EQUATIONS OF STRUCTURE FOR VALENT CRYSTALS AND THE LOCAL VALENCY BALANCE

F. F. Grekov

Physical principles underlying the local valency balance rule are discussed. It is shown that crystal stability does not obey the rule. Some more general rules of valent crystal structures are considered, and the corresponding equations, including Pauling's rules for one-anion crystals as a particular case, are given. The equations may be used for analyses and predictions of complex structures.

Local valency balance (LVB) is one of the few principles that claim quantitative solution of the principal problem of crystal chemistry (relationship between crystal structure and composition), posed more than 60 years ago. According to Pauling [1], in a stable "ionic" crystal, the sum of valence forces applied to the "anion" equals (or approximates) its formal charge. Initially the formulation pertained to the ionic model only, but subsequently it was extended to all crystals, especially to those of oxide nature, in which formal valency relations are valid.

This is a rather general rule, which is validated by enormous experimental material. Nevertheless, it demands justification because of some inexplicable exceptions [2]. Some common remarks were made in early works [1, 3] with respect to "the least lengths of force lines" as a condition of crystal stability. However, no energy calculations consistent with modern knowledge on chemical bonding have been made.

There were several attempts to explain the exceptions and improve LVB by applying corrections for dispersion of interatomic distances [4-6]. In these papers, however, as well as in a recent computation using characteristics of Dirichlet polyhedra around atoms [7], the physical basis for the corrections remains vague, and the field of their application is limited. It is unlikely that this approach will help us find a universal empirical crystal-chemical model to correlate structure with stability for all inorganic compounds of normal valencies.

The aim of this work is to resolve this contradiction of the fundamental crystal-chemical principle without any empirical assumptions.

Let us first address crystal stability. The rule is thought to be more valid in natural minerals, because they are more stable than synthetic ones. However, natural minerals are stable in specific (geological) conditions and have specific structure and composition inherent, e.g., in silicates, which are basic compounds in the mineral world. It will be shown below how the specifics of silicates are related to LVB. Clearly, the origin of a compound cannot serve as a measure of its stability. There are synthetic and mineral isomorphous compounds in which LVB is satisfied, but some of them occur in nature, whereas others do not. This is exemplified by structural analogs in oxide and nitride systems. Stable silicates phenacite $Be_2SiO_4$ and willemite $Zn_2SiO_4$ are isostructural to silicon nitride $Si_3N_4$; bromellite $BeO$ and zinctite $ZnO$ are isostructural to aluminum nitride $AlN$. In all of these structures, LVB is valid, although nitride minerals do not occur in nature. However, this does not mean that they are unstable. On the contrary, silicon and aluminum nitrides are very stable to thermal, chemical, or radiation effects due to their high metal-nitrogen bond energies [8]. The absence of nitride minerals in nature is explained by competition with free nitrogen, which has very stable intramolecular bonds. On the other hand, stable oxide minerals in which LVB is invalid are known.

An objective criterion of crystal stability to be correlated with LVB is the Gibbs energy of crystal atomization. In this case, the effect of interatomic interactions, underlying Pauling's rule, is not masked by thermodynamic properties of crystal decomposition products. As far as we know, no such calculations using thermochemical data were carried out.
Direct calculations of atomization energies for two or more coordination variants would be the most convincing proof of the LVB effect on crystal stability. However, the calculation encounters insurmountable difficulties. First, the model of point charges localized on atomic centers is not consistent with the real picture of electron distribution, providing chemical binding. As follows from the deformation electron density maps [9], the real potential relief is so complex that it is impossible to discuss the lengths of force lines or to optimize the potential of Coulomb interactions in a complex system in another way. Second, even if the potential relief did not abound in unexpected features, the calculation should not deal with formal charges, which are the only types of charges used in LVB theory. Rather, it should consider effective charges, which do not coincide nor correlate with formal charges.

Let us consider the valence force, which is a basic notion of LVB theory. The valence force of a cation is an average fraction of valence electrons of the cation per anionic ligand. In other words, the magnitude of valence force demonstrates the intensity of the electron density redistribution between different cation–anion bonds during crystal formation. This redistribution is postulated to be equal for all bonds of the cation. The greater the differences between ligands, the greater the inequality of redistribution. Corrections for differences between ligands are usually applied by analyzing bond lengths or characteristics of Dirichlet polyhedra. It is not questioned whether it is reasonable to construct the initial system of valence forces in a classical way or to apply corrections to an incorrectly built parameter system. The incorrectness of the notion of "valence force" is evident if the crystal contains elements that are different anionogens, e.g., oxygen and halogen or oxygen and nitrogen. Balance is severely violated in these cases [10]. Anions of different chemical nature must certainly accept different fractions of electron density of the cation. This must be admitted based on the physical sense of this effect and experimental results unless one chooses to adhere to tradition [9]. When anionic ligands are atoms of the same element that differ crystal-chemically, e.g., bridging and apical oxygens in silicate groups, we also have no reason to believe that different oxygen atoms take equal fractions of electron density from coordinating silicon. On the contrary, differences in oxygen coordination are convincing evidence of radical differences in electron density distributions in the vicinity of the atom. In many-anion systems, valence forces are evidently estimated with so random approximations that these estimates may not serve to predict stability or select variants of coordination.

At the same time, in stable (and metastable) valent crystals, the coordination numbers (CN) and group indices (GI, i.e., formal charges or oxidation levels) of the elements involved in the crystal obey the mathematical relation of the form

$$F(GI, CN) = 0,$$  \hspace{1cm} (1)

which is satisfied either exactly or approximately.

Discussing the sense of this empirical equation, we would naturally try to make one group of variables (GI or CN) the argument, and the other will be the function. It is necessary to understand whether the group indices of the elements dictate a certain coordination or, vice versa, the coordination scheme may be realized only for a certain set of elements. Both questions are answered negatively. Indeed, for a given set of atoms (GI), we usually have polymorphic modifications and isomers with so different structures that no direct relationships between the electronic structures of atoms and their mutual dispositions may be established. This is also indicated by the existence of different morphotropic modifications. For a given set of valent states of atoms, there is no chemical mechanism that would lead to a definite coordination, irrespective of the thermodynamic conditions or the structure of the core electron levels. Analyzing experimental data on heterovalent substitutions and isomorphism, one can again conclude that a given spatial position of atoms may be realized for various (although restricted) sets of elements. Here again we cannot reveal chemical effects dictating a definite set of valent states of participant atoms for a given structural variant. Thus relation (1) is a many-valued function whose physical sense may not be clarified without using additional variables.

As shown in [11], such variables may be stoichiometric indices (SI). There is a strictly defined and chemically verified dependence

$$\Phi(GI, SI) = 0,$$  \hspace{1cm} (2)

known as Pearson's rule [12], which is valid for all valent compounds. A given combination of chemical elements exhibiting normal group valency unambiguously defines a set of stoichiometric indices of a crystal.

Also, there is a strictly defined and geometrically verified dependence between the composition of coordination polyhedra and stoichiometry of a crystal:

$$\varphi(CN, SI) = 0.$$  \hspace{1cm} (3)