The Correlation between Bonding Relationships and Ionic Volume Increments Exemplified by Metal Hydrides and some Intermetallic Compounds

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Introduction

In 1934 W. Biltz published a book entitled „The Volume Chemistry of Solids“ [1] trying to approximate the volume of solids by a sum of individual atomic volume increments. In order to determine these increments, statistical averages based on the data available at that time were used. Additionally, deviations from these increments were discussed by Biltz, particularly, if strong polarization of anionic partners are present, e.g., in metal hydrides.

A comparison of the model developed by Biltz with modern quantum mechanical calculations of atomic volumes gives insights into bonding relationships which are not available by the discussion of interatomic distances alone.

The determination of partial volumes of atoms on a quantum mechanical basis was mainly founded by the work of Bader [2,3]. According to Bader's work, a subsystem, such as an atom in a crystalline compound, is bound by the surface of zero flux of the electron-density-gradient vector field. This allows the determination of the charge distribution among the atoms within molecules.

The analysis of the electron localization function (ELF) permits further insight into the bonding situation again in real space [4,5].

Metal-hydrogen compounds

The volume increments of hydrogen in metal hydrides determined by the Biltz method versus the partial volumes determined by the Bader method [6] are plotted in Fig. 1. Only binary compounds are shown. The surprising result is an almost linear relation between both series. The decreasing ionic

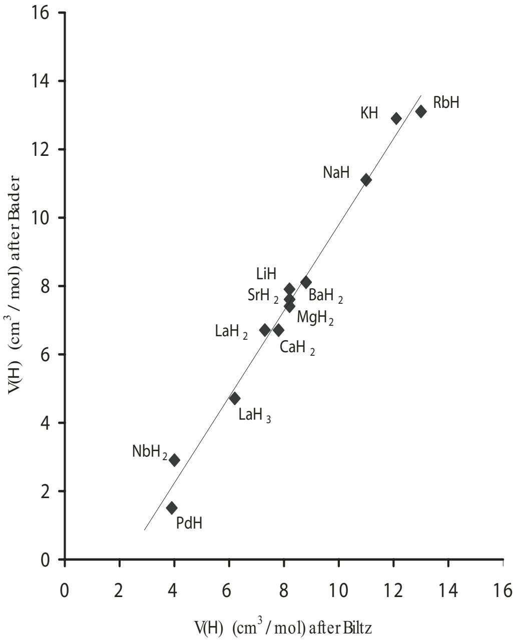

Fig. 1: Volumes V(H) of hydride ions in selected binary metal hydrides according to Biltz, plotted versus the volumes calculated according to Bader.

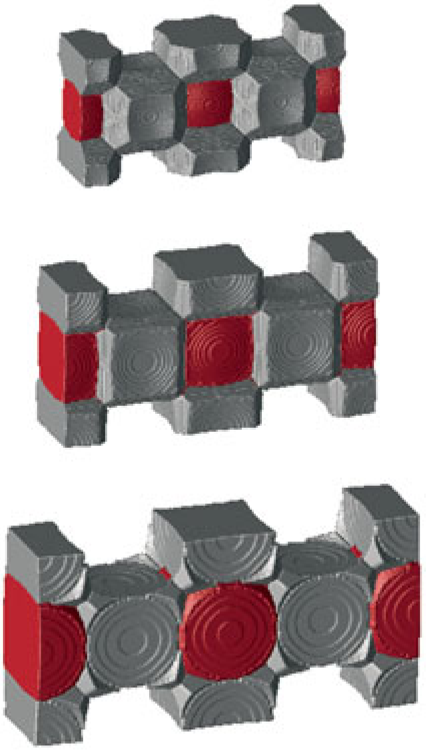

Fig. 2: The atomic volumes of the hydrides of Li, Na, and K (red marked; top to bottom). The representation shows the structures true in scale.

character, ranging from the alkali metal hydrides to the transition metal hydrides NbH_2 and PdH, leads to an analogous decrease of the partial volume of hydrogen in both sequences (according to Biltz and to Bader). In Fig. 2 the atomic volumes determined by the Bader method for the alkali metal hydrides of Li, Na and K (red marked), crystallizing in the rock salt structure, are shown true in scale.

The next example (Fig. 3) shows results on the lanthanum hydrides LaH_2 and LaH_3. The atomic arrangement of LaH_2 corresponds to that of the CaF_2 structure type. The Bader analysis divides the space according to Fig. 3b. In LaH_3 the additional fourfold position (½ ½ ½) is occupied with hydrogen atoms (Fig. 3d). Exactly in this position, the ELF analysis concerning the metallic compound LaH_2 (Fig. 3a) shows an extra volume (green) occupied with nearly half an electron. It can be suggested that the additional hydrogen atom picks up this electronic charge forming the nonmetallic compound LaH_3.

In Fig. 4 the volume increments of hydrogen determined by the Biltz method for some ternary hydrides are plotted versus the partial volumes according to Bader. The straight line is taken from the diagram of the binary compounds (Fig. 1). Ternary hydrides of the main group metals (black symbols) investigated by us correspond to the straight line found for the binary compounds. The same is valid for such ternary hydrides which contain a transition metal in a middle or high oxidation state (green symbols). However, we observed drastic deviations for systems with low oxidation states (red symbols). A parallel straight line seems to exist for the compounds $A_2[MH_2]$, where A means Li or Na and M stands for Pd or Pt with the oxidation number 0.The reason for this deviation is that the volume increments of the transition metal atoms after Biltz, taken from the structure of the elements, are too small. For the metal palladium the ELF analysis suggests a d^9 configuration for the palladium core and one electron in the bonding region. However, for the $A_2[MH_2]$ compounds the ELF analyses imply a d^{10} configuration and a correspondingly larger volume. If a transformation of the red marked V(H) values to the straight line is taken into account the palladium atom gets a volume increment of about 13 cm^3/mol. In the metal the volume increment is only 8.9 cm^3/mol. The volume of a palladium atom in the metal is clearly smaller than an atom with the oxidation state zero in a compound. The same is valid for platinum.

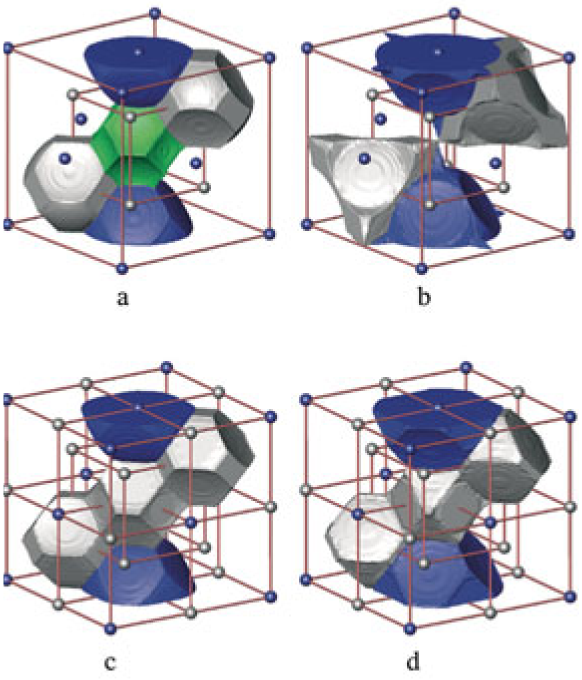

Fig. 3: The atomic volumes of the lanthanum hydrides LaH_2 and LaH_3; (a) LaH_2, ELF representation; (b) LaH_2, calculation according to Bader; (c) LaH_3, ELF representation; (d) LaH_3, calculation according to Bader. The volumes of the lanthanum ions are marked blue, those of the hydrogen ions silver. The volume marked green shows an extra volume occupied with nearly 1/2 electron (see text).

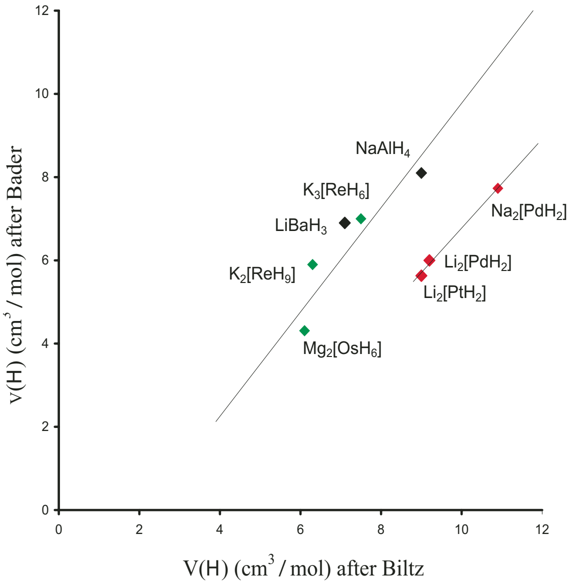

Fig. 4: Volumes V(H) of hydride ions in selected ternary metal hydrides according to Biltz, plotted versus the volumes calculated according to Bader

Intermetallic compounds

Compounds in which small cations polarize large anions are not rare. The metal hydrides are only one example. An analogous group of compounds are the metal nitrides [7]. Our investigations concerning the intermetallic compounds are just at the beginning and confine themselves to some aluminum-platinum compounds [8-10]. Their formation in the platinum-rich region leads to a drastic decrease of the volume in comparison to the expected value after Vegard's law (Fig. 5). The reason for that could be a charge transfer system. We suggest that the loss of electrons of the aluminum atoms is followed by a larger decrease of the volume increments than the compensating increase caused by the reception of electrons by the platinum atoms. The quantum mechanical model after Bader confirms this prediction for the two compounds $AlPt_3$ and AlPt. For the compound Al_2Pt the contrary confirms the experimental result. Here, the decrease of the volume increment of the aluminum atoms does not compensate the increase caused by the platinum atom. The result is a volume dilatation. Fig. 6 shows volumes of the platinum atoms calculated true in scale after Bader for the three aluminum-platinum compounds $AlPt_3$ ($AuCu_3$ structure type), AlPt (CsCl type), and Al_2Pt (CaF_2 type).

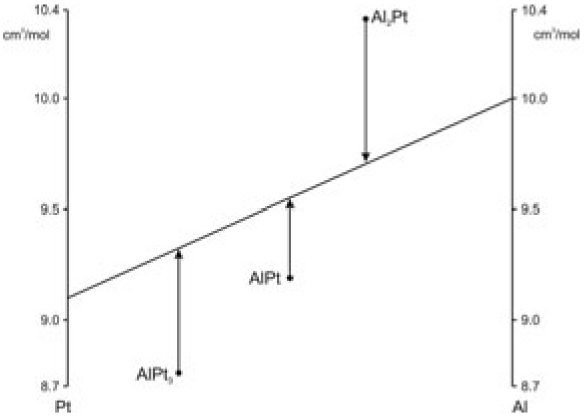

Fig. 5: Volumes of some aluminum-platinum compounds in comparison to the expected values after Vegard's law.

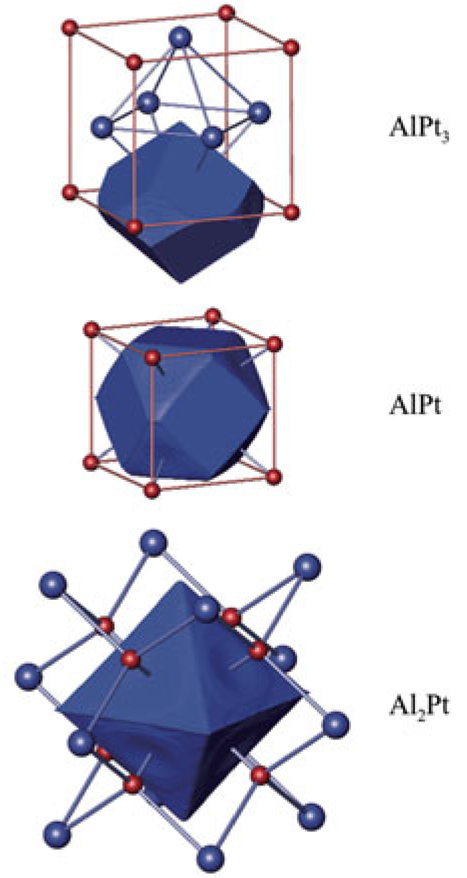

Fig. 6: Volumes of the platinum anions calculated true in scale after Bader for the three aluminum-platinum compounds $AlPt_3$, AlPt, and Al_2Pt (Al red, Pt blue).

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