

V.I. Vernadsky's contribution to crystal chemistry



In 2013 we celebrate the 150th anniversary of the birth of Academician Volodymyr Ivanovych Vernadsky, an eminent scientist, world-wide known for his contributions to biogeochemistry and the concept of noosphere. In 1918 Volodymyr Vernadsky founded the Ukrainian Academy of Sciences, which set up the conditions for the development of modern Ukrainian science.

V.I. Vernadsky contributed to many fields of science, among which mineralogy, and crystallography. In 1885 he wrote his candidate work "On the Physical Properties of Isomorphic Mixtures" and then a thesis "On the Fibrolite Group and the Role of Alumina in Silicates", where he, for the first time, used the term "isomorphic substitution". In order to obtain the post as a privat-docent at Moscow University in 1891, he gave a lecture entitled "On Polymorphism as a Fundamental Property of Matter", where he demonstrated that polymorphism is a natural property of solids. In his work he also studied the occurrence of what is now well-known as a metastable state. The PhD thesis of V.I. Vernadsky "On the Gliding Phenomena in Crystalline Matter", published in 1897, was formally dedicated to the shear deformation in crystals, but was, in fact, a prominent work on general crystallography and crystal physics. Short time after, he published a series of articles with the common title "Outlines of Physical Crystallography", which in 1909 were collected into "Lectures on Physical Crystallography". These lectures, from a modern point of view, include chapters on crystal chemistry and physical-chemical analysis. The author himself called this scientific section "chemical crystallography". Special attention was paid to crystal and surface energy, effects of crystallization, and polymorphism. To a certain extent, this work may be considered as the first lectures in crystal chemistry. His important works "On Empty Spaces in Isomorphic Mixtures" and "On the Isomerism in the Group of Alumino- and Ferrisilicates" were published shortly after.

The relation between the symmetry and properties of a crystal was analyzed by Volodymyr Vernadsky in his lectures of crystallography in the chapters "The Law of the Ellipse and its Symmetry" and "A Comparison between Ellipsoidal Symmetry and the Symmetry of Crystal Classes". Ideas for the description of the physical properties of anisotropic materials, taking into consideration their symmetry, are proposed in the chapter entitled "Several Observations on the Nature of Physical Effects, which are Expressed by the Law of the Ellipse".

However, the main "symmetric" relish of V.I. Vernadsky in the theory of solids was the theory of space groups, and also the concept of "crystal space". In the work "On the States of the Physical Space" he introduces the concept of a multidimensional space. Another important concept in crystallography and crystal chemistry, "pseudosymmetry", was also proposed by V.I. Vernadsky.

In his lectures on physical crystallography dedicated to the processes of crystallization, Volodymyr Vernadsky writes about the twin laws, and gives a classification, which still remains valid for the macroscopic theory of twinning.

Among the different aspects of crystals and physical properties, enantiomorphism appeared particularly interesting to V.I. Vernadsky. He considered 219 space groups, while the 11 space additional groups, which can reproduce others, were not included in his classification. Right- and left-handed enantiomorphous structures were considered to have different spatial properties. In the context of crystal chemistry, his considerations meet modern ones – enantiomorphous molecules and crystals were considered to be identical by their chemical nature, but to have different chemical and physical properties, caused by differences in symmetry.

In his work "On Empty Spaces in Isomorphic Mixtures" Volodymyr Vernadsky proposes an energy theory of solid solutions. He was the first to explain the decomposition of solid solutions into separate phases, and to observe phase equilibria involving solid solutions. An important concept in crystal chemistry, "isomorphic series", was for the first time formulated in one of his most famous works, "The Paragenesis of Chemical Elements in Earth's Crust" (1909).

The works by V.I. Vernadsky gave a significant incentive to the progress of crystal chemistry in Ukraine, and his ideas lay the foundation also for the development of crystal chemistry of intermetallic compounds. For instance, the concepts of isomorphism in solid solutions based on intermetallic compounds were further developed in the works by the founders of Lviv School on Crystal Chemistry, E.I. Gladyshevskii and P.I. Krypyakevych.

Only today, possessing a large amount of accumulated knowledge and advanced experimental methods, we can fully appreciate the scientific work of Volodymyr Ivanovych Vernadsky, his progressive ideas and foresight.

Roman GLADYSHEVSKII