Local ‘impurities’ in crystal structures

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Structure-property relation is one of the most important guidelines in the development of new tailor-made materials and compounds. Usually, the regular crystal structure determination results in an idealized model typically ignoring any kind of deviation – in particular from the translational symmetry - which, however, may have significant impact on properties of the particular sample. This phenomenon appears to be not very rare in the crystal structures of intermetallic compounds. The reconstruction of the real local atomic arrangement in such cases is sometimes possible by applying high-resolution X-ray diffraction, but in general requires a combination of the latter with high-resolution transmission electron microscopy and theoretical calculations.

Due to the special features of covalent bonding in intermetallic compounds [1], in particular its multi-center character [2], they often show flexibility of structural patterns with respect of the valence electron concentration [3]. This may result in the coexistence of different structural motifs within the same crystal structure. Usually the regions of the minority pattern are embedded in the matrix formed by the majority pattern. In the previous report period this was firstly shown on example of two types of crystal structure – $YCrB_4$ and $HoGa_5Co$. Precise crystal structure determination (in combination with high-resolution transmission electron microscopy (HRTEM) study) made on a large single crystal of α-$TmAlB_4$ (structure type $YCrB_4$) revealed the presence of spatially confined segments of the $ThMoB_4$ type [4]. By long-term experiments, it was shown to be a problem of crystallization kinetics [5]. $CeIn_5Ir$ and $CeIn_5Co$ (structure type $HoGa_5Co$) are prominent representatives of strongly correlated electron systems as well as prototypical heavy fermion superconductors. When tunneling microscopy data were not in accordance with the established structural model a detailed reinvestigation with high quality data revealed a minor contribution from a closely related structure type $TlPd_5As$ [6]. The sole difference is in the way transition metal atoms occupy the slabs of empty cubes formed by indium. The latter are characteristic of the fluorite type, one of the simplest crystal structures.

Considering calcium fluoride CaF_2 or its anti-type Li_2O as a prototypical ionic structural pattern, any AB_2-type compound adopting its respective structure type is expected to be largely ionic in the first place. Along these very basic crystal chemical ideas it is quite unexpected that the intermetallic compound Al_2Pt adopts the anti-fluorite Li_2O-type structure. A detailed structure determination for well-defined single crystals of Al_2Pt reveals a minute but very significant deviation from the ideal atomic arrangement. In the fluorite-type structures, every atom of the minority component (cation) is coordinated by eight atoms of the majority component (anion) in an ideal cubic arrangement (Figure 1, top left). As there exist as many such cubic sites as anions in the basic motif every other of these cubic sites remains empty to comply with the ideal composition AB_2. Finally, all atoms of the minority component are located on a perfect tetrahedral network while all empty sites are located on an identical but inverted tetrahedral network. All single crystals of Al_2Pt studied till now showed a distribution of Pt atoms at both possible positions in a 97 : 3 ratio within very narrow limits (Figure 1, top right and bottom). Within experimental limits there are no indications for deviation from ideal composition for any crystal under investigation. The very consistent ratio of 97 : 3 excludes a statistical formation of respective domains there has to be a well-defined driving force that gives rise to this systematic deviation from the ideal structural arrangement. Besides efforts to develop a deeper understanding of this particular case it is even more compelling to check if identical or similar features occur with other related compounds. Even more fascinating seems the idea that such deviations may occur for other prominent structure types which are typically described on the basis of close packed anions with cations occupying only part of available vacancies. Ultimately, a better understanding of these non-ideal structural arrangements will allow to control their formation as a kind of ‘structural doping’ which should allow for influencing particular properties.

Closely related to Al_2Pt is Al_2Ru, an intermetallic compound with semiconducting properties. Excellent data which were targeting at the reconstruction of electron density revealed very fine structural details which required adequate analysis [7]. A contribution of only 0.34 % in terms of a different stacking sequence was taken as a very special case of polytypism (Figure 2). As an interesting example to further elucidate this

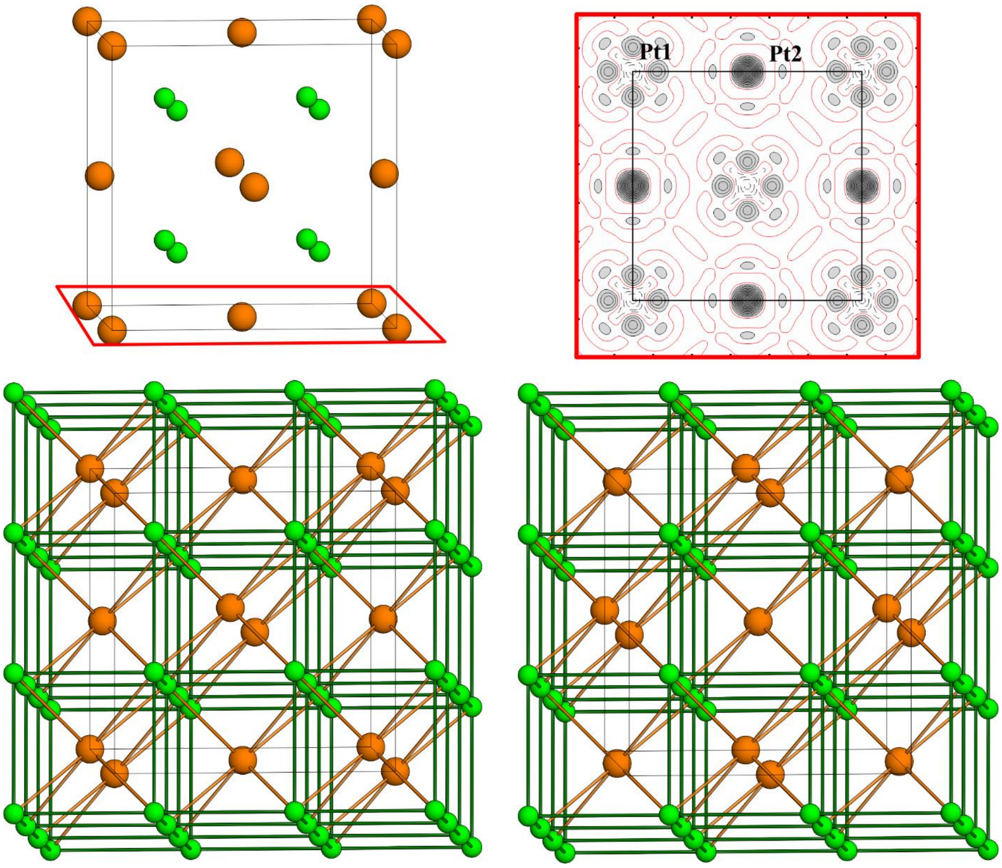

Fig. 1: Crystal structure Al_2Pt: (top left) ideal atomic arrangement of the Li_2O type (anti-fluorite pattern, orange - Pt, green - Al); (top right) difference electron density in the (001) plane revealing the second platinum position; (bottom) atomic pattern in the majority (left) and minority (right) structural patterns shown with the same coordinate system. Black lines show the unit cell boundaries.

problem, single crystals of the 'hidden' compound Cr_2Al were recently obtained for the first time [8]. Preliminary results confirm the assigned $MoSi_2$ structure type, high-level analysis along with a reinvestigation of the parent compound are ongoing. A very detailed comparison of these two compounds may provide insight as to which extend entropy is a main driving force in the formation of such structural 'impurities'. $MoSi_2$ is a very well-known high-temperature material, while Cr_2Al exists only below about 900 °C.

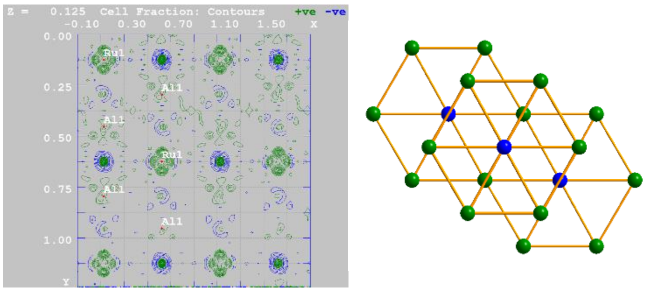

Fig. 2: (left) Difference map after the refinement of a $TiSi_2$ type model for Al_2Ru; pronounced peaks reflect the shifted pattern of Ru atoms; (right) AB-type stacking for Cr_2Al (Al blue) as well as for stacking faults in Al_2Ru (right).

The real structure of boron carbide is a more complex example exhibiting local structural modifications [9]. In the ideal structure model with composition $B_{13}C_2$, the boron icosahedra B_{12} are interlinked by three-atomic chains CBC into a 3D framework (Figure 3a). Detailed crystal structure investigation reveals partial occupation of the vertices of the icosahedra by carbon (Figure b and e). Moreover, defects at the boron site and disorder around the boron and carbon positions in the chain (Figure 3c and f) were observed employing high-resolution X-ray diffraction data. Due to its complexity, the real structural pattern behind such an average picture could not be reconstructed from the X-ray diffraction data, it was recovered only by combined application of theoretical calculations [1] and HRTEM [10]. The combination of three techniques revealed (for carbon-rich compositions) several different atomic configurations of and around the chain, which show similar stability, so that the real crystal structure should be considered as a mixture of different variations [9].

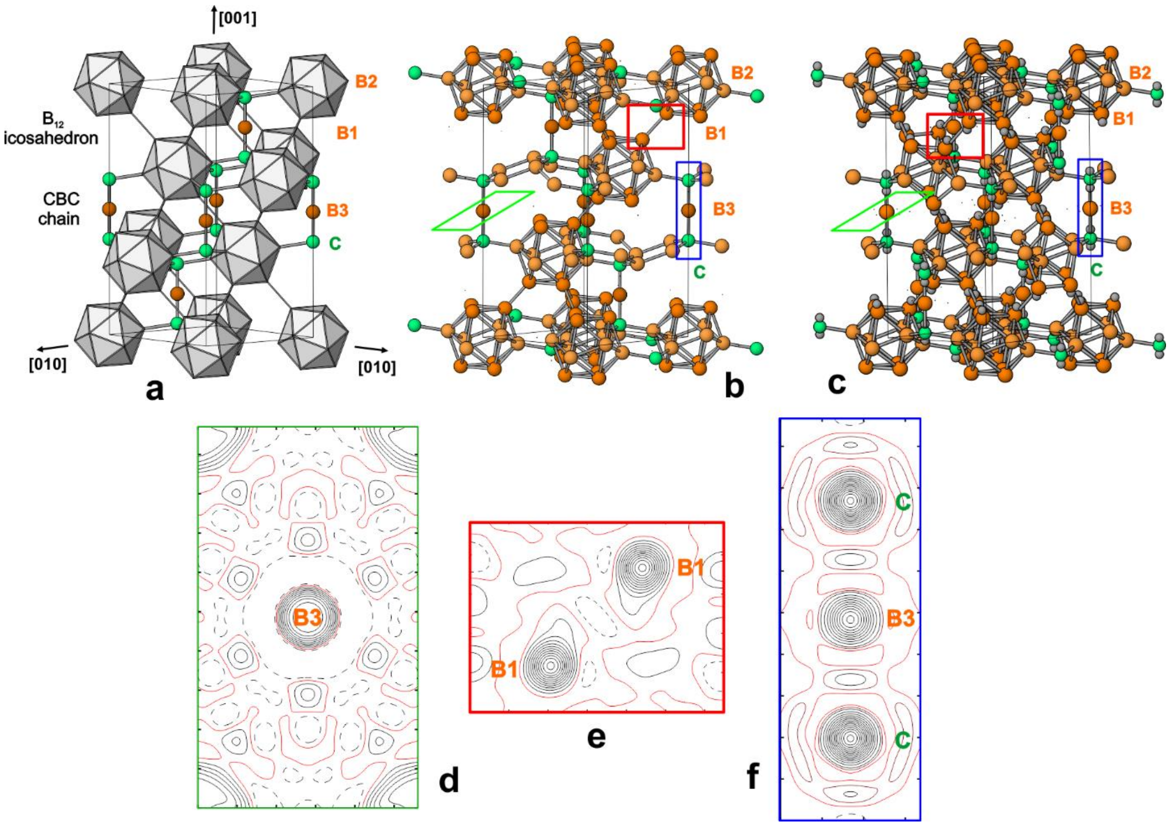

Fig. 3: Crystal structure of boron carbide: (a) ideal model with the composition $B_{13}C_2$; (b) positions of selected planes and distribution of difference electron density in them (d-f); (c) locations of the maxima of difference electron density within the ideal model.

The appearance of different local atomic arrangements within the same majority matrix seems to be a quiet common phenomenon. Recently, deviations from translational symmetry were found in the intermetallic clathrate $Ba_{7.81}Ge_{40.67}Au_{5.33}$ by combination of X-ray powder diffraction methods with HRTEM. The reason for this crystallographic feature is the random formation of Ba-Au bonds causing displacement of Ba and Au atoms from the ideal positions of the clathrate-I structure pattern [11, 12]. Another example of structural complexity of this kind is found in a ternary compound of ytterbium with gallium and platinum, $Yb_4Ga_{24}Pt_9$. The deviations from the ideal structure are caused by non-periodic faults in stacking of two slabs with different compositions R_4E_6 and $E_{12}T_6$, respectively, in the crystal structure (R – rare-earth metal, E – triel element, T – transition metal [13, 14]).

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