A Unified Bonding Picture for the Metallic Triel Elements**

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The elements of the boron group (the triel elements) have a unique position in the periodic table, being situated at the borderline between metallic bonded elements with either a close-packed or the body-centered cubic structure and the covalently bonded tetrel elements crystallizing in the diamond structure. As a peculiar consequence all the triels display different ground-state structures at ambient conditions[1] (of which some are displayed in Figure 1): in α-rhombohedral

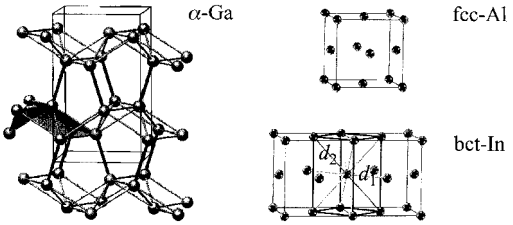

Figure 1. The structures of orthorhombic α-Ga (left), and fcc-Al and tetragonal In (right). In the α-Ga structure the local (1+6) coordination of the atoms is emphasized.

boron B_{12} icosahedra are arranged as in a cubic close-packing of spheres, whereas aluminum crystallizes in the simple face-centered cubic (fcc) structure type. α-Gallium again has a rather complicated, orthorhombic structure, consisting of corrugated 3^6 nets that are stacked and connected by short distances along the stacking direction yielding a local (1+6) coordination for each Ga atom. Indium adopts a tetragonal body-centered (bct) structure which corresponds to a distorted fcc arrangement in which the environment of 12 nearest neighbors is split into two sets. The c/a ratio is 1.521 and is thus larger than that for the ideal case of the fcc structure $(\sqrt{2})$. Finally, thallium attains an almost ideal hexagonal close-packed (hcp) structure with a c/a ratio of 1.598 (the ideal value is $\sqrt{8/3}$). The contrast to the simple structure–bonding situation of the neighboring tetrel group is striking and has fascinated chemists for a long time. There, the tetrahedral coordination of atoms is easily linked to the electron count of four which leads to the simplified picture of covalent two-electron two-center bonds in solids formed by atomic sp^3-hybrid orbitals. Prerequisite to this bonding picture is the strong interaction between the atomic valence states giving rise to an opening of a s–p hybridization gap in the band structure.[2] The decrease of the number of valence electrons to three in the triels seems to terminate the clear link between electron count and geometrical structure in elemental solids and the obscure region of metallic bonding is entered. However, importantly the transition from covalent (saturated) bonding to metallic (unsaturated) bonding does not occur abruptly. For the two most electronegative triel elements, boron and gallium, a distinct relation between electron count and ground-state structure can still be established on the basis of (localized) multicenter bonding, which results in two structural solutions for an electron count of three, optimal structures are α-rhombohedral B (semiconducting) and α-Ga (metallic).[3]

Herein we present an intriguing, general bonding picture for the metallic triels, which we have extracted from high-accuracy full-potential calculations of these elements in different structural variations (see Computational Methods). We will see that this bonding picture is astonishingly closely connected to the simple one of the tetrels. To make progress towards a unified bonding picture we state that from a chemical point of view the problem of structural stability of solids is preferably tackled by dividing the total energy into the band energy E^{band}, which represents the sum over the occupied one-electron states, and a part containing the remaining contributions, of which the electrostatic (Madelung) energy is the most significant. E^{band} favors the formation of open packed structures in which the atoms are closer to each other and thus covalent bonding can be realized. The electrostatic contributions display an antagonistic behavior with the tendency to stabilize high-symmetry close-packed structures. Therefore, we expect for the metallic triels with their distinguished location in the periodic table a delicate balance of these contributions to the total energy.

We computed the total energies and E^{band} of different structures for Al, Ga, In, and Tl at their experimental ground-state volumes. In the case of Tl a second set of calculations was performed with nonrelativistic radial functions within the muffin-tin spheres (NR-Tl) in order to examine the influence of (scalar) relativistic effects on structural stability of this element. As competing structures we considered the fcc structure and its bct distorted variants with different c/a ratios around the ideal fcc value of $\sqrt{2}$, the hcp structure at different c/a ratios around the ideal value of $\sqrt{8/3}$, and finally the α-Ga structure. Figure 2 summarizes the total energy differences of the α-Ga structure and the two ideal close-packings. As expected, the energy differences between the close-packed structures are very small ($\approx$25 meV per atom at the most (Al)), whereas the low-symmetry α-Ga structure is energetically clearly separated from the close-packings and is obtained correctly as the ground-state structure for gallium. In the left-hand panel of Figure 3 we focus on the structural competition between the fcc- and hcp-based structural variation for the metallic triels. We note that, with the exception of Tl, the fcc-related structures are always lower in energy than the hcp ones. For Al the tetragonal variations lead

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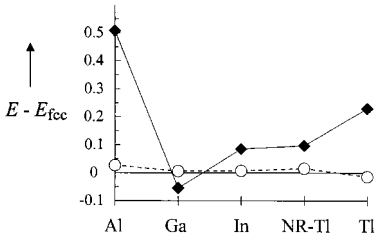

Figure 2. Total energy differences (in eV per atom) for the metallic triels in the α-Ga (solid diamonds), hcp (open circles), and fcc structure. The energy differences are referenced to the fcc structure.

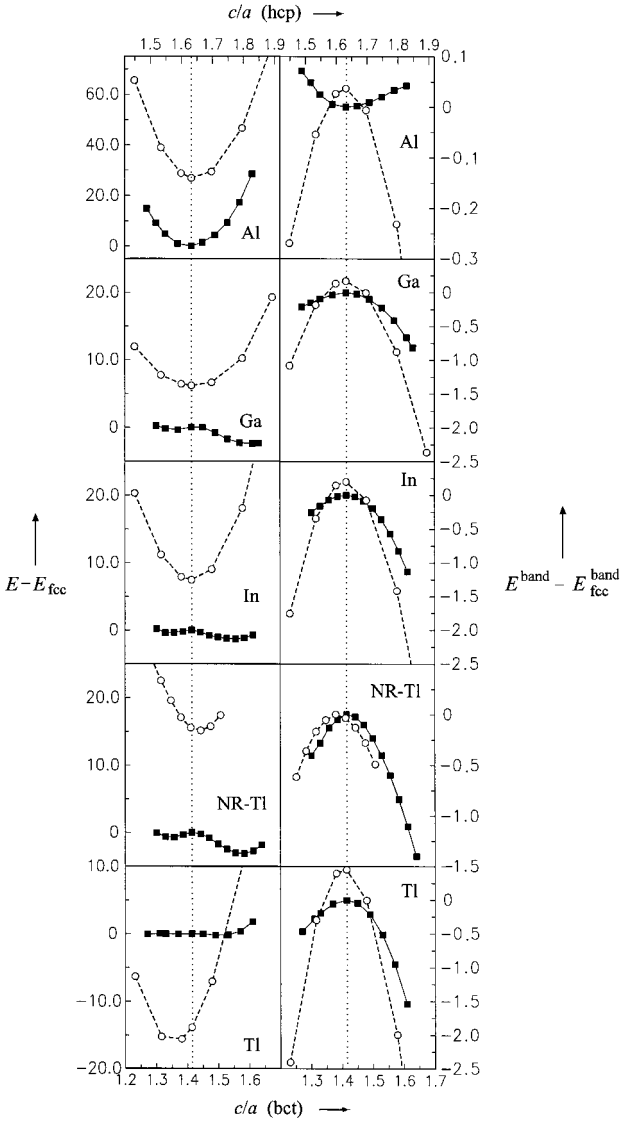

Figure 3. Left: Total energy changes (in meV per atom) as a function of c/a for the metallic triels in fcc- (solid squares) and hcp-based (open circles) structural variations; right: The corresponding changes in the band energies (in eV per atom!). The dotted lines mark the c/a ratios for ideal close-packings.

to a parabolic total energy versus c/a curve, where the minimum corresponds to the c/a ratio of the fcc structure, which is also the ground-state structure. For Ga and In, however, the bct energy curve exhibits double-well behavior with two minima and a local maximum exactly at a c/a ratio corresponding to the ideal fcc structure. In the case of In the deeper minimum at a c/a ratio of 1.55 (at 0 K) is in agreement with the observed In ground-state structure and compares very well with the experimental value of 1.521 (at 298 K). The stabilizing energy of the ground-state structure with respect to the fcc structure is extremely small (below 2 meV per atom).[4] For Ga the bct structure is a high-pressure modification (Ga-III) that appears at pressures around 15 GPa.[5] The deeper minimum of the bct energy curve at $c/a \approx 1.61$ for the ground-state volume V_0 compares also well with that of the experimental Ga-III structure (1.58 at $V/V_0 = 0.9$). The stabilization energy with respect to the fcc structure is about 4 meV per atom.[6, 7] Finally, for Tl a remarkable result is obtained: the hcp ground-state structure appears as a consequence of scalar relativistic effects. Without considering these effects (NR-Tl), the bct-In structure with a c/a ratio of about 1.58 is almost 20 meV per atom more stable than the hcp structure. Interestingly, this stabilization of a close-packing by relativistic effects was also found for the neighboring element Pb.[8] There the omission of relativistic effects reveals the diamond structure is more stable than the ground-state fcc packing. The trends in the band energies along the distortion paths of the close-packings are displayed in the right-hand panel of Figure 3. The E^{band} curves have—with the exception of bct-Al—a maximum at the c/a ratios corresponding to ideal close-packings thus favoring the formation of distorted structures. Therefore, we may identify E^{band} as the leading contribution to the stability of the ground-state structures of Al, Ga, In, and NR-Tl. E^{band} is optimized with respect to the counteracting (weaker) Madelung contribution to the total energy. Remarkably, for Al E^{band} attains a minimum for the ideal fcc structure with respect to the tetragonal distortion, that is for this element E^{band} supports a close-packed arrangement. For Tl however the electrostatic part overcompensates E^{band}: the (almost) ideal hcp structure is obtained as the ground-state structure despite a maximal value of E^{band} at the corresponding c/a ratio.

To proceed further to a unified bonding principle for the metallic triels we need to analyze E^{band} in more detail. An important feature influencing E^{band} in elemental main group solids is the interaction between the valence s and p bands. Generally, this interaction (s–p mixing or hybridization) can take place in the band structure of any structure, provided that the corresponding Bloch functions belong to the same irreducible representation of the space group. Figure 4 sketches roughly the consequences of s–p mixing. The pure s and p energy bands are bonding at their bottom and antibonding at their top (left part of Figure 4) and when the dispersion of the bands is large enough, their interaction leads to an opening of a hybridization gap (right part of Figure 4). Accompanied with the gap formation is a change in the bonding characteristics of the bands: the lower band becomes completely bonding, whereas the upper one turns into a completely antibonding one.[9] Such hybridization gaps often correspond to only local band gaps at highly symmetrical k points and do not have to coincide with the Fermi level. While the occurrence of s–p mixing is determined by symmetry, the strength of s–p band interaction is dependent on the size of the energy separation between the atomic s and p levels, the kind of structure (in open packed structures interactions

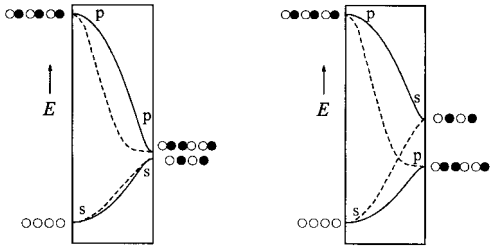

Figure 4. Schematic representation of the interaction between s and p valence bands in the band structures of main group elemental solids (based on ref.[9]). Weak interaction is shown in the left-hand part, strong interaction in the right-hand part. The dashed lines approximate the dispersion of the unhybridized (noninteracting) bands. The orbital combinations indicate the bonding character of the bands.

between atoms are stronger) and the volume (external pressure increases the band widths). The degree of stabilization by strong s–p mixing is crucially dependent on the electron count of the elements. Maximum stabilization is obtained for a band filling, which corresponds to a completely filled lower band in Figure 4. This is exactly the situation for the tetrels in the diamond structure where the s–p hybridization gap corresponds to a real band gap at the Fermi level. The electron count of the triels, however, is not sufficient to produce a fully occupied completely bonding s–p hybridized band throughout the Brillouin zone. Nevertheless one might expect that s–p mixing is still a decisive ingredient to the bonding in the metallic triels. To corroborate this idea we calculated the ratio between the total number of p and s states (N_p/N_s) inside the muffin-tin spheres as a measure of the degree of s–p mixing in the structures under consideration.

In Figure 5 the N_p/N_s ratios for the metallic triels in the α-Ga structure and the two different close-packings are shown.[10] Two important results can be extracted from

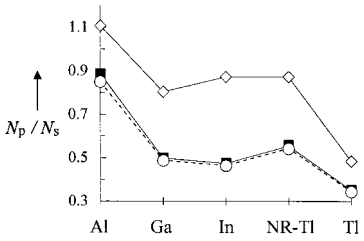

Figure 5. The ratio of the number of p states and s states in the muffin-tin spheres (N_p/N_s) for the metallic triels in the α-Ga (open diamonds), and the ideal fcc (solid squares) and hcp structures (open circles, broken line for clarity).

Figure 5. First, in the low-symmetry α-Ga structure the highest degree of s–p mixing (highest values of N_p/N_s) can be expressed and second the "inherent hybridization capacity" of the different atoms is revealed. Al shows the highest N_p/N_s values in the considered structures, whereas those for Ga, In, and NR-Tl are lower but in a quite narrow range. Clearly distinct from the other triels is Tl which attains very low N_p/N_s values. The trend in the "inherent hybridization capacity" of the triel elements, Al > Ga ≈ In ≈ NR-Tl > Tl, reflects exactly that of the separation of the atomic s and p valence states of these elements: $\Delta\varepsilon_{sp}(Al) = 3.60\ eV < \Delta\varepsilon_{sp}(Ga) = 4.71\ eV \approx \Delta\varepsilon_{sp}(In) = 4.34\ eV < \Delta\varepsilon_{sp}(Tl) = 5.61\ eV$.[11] Figure 6 displays the N_p/N_s ratios for the fcc and hcp structural variations. Again, two results are important. First the metallic triels in the fcc-related structures can express a slightly higher degree of s–p mixing than in the hcp-related ones and second the obtained N_p/N_s values as a function of c/a exhibit a trend that is reverse that for the corresponding band energies. For the favored tetragonal structural variations, the N_p/N_s ratio gains a maximum value for Al and a minimum value for Ga, In, and NR-Tl at $c/a = \sqrt{2}$. Consequently, taking the fcc structure as a reference, the apparent tendency for the metallic triel elements is to adopt a ground-state structure in which the N_p/N_s ratio is either maximal (Al) or increased by distortion (Ga, In, NR-Tl). The degree of distortion (bct or α-Ga structure), however, is governed by the counteracting electrostatic contributions. Only for the most electronegative metallic triel (Ga), where E^{band} is dominating most and the ability to form strong homonuclear bonds is highest, the α-Ga structure can be adopted.

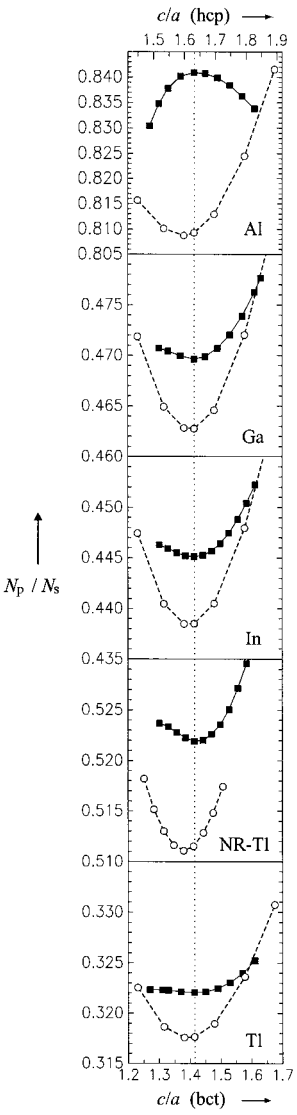

Figure 6. Ratio of the number of p states and s states in the muffin-tin spheres (N_p/N_s) as a function of c/a ratio for the metallic triels in fcc- (solid squares) and hcp-based (open circles) structural variations. The dotted line marks the c/a ratios for ideal close-packings.

With these results we may now formulate the bonding principle for the metallic triels Al, Ga, In, and NR-Tl: Metallic triels adopt a ground-state structure in which s–p mixing of the valence bands (and thus E^{band}) is optimized with respect to the electrostatic contributions of the total energy. As shown in Figure 4, this optimization of s–p mixing raises s–s antibonding states above the Fermi level for the *largest* possible part of the Brillouin zone. It should be remembered that for the tetrels in the diamond structure s–s antibonding states are situated above the Fermi level for *all* parts of the Brillouin zone. For a final elucidation of this bonding principle we compare a particular section (the direction L – W) of the fcc band structure of the considered elements (Figure 7). The direction L – W in these band structures mirrors perfectly the s–p band interaction as sketched in the simple Figure 4. For Al the relatively small s–p separation of the atomic levels

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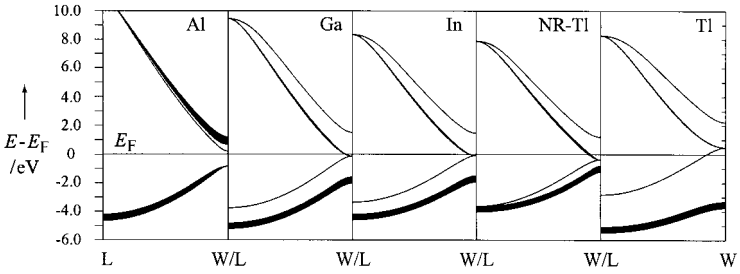

Figure 7. Band structure along the direction L – W for the metallic triels in the fcc structure. The s orbital character of a band is proportional to the "fatness" of the lines used in the plots. Note that just one of the three p bands can interact with the s band. While for Al s – p mixing is most effective, in Tl relativistic effects suppress completely this interaction.

ensures large s – p mixing, which results in a s – p hybridization gap (a local band gap) at the Fermi level at W. A distortion of the fcc structure decreases the amount of s – p mixing for Al (see Figure 6). Thus, the fcc ground-state structure appears as most stable for *electronic* reasons.[4] In Ga, In, and NR-Tl with a larger atomic s – p separation, however, substantial s – p mixing in the fcc structure is prohibited. As a consequence a distortion to a low-symmetry structure takes place where a higher degree of s – p mixing can be achieved. Interestingly, with pressure the dispersion of s and p valence bands is increased and bct-Ga (Ga-III) and bct-In transform to the fcc structure at such a compressed volume that the amount of hybridization between the s and p valence bands becomes comparable to that for fcc-Al at ambient pressure.[6] Thus, the structural phase transition bct → fcc for these elements is *electronically* driven. Finally, Tl does not follow the bonding principle of optimum hybridization. Relativistic effects increase the separation of the atomic 6s and 6p states to such a degree that effective s – p mixing is virtually suppressed in all considered structural alternatives. Owing to this relativistic s – p dehybridization[12] E^{band} is overcompensated by the Madelung part of the total energy and the hcp ground state structure appears as most stable for *electrostatic* reasons.

Computational Methods

Total energy calculations for Al, Ga, In, NR-Tl, and Tl in the considered structural alternatives were performed at constant volumes which corresponded to the respective experimental ground-state volumes (V_0 (Al) = 16.617, V_0 (Ga) = 19.588, V_0 (In) = 26.164, V_0 (Tl) = 28.584 Å^3 per atom). We applied the full-potential linearized augmented plane wave (FLAPW) method[13] and the the full-potential linear muffin-tin orbital (FP-LMTO) method.[14] The size of the atomic muffin-tin sphere for a particular element was the same in all structures; between the sphere sizes of the different elements a certain relation was introduced.[10] In full-potential techniques within the local-density approximation basis functions, electron densities, and potentials are calculated without any shape approximation. These methods belong to the most accurate ones to date concerning studies of structural stability.[15] The calculated energy differences and band structures were found to be virtually identical for the two full-potential techniques. The presented energy differences for Al, Ga, In, and Tl were obtained from FP-LMTO calculations, the presented band structures and the energy differences for NR-Tl are results from FLAPW calculations.

Concerning the FLAPW calculations, well-converged plane wave sets with a cut-off parameter $R_{mt}K_{max} = 9.0$ were used for all elements. The Ga 3d, In 4d, and Tl 5d states were treated as local orbitals. The exchange – correlation potential was parametrized according to Perdew et al.[16a] The reciprocal space integrations in the irreducible tetragonal Brillouin zone were performed with the tetrahedron method. Concerning the FP-LMTO calculations, we made use of valence band s, p, and d basis functions for all elements. For Ga, In, and Tl pseudocore d states were included in the basis as well, that is the resulting basis always formed a single, fully hybridizing basis set. The exchange – correlation potential was parametrized according to Hedin and Lundqvist.[16b] For sampling the irreducible wedge of the Brillouin zone we used the special k points with a Gaussian smearing of width 20 mRy. To ensure convergency several standard tests were performed for both methods, such as the effect of increasing the number of k points used in the summation over the Brillouin zone.

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