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Editorial

Compounds with Polar Metallic Bonding

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Recently, I witnessed a discussion amongst solid state chemists whether the term *polar intermetallic bonding* was necessary or dispensable, whether a conceptual discernation of this special class of intermetallic compounds was indicated or spurious. It quickly outcropped that the reason for this discussion is the ambiguity of the term *polar*. Most chemists associate *polarity* immediately with bond polarity in a classical van Arkel-Ketelaar triangle picture [1,2]. And as introduction of ionic polarization into a covalent bond is a very common case also in intermetallic systems, the term *polar intermetallic phases* indeed may seem dispensable. However, the term has existed in the literature for many decades, and there is a good reason for this. Polarity in intermetallic phases causes a number of effects, and the underlying structure-property relationships justify summarizing this class of intermetallic compounds with one common epithet. The conceptual difficulty with it is due to multiple meanings of the term. There are several instances of *polar metal* or *polar metal-metal bonding* in the literature, and as they originate from different scientific backgrounds it is not always clear to the public in which sense *polarity* is being referred to by the author.

Not only Coulombic, but all kinds of dipoles are appropriate to create polarity in an intermetallic phase. The different aspects of macroscopic polarity have one common condition, and it is a crystallographic one. Dipole interaction in a long-range ordering is only observed when inversion symmetry or mirror planes perpendicular to the dipole axis are absent. Therefore the crystallographic meaning of *polar* is the absence of special symmetry operations [3,4]. The perhaps largest number of scientific publications on *polar metals* concentrates on electron conducting materials showing some kind of ordering of electric dipoles in the structures. The coexistence of ordered electric dipoles, as e.g., in ferroelectrics, and metallic behavior comes as a surprise as it would normally be forbidden by Gauss' law: Due to charge screening the effective field within an electron conductor has to be zero, ruling out any kind of cooperative long-range dipole ordering. This rule can be broken in cases of weak electron-phonon coupling, and it is observed in a large and growing number of perovskite-type materials [5–8]. These materials show great potential in future data storage systems with high density and long lifetimes [9,10]. Also the presence of magnetic dipoles and their long-range ordering leads to a form of polarity within an intermetallic phase, and ferromagnetic behavior is by far the more common case. The interface created by contacting a semiconductor with a metal results in a Schottky barrier, and its height depends on electron concentrations, doping and other parameters. The height of the Schottky barrier creates polarity at the metallic interface often referred to in literature as polar bonding [11,12]. And finally, in coordination chemistry, a covalent bonding between the metal centers of a heterodimetallic coordination compound is described as a polar metal-metal bond when the electronegativity differences between the metal atoms is pronounced [13]. This shows how different the meaning of *polar metallic bonding* can be understood, depending on the context.

The Special Issue of *Crystals* entitled *Compounds with Polar Metallic Bonding* presented here is a compilation of eight original articles based on the most recent research projects. It may therefore be seen as a snapshot view on the subject, and it is my great pleasure to see so many different interpretations of the term *polar metallic bonding* assembled here. The broad spectrum of the different meanings of *polarity* in intermetallic compounds is brought forward by a plethora of modern synthetic approaches, structural studies, interpretations of chemical bonding and application-driven materials science. We are extremely happy to have attracted prominent and outstanding members of the intermetallic community to contribute with articles of highest quality to this compilation and we owe them the deepest gratitude:

- Corinna Lorenz, Stefanie Gärtner and Nikolaus Korber report in their article 'Amoniates of Zintl Phases: Similarities and Differences of Binary Phases A_4E_4 and Their Corresponding Solvates' [14] about Zintl chemistry, presenting chemical examples for highest polarity, the complete electron transfer from less noble metal to an electronegative metal. Intermetallic phases of this kind can be dissolved in and recrystallized from polar solvents. Crystalline solvates of Zintl phases may be seen as 'expanded metals' and cross the border from intermetallic phases to coordination compounds in an impressive way.
- Alexander Ovchinnikov, Matej Bobnar, Yurii Prots, Walter Schnelle, Peter Höhn and Yuri Grin present a communication with he title '$Ba_4[Mn_3N_6]$, a Quasi-One-Dimensional Mixed-Valent Nitridomanganate(II,IV)' [15] and give a beautiful example of both sophisticated modern solid state synthesis and of modern interpretation of the chemical bond in a semiconducting material with long-range ordering of magnetic dipoles. The interplay of magnetic and electronic properties is most interesting in this chain compound.
- Yufei Hu, Kathleen Lee and Susan M. Kauzlarich report on 'Optimization of $Ca_{14}MgSb_{11}$ through Chemical Substitutions on Sb Sites: Optimizing Seebeck Coefficient and Resistivity Simultaneously' [16]. Their reseach on thermoelectric materials within the class of Zintl compounds has gained great atention over the years. Getting control over thermal end electric conductivity via structural modification is a highly difficult task, and the article present in this Special Issue gives an excellent example.
- Riccardo Freccero, Pavlo Solokha, Davide Maria Proserpio, Adriana Saccone and Serena De Negri report on '$Lu_5Pd_4Ge_8$ and $Lu_3Pd_4Ge_4$: Two More Germanides among Polar Intermetallics' [17]. Their structural and theoretical study shows the compounds to consist of a network of negatively polarized Ge and Pd atoms whereas Lu acts as a counter-cation, being positively polarized.
- Michael Langenmaier, Michael Jehle and Caroline Röhr present an article entitled 'Mixed Sr and Ba Tri-Stannides/Plumbides $A^{II}(Sn_{1-x}Pb_x)_3$' [18], dealing with a mixed-crystal series in which the continuous chemical exchange causes the transition from ionic to metallic bonding. This is a most instructive example how chemical bonding can be directly manipulated by chemical means. Modern ways of conceptualizing electron distributions in the sense of counting rules are presented next to high-level DFT calculations of the electronic structures and also geometric analyses.
- Asa Toombs and Gordon J. Miller show a detailed structural study on 'Rhombohedral Distortion of the Cubic $MgCu_2$-Type Structure in Ca_2Pt_3Ga and Ca_2Pd_3Ga' [19]. They give an excellent example on how electronic structure and crystallographic distortion mutually interact.
- Fabian Eustermann, Simon Gausebeck, Carsten Dosche, Mareike Haensch, Gunther Wittstock and Oliver Janka present an article entitled 'Crystal Structure, Spectroscopic Investigations, and Physical Properties of the Ternary Intermetallic REPt$_2$Al$_3$ (RE = Y, Dy–Tm) and RE_2Pt$_3$Al$_4$ Representatives (RE = Tm, Lu)' [20]. Here, structural and chemical modifications go hand in hand with symmetry reduction, magnetic interactions and with gradual polarity changes.
- Simon Steinberg and Richard Dronskowski present a review on 'The Crystal Orbital Hamilton Population (COHP) Method as a Tool to Visualize and Analyze Chemical Bonding in Intermetallic Compounds' [21]. This comprehensive study gives a summary and overview on fundamental concepts of recognizing the chemical bonding in intermetallic compounds. They give a coherent

introduction into the well-established COHP method, the 25th anniversary of which gave rise for this review. With the examples of cluster-based rare-earth transition metal halides and of gold-containing intermetallic series they illustrate polarity and its expression in terms of bond analyses. The relevance of such considerations on material chemistry is emphasized with respect to phase-change materials and to magnetic materials.

The world of intermetallic compounds with polar metallic bonding is a rapidly growing one. It is a fertile ground on which novel materials emerge, due to the unique ability of polar intermetallics to provide new and unexpected combinations of properties. This Special Issue may be taken as an excellent example on how much further work is needed in order to purposefully direct material research in this field, and, indeed, how valuable basic research on chemical systems and development of concepts for elucidation of electronic bonding situations is with this respect.

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