# **Chemical Bonding in Intermetallic Compounds: Concepts and Tools**

Frank R. Wagner<sup>#</sup>, Miroslav Kohout<sup>##</sup>, Riccardo Freccero, Daniel Menendez-Crespo, Carina Bergner

The chemical bonding investigations ultimately aim to encompass all theoretical studies necessary to understand chemically the structure and the chemo-physical properties of intermetallic phases. The three topics presented hereafter represent progress in concurrent research on extending the 8-N rule to polar bonding situations, and the technical realization of energy evaluations of chemical bonding in position space within the IQA method for crystalline systems.

## The 8–N rule in polar intermetallic phases

In many polar intermetallic phases, e.g. with alkaline earth or rare earth metals, there are indications, like unusual distances and connectivities, or metallic properties, that the actual bonding scenario is significantly different from the conceptual Zintl or Wade picture. In order to quantify polar bonding effects and to incorporate them into the 8-N rule, chemical bonding was analyzed in position space employing the ELI-D (electron localizability indicator) /QTAIM (quantum theory of atoms in molecules) basin intersection technique. The key feature of the procedure is the decomposition of a polar-covalent bonding electron pair into fractions of shared and unshared electrons, which makes the effective QTAIM atomic charges consistent with the formal charges, and leads to an augmented Lewis picture. In the first study of this kind, semiconducting main group Nowotny-Juza phases  $A^{(\leq 2)}A^{(\leq 13)}E^{(\geq 14)}$  compounds, with 8 valence electrons and a polar-covalent [A'E] zinc blende type partial structure, have been successfully related to the 8-N rule [1, 2]. In the second, complementary study, a series of virtually isostructural compounds  $La_2MGe_6$  (M = Li, Mg, Al, Zn, Cu, Ag, Pd)



Fig. 1: Classification of homo-atomically 2- and 3connected Ge species according to the extracted amounts of 2-electron covalent bonds ( $N_{cb}$ ) and lone pairs ( $N_{lp}$ ). Large spheres mark the domains of (2b, 2lp), (3b, 1lp), and (4b, 0lp) scenarios.



Fig. 2: "Excess" electrons in LuGe forming a cluster via 4-atomic Lu<sub>4</sub> bonds found as a separate bonding basin of pELI-D.

with a fully covalent anionic partial structure of 2- and 3-connected Ge species displaying additional polarcovalent bonding with the surrounding cations was analyzed [3]. All compounds, including the ones with M = Mg, Zn displaying the Zintl electron count, feature a metallic DOS, with the Fermi level located in a pseudo gap. The common reason for the tolerance of the structure with respect to the electron count seems to be the La species, whose incomplete charge transfer accompanied by polar-covalent La-Ge bonding already pushes each compound away from a Zintl scenario (Fig. 1) and paves the way for a more intermetallic kind of bonding with variable electron counts. The specific behavior of La in these systems has been verified by comparison with binary LaGe crystallizing at high temperature in the FeB type of structure with 2-connected Ge species forming equidistant zigzag chains. Consistent with its effective charge Ge<sup>1.1-</sup>, the bonding scenario of the Ge species lies already in the domain of (3b, 1lp) bonding (Fig. 1). Concerning La<sup>1.1+</sup>, the remaining valence electrons are itinerant and were found to yield polycationic bonding, which was the topic of a separate study on LuGe and LaGe. [4]

The compound LuGe in the FeB structure type has been prepared by high-pressure, high-temperature synthesis (<u>https://www1.cpfs.mpg.de:2443/CMS\_04</u>). Quantum chemical position space analysis of chemical

bonding in the framework of ELI-D topological analysis for both phases established a chemical role of the "excess electron"  $R^{3+}$  (2b)Ge<sup>2-</sup> × 1e<sup>-</sup>. [4] The situation is reminiscent of the one in GaSe, which can be written according to  $Ga^{3+}$  (0b)Se<sup>2-</sup> × 1e<sup>-</sup> =  $(1b)Ga^{2+}(0b)Se^{2-}$ . The "excess" electron of each  $Ga^{2+}$  is chemically involved forming a Ga-Ga dumbbell, which leads to semiconducting behavior. The "excess" electrons of Lu and La atoms were found to form 4atomic  $R_4$  bonds (Fig. 2), which conceptually classifies these compounds to be located at the boundary between Zintl valence compounds and polar intermetallic phases. Still, there is a decisive difference between GaSe and LuGe. The polycationic partial structure of LuGe and LaGe is the result of a largely incomplete charge transfer, i.e. Lu<sup>1.3+</sup>Ge<sup>1.3-</sup> and La<sup>1.1+</sup>Ge<sup>1.1-</sup> instead of  $R^{3+}$ Ge<sup>3-</sup>, which should yield a structure with  $\text{Ge}_2^{6-}$  dumbbells and separate  $R^{3+}$ cations. From a physical point of view, another comparison may be interesting: In  $RB_6$  compounds, the situation concerning "excess" electrons is somewhat similar, i.e.  $R^{3+}(B_6)^{2-} \times 1e^{-}$ . There is a notable difference between both situations, which concerns the chemical involvement of the "excess electrons". From our position space analysis, the "excess" electrons in  $RB_6$  are less involved in polyatomic R bonding than the ones in LuGe.

## Implementation of the IQA method for crystals

A complete picture of chemical bonding in real space requires a description of the electron population distribution along with detailed component energetics. The method of interacting quantum atoms (IQA) is based on the QTAIM space partitioning and represents a complete scheme of total energy decomposition for a chemical system within the Born-Oppenheimer approximation into mono- and diatomic contributions in position space. This powerful method was only available for molecules. In an explorative computational study on crystalline compounds with the MgAgAs type of structure, a point charge approximation of the diatomic coulomb and exchange contributions has been successfully applied to predict yet unknown compounds to adopt this structure type [5]. As a continuation, a project has been set up to implement the precise IOA method for crystalline materials. The program FHI-aims (Prof. M. Scheffler, FHI Berlin) was chosen to deliver the crystalline wave function on which the analyzed densities are based. An interface module to connect the output wave function to our native position space code DGrid [6] has been developed, and included into the FHI-aims code as an official output option (since version 200112, from Jan. 2020). The IQA methodology has been adapted and implemented in a new software package (ChemInt) that takes QTAIM atoms as fundamental constituents. It works also for molecular systems and can operate with Hartree-Fock or Density Functional Theory wave functions. Besides, ChemInt relies on DGrid to evaluate wave functions created with FHI-aims or ADF programs, among others. A key characteristic for its applicability has been the parallelization of the code. Questions like, which atomic interactions are more relevant in a system of interest, how atomic selfenergy and atomic interaction energies are balanced to achieve a lower energy, as well as whether it is the classical Coulomb or the exchange-correlation energy which is more important for the stability of a bond or fragment can be addressed by this new method. [7]

#### **External Cooperation Partners**

Angel Martín Pendás (Univ. of Oviedo, Spain); Adriana Saccone (Univ. of Genova, Italy); Christian Carbogno, Matthias Scheffler (FHI Berlin).

## References

- [1] 8–N Rule and Chemical Bonding in Main Group MgAgAs-Type Compounds, D. Bende, F. R. Wagner, and Y. Grin, Inorg. Chem. 54 (2015) 3970, doi.org/10.1021/acs.inorgchem.5b00135
- [2] Heteropolar bonding and a position-space representation of the 8–N rule, F. R. Wagner, D. Bende, and Y. Grin, Dalton Trans. 45 (2016) 3236, doi.org/10.1039/c5dt04140f
- [3]\* Polar-Covalent Bonding Beyond the Zintl Picture in Intermetallic Rare-Earth Germanides, R. Freccero, P Solokha, S. De Negri, A. Saccone, Y. Grin, and F. R. Wagner, Chem. Eur. J. 25 (2019) 6600, <u>doi.org/10.1002/chem.201900510</u>
- [4]\* "Excess" Electrons in LuGe, R. Freccero, J.-M. Hübner, Y. Prots, W. Schnelle, M. Schmidt, F. R. Wagner, U. Schwarz, and Y. Grin, Angew. Chem. Int. Ed. 60 (2021) 6457, <u>doi.org/10.1002/anie.202014284</u>
- [5] Chemical Bonding Analysis as a Guide for the Preparation of New Compounds: The Case of VIrGe and HfPtGe, D. Bende, F. R. Wagner, O. Sichevych, and Y. Grin, Angew. Chem. Int. Ed. 56 (2017) 1313, doi.org/10.1002/anie.201610029
- [6]\* Electron localizability indicator and bonding analysis with DGrid, M. Kohout, from: Complementary Bonding Analysis, Ed. S. Grabowsky, pp. 75-112, DeGruyter, 2021, <u>doi.org/10.1515/9783110660074-004</u>
- [7] Interacting quantum atoms method for crystals, D. Menéndez-Crespo, F. R. Wagner, E. Francisco, A. Martín Pendás, Y. Grin, and M. Kohout, submitted.

<sup>&</sup>lt;sup>#</sup> Frank.Wagner@cpfs.mpg.de

<sup>##</sup> Miroslav.Kohout@cpfs.mpg.de