Electron density and chemical bond in intermetallic compounds

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In respect to the periodic table of elements, intermetallic compounds contain only elements located at the Zintl line and to the left of it. The low number of electrons in the last shell (ELSA) hinders the application of bonding concepts based on the 8–N rule to understand the composition and crystal structure [1]. As to the chemical bonding concepts, intermetallic compounds do not follow classical valence rules. It is impossible to consider all shortest interatomic contacts as 2c-2e bonds in such crystal structures. Also, the extension necessary for the bonding analysis in boron compounds [2] - being remarkable step in the development of quantum chemistry - was not sufficient to explain composition and crystal structure of intermetallic compounds in general. The demand on new bonding concepts for this family of inorganic materials is still actual. One of the possible ways to develop new concepts is opened by Hohenberg-Kohn theorems [3]. If the true electron density of the ground state yields the lowest energy and determines properties of the system, it makes a sense to describe also chemical bond using electron density in order to have a direct link to the properties.

One of the quantum chemical tools suitable for this purpose, is the bonding analysis based on electron density in position space, the electron localizability approach [1]. First considered as a way to establish the connection between the classical and quantum chemical perspective of chemical bond, this approach develops into a powerful tool for investigative studies of atomic interactions, especially in solids. The position-space partitioning for this analysis is based on the electron density distribution, which is an observable property of the system [4]. Still under investigation is the question, what chemical and physical information can be obtained employing this approach.

Analysis of atomic shapes obtained from the topology of electron density within the Quantum Theory of Atoms in Molecules (QTAIM) [5] allows not only the quantization of atomic volumes and effective charges, but by description applying solid angles allows to estimate the effective topological coordination numbers (*tCN*) [6]. The latter may contain also the information about atomic interactions in complex crystal structures of intermetallic compounds.

The Topological Octet Rule Implementation (TORI) approach [7] allows to expand the basic Lipscomb's model construction of localized 2c-2e and 3c-2e bonds by dropping the 2-electron component and to analyse the fulfilment of the octet rule in both, local and cluster-wise ways in multiatomic clusters. This may open a conceptual way to establish the bonding pattern analysing the topological characteristics of clusters only.

Chemical bonding influences total electron balance in thermoelectric materials regulating the charge carrier concentration (transport properties) and controls heat transport. The co-existence of different bond types in substances (bonding inhomogeneity) supports reduction of the lattice thermal conductivity effecting most probably the speed of sound [8]. The anisotropy in spatial distribution of regions with different bond types (bonding anisotropy) affects the directional dependence of thermal and electronic transport.

Recent developments in electron-localizability approach make also the quantitative description of the surface state possible, allowing the interpretation of the experimental results in catalysis on intermetallic compounds [9,10].

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