Pseudoatoms and preferred skeletons in crystals

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The generalization of the Zintl–Klemm concept provides a universal formulation of a crystal structure in terms of universal building skeletons formed by Klemm's pseudoatoms: atoms that behave structurally according to their formal total electron charge. An important difference in this novel view is that charge is considered to be transferred, in the strict Zintl's sense, from the donor cations to the building skeleton as a whole, not specifically to a given atom or ion. Although application is restricted to (IV)–(IV) compounds (group 14 structures), the principle seems to be universal and can be applied to understand, to relate and to predict the structure of complex compounds on the basis of more simple structures, *e.g.* a given AB skeleton provides the building block for A_2B, AB_2, ABX_m *etc.* compounds of a very different nature. The application of such a principle only requires information on the constituent atoms and on the existing phases of the p-block elements (observed under ambient and high-pressure and/or high-temperature conditions). The ideas introduced here demonstrate, for the first time, that a generalization of the Zintl–Klemm concept is possible and that such a generalization helps to establish a univocal link between chemical composition (in terms of pseudoatoms) and the crystalline structures observed experimentally.

1. Introduction

The great challenge, as yet unmet, of solid-state chemistry is the understanding of the fundamental principles governing the formation of crystal structures. It is generally admitted that the rules enumerated in the 1930s, which are based almost exclusively on atomic sizes and electrostatic forces, have not allowed either the understanding or the prediction of crystalline structures. Moreover, their description has been, in many instances, a rather cumbersome task.

Despite the astonishing developments of computational methods and their impact in the prediction of a number of properties of crystals (mechanical, electrical *etc.*), first-principles calculations were not able to predict crystal structures, since an initial set of candidate structures is always required before performing a geometry optimization. In binary compounds, possible alternative structures can be proposed, for instance, from the empirical Pettifor structure maps (Simak *et al.*, 1997). The works of Jansen and co-workers (Schön & Jansen, 1996; Jansen, 2002) have shown the first steps towards prediction and synthesis planning. More recent studies have demonstrated that a combination of data mining and quantum mechanical calculations (Fischer *et al.*, 2006), and the use of evolutionary algorithms (Hart *et al.*, 2005; Oganov & Glass, 2006) provide appealing alternatives for structure prediction. In the case of data-mining-based

methods, the increasing information included in structural databases helps to ease the task. In any case, it should be emphasized that even if some kind of prediction is currently feasible (Schön & Jansen, 1996; Jansen, 2002), the crucial aspect, *i.e.* the understanding of the crystalline state, is still at a primitive level. In our opinion, one of the reasons for this poor advancement in the understanding of crystal formation concerns the almost unique accepted way of looking at crystal structures: the so-called cation-centred anions polyhedra. Only in the last few decades have attempts to develop alternative approaches to describe the structures of crystals been made. Among others, we mention the ideas introduced by O'Keeffe & Hyde (1985), Borisov (2000), and Vegas & co-workers (Vegas, 2000; Vegas & Jansen, 2002; Santamaría-Pérez & Vegas, 2003; Santamaría-Pérez et al., 2005; Vegas et al., 2006), who have provided new insights into the analysis of the cation arrays in oxides. These works have led to an important conclusion: cations seem to govern the skeletons of crystals. The most recent works are especially illuminating in this regard, since these authors succeeded in rationalizing and explaining the structures of aluminates and silicates by applying the Zint–Klemm concept (ZKC; Zintl & Dullenkopf, 1932) to the cation arrays of these families of oxides (Santamaría-Pérez & Vegas, 2003; Santamaría-Pérez et al., 2005). These somewhat surprising results indicate that cations in silicates/aluminates behave as real Zintl phases and that the aluminates/silicates polyanions are real Zintl polyanions in which the O atoms are located in the vicinity of both bonding and lone pairs.

The Zintl–Klemm concept, one of the most simple but powerful concepts in solid-state chemistry, is also among the most widely accepted in different areas of chemistry. Such a concept was introduced to rationalize the structures of the later so-called Zintl phases. Typical Zintl compounds are formed when a very electropositive element reacts with a *p*-block element with medium electronegativity. The ZKC requires the formal charge transfer of the valence electrons from the electropositive element to the electronegative. The negatively charged atoms (the so-called Zintl polyanions) form partial structures with directed bonds obeying the '8-N rule' that are similar to the structures found in the (neutral) main-group elements having the same number of valence electrons. Although the ZKC is mainly applied to intermetallics (Zintl phases), the issue of extending the Zintl–Klemm concept to transition metals (assuming that transition metals act electropositively; Kauzlarich, 1996), anionic transition metals (Karpov et al., 2004) and the aforementioned example of aluminates and silicates has been addressed.

The present work represents a step forward in the generalization of the ZKC, as our goal here is to demonstrate that the ZKC provides the key to understand more complex structures, provided that a formal charge transfer between cations takes place in the crystal. In other words, it appears that the ZKC concept is more universal than previously thought.

Our initial motivation in the present study was to understand the structural correlations observed for different families of homologous compounds (wide sense), in an attempt to generalize the so-called anions on a metallic matrices (AMM) model recently developed (Vegas et al., 2006; Marqués et al., 2006). This model, which gave a successful interpretation of the structures of silicates and aluminium halides, provides a direct interpretation of the particular structures shown by oxides by considering that the crystal structure can be understood as a metallic matrix (or Zintl polyanion) acting as a host lattice for the non-metallic atoms, the formation and localization of the anions in the compound being driven by the geometric and electronic structures of the metallic sub-structure.

2. Preferred skeletons

After the analysis of several hundred compounds, we found that a number of *preferred skeletons* (PS) appeared in a recurrent fashion either in the structure itself (in binary and ternary alloys) or in the cation subarrays (in ternary and quaternary oxides). We also found that the number of such PS was certainly limited to those of the *p*-block elements, specifically those of Group 14. We soon realised that the cationic substructures of oxides could be rationalized in terms of the PS exhibited by binary alloys. Furthermore, all the cationic substructures in the oxides could also be explained in terms of the ZKC. Thus, if we assume that a generalization of the ZKC holds, a universal principle seems to work as follows: In any oxide, a pair of cations tends to produce skeletons characteristic of the *p*-block elements in such a way that the valence electron count (VEC) is satisfied and the 8-N rule is maintained.

As already noted above, it appears that the PS are those of Group 14, as a more or less homogeneous charge distribution would be a stability factor for a given structure. The analysis of the relative occurrence of a given PS reveals that those derived from (IV)–(IV)-type compounds (diamond, blende, $SrAl_2$ etc.) are certainly quite common. Thus, it seems that if the number of valence electrons that can be shared by the structure completes an octet, the compound tends to acquire a PS of an element of Group 14. It therefore appears that some sort of '(IV)–(IV) rule' holds in the formation of a given compound [a well known fact in (IV)–(IV), (III)–(V) and (II)–(VI) binary semiconductors]. Thus, whenever possible, a pair of cations tends to acquire a full-octet configuration, giving rise to a (IV)–(IV)-like structure. If the number of valence electrons is smaller than eight, it appears that a pair of cations tend to acquire electron charge from others present in the structure whatever type it is (*i.e.* they can be of the same kind) to fulfill the octet configuration. In order to achieve this, the necessary formal electron transfer between cations seems to be produced to form what we have named the *building skeleton* (BS).

Within this view, the BS is considered to be formed by pseudoatoms in the original Klemm's sense, *i.e.* atoms that behave structurally according to their formal total electron charge (pseudoatoms will be labelled with the Ψ prefix in the following). As a result, we propose that a given structure

should be universally formulated as $D_n[BS]X_m$, where D is the donor cation, the BS cations can be regarded as cations *ex-officio* (Parthé & Engel, 1986; Parthé & Chabot, 1990) and, if present, X represents the anion. An important outcome of this view is that charge can be transferred, in Zintl's sense, to the BS as a whole and not specifically to a given atom or ion. To illustrate this idea we shall consider the example of Na_3P, where two Na atoms formally donate charge to the $(NaP)^{2-}$ entity (namely $\Psi-AlP$) that forms graphite-like layers (typical of the group 14 elements) with two Na^+ cations (closed-shell-like) intercalated between them. Accordingly, Na_3P should be reformulated as $Na_2[NaP]$.

In order to demonstrate the general applicability of the generalized ZKC we shall first analyse three binary structures: ZnS (blende), NiAs and MnP, and related structures. The prototypical structure of blende [a (II)–(VI) compound] can
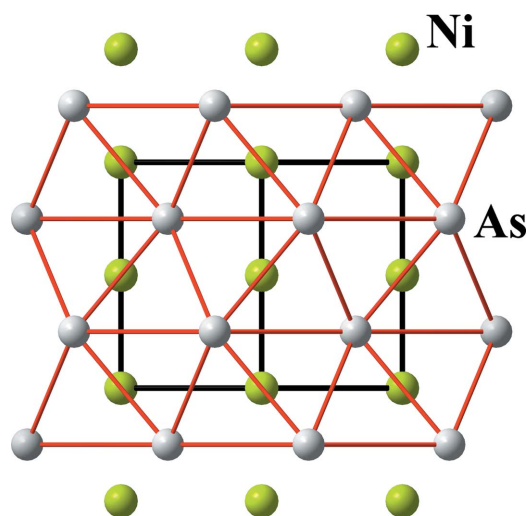

Figure 1
The NiAs structure viewed along [110]. The As atoms (grey circles) are connected by lines to depict the octahedra filled with the Ni atoms (green).
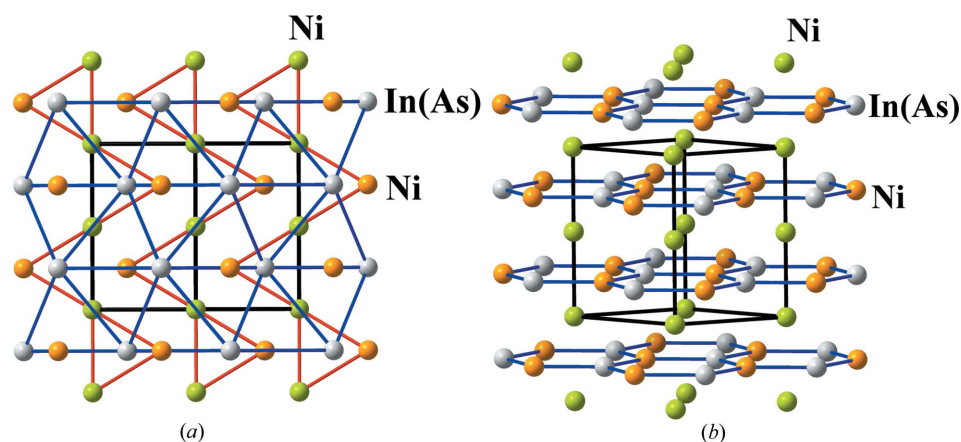
be considered as a substructure of diamond. It is well known that many other ternary compounds, like the prototypical Zintl compound LiAlSi, or MgAgAs, can be regarded as stuffed blendes. Early first-principles calculations in LiAlSi were unable to confirm the charge transfer from Li to Al (to convert it into a Ψ-Si) leading to a widespread critique of the Zintl model. The reader is referred to the article of Seifert-Lorenz & Hafner (2002) for a discussion on the current understanding of the ZKC in terms of first-principles calculations. Both compounds LiAlSi and MgAgAs exhibit diamond-like skeletons BS, which are formed by (AlSi) and (AgAs) entities, respectively. Assuming that the ZKC holds, these structures can be rationalized if one considers that the Li (Mg) atoms formally provide one (two) electron(s) to the BS. While in the first case, the BS is well defined as [Ψ-Si Si] or [Al Ψ-P] in terms of pseudoatoms, in the second case, given the capability of Ag to behave as a Zintl acceptor, it could be hypothesized that the electron donation from Mg turns the Ag atoms into (Ψ-In). Thus, the BS (Ψ-In) As forms a diamond-like structure with the BS atoms following the structural trend observed in (III)–(V) compounds. In fact, let us note again that InAs itself forms a blende-type structure. In any case, since at present we cannot determine whether charge is localized on a given atom, we prefer to refer to the BS as a whole.

The second structure to be considered is NiAs and its stuffed variant Ni_2In. NiAs is usually described as an h.c.p. (hexagonal close packing) of As atoms with all the octahedral voids occupied by Ni atoms (Fig. 1). An inverse description is a simple hexagonal array of Ni atoms with one half of the trigonal prisms occupied by As atoms (Fig. 2a). If the empty trigonal prisms are filled with additional atoms, the Ni_2In-type structure is produced. Such filling leads to a structure in which h.c.p. layers of Ni^{2+} cations alternate with graphite-like layers formed by $(NiIn)^{2-}$ entities (Fig. 2b). Such an interpretation in terms of graphite-like layers was already considered by Zheng & Hoffmann (1989). At this point, we provide a new re-interpretation of the Ni_2In structure within the generalized ZKC, since the important question is why Ni_2In forms such a structure. Within the generalized ZKC, the Ni atoms formally transfer two electrons to the BS, turning the In atoms into Ψ-Sb atoms, the final formula being Ni[NiIn], with the BS [NiΨ–Sb] having the NiAs-type structure, just the structure of NiSb itself. Thus, Ni_2In is really an Ni-stuffed NiAs structure and, to our knowledge, this is the first time that a simple and rational explanation is given for this compound.

A similar reasoning could be made for the MnP structure, which is intimately related to NiAs. MnP can be described as a distortion of

Figure 2
(a) The NiAs structure of Fig. 1 viewed along [110] stuffed with an additional Ni atom (orange) to form the Ni_2In structure. The blue contacts form the As octahedra shown in red in Fig. 1. The red contacts represent the trigonal prisms of Ni atoms which are occupied by the As atoms. (b) Perspective view of the same structure in which the graphite-like NiAs layers are highlighted.

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NiAs in which the P atoms form a distorted h.c.p. array with all the octahedral voids occupied by Mn (Fig. 3a). In the same manner that Ni₂In can be derived from NiAs, the Co₂Si-type structure, and hence the cotunnite structure, can be derived from MnP. The reality is that MnP is the parent skeleton of a (vacant) cotunnite-like structure. If an additional atom is inserted into one half of the tetrahedral voids of MnP, then the cotunnite structure is formed (Fig. 3a). The additional atom together with the Mn atoms form trigonal prisms where the P atoms are lodged (see Fig. 3b).

Summarizing, the following phase relations hold:

Compound	Structure type	D + BS	BS	BS structure
Ni₂In	Ni₂In	Ni + NiAs	NiΨ–Sb	NiAs
Mn₂Ge	Ni₂In	Mn + MnGe	MnΨ–Se	NiAs
Co₂Si	Co₂Si (cotunnite)	Co + CoSi	CoΨ–P	MnP

In fact, Co₂Si (Fig. 3b) has the cotunnite structure. Interestingly, the ternary compounds MnNiSi and CoVSi have the same structure as Co₂Si, confirming the underlying transformations expressed in the above diagram. Let us note here that all the above structures present BS of the (IV)–(IV)-type, including the cotunnite structure. Thus, a diamond-like net is found in stuffed blendes, the Ψ-Si skeleton of SrAl₂ is found in cotunnites, and graphite-like layers are characteristic of the Ni₂In-type structures. It is also important to point out that the transitions between these phases always involve the stabilization of Group 14 structures. The interesting conclusion of the above structural sequences is that they demonstrate how these structures convert into each other. As a matter of fact, the fluorite (stuffed blende) → cotunnite → Ni₂In sequence has already been observed in several compounds (Vegas *et al.*,

2001). Furthermore, the NiAs → MnP phase transition also exists in FeS, a compound that provides an excellent example of the generalized ZKC involving phase transitions within the same compound. Thus, besides the NiAs and MnP structures, FeS also adopts the PbO-type structure, a mineral known as mackinawite (*P4/nmm*), which is also found in BaO, BiIn, CuFeTe₂, FeSe, and in more than a hundred 2:1 compounds (*e.g.* Mn₂As, Cr₂As, Fe₂As, NaMnAs, CaMnGe, Cu₂Sb, among others). In all these compounds the PbO-like BS also fulfils the octet configuration, forming a four-connected net typical of (IV)–(IV) compounds. This is the case for the Zintl phase NaAlSi, where the (AlSi)⁻ BS is identical to those found in the compounds listed above (in contrast to the stuffed blende structure adopted by the analogous LiAlSi). Finally, it is worth mentioning that in the ternary sulfide KLiS, the BS (LiS)⁻ is of the same type. It should be pointed out that the structure of KLiO was interpreted assuming that the K atom donates its valence electron to the (LiO)⁻ system, thus accounting for the formation of **4·8²** planar nets, which were seen as an analogy of the **6³** graphitic layers; no mention to the ZKC was made though (Sabrowsky *et al.*, 1985).

3. The phases of Na₂S and their related oxides

Now we shall show that the generalized ZKC can be used to re-interpret and rationalize on a common basis the structures of ordinary compounds, like Na₂S and its related oxide Na₂SO₄. As is well known, Na₂S crystallizes in the antifluorite structure at ambient conditions and undergoes two high-pressure phase transitions to cotunnite- and Ni₂In-type structures. It has been suggested that the transition sequence *fluorite → cotunnite → Ni₂In* might lead, at higher pressures, to the MgCu₂ structure of the cubic Laves phases (Vegas *et al.*, 2001; Vegas & Jansen, 2002). Although such a transition has never been observed in a binary alloy, it has been observed in related oxides: the well known olivine (Ni₂In) → spinel (MgCu₂) transition. As far as we know, the only theoretical prediction for this transition refers to Na₂S (Schön *et al.*, 2004), which could reach the Laves phase structure at a pressure of the order of 1 Mbar. In any case, according to the generalized ZKC, if we assume that one Na donates one electron, the BS becomes (NaS)⁻ with eight valence electrons. Since the polyanion can be considered isostructural to ZnS, Na₂S therefore adopts a stuffed blende structure (as is well known a fluorite structure can be seen as a stuffed blende). This arrangement has been found in the BS of the high-temperature phase of Li₂SO₄, which essentially can be regarded as an oxygen-stuffed fluorite. Let us
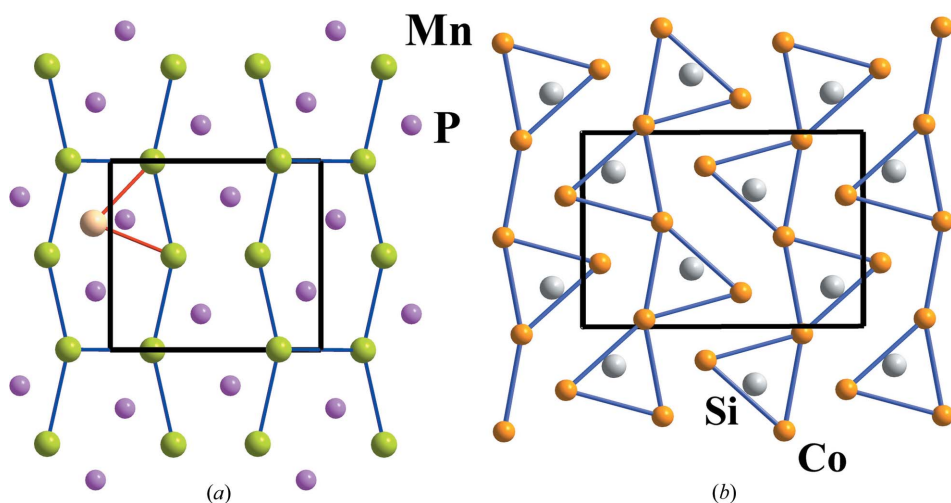

Figure 3
(a) The MnP structure projected on the *ab* plane. The Mn atoms are green spheres and violet spheres represent the P atoms. By inserting an additional atom (golden sphere) this structure converts into the Co₂Si-type structure projected in (b). Co atoms form the trigonal prisms and are represented as orange spheres and the Si atoms as grey spheres. Note that the P atoms in (a) are equivalent to the Si atoms in (b).

recall that Li_2S is antifluorite at ambient conditions and it undergoes a phase transition to anti-cotunnite at high pressure (Grzechnik *et al.*, 2000).

Probably the most convincing explanation of what occurs in fluorite-type compounds is exemplified in Ag_2Te. Careful structure refinements (Sakuma & Saitoh, 1985; Schneider & Schulz, 1993) lead to a disordered structure (anti-fluorite) in which the Te atom is fixed at $(0, 0, 0)$ and one Ag at $8(c)$ $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ with an occupation factor of 0.647 (almost four Ag atoms), while the second Ag atom is disordered at $32(f)$ $(x = 0.422)$ with an occupation factor of 0.0881. That is, a blende-type structure is formed by the BS $(AgTe)^-$, but the second Ag atom seems to be rattling around in the structure searching for available electronic charge to stabilize. Similar features are observed in all copper and silver chalcogenides. In the case of Ag_2S, Tomaszewski (1992) reports the transitions: $P2_1/n \rightarrow$ (450 K) $Im3m \rightarrow$ (860 K) $Fm\bar{3}m$. We have not found any structure determination of the $Im3m$ phase. The room-temperature phase is cotunnite, which exhibits a phase transition to anti-fluorite at 860 K, so the fourfold connectivity is maintained across the phase transitions. The important issue here is that the generalized ZKC explains the BS of these compounds, including that of the cotunnite structure.

Let us emphasize the fact that the cotunnite structure has never been interpreted as a (IV)–(IV)-like structure, but it should within the generalized ZKC by assuming a charge transfer occurs between a pair of atoms of the same species to stabilize octets, leading to the formation of (IV)–(IV) skeletons. As noted earlier in this paper, this view might be questioned at first sight, because it indirectly implies the possible existence/formation of negatively charged cations (cations *ex-officio*). However, several experiments exist that indicate the existence of such entities (*e.g.* potassides) even in the solid state (Tinkham & Dye, 1985; Nakayama *et al.*, 1994; Terskikh *et al.*, 2001), so it is conceivable that these ions might coexist in other compounds, regardless of the fact that such entities could be (or not) identified in conventional diffraction experiments.

The previous discussion is relevant because Na_2S transforms to cotunnite at high pressures (Vegas *et al.*, 2001). This transition, which takes place in several binary compounds, also occurs in oxides. An interesting example is provided by $Cs[LiCr]O_4$, a cotunnite-like compound at room temperature, which undergoes two phase transitions at high temperatures: one to olivine-like (*Pnma*) at 427 K, and a subsequent transition to anti-fluorite ($F\bar{4}3m$) at 573 K (Tomaszewski, 1992).

The most accepted description of cotunnite depicts this structure as a set of trigonal prisms (formed by either Na atoms in Na_2S or LiCs entities in $CsLiCrO_4$) that are occupied by the nominal anion. The prisms form zigzag chains, as in Co_2Si (directly related to those found in the Ni_2In structure), in which the cation array can be regarded as a stuffed MnP-type structure (Fig. 4). In our example, the MnP array is formed by the Cs(Mn) and Cr(P) atoms. Thus, if Li is inserted into the structure, the trigonal prisms are formed. Here, the similarity with Na_2S is explained by assuming that Cs donates its valence electron, so a BS of the type (Ψ–BeCr) is formed, in which Cr is structurally equivalent to S, as is well known. In the case of Na_2S, to show a similar behaviour, one must admit some sort of disproportion between the two Na atoms, so that one Na atom donates its electron to the BS $(NaS)^-$ forming a (Ψ–MgS) array.

In any case, the important comparison is that in both Na_2S and $CsLiCrO_4$, the arrays correspond to (II)–(VI) compounds, which lead to a (IV)–(IV)-type array typical of the binary alloys. Thus, if we connect the pairs (Na–S) and (Li–Cr), respectively, a three-dimensional four-connected net is formed. This net corresponds to the Zintl polyanion $(Al_2)^{2-}$ (Ψ-Si) in the Zintl phase $SrAl_2$ (Fig. 4). Thus, skeletons of either elements or pseudo-elements of Group 14 are always obtained. An interesting observation is that these examples represent new cases of how cations undergo their own phase transitions, in spite of the presence of O atoms (Vegas & Jansen, 2002).

At still higher pressures, the cotunnite-like Na_2S transforms into a hexagonal phase of the Ni_2In-type. To understand this transition we must recall that cotunnite is a filled MnP-type structure, whereas Ni_2In is a filled NiAs-type structure. However, the important issue here is that the MnP $\rightarrow$ NiAs transition has been never experimentally observed in CrS, so it is concluded
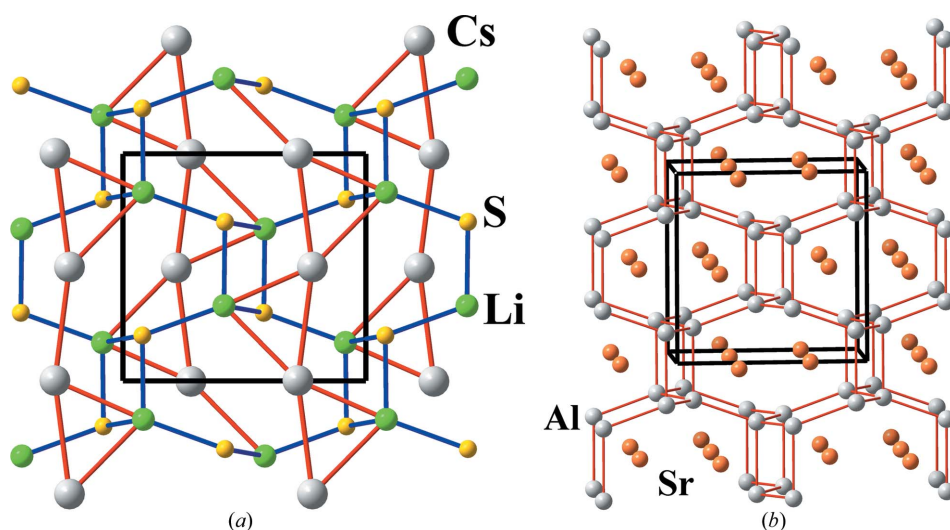

Figure 4
(*a*) The $CsLiSO_4$ structure projected on the *ab* plane. The cation array: Cs (grey), Li (green) and S (orange) form a cotunnite-like structure, in which Cs and Li form the trigonal prisms centred by S. The cotunnite structure is outlined by red contacts, to be compared with that shown in Fig. 3(*b*). We have drawn in blue the Li–S contacts to show that they form a four-connected net similar to that of the $SrAl_2$ structure represented in (*b*). Red contacts connect the Al atoms (grey spheres). Orange spheres represent Sr atoms.

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that the cotunnite $\rightarrow$ Ni$_2$In transition is a consequence of the former transition. This necessarily implies that the MnP $\rightarrow$ NiAs transition takes place in the BS even in the presence of additional atoms in the structure. In fact, the MnP–NiAs phase transition is implicit in the K$_2$SO$_4$-type $\rightarrow$ olivine-type transition, which takes place, for example, in K$_2$SO$_4$ itself. Thus, the structures of binary alloys seem to be preserved and the BSs undergo their own phase transitions even in the presence of additional cations or O atoms. In any case, the interesting fact is that both structures are intimately related and that they are found in many compounds (Na$_2$S, Ni$_2$Si, Co$_2$Si, Ca$_2$Si, Ca$_2$SiO$_4$, K$_2$SO$_4$, Na$_2$SO$_4$ etc.).

An interesting observation is that the Ni$_2$In type is sometimes stable under high-pressure conditions, while in other instances, the Ni$_2$In structure is obtained at high temperature, always starting from a cotunnite-type phase. In some cases, like in Ca$_2$SiO$_4$, the cotunnite-like structure seems to be metastable and, when heated, it converts irreversibly into the $P6_3/mmc$ Ni$_2$In-type phase. In other cases, as in K$_2$SO$_4$, the cotunnite-like structure is the stable phase at room temperature; the Ni$_2$In phase being obtained at high temperature.

An interesting exception is Na$_2$SO$_4$, for which the cotunnite-like phase is unknown; the room-temperature phase being the mineral thenardite (*Fddd*). Considering the idea that oxidation can be equivalent to the application of pressure (Vegas & Jansen, 2002), it should be expected that Na$_2$SO$_4$ could have stabilized the MgCu$_2$ structure, by adopting the spinel structure (it should be noted that the arrangement of atoms in spinel MgCu$_2$ is also adopted by Si in the high-pressure spinel Si$_3$N$_4$). However, the sulfate presents the thenardite structure, where the BS (Na$_2$S) is of the TiSi$_2$-type. Although this structure has no directed bonding, it presents some remarkable features which are worth discussing. The first striking feature is that cations adopt the structure of a compound where atoms of the Group 14 are involved. The second feature is that the S atoms (equivalent to Ti in TiSi$_2$) form a diamond-like array similar to that which is found in spinels. The third characteristic is that the Si (Na atoms in Na$_2$SO$_4$) atoms form fragments of the Al-subarray in the MgAl$_2$O$_4$ spinel or Si in Si$_3$N$_4$. All these features clearly indicate that the structure of thenardite is halfway between the olivine and the spinel structures. So it could be inferred that the TiSi$_2$ structure is an intermediate in the Ni$_2$In $\rightarrow$ MgCu$_2$ transition. Consequently, thenardite might well be an intermediate structure in the olivine $\rightarrow$ spinel transition which takes place in the earth mantle. Although one may think that this reasoning would be somewhat controversial as the complete transition olivine $\rightarrow$ thenardite $\rightarrow$ spinel has never been observed, it must be pointed out that the complete transition path can be reconstructed from the observed transitions in two closely related compounds. Thus, let us consider the transition thenardite $\rightarrow$ olivine which takes place at high temperature in Na$_2$SO$_4$. Subsequently, this path is completed with the transition spinel $\rightarrow$ thenardite which takes place at high temperature in Na$_2$MoO$_4$. Thus, the following general scheme is proposed

$$\text{spinel} \longrightarrow \text{thenardite} \longrightarrow \text{olivine}$$
$$\text{Na}_2\text{MoO}_4 \qquad\qquad \text{Na}_2\text{SO}_4$$
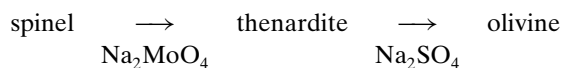
At this point, the thermal behaviour of thenardite merits a special comment, because when it is heated three phases with a cation array of the Ni$_2$In-type appear, namely *Cmcm* (filled CuSO$_4$-type), *Pnma* (olivine) and the $P6_3/mmc$ phase. The third one is, in fact, an oxygen-stuffed Ni$_2$In alloy, the other two phases being orthorhombic distortions of the former. To the best of our knowledge, Na$_2$SO$_4$ is the only compound that presents these three phases. Thus, when thenardite is heated the following sequence is found: $Fddd \rightarrow Cmcm \rightarrow Pnma \rightarrow P6_3/mmc$. In the case of Ag$_2SO_4$, only one transition has been reported: $Fddd \rightarrow P6_3/mmc$. In the three high-temperature phases the structural features are quite similar: their cation arrays are of the Ni$_2$In-type. Moreover, the hexagonal phase is just that of the high-pressure phase of Na$_2$S (also $P6_3/mmc$). It should be noted that whereas the graphite-like layers are irregular in the orthorhombic phases, they are completely regular in the hexagonal variant. Such regularity is also true of the same rotational disorder observed in the oxygen-stuffed anti-fluorites. Thus, the XO_4^{2-} anions (SO$_4^{2-}$, SiO$_4^{2-}$) are completely disordered in the $P6_3/mmc$ phases. The reason for this could be that in the orthorhombic phases the layers (NaS, CaSi, AgS) show Na–S contacts of different lengths, which would correspond to hypothetical single/double bonds. However, in $P6_3/mmc$, all the distances are equal, mimicking an aromatic ring configuration. In these conditions each Na–S contact (with 1.5 electrons on average) does not fulfil the stability conditions found in the other phases, as oxygen tends to share a pair of electrons. The fact that disorder is not only a thermal effect is exemplified by ZnSO$_4$. At room temperature this compound is VCrO$_4$-type, but transforms into a high-cristobalite structure at 973 K (Spiess & Gruehn, 1979), in which the ZnS subarray recovers the blende structure and where the O atoms are not disordered but fixed near the midpoint of the Zn—S bonds. Let us recall that the $P6_3/mmc$ structure of Na$_2$SO$_4$ is stable (with disorder at 520 K) at lower temperatures (450 K below) than ZnSO$_4$. In the case of the related compound GaPO$_4$ (Haines *et al.*, 2006) thermal disorder is induced at 1303 K with the O-atom density forming a continuous ring around the vector joining neighbouring Ga and P atoms. This type of disorder, however, is closer to the image of fixed O atoms near the bond pairs than the rotational disorder observed in both high-temperature phases of Na$_2$SO$_4$ and Li$_2$SO$_4$.

4. Concluding remarks

The above examples demonstrate that the generalization of the ZKC allows for a universal definition of a crystal structure in terms of the general formula $D_n[\mathbf{BS}]X_m$ involving pseudo-atoms. The universal principle we introduce here just needs information about the constituent atoms and on the known phases of the *p*-block elements, which can exist at ambient conditions, or under high-pressure/temperature conditions. We believe this is a novel, powerful tool to understand crystal

structures. In addition, the principle can be applied to predict the structure of complex compounds from simpler ones, *e.g.* a given *AB* skeleton is the building block for A_2B, AB_2, ABX_m, ... compounds of a very different kind. The low-temperature phase α-NaCoPO$_4$ provides a good example of this. In this structure, the CoP subarray is of the NiAs type, because the Na atom provides one electron to the P atom converting CoP into a Ψ-(CoS) skeleton (also NiAs-type). The striking feature is that this array is maintained in NaCoPO$_4$. Thus, the CoS structure remains when more (Na atoms) and more (O atoms) atoms are added into the structure. Interestingly, when this compound is heated, the high-temperature phase β-NaCoPO$_4$ adopts a structure that has been related to a stuffed tridymite structure (Hammond & Barbier, 1996), in which the CoP subarray forms a four-connected net characteristic of (IV)–(IV) compounds. Again, such types of transformations, as discussed in the article, are precisely those often observed in binary compounds.

We believe that the principles discussed here serve to rationalize the observed structures and to put them on a general basis. Surely, they will also help to make reliable predictions of the structural features of new crystalline materials. Our interest now is to join the efforts of scientists of different fields to solve the challenges following from these principles, perhaps the high-pressure community and, of course, theorists developing first-principles calculations. We are aware that our contribution is very likely only the first step in future developments, so now it works only at a qualitative level, so new ideas are welcome to quantify the unexpected regularities uncovered here. The ideas introduced throughout this work demonstrate, for the first time, that there exists a univocal link between chemical composition (in terms of pseudoatoms) and structure: the generalized Zintl–Klemm concept.

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