STRUCTURAL CRYSTALLOGRAPHY[1]

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For the branch of science concerned with the internal structure of crystals, various names, such as leptology or leptonology (Rinne), roentgenography (V. Goldschmidt), x-ray crystallography (the title of a recent book by R. W. James, New York, 1930), crystal stereochemistry (Rinne), new or modern crystallography, and possibly others have been used.

Objections may be raised to all of these. Leptology (from the Greek, *lepton*, fine or delicate) is perhaps the best, if one is to use an entirely new term, but this hardly seems necessary or even desirable. Roentgenography is unsuitable since it is widely used in a different sense, *viz.*, for the art of producing x-ray photographs especially for medical and dental work. Of the various terms enumerated, x-ray crystallography is perhaps the one most generally used. This term is a good one in that it implies that the science under discussion is a branch of crystallography, but x-rays are simply means used in the elucidation of crystal structure. It is also true that the theoretical aspects of this science were well developed before x-rays were used or even discovered. The term stereochemistry has long been used in a special sense in organic chemistry. The use of "new or modern crystallography" as contrasted with older or classical crystallography is in my opinion unfortunate as it implies that geometrical crystallography is out of date. As Victor Goldschmidt[2] has expressed it, "The morphologists are old-fashioned folk; their methods are superseded." Without the background of geometrical crystallography a science dealing with the internal structure of crystals could never have been developed. Again it is certainly true that the use of x-rays does not furnish complete information about a crystal; there are yet further advances to be made, especially in regard to the surface features of a crystal. Such a term as modern crystallography, therefore, has at best only a temporary value.

For this division of crystallography concerned with the internal structure of crystals, I propose the term *structural crystallography*

[1] Paper read before the eleventh annual meeting of *The Mineralogical Society of America* at Toronto, December 30, 1930.

[2] *American Mineralogist*, Vol. **16**, p. 32, 1931.

coördinate with geometrical, physical, and chemical crystallography. We then have the following classification:

Crystallography { Geometrical, Structural, Physical, Chemical }

Crystallography is often used in the narrow or restricted sense of geometrical crystallography or crystal morphology, but there are many arguments in favor of the broad use of the term. The internal structure, the transmission of radiant energy through crystals, and the relation between crystal form and chemical composition are so closely related to the external form that they demand treatment in the complete science of crystals which we call crystallography.

A quarter of a century or so ago it was common to find the term crystallography used in the restricted sense, but there is an increasing tendency to employ it with the more comprehensive meaning. In books published within the last decade I find that in only five[3] is crystallography used in the narrow sense of geometrical crystallography. Only one English dictionary, the Standard, gives a broad definition of crystallography, but dictionaries are often out-of-date when it comes to scientific terms.

To some a three-fold division of crystallography with structural crystallography as a subdivision of physical crystallography is preferable. Professor E. H. Kraus[4] so expressed himself. The same view is apparently held by Niggli, for the sub-title on the cover page of the "Zeitschrift für Kristallographie" is "Kristallgeometrie, Kristallphysik, Kristallchemie." While the strictly experimental side of structural crystallography might logically be placed under physical crystallography, the consideration of space-lattices, and space-groups could be included under geometrical crystallography. But these two parts of crystallography should be considered together and not in separate divisions. The objects and methods of structural crystallography are so different from those of other branches of crystallography that it should stand as an independent division of the complete science of crystallography.

[3] Ford, *Manual of Mineralogy*, 14th ed., New York, **1929.**
Dana-Ford, *Text-book of Mineralogy*, 4th ed., N. Y., **1932.**
Evans and Davies, *Elementary Crystallography*, London, **1924.**
Barker, *Systematic Crystallography*, London, **1930.**
Winchell, *Elements of Optical Mineralogy*, 3rd ed., N. Y., **1928.**

[4] Oral communication. December 30, 1930.

The following tabulation presents a brief summary of some of the important events in the development of structural crystallography.

Important Events in the Development of Structural Crystallography

1849	Bravais	14 Space-Lattices
1879	Sohncke	65 Point-Systems
1890	Fedorov	230 Space-Groups
1891	Schoenflies	
1894	Barlow	
1904	Groth	"Crystals consist of n interpenetrating point-systems of atoms"
1905	Friedel	Law of Rational Symmetric Intercepts
1912	Laue, Friedrich, Knipping	Crystal Structure revealed by x-rays
1913	Bragg, W. H.	x-ray Spectrometer
1914	Canac	Determination of Axial Ratio by x-Rays
1915	Nishikawa	Application of Space-Groups
1916	Debye and Scherrer	Powder Method
1917	Hull	
1922	Schiebold	Rotating Crystal Method
1926	Greenwood	x-Ray Goniometer

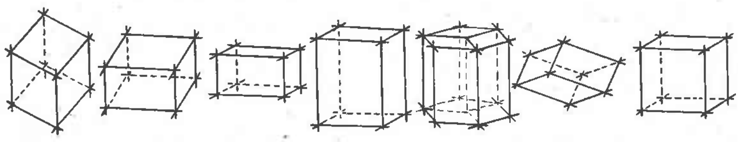
Contrary to general opinion this science did not spring suddenly into existence with the discovery in 1912 that a crystal may act as a diffraction grating for x-rays. More than half a century before, Bravais made a substantial contribution toward the solution of the problem of crystal structure from the theoretical side. This theoretical work culminated in the discovery of the 230 space-groups at the hands of Fedorov in 1890. In 1904 Groth in an address before the British Association for the Advancement of Science stated that "a crystal consists of n interpenetrating point-systems of atoms," which was verified about a decade later. In 1905 Friedel formulated the law of rational symmetric intercepts,[5] which practically proved the existence of space-lattices in crystals, seven years before direct proof was furnished by the work of Laue and his associates in 1912.

The direct experimental approach to the problems of crystal structure has given a wonderful impetus to the study of structural

[5] See article by author, *American Mineralogist*, Vol. **10**, p. 181, 1925.

crystallography and its growth has been much more rapid than that of the other divisions of crystallography. The results of x-ray analysis have for the first time aroused the interest of chemists and physicists generally in crystals. There is some danger that structural crystallography through its great achievements may dominate crystallography just as the latter was once dominated by geometrical crystallography. That in my opinion would be unfortunate. All divisions of crystallography are useful; the neglect of any one of them may be detrimental to the others.

Before concluding I wish to point out that there are seven fundamental or primary space-lattices. This has not been generally recognized. Seven of the 14 Bravais lattices may be derived from the other seven or primary lattices by translations. Thus the body-centered cube is derived from the cube by a translation equal to one-half the cube-diagonal. The 14 Bravais lattices are of course very important in x-ray analysis, but the recognition of the seven fundamental lattices simplifies the study of elementary structural crystallography. Unit cells of the seven fundamental lattices are illustrated by the accompanying figures:



The Seven Primary Space-Lattices. (From left to right these are: triclinic, monoclinic, orthorhombic, tetragonal, hexagonal, rhombohedral and isometric.)

Since all crystals have one of them as an ultimate framework, these seven fundamental lattices suggest a basis for the definition of crystal systems. Satisfactory definitions of the crystal systems are sadly lacking in nearly all text-books and treatises on crystallography. In fact some crystallographers, especially those of the French school, make the character of the space-lattice the basis for the crystal system; in this they follow the example of Bravais. This gives seven crystal systems, the holosymmetric class of each system having the symmetry of one of the primary space-lattices.

Let us note the relation between the crystal systems and the primary space-lattices which is expressed in the following tabulation. In the triclinic, monoclinic, orthorhombic, tetragonal, and isometric systems there is a clear-cut correspondence, but when we

Primary Space Lattices for the Various Crystal Systems

Triclinic System	Oblique Rhomboidal Prism	Γ_{tr}
Monoclinic System	Oblique Rectangular Prism	Γ_m
Orthorhombic System	Right Rectangular Prism	Γ_o
Tetragonal System	Right Square Prism	Γ_t
Hexagonal System		
Rhombohedral Subsystem	{ Rhombohedron	Γ_{rh}
	{ Hexagonal Prism with centered base	Γ_h
Hexagonal Subsystem	Hexagonal Prism with centered base	Γ_h
Isometric System	Cube	Γ_c

come to the twelve classes with a single axis of 3-fold or 6-fold symmetry there are difficulties. These twelve classes are either placed in one system, the hexagonal, or in two systems, the hexagonal and the rhombohedral. The difficulty in using two systems and making the lattice the basis of the system is that each of the five classes [A_3, $Æ_6$(C), $A_3 \cdot 3A_2$, $A_3 \cdot 3P$, $Æ_6 \cdot 3A_2 \cdot 3P$(C)][6] placed in the rhombohedral system may have either the hexagonal prism or the rhombohedron as the fundamental lattice. This means that the crystals of these five classes may belong to either the hexagonal or the rhombohedral system. Now this gives to the crystal system a meaning different from the original meaning of the term. The term crystal system is now so firmly established in the original sense that it is too late to make a change, even if that change were desirable, which is very doubtful. It is clear, then, that crystal systems cannot be based upon space-lattices.

The most satisfactory disposition of the twelve classes mentioned is to place them in one system, the hexagonal, with two subsystems: the hexagonal subsystem of seven classes each with the hexagonal prismatic lattice and the rhombohedral subsystem of five classes each with both the hexagonal prismatic and the rhombohedral lattices.

[6] The character $Æ_6$ is used as a symbol for a composite six-fold axis of rotatory-reflection.