeshed lattices of tegragonal prisms have coördinates

$$m,\ n,\ pc,$$
$$m + 1/2;\ n + 1/2;\ (p + 1/2)c$$

[1] A. W. Hull, PHYS. REV., 10, 661, 1917.

[2] C. Runge, Phys. Z., 18, 509, 1917.
Johnsen u. Toeplitz, Phys. Z., 19, 47, 1918.

[3] The term *axial ratio* is used in its strict sense, viz., the ratio of the fundamental translation distances of the point lattice along the vertical and lateral axes respectively.

For the hexagonal and tetragonal systems this is equal to the ratio of altitude to side of the unit triangular prism and tetragonal prism respectively.

and constitute a single lattice of body centered tetragonal prisms.

The three intermeshed triangular lattices have coördinates

$$m, n, pc,$$
$$m + 1/3; n + 2/3, (p + 1/3)c,$$
$$m + 2/3, n + 1/3, (p + 2/3)c.$$

This gives complete rhombohedral symmetry, and is equivalent to a single lattice of rhombohedra of which the edge is $\sqrt{1/3 + c^2/9}$ times the edge of the unit triangle, and the angles between edges *i.e.*, the face angles of the rhombhedra, are each equal to $2csc^{-1}2\sqrt{1/3 + c^2/9}$.

The four intermeshed tetragonal prisms have indices

$$m, n, pc,$$
$$m + 1/2, n + 1/2, pc,$$
$$m + 1/2, n, (p + 1/2)c,$$
$$m, n + 1/2, (p + 1/2)c,$$

and constitute a single lattice of face-centered tegragonal prisms.

USE OF PLOTS. EXAMPLES.

As illustrations of the use of the plots the complete analysis of zinc, cadmium and indium will be described.

Zinc.

Zinc has atomic weight 65.37, density 7.1, and crystallizes, according to Groth (measurements of Williams & Burton) holohedral hexagonal, with axial ratio 1.3564.

Powder photographs of pure zinc prepared in different ways gave identical patterns (using molybdenum monochromatic X-rays) with the spacings shown in Table I.

TABLE I.

Zinc

Intensity of Line (Estimated).	Planar Spacing in Ångstroms.	Intensity of Line.	Planar Spacing.
10	2.473	2	1.088
4	2.315	2	1.044
20	2.080	1	.947
4	1.684	2	.908
5	1.339	4	.857
5	1.333	2	.824
1	1.235	2	.770
4	1.173	1	.749
2	1.152	6	.734
4	1.121	3	.667
		2	.654

In order to compare these observed spacings with the theoretical ones of the plots, a strip of paper is placed beneath the scale of abscissas of the plot (position 1, Fig. 1) and the values of planar spacings from Table I. laid off along its edge. This strip with its pattern of lines is then moved over the plot, with its edge always parallel to the axis of abscissas, until a position is found where its pattern exactly coincides with that of the plot. "Position 2," Fig. 1, shows the best fit that can be obtained at the accepted axial ratio 1.356, and "position 3," Fig. 2, the correct position, at axial ratio 1.860. The agreement is exact. The plot shows that the second spacing, viz: 2.315 Å. belongs to the form $1\,0\,\bar{1}\,0$, hence the side of the unit triangle, which is $2/\sqrt{3}$ times the $1\,0\,\bar{1}\,0$ spacing, is 2.670 Å. The number of atoms per unit triangular prism is

$$n = \frac{\sqrt{3}}{4}\frac{a^3 c\rho}{M} = 1.00$$

a = side of elementary triangle in cm.
c = axial ratio,
ρ = density,
M = mass of 1 atom in grams.

which is correct for two intermeshed triangular prism lattices. *The zinc lattice is therefore similar to that of magnesium (hexagonal close-packed) except that it is elongated 14 per cent. in the direction of the principal hexagonal axis.* The arrangement is that of *closest packing of prolate spheroids*, indicating that the zinc atom is polar and elongated, as suggested by Langmuir.[1]

Cadmium.

Filings of pure cast cadmium were photographed with Mo. monochromatic X-rays and gave the spacings in Table II.

TABLE II.

Cadmium.

Intensity of Line (Estimated).	Planar Spacings in Ångstroms.	Intensity of Line.	Planar Spacing.
20	2.817	1	1.225
10	2.585	2	1.165
60	2.336	2	1.060
12	1.900	2	1.025
10	1.515	2	1.023
8	1.490	(wide, 4 not resolved)	.958
1	1.400	1	.918
10	1.313	3	.861
6	1.257	2	.820

[1] Langmuir, Arrangement of Electrons in Atoms and Molecules. J. Amer. Chem. Soc., 41, 879, 1919.

The scale of abscissas on the plots is not quite long enough to enable all the values of planar spacings in Table II. to be laid off directly. They may be brought within the range of the plot, however, by dividing them all by 2; or the first two spacings may be laid off with the strip in position 1, and the rest in position 2, Fig. 3. The strip is then moved about on the plots until the correct position is found. This is shown at position 3, Fig. 3, at axial ratio 1.89. The best fit that can be obtained at the commonly accepted axial ratio 1.335 is shown in position 4, Fig. 4, and position 5, Fig. 4, shows the next most plausible guess, at axial ratio 1.633, which is hexagonal close packing. This fit is very bad, but close enough to tempt one to look for the correct axial ratio in the immediate neighborhood of 1.633. This would be a false lead, however, since the order of many of the lines, notably the first two, reverses in passing from axial ratio 1.633 to 1.89.

From the value of the 1 0 $\bar{1}$ 0 spacing, as identified by the plot (position 3, Fig. 3), the side of the elementary triangle may be calculated, viz.,

$$a = \frac{\sqrt{3}}{2} d_{10\bar{1}0} = 2.980\ \text{Å}.$$

The number of atoms per unit triangular prism is

$$\frac{\sqrt{3}}{4} \frac{a^3 c\rho}{M} = 1.005,$$

which is sufficiently close to the correct value, 1,000, for two intermeshed triangular prism lattices in close packed arrangement.

The cadmium lattice is therefore a close-packed arrangement of elongated atoms, like that of zinc, the elongation being 16 per cent., as compared with 14 per cent. for zinc.

Indium.

A photograph of finely powdered indium, of unknown purity, gave the following lines (Table III.).

TABLE III.

Indium.

Intensity of Line (Estimated).	Planar Spacings in Ångstroms.
40	2.70
1	2.42
10	2.29
4	1.675
1	1.617
2	1.450
4	1.392
4	1.348
1	1.150
2	1.080

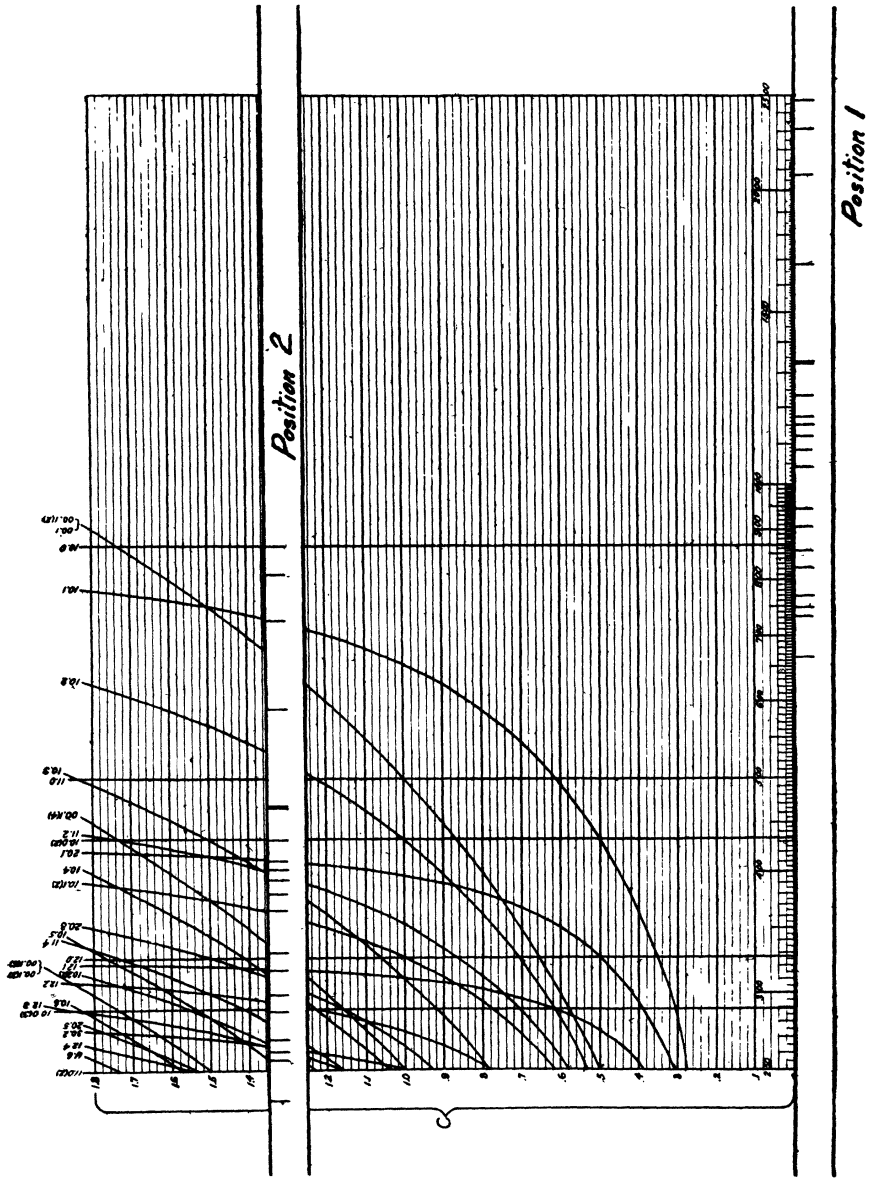

Fig. 1.

Zinc spacings compared with triangular close packing plot.

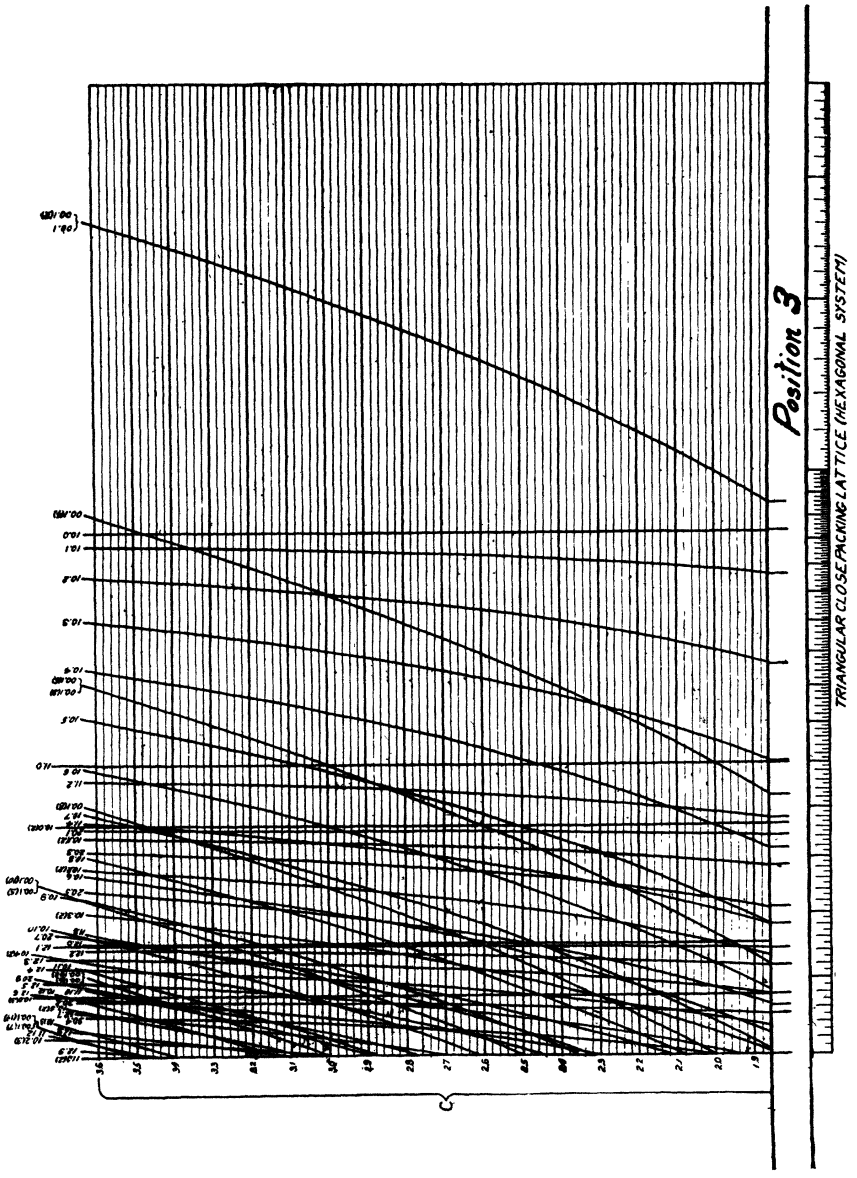

Fig. 2.

Zinc spacings compared with triangular close packing plot.

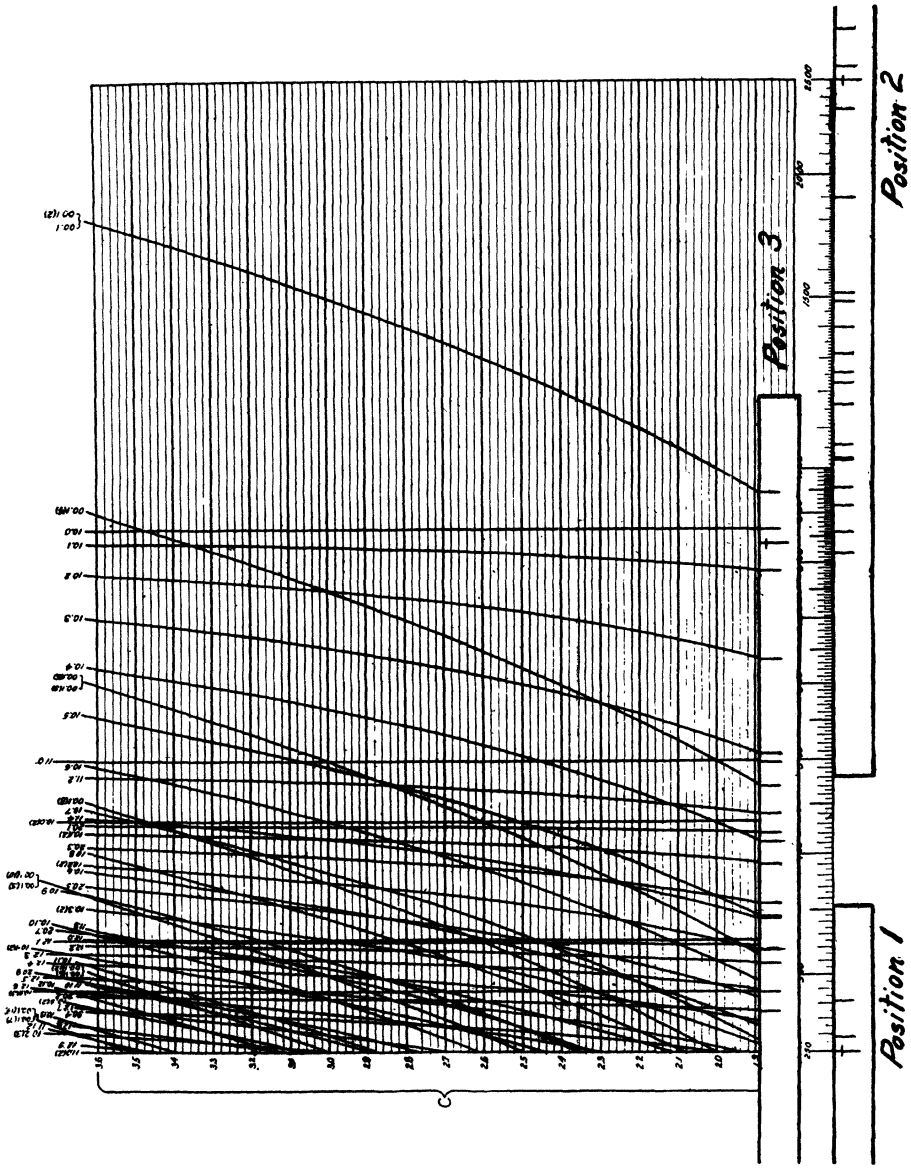

Fig. 3.

Cadmium spacings compared with triangnlar close packing plot.

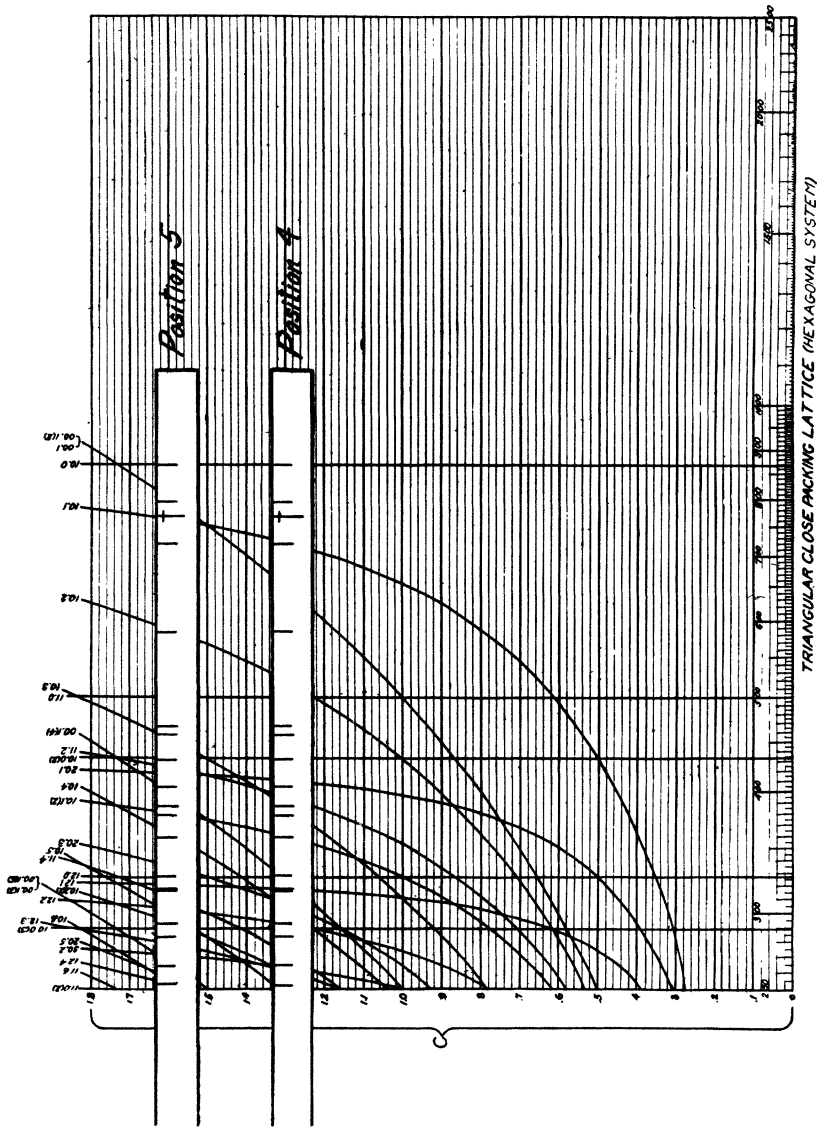

Fig. 4.

Cadmium spacings compared with triangular close packing plot.

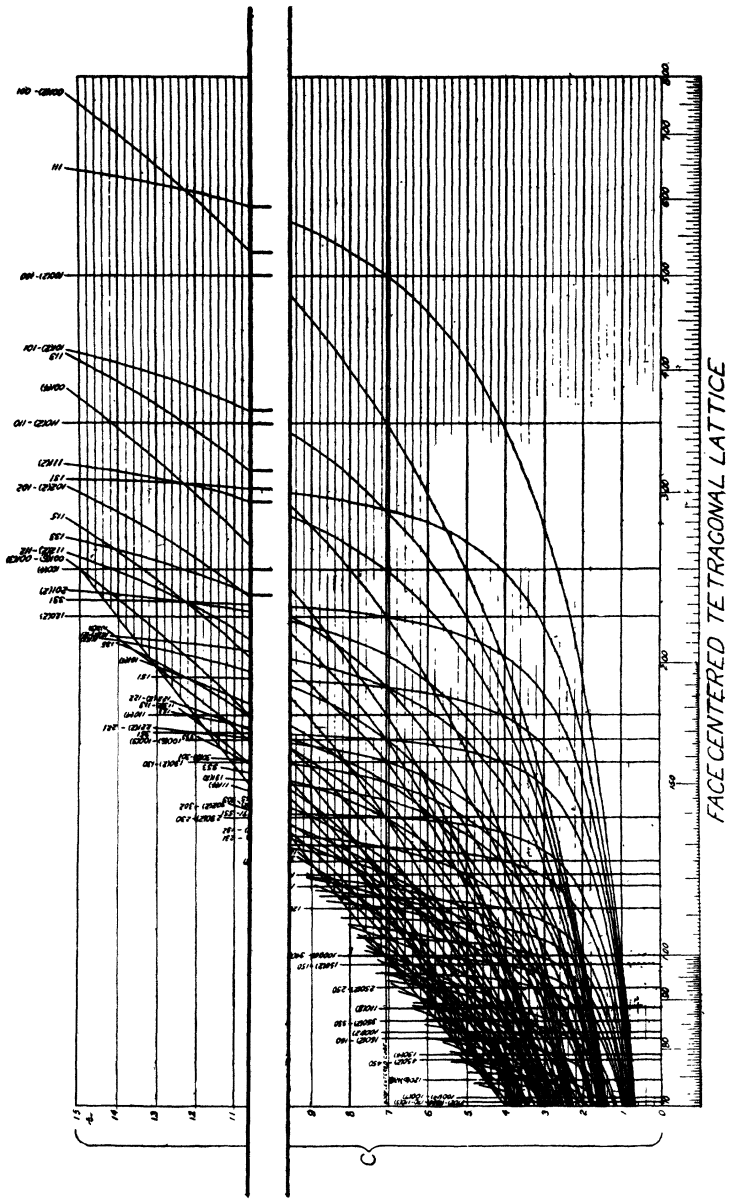

Fig. 5.

Indium spacings compared with face-centered tetragonal plot.

The spacings in Table III. are laid off on a strip of paper, and this strip moved about on the different plots until a position is found (Fig. 5) where the pattern exactly fits the plot.

The only data on indium given by Groth is an observation of Sachs that it crystallizes in regular octahedra. Inspection of the film showed at once that it was not cubic, and this was checked by trying the strip of paper on the tetragonal plots at axial ratio 1. It remained, therefore, to move the strip over the different plots until a position was found on one of them which matched the pattern of lines on the strip. In this case it took less than five minutes to find the correct position, as shown on Fig. 5, position 3.

The plot shows that the third spacing, 2.290Å., is half the fundamental spacing of the 100 planes (second order reflection from 100) of a simple tetragonal lattice. Hence the side of the unit square is $a = 4.58$Å., the height of the unit prism is $ca = 1.06 \times 4.58 = 4.86$Å., and the number of atoms per unit prism, taking the density of indium as 7.45 is

$$n = \frac{a^3 c\rho}{M} = 4.00,$$

which is correct for a face-centered tetragonal lattice.

The lattice of indium is therefore similar to that of aluminum (cubic close-packed) except that it is elongated 6 per cent. in the direction of the principal axis. This lattice, like that of zinc and cadmium, is a close packed arrangement for oblate spheroids, indicating that the indium atom also is slightly elongated.

GENERAL REMARKS.

The plots reproduced in Figs. 6–11 are all drawn to the same scale, and photographed without distortion, so that experimental values laid off on a strip of paper according to the scale at the bottom of any one of the plots may be used on all the plots.

These plots cover all possible arrangements of atoms in the cubic, hexagonal (including trigonal) and tetragonal systems. Only three specific arrangements have been given for each system, viz., simple prism, centered, and face-centered arrangements in the cubic and tetragonal systems, and simple prism, close packed, and rhombohedral arrangements in the hexagonal system. It is obvious, however, that these and all other possible arrangements are obtained from the simple tetragonal and triangular prism lattices respectively by simply omitting part of the lines. This will be more obvious, perhaps, if stated in the form of two fundamental principles:

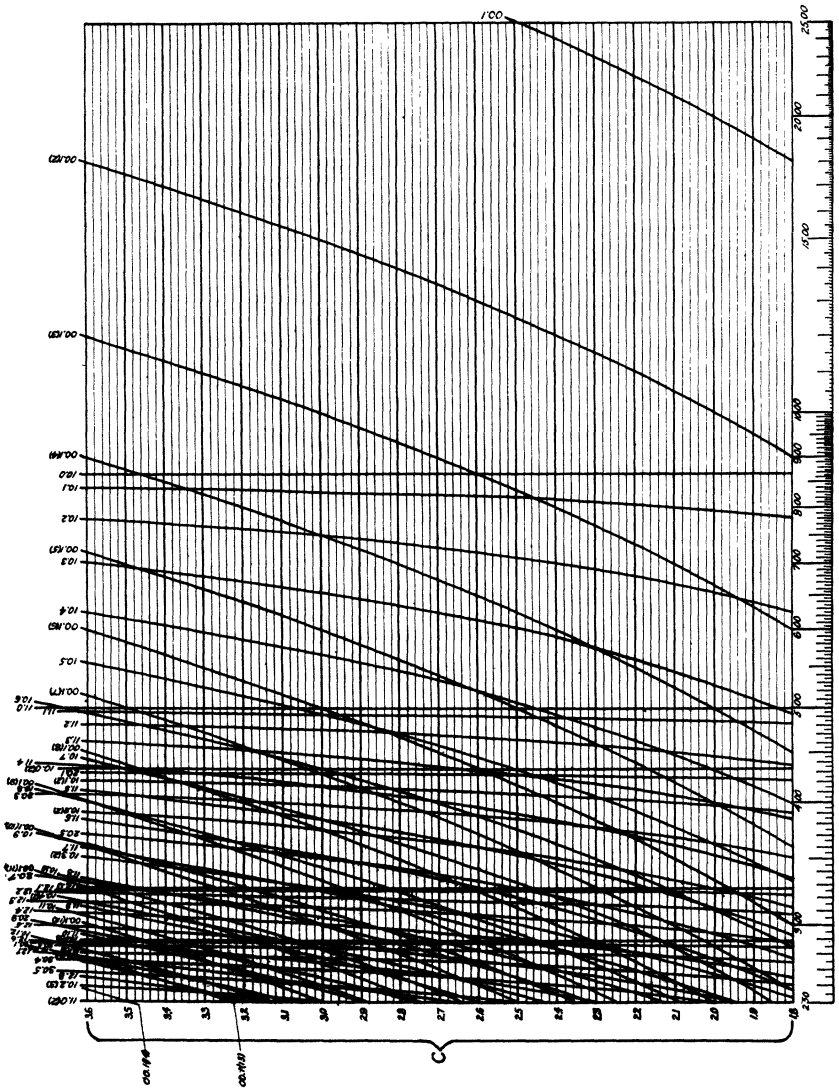

Fig. 6A.

Simple triangular lattice (hexagonal system).

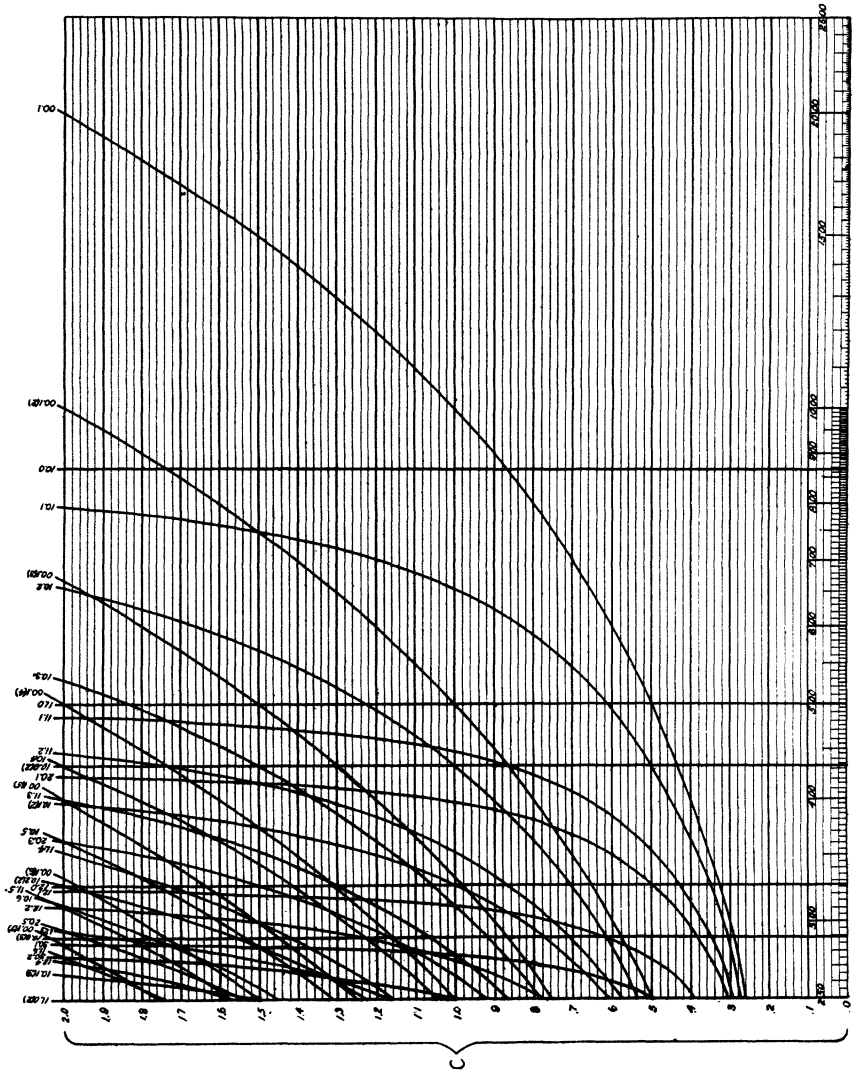

Fig. 6B.

Simple triangular lattice (hexagonal system).

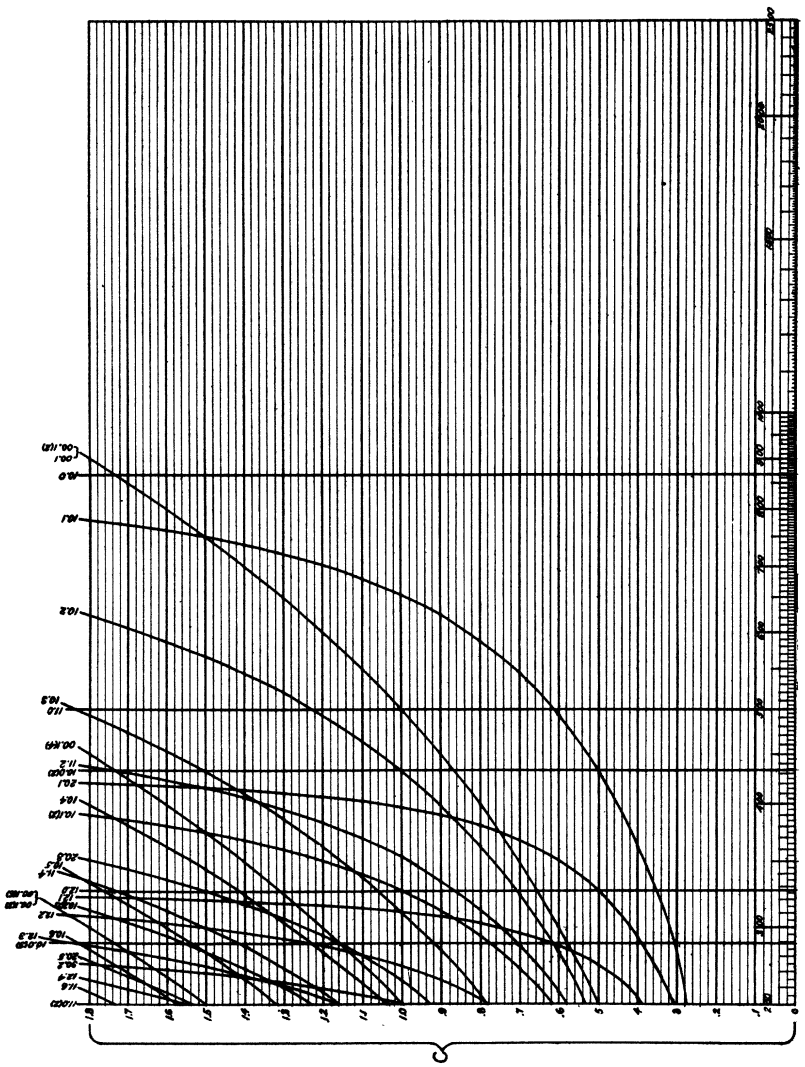

Fig. 7A.

Triangular close packing lattice (hexagonal system).

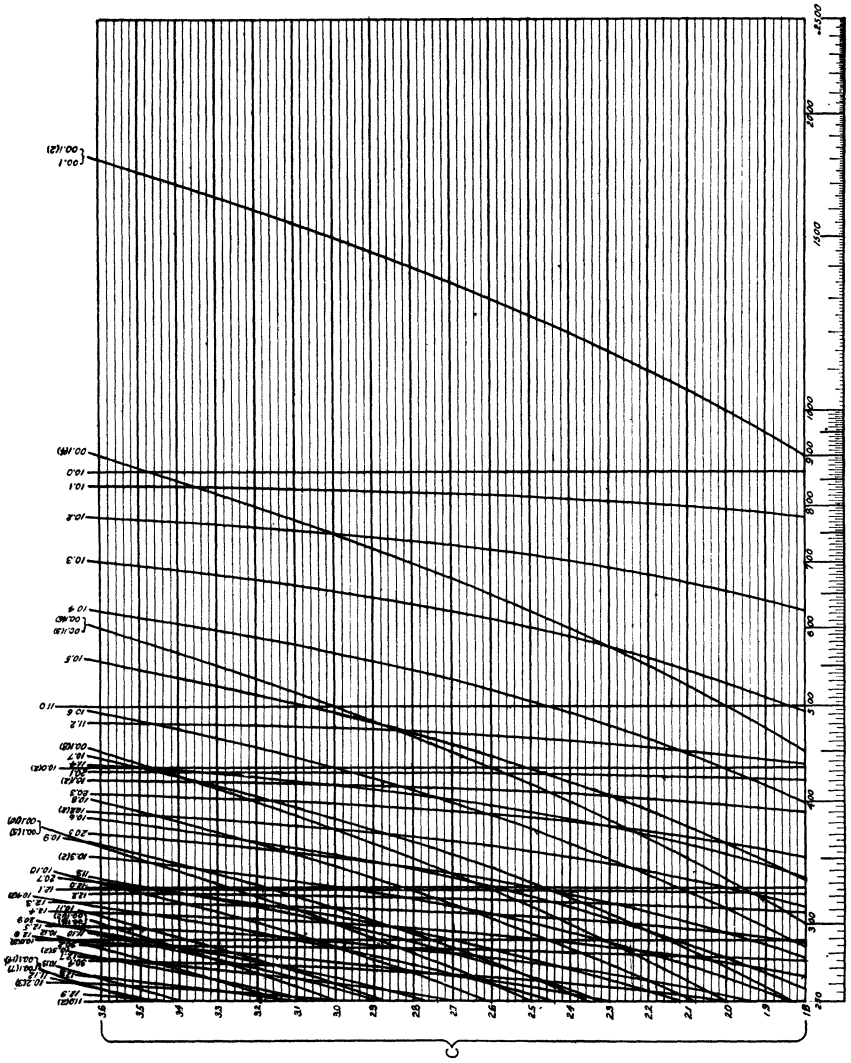

Fig. 7B.

Triangular close packing lattice (hexagonal system).

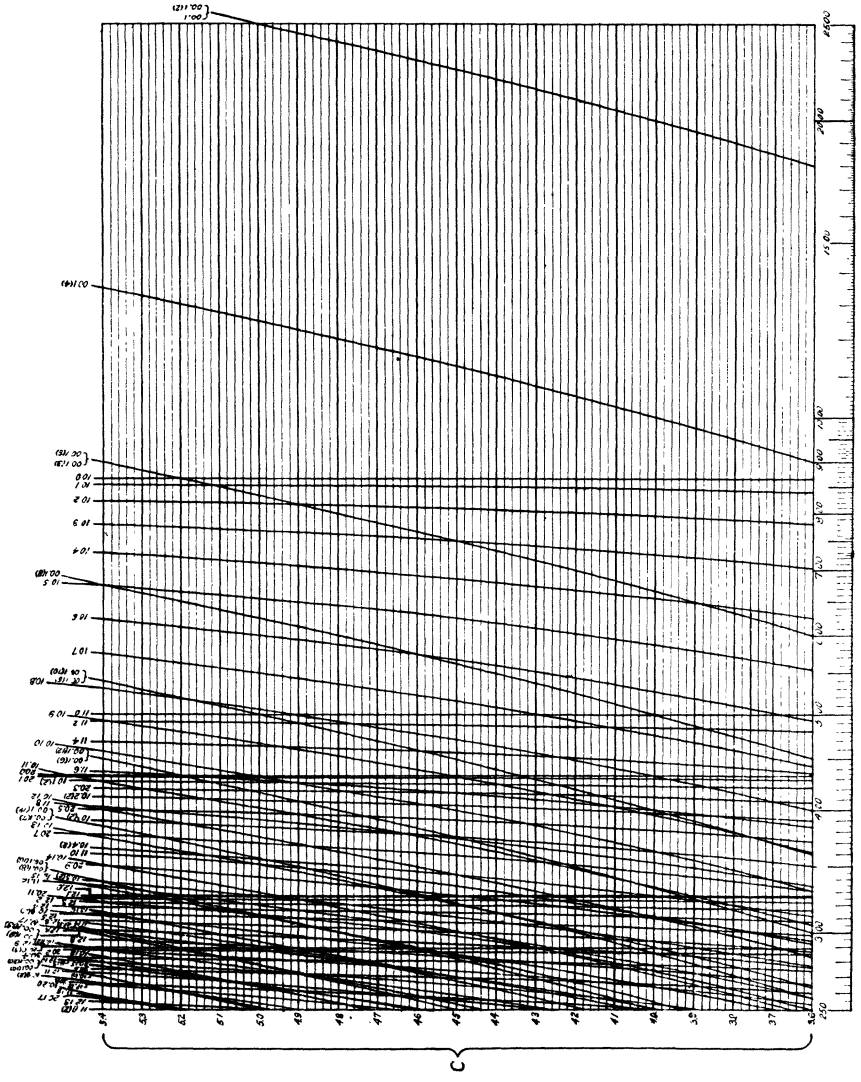

Fig. 7C.

Triangular close packing lattice (hexagonal system). [Scale 1 per cent. larger than the others.]

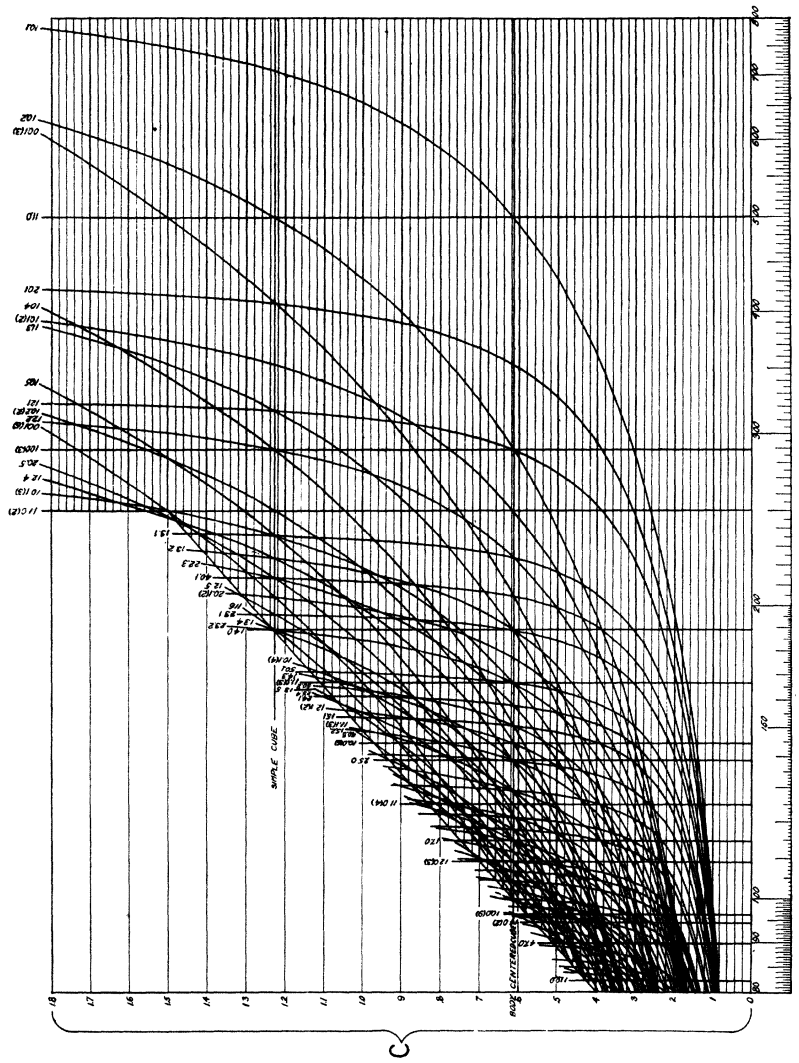

Fig. 8A.

Rhombohedral lattice (hexagonal system). [Scale 1 per cent. smaller than the others.]

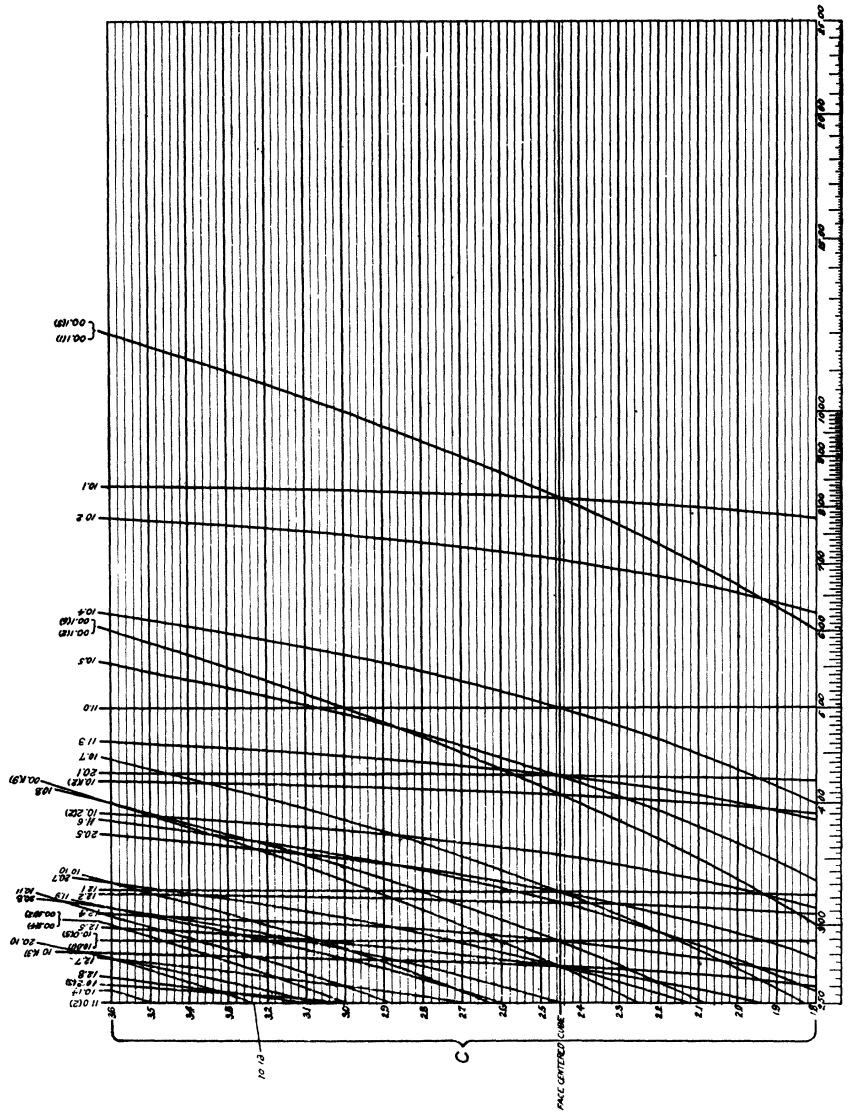

Fig. 8B.

Rhombohedral lattice (hexagonal system).

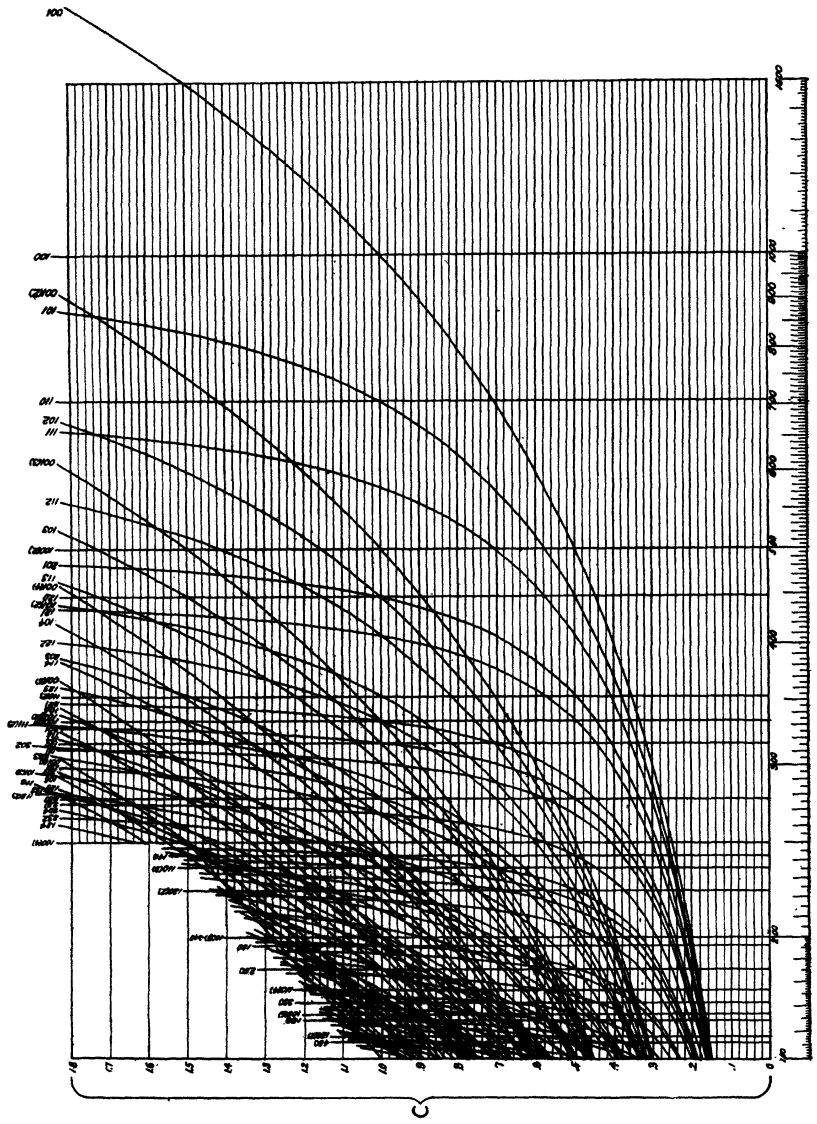

Fig. 9.

Simple tetragonal lattice. [Scale ½ per cent. smaller than the others.]

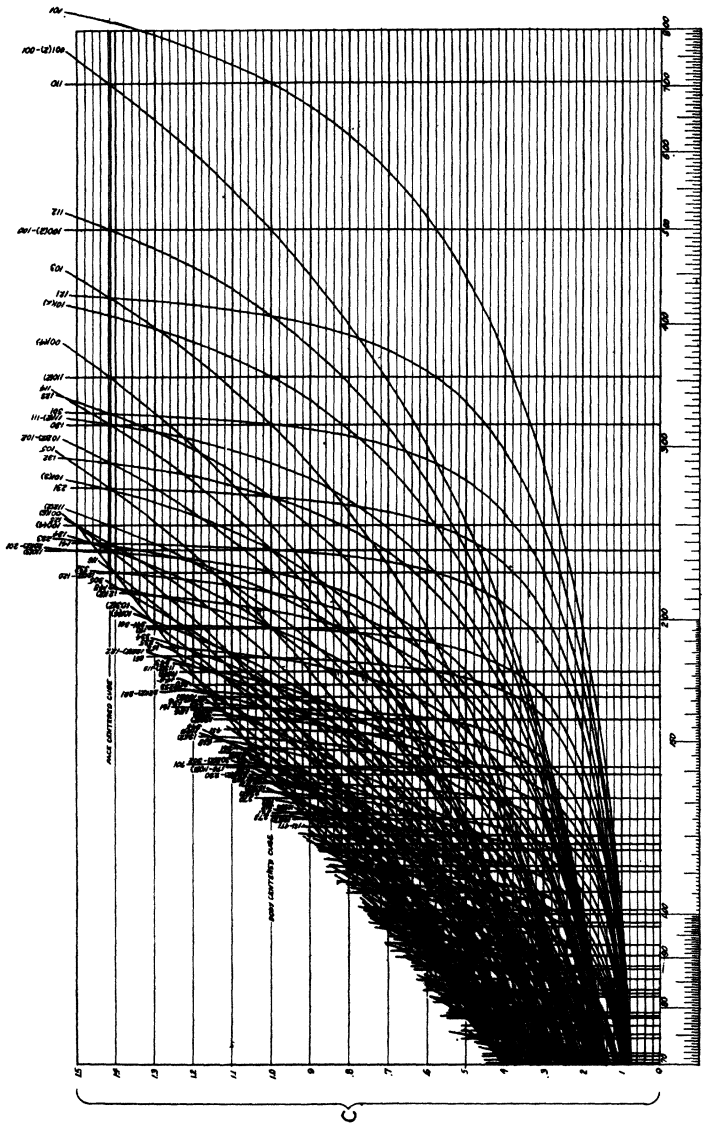

Fig. 10.

Body-centered tetragonal lattice.

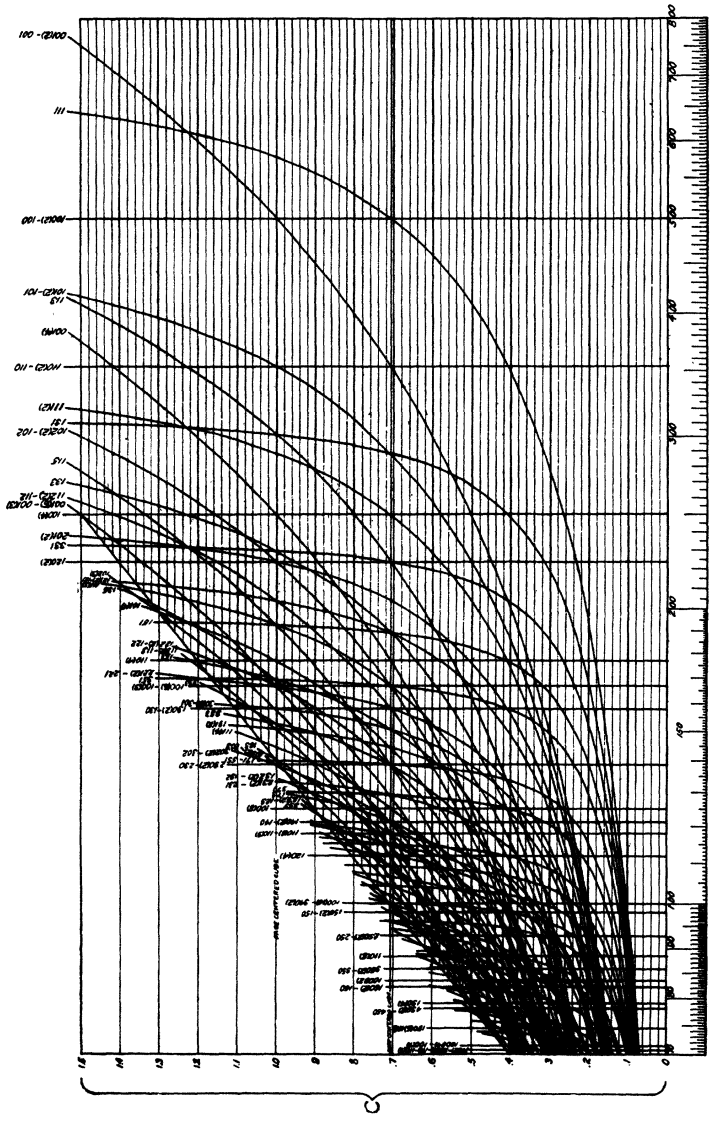

Fig. 11.

Face-centered tetragonal lattice.

1. All possible arrangements of atoms in the cubic, tetragonal, or hexagonal systems may be obtained by the combination of one or more identical simple space lattices of cubes, right tetragonal prisms, and right 60° triangular prisms respectively.

2. The intermeshing of two or more identical lattices weakens or causes to disappear some of the lines due to a single lattice, but can add no new lines.

The cubic forms may be found on either the tetragonal or hexagonal plots. For example, the simple cube is given by the simple tetragonal lattice with axial ratio 1.00, or the rhombohedral lattice with axial ratio 1.225; the centered cube by the centered tetragonal lattice with axial ratio 1.00, the face-centered tetragonal lattice with axial ratio .707, or rhombohedral lattice with axial ratio .612; the face-centered cube by the face-centered tetragonal lattice with axial ratio 1.00, the centered tetragonal lattice with axial ratio 1.414, or the rhombohedral lattice with axial ratio 2.45.

For the other three crystal systems, the orthorhombic, monoclinic, and tri-clinic, the graphical solution is less simple, since the relative crystal spacings must be expressed as a function of 2, 3, and 5 variables respectively. No simple method of representing these relations in a single plot is available, but in practice it may be found that many crystals belonging to these systems approximate sufficiently closely to one of the systems of higher symmetry, represented in Figs. 6–11, to enable the correct lattice to be guessed approximately from these plots, and found by a few trial calculations.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
Schenectady, N. Y.