MODERN EXTENSIONS OF HAÜY'S LAWS OF CRYSTALLOGRAPHY

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It is perhaps not generally appreciated to what an extent modern work on crystal structure is based upon the fundamental principles enunciated by Haüy over 125 years ago. The terminology may be different, but the ideas remain the same. He spoke of "integral molecules," we say "crystal molecules," "unit cells of the space lattices," etc. He adopted as the shapes of these units the parallelopiped, octahedron, tetrahedron, hexagonal prism, rhombic dodecahedron, and hexagonal bipyramid. We still use some of these, altho certain changes in the list have been required as a result of subsequent investigations. His law of rational indices has held firm, and has furnished a starting point for many subsequent generalizations. The point-system or space-lattice theory of crystal structure is a direct extension of it. Professor Goldschmidt's recognition of harmony and complication in the symbols of zones of forms is another. And now that the use of X-rays has furnished, especially in the hands of the Braggs, a means of demonstrating the reality of space-lattices and the occupation of their nodes by atoms, rather than by chemical molecules, it is possible to go still further.

The Russian crystallographer, E. S. Fedorov, has been during the past few years carrying on extensive researches on what he terms "crystallo-chemistry," and, aided by the Braggs's working out of the structures of a number of simple salts, has recently formulated certain laws and principles extending Haüy's original law into this field.[1] Being written in Russian,[2] his papers are comparatively inaccessible to English-speaking scientists, but it has fortunately been possible to have very full and accurate abstracts of them published in *Chemical Abstracts.*[3]

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[1] The fundamental law of crystallochemistry. *Bull. Russ. Acad. Sci.*, 1916, 435–454; The chemical side of crystalline structure, *ibid.*, 547–553; Note on the determination of the densities of atoms in crystal faces, *ibid.*, 1675–1688.

[2] As there is in the Russian alfabet no letter exactly equivalent to our "h," the name "Haüy" becomes "Gaui" when transliterated.

[3] Chem. Abstr., **12**, 8–13, 1918 (on 3d line for Bross read Bragg).

The principal points made by Professor Fedorov are: The space arrangement of atoms in three crystallographic directions, and the units to be used in the corresponding axes, may be expressed rationally, altho, because of our inability to determine the positions of the atoms with absolute exactness, only approximately rational relations are as a rule obtained. Planes determined by any three atoms are possible crystal faces, but the greater the density of a face the more important it is, crystallographically speaking, and the more likely to appear on the actual crystal. The importance of planes is increased by the presence in them of dissimilar atoms, capable of attracting one another, and due to similar chemical attractions the bond between parallel planes is made stronger. The nearest distance between unlike atoms in any space-lattice is in general inversely proportional to their chemical affinity, altho exceptions may occur when an atom of one kind holds two or more of another. Thruout these theorems the influence of Haüy's law of rational indices can be clearly traced.

An extension of the idea of arrangement of atoms in layers into the field of optical properties has recently been attempted by the writer. Thus far only tetragonal crystals have been studied, but in a number of substances which crystallize in this system there has been found to be a correlation between crystallographic axial ratio and refractive indices. Deriving from the indices, by the use of the Lorentz-Lorenz formula, the "refractions," the following inverse relationship has been found to hold in certain simple compounds:

$$\frac{\omega^2 - 1}{\omega^2 + 2} : \frac{\epsilon^2 - 1}{\epsilon^2 + 2} = c : a.$$

It is of course necessary that the true axial ratio, based on all the layers of atoms present, be used; and in many cases this is not the same as the standard axial ratio, which is obtained by taking the most prominent pyramid form to be (111). There are, furthermore, many disturbing factors, such as irregularity of the layers, asymmetric arrangements of atoms, which produce rotation of the plane of polarized light, and the presence of absorption bands and other color phenomena, such as pleochroism. Because of the presence of one or more of these features, the effects of which cannot as yet be evaluated, this rule fails to hold with complex compounds, but it does hold for enough simple ones to indicate that it is a fundamental relationship.

In a preliminary paper on this subject, recently published,[4] a few organic compounds were considered. Similar relations prove to hold with the minerals of the zircon group, the crystallographic features of which were first established by Haüy.

In cassiterite the refraction ratio is 0.945, the alternate axial ratio 0.951; in rutile the values are 0.926 and 0.911 respectively. The practical identity of the two ratios shows that in these minerals the space-lattice must have the same number of layers of atoms in the horizontal as in the vertical direction. In zircon and xenotime the refraction ratios are not equal to either axial ratio, but to 3/2 the standard one. This is interpreted to show that in the unit cells of these minerals there are three layers of atoms horizontally for every two vertically. It is accordingly possible to tell in this way something about the space-lattices of crystals, and when the refraction data are combined with the observed symmetry relations, to work out in detail probable arrangements of atoms for the substances. A few minerals in addition to those of the zircon group have also been studied in this way, but in most cases the presence of disturbing factors prevents the complete recognition of their structure. Further work is planned, however, to evaluate as far as possible the influence of these factors, as well as to apply this method of study to substances crystallizing in other systems than the tetragonal.

How slowly could such investigations progress had not Haüy blazed the way by his clear recognition of the significance of cleavage and the rationality of indices!

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[4] *J. Wash. Acad. Sci.*, **8**, 277–285, 319–327; 1918.