Chemical Bonding in Intermetallic Phases

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The chemical bonding investigations ultimately aim to encompass all the theoretical studies necessary to chemically understand the structure and chemo-physical properties of intermetallic phases. The employed ChemBond descriptors have to be i) applicable for molecular systems and solids alike, ii) independent of the type of basis set used to describe the electronic structure, and iii) defined at correlated and relativistic levels of theory. Finally, firm connection to bonding energetics is a necessary ingredient of such a complete chemical bonding framework. In this area, the work during the report period presents a snapshot covering all aspects ranging from conceptual studies on the 8–*N* rule and application of already settled methodology to actual ChemBond situations in catalysts, thermoelectrics, and other chemically interesting compounds, to transitions towards new methodology as the Interacting Quantum Atoms (IQA) method for solids.

While most of the ChemBond studies are triggered by the experimental studies performed in the department, the ChemBond group also undertakes systematic chemical bonding studies in prototype crystal structures and compound classes. The results of these studies serve to calibrate and refine the methodology employed. They are of ultimate importance for the ChemBond investigations of singular compounds from experimental studies.

Boron, Aluminium and Gallium compounds

On the basis of systematic ChemBond studies of MB_2 (M = main group metal) and TB_2 (T = transition metal) compounds with AlB_2 type of structure and MB_6 compounds focusing on 3-centre bonding B–B–T and B–B–B, respectively, reported in the previous Scientific Report [1], subsequent studies of trielide intermetallic phases were performed.

The important connection between theoretical ChemBond studies and experiment was investigated in cooperation with the competence group *Structure* in the course of an experimental electron density reconstruction study for VB, V_3B_4 and VB_2 from X-ray diffraction data [2]. The previous theoretical findings on VB_2 could be confirmed by topological analysis of the reconstructed electron density, and a consistent picture of polar V–B bonding and covalent B–B bonding was obtained. However, for a detailed chemical bonding analysis, information beyond the electron density, i.e. of the pair density, is still necessary.

As an immediate follow-up of the TB_2 study, the corresponding digallides MGa_2 and TGa_2 with AlB_2 type of structure, and the late-T compounds TB_2 with RuB_2 and OsB_2 strucure type were investigated [3]. A negative deviation from the Vegard's rule for the average atomic volume vs. yttrium content has been found by collection of crystallographic data for all known binary Y–Ga phases. Analysis of the calculated electron density employing the QTAIM method revealed an increase of the atomic volumina of both Y and Ga with the yttrium concentration. The non-linear increase is caused by a strengthening of covalent Y–Ga interactions with stronger participation of genuine penultimate shell electrons (4d electrons of yttrium) in the valence region. With increasing yttrium content, the polarity of the Y–Ga bonding decreases and the increasing covalence of the bonds is going along with their delocalization from two-centre to multi-centre type [4].

In a collaborative study with the department Tjeng (see report Wirth), the favourable cleavage plane of CaB_6 and LaB_6 was quantum chemically computed and the surface termination determined. It turned out that the shorter inter-octahedral bond is more easily broken than four intra-octahedral ones [5], which is consistent with the calculated B–B delocalization indices (DIs) and derived ChemBond scenario reported earlier [1].

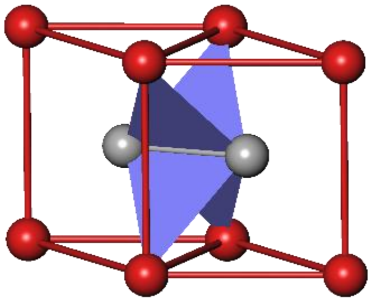

Fig.-1: Schematic view of the four nested 3-centre B–B–T bonding scenario obtained for $SnNi_{21}B_{20}$ and generally proposed for B@T_6 trigonal prismatic boron chains.

In continuation of the work on more complex intermetallic borides like $AlNi_9B_8$ [1], chemical bonding in $SnNi_{21}B_{20}$ [6] was thoroughly investigated (see report Leithe-Jasper), where the smaller size of the unit-cell permitted the incorporation of 3-centre DIs in the bonding discussion. The previously reported $Ni_6@B_{20}$ structural motif was uncovered to be a part of the $B@Ni_6$ trigonal prismatic framework, where instead of a 2-centre type, each B–B bond forms the central part of four nested B–B–Ni 3-centre bonds (Fig. 1). In retrospect, a similar situation can now also be assigned to the B–B bonds analyzed before in $AlNi_9B_8$, and this serves as a general model for $B@T_6$ boron chains in trigonal prismatic transition metal coordination.

Metal-rich borides $T^{(5)}{}_7Fe_3B_8$ were found to form a Kagomé-type Fe framework with 2-centre Fe–B and B–B bonds, but with additional 4-centre bonds involving $T^{(5)}$ metals [7]. A similar type of bonding was found for Eu_2GaPt_2 and Ca_2SiIr_2 [8].

Approaching the triel-richer side, semiconducting $FeGa_3$ and its isostructural $T^{(8)}Tr_3$ homologues have been shown to reveal interesting doping opportunities for thermoelectric engineering and physically emergent behavior [1]. The pure compound $FeGa_3$ displays a non-trivial covalently bonded dumbbell Fe–Fe and Fe–Ga–Ga 3-centre type delocalization of the Fe–Ga bonds. Fe–Fe bonding was shown to be of a partially compensated type somehow related to the situation in the triply bridged Fe_2 unit in $Fe_2(CO)_9$. Interestingly, although being quite rich in Ga-content, direct Ga–Ga interactions do not play a primary role. In the course of this study (see report Cardoso), the structure was found to tolerate self-doping by Fe producing ferromagnetic in-gap states [9], which explains a number of controversial physical properties measurements.

In the course of systematic chemical bonding studies of all known TGa_3 phases with $FeGa_3$ type of structure [10], the prediction of a new thermoelectric compound WGa_3 with $FeGa_3$ type of structure and favourable thermoelectric parameters has been presented [11].

On the more triel-rich side in the composition range of $SrAl_4$, covalent triel–triel interactions are found to determine the main structural motif. In the combined experimental and chemical bonding study [12] of $SrAl_{4-x}Si_x$ ($0 \le x \le 2$), a step-wise transition of a 3d nido-type Al-network towards the known 2d $[AlSi]^{2-}$ four-bonded semiconducting network $SrAl_2Si_2$ at ambient pressure is contrasted with a novel superconducting phase obtained from high pressure synthesis (see report Schwarz) yielding a metastable $BaZn_2P_2$ type of network.

The complex balancing of several types of defects in boron carbide (ordered model: $B_{13}C_2 = B_{12} + CBC$) leading to semiconducting behaviour has been the focus of a combined computational (in cooperation with M. Scheffler) and experimental study (see report Ramlau) of the carbon-rich side of the composition range. Increasing carbon concentration was generally modeled by gradual replacement of B_{12} boron atoms. Of special interest, however, is then the replacement of the ideal linear chain motif CBC by energetically preferred boron-rich configurations CB_2C, BB_2B, CB_2B, and CBCB, which is a clear chemical bonding effect probably driven by 3-centre bonding in the rhombic units [13].

Intermetallic Germanides beyond the 8–*N* scenario

A new modification of $EuGe_3$ (see report Schwarz) with triangular Ge_3 units being linked to Eu atoms with polar bands was discussed in [14]. With alkaline earth atoms (*AE*), superconducting trigermanides $AEGe_3$ were found to display Ge_2 dumbbells interlinked by Ca–Ge multicentre bonding [15].

A number of isostructural M_2LaGe_6 compounds with a covalently bonded framework of two-bonded and three-bonded Ge species have been investigated within a common project with A. Saccone. With two-valent M = Mg atoms the compounds formally obey the 8–N rule, while M = Li leads to electron deficiency as expected. Unexpectedly, however, with M = Zn the introduced Ge–Zn covalence also introduces quantifiable electron deficiency of the Ge–Ge bonds. The project started as a diploma thesis [16] and is now being continued with further different atoms M in a common PhD thesis project.

Intermetallic catalysts (see Antonyshyn)

GaPd represents the prototype compound for the newly established site isolation concept for catalytically active intermetallic phases [1]. A chemical bonding study [17] devoted to this remarkably active catalytic compound clearly shows polar-covalent Pd-Ga bonding with a heteroatomic coordination number of 7 for both atom types. Whereas the valences of Ga are found to be saturated by Pd coordination, the Pd atoms additionally show six homoatomic bonding interactions, which confirms an old model proposed by L. Pauling in 1948. In cooperation with the groups of M. Scheffler and M. Armbrüster the bonding features of the (111) surface of GaPd with respect to CO adsorption was visualized and quantified [18]. In a study to further optimize the catalytic properties of the Ga–Pd system by changing to the Ga–Sn–Pd system results in a lower catalytic activity for $Ga_{2+x+y}Sn_{4-x}Pd_9$ [19]. The reason was found to be the suboptimal spatial arrangement of the heteroatomic two-centre bonds, which hinders the formation of active sites on the surface.

CaAg crystallizes in the CrB type of structure and displays a metallic density of states. Chemical bonding analysis reveals strongly polar Ca–Ag bonding with multicentre character, whereas Ag–Ag bonding along [001] linear chains is mostly of the 2-centre type. As a result, the analysis suggests the Ca-terminated (010) plane being the preferred cleavage plane, which was shown to be consistent with surface energy calculations and the experiment [20].

$CaAg_2$ crystallizes in the KHg_2 type of structure and displays a metallic density of states. Chemical bonding analysis of the bulk features polar multicentre bonds. Chemical bonding of a slab model for the most stable (100) surface reveals dangling bonds located at the Ag sites. Interestingly, the effective charges of the surface atoms do not deviate significantly from those within the bulk suggesting that the introduction of highly electronegative species at the surface may lead to ionic bonds with Ca and aggregation of Ag atoms [21].

Intermetallic compounds in thermoelectrics

Intermetallic clathrates based on Si or Ge networks have attracted attention as possible thermoelectric materials. While “band structure engineering” of the charge carriers is found to be rather successful, tailoring of the thermal conductivity is more difficult. In a systematic study on intermetallic clathrates [22], it was shown that the anisotropic distribution of different types of bonding (bonding inhomogeneity) causes a marked difference in the thermal conductivities of these materials. In a subsequent study [23] of phonon life times in $Ba_{7.81}Ge_{40.67}Au_{5.33}$ (see report Baitinger) it was found that in the non-ordered formation of polar Ba–Au bonds the crystal structure loses –in a strict way of thinking– the translational symmetry and reveals a very low thermal conductivity. Bonding inhomogeneity, produced by anisotropic distribution of 2-centre and 3-centre bonds in CdSb, was also found to be responsible for the strong differences in thermal conductivity along different crystallographic directions [24].

In the binary Si- and Ge-based clathrates, the formation and distribution of defects is crucial for their understanding. In a computational study [25] in cooperation with the M. Scheffler, the defect and non-defect experimental compositions were verified, and the role of electron localization and symmetry breaking discussed (see report Baitinger).

Covalence and ionicity in intermetallic phases

The systematic investigation of main group compounds crystallizing in the MgAgAs type of structure by means of ELI-D/QTAIM basin intersection method has led to a generalized view on the 8–N rule suitable also for polar bonds in the polyanionic partial structure. In this way, discrepancies between the formal and the effective atomic charges could be resolved [26].

Based on careful IQA calibration studies on large molecular models of zinc blende type compounds [27], our previously published semi-quantitative method to predict the site preference in compounds with MgAgAs type of structure [1] was raised on the quantitative level of the point charge approximation of the IQA method (PCA-IQA) for solids. While full IQA for solids is not yet available, our PCA-IQA study was the first application of this type in solids.

The potential of this novel methodology for solids was demonstrated by predicting six compounds with MgAgAs type of structure. The key point was an uncovered synergism of ionic and covalent interactions for certain element combinations (Fig. 2). The majority

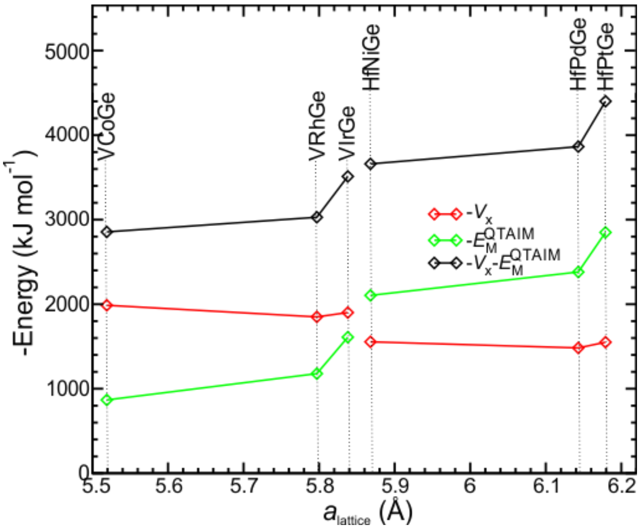

Fig.-2: Synergism between covalent (V_x) and ionic (E_{Mad}^{QTAIM}) interactions for VIrGe and HfPtGe in the MgAgAs structure type.

of these compounds could then be subsequently synthesized in the laboratory [28].

The complete research project has been summarized in the *Jahrbuch der Max-Planck-Gesellschaft 2017* [29].

Semiconductor–metal relations

The cubic diamond structure of elemental tin is known to be unstable above +13 °C, where the tetragonal β-Sn structure is formed displaying a 4+2 coordination and metallic properties. At higher pressures all the lighter group 14 elements can be converted to the metallic β-Sn phase with the exception of carbon. In a systematic study of all group 14 elements, the reason for this exceptional behaviour of carbon was computationally investigated and traced back to chemical bonding arguments from various chemical bonding descriptors in position space [30, 31]. It turned out, that the absence of the cubic diamond to β-Sn transition for carbon is reflected by the ELI-D topology and by the sum of the electron density values at the bond critical points connected with an atom. While the appearance of the β-Sn structure is connected with the occurrence of six ELI-D attractors around each atom in Si, Ge, and Sn, for C this situation is never reached, because before the two further ELI-D attractors are formed, the four initial bonds of the diamond structure are already split, i.e. the initial bonds appear significantly broken before the new bonds are fully established.

Two further very basic studies on the principal behaviour of chemical bonding indicators in position space during a Mott transition have been performed. They will be reported in the separate methodological part of the ChemBond reports (see report Kohout)

The compound Sr_3LiAs_2H has been initially obtained from an approximately equiatomic sample SrLiAs. Refinement of the diffraction data revealed a structure with the composition Sr_3LiAs_2, which, consistent with the 8–N rule, displays a metallic band structure with the DOS(E_F) located on a local maximum. A subsequent NMR study confirmed the presence of hydrogen in the sample. With the aid of ELI-D, possible location of hydrogen in this structure was investigated and this improved structure with interstitial hydride refined. In accordance with the 8–N rule, the Zintl phase Sr_3LiAs_2H displays a band gap [32].

Ag_2S is a semiconducting compound with a band gap of about 0.9 eV. Surprisingly, this compound displays a ductility and plastic deformability like a metal. It was shown that these mechanical properties are based on an especially robust arrangement of covalent bonds using position space ELI-D and Hilbert space COHP method [33].

f-metal–d-metal bonding

The diamagnetic metallic compound $ThPt_2$, was found to crystallize in a unique type of close packed tetragonal structure. Consistent with the large electronegativity difference a sizable charge transfer according to $Th^{+1.78}$ $Pt^{-1.22}$ $Pt^{-0.59}$ was obtained from the QTAIM method, which led to highly polar Pt–Th bonding in the ELI-D/QTAIM framework. Pt atoms were found to build up a three-dimensional network by 2-centre bonds [34].

For the intermediate valence intermetallic phase $YbIn_{1-x}Au_{1+x}$, the QTAIM method yields a sizeable charge separation according to $Yb^{+1.1}$ $Au^{-1.25}$ which favours well-known charge-supported dative bonding Au→Yb characterized already in earlier studies. The auridic character of gold species was confirmed by Mössbauer spectroscopy [35].

Multicentre bonding ($b^m > 3$)

A new phase Al_3AuIr crystallizing in the Ni_2Al_3 structure type has been found in the Al-Au-Ir system. Consistent with the Hume-Rothery mechanism, the compound displays a pseudo gap at the Fermi level. Chemical bonding analysis reveals an anisotropic distribution of two- and multicentre (4c + 5c) bonds, which explains the preferential cleavage of the material perpendicular to [001] [36].

Superconducting $Be_{21}Pt_5$ was found to crystallize in a γ-brass related structure (see report Amon). With the low valence electron concentration VEC < 2 electrons per atom, chemical bonding is characterized by a high degree of multicentre bonding. Especially 8- and 14-centre bonding was described for the first time using position space techniques [37].

Superconducting hp-CuBi (see report Schwarz) features two-dimensional sandwich-like Bi–Cu–Bi slabs characterized by 4-centre Bi–Cu–Cu–Cu interactions. The inter-layer interactions are of van der Waals type between the Bi lone pairs. The compound represents the hitherto missing example of spatial lone-pair separation in two-dimensional structural segments among the intermetallic compounds of bismuth [38].

Outlook:

With the implementation of the IQA method for solids (work in progress since Jan. 2018), the important step towards energetic interpretation of position-space chemical bonding features will be accomplished in the near future. As the IQA-PCA study [28] has already demonstrated, the old but slightly forgotten concept of Madelung energy will become revived but at a higher level. The quantitative interplay of covalence and ionicity in intermetallic phases will become a fascinating topic for study and can even develop into one of the basic ingredients for structure-property-reactivity predictions.

External Cooperation Partners

M. Scheffler, C. Carbogno (FHI Berlin, Germany), J.-F. Halet (Université de Rennes, France), R. Gautier (ENSC Rennes, France), A. Saccone (Università di Genova, Italia), M. Armbrüster (Technische Universität Chemnitz, Germany)

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