

DOI: <https://doi.org/10.24297/jap.v19i.8982>**High-symmetry approximations of AX₃ crystal structures retrieved with the method of hierarchical trees**Panfilov A.G.¹, Vaganov S.A.¹¹Ioffe Institute, Saint-Petersburg, Russia

a.panfilov@mail.ioffe.ru, sv.exciton@mail.ioffe.ru

Abstract

The hierarchical trees have been constructed for the AX₃ crystal family, significant steps of this construction being explained in detail. It has made possible to establish the archetypes of the crystal structures that are high-symmetry approximations for subfamilies of the crystals under consideration.

Keywords: AX₃ crystals, structure types, hierarchical trees, high-symmetry approximations

Introduction

A crystal structure is considered to be specified if the space group and Wyckoff positions occupied by atoms are determined. Hence, the record of the form [G166, (3a+6c)+(3b+6c+18h)] implies that the structure can be characterized with the space group 166 (D_{3d}⁵ in the Schönflies notation or R-33m in the short International notation) whereas the Wyckoff positions 3a and 6c are occupied by atoms of one sort while 3b, 6c, and 18h by another sort.

When a phase transition with decreasing symmetry takes place, the crystal structure changes so that the remaining symmetry elements determine both a new space group (usually, a subgroup of the initial one) and a set of occupied Wyckoff positions, which initial Wyckoff positions go into. To obtain the low-symmetry structures, the procedure proposed by (Megaw, 1973) and (Bärnighausen, 1980) can be used. This procedure takes into account not only group-subgroup symmetry relations but also the splitting schemes of the occupied Wyckoff positions. The dendroid constructions branching from a high-symmetry structures are known as the Bärnighausen trees (Koch, 1984), (Bock and Müller, 2002), (Müller, 2004).

Depending on the nature of a system, two approaches have proved to be efficient. The first one is to obtain the derivative crystal structures by the substitution of atoms in the crystal lattice by atoms of different types (Baur, 2007). The second one is to study the chains of continuous structure changes in a constant-composition crystal (when analyzing the structural changes during phase transformations). The latter approach allows one to predict the low symmetry and intermediate structure types which may not have been yet observed. It is also useful when analyzing periodic superlattices (Evarestov et al., 1993), (Kitaev et al., 1997).

The up-to-down-symmetry construction of the Bärnighausen trees, which is their characteristic feature, does not allow one to find out a higher symmetry structure for a given crystal structure unless a huge number of variants is thoroughly considered. At the same time, such a high-symmetry approximation is helpful in simplifying the descriptions of various crystal properties (mechanical, electrical, optical, etc.) when the low-symmetry addition either slightly changes the material property or does not contribute at all. Noteworthy, just the distinction between a high-symmetry description and experimental data indicates the contribution of such a low-symmetry addition.

At the Bilbao University, the method of constructing the reverse "down-to-up-symmetry" trees had been developed (Kitaev et al., 2015) and evolved into several on-line tools which are freely available on the Bilbao Crystallographic Server (BCS. n.d.), (Aroyo, Kirov, et al., 2006), (Aroyo, Perez-Mato, et al., 2006).

This method allows one to establish a higher-symmetry structure type (aristotype) for a given lower-symmetry structure type (hettotype) and to classify structures by the hierarchical families. Hence, below we call the trees constructed in this way "hierarchical trees". When a few aristotypes are possible and locations of atoms in the lattice (i. e. atomic packing) are known from experiments ("structural conditions"), the hierarchical-tree method allows one to choose the most probable aristotype structure among several ones.

Although the construction of the hierarchical trees somehow resembles that of the Bärnighausen ones, there are some nuances. In this paper, using the crystal family of the AX_3 compounds as a representative example, we dwell upon principal distinctions between construction of the Bärnighausen trees and that of the hierarchical ones. To do that, a number of real crystal structures are considered, such as [G140 4a+(4b+8h)], [G204 8c+24g], [G167 6b+(18e)], [G59 2a+(2b+4f)], and so on.

Constructing the hierarchical tree

Minimal supergroups

Let us first consider the hierarchical tree with the root crystal structure [G140, 4a+(4b+8h)] as a rather simple case. Ir_3Si , Pt_3Si , (and so on) crystals are among the ones belonging to this hettotype (Springer Materials n.d.), see Fig. 1.

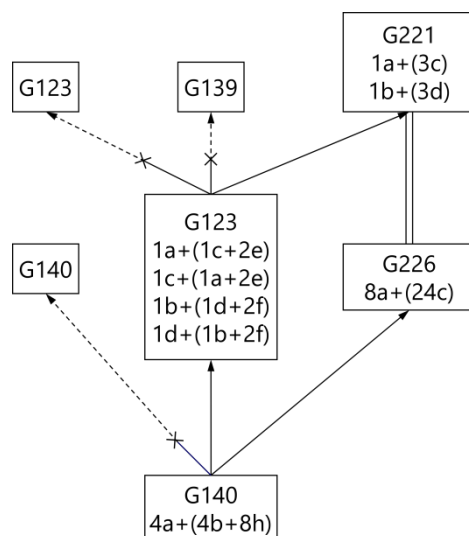


Figure 1. The hierarchical-tree construction for the [G140, 4a+(4b+8h)] structure type

As for the space group G140, there are three minimal (that is the closest in symmetry) supergroups, namely G123, G226, and G140 itself. The procedure of determining the minimal supergroups of the space groups has been explained in detail (Koch, 1984), (Igartua et al., 1996) and is realized at the Bilbao Crystallographic Server (Ivanchev et al., 2002). The search for possible aristotypes can be performed as a stepwise procedure over a chain of minimal supergroups of the root-structure space group (Capillas et al., (2011), (Kitaev et al., (2015).

The splitting of the Wyckoff positions

Probably, the most principal nuance while building the hierarchical trees is as follows. When a transition from a group to subgroup (designated as "group\subgroup" later in the text) is considered, the new Wyckoff positions, which the initial Wyckoff positions go into, can always be pointed out. The correspondence between the positions can be always found out. On the contrary, for the group-to-supergroup transition (designated as "group\supergroup" later in the text), it is frequently impossible to indicate the new Wyckoff positions, that implies the absence of a higher-symmetry aristotype (supergroup) structure for the given hettotype structure. This restriction can be illustrated by contradistinction of two examples presented in Fig. 1, namely $G123 \not\rightarrow G221$ (see Table 1) and $G123 \not\rightarrow G139$ (see Table 2).

For the [G123, 1a+(1c+2e)] structure, the increasing-symmetry transition $G123 \rightarrow G221$ is possible:

Table 1. Correspondence between the Wyckoff positions (space groups G221 and G123)

Supergroup	G221	1a	1b	3c	3d	6e	6f
Group	G123	1a	1d	1c+2e	1b+2f	2g+4h	2h+4o

One can see that, when the symmetry decreases ($G221 \rightarrow G123$), atoms occupying the Wyckoff position 3c of the aristotype structure selected as an example (first line in the Table 1) take in not one but two Wyckoff positions, namely 1c and 2e in the hettotype structure so that "Wyckoff position splitting" occurs. Vice versa, when the

symmetry increases ($G123 \nearrow G221$), atoms of one sort which occupied different Wyckoff positions 1c and 2e (last line in the Table 1) take the unified 3c position in the aristotype structure. In other words, the movement upward the hierarchical tree to a higher symmetry structure is possible.

On the contrary, for the same [$G123, 1a+(1c+2e)$] structure, the increasing-symmetry transition $G123 \nearrow G139$ is impossible:

Table 2. Correspondence between the Wyckoff positions (space groups $G139$ and $G123$)

Supergroup	$G139$	2a	2b	4c	4d	4e
Group	$G123$	1a+1d	1b+1c	2f+2e	4i	2g+2h

One can see that, when the symmetry decreases ($G139 \searrow G123$), atoms occupying the Wyckoff position 2a of the aristotype structure selected as an example (first line in the Table 2) take in not one but two Wyckoff positions, namely 1a and 1d in the hettotype structure. However, in the case of the considered [$G123, 1a+(1c+2e)$] structure, the 1a Wyckoff position is fulfilled while 1d one is not. It implies that, when the symmetry conversely increased ($G123 \nearrow G139$), atoms of the 1a position ($G123$) would occupy merely half of the 2a position ($G139$) locations, and the crystal would not form. In other words, for the given hettotype structure [$G123, 1a+(1c+2e)$], one can not indicate an aristotype structure with the space group $G139$ and fully occupied Wyckoff positions.

The crossed arrows in Fig. 1 (and in the subsequent figures as well) just indicate that these transitions are just impossible. This discourse is naturally valid for the other three structures with the space group $G123$ presented in Fig. 1.

Analogously, it is impossible to point out the Wyckoff positions for transitions $G140 \nearrow G140$ and $G123 \nearrow G123$. Although the symmetries of group and supergroup coincide in these cases, it is not determinative. Even if the symmetries of group and supergroup are the same, sometimes, the "group \nearrow supergroup" transition is still possible. For example, the below discussed structure [$G59, 2a+(2b+4f)$] is the aristotype one for the structure [$G59, (2a+4e)+(2b+4e+4f+8g)$] (one of crystal phases of the $NbPd_3$ compound). At the same time, there is no aristotype structure with the same space group $G59$ for the structure [$G59, 2a+(2b+4f)$] itself (on the next "hettotype-aristotype" step).

Physically identical and non-characteristic structures

Another nuance of the hierarchical-tree construction is related to the situation when two or more mathematically different descriptions of a given crystal structure (i.e. in those descriptions, space groups and/or Wyckoff positions are different) nevertheless specify the same atomic coordinates in the real space. When it happens with atoms of each sort, the corresponding crystal structures (two or more) are physically identical. For example, the Wyckoff-position set $1a+(1c+2e)$ presented in Fig. 1 ($G123$) is physically equivalent to the sets $1c+(1a+2e)$, $1b+(1d+2f)$, and $1d+(1b+2f)$. Below, we give only one of the physically equivalent sets. Since the choice of one of such equivalent sets is arbitrary, we will use alphabetically first set unless another description was established historically.

Structures may be physically identical not only in the case of the same space group. It is also possible that all atoms of a crystal still occupy the same positions in the real space when the formal symmetry increases/decreases. As an example, two structures [$G221, 1a$] and [$G207, 1a$] imply the same spatial distribution of atoms, although mirror plane being formally absent in the latter case. The structure with a lower symmetry (here, [$G207, 1a$]) is considered as non-characteristic. It is obvious that, in a real crystal, the group \nearrow supergroup transition suggests in fact straightforward transition to the corresponding characteristic highest-symmetry structure. In other words, the real phase transitions take place between characteristic structures.

In the above considered case illustrated by Fig. 1, the structure [$G226, 8a+(24c)$] describes the spatial distribution of atoms (their coordinates in a crystal) just as the characteristic structure [$G221, 1a+(3c)$] does. That is to say, although mathematically different, the two descriptions are physically identical, what is indicated with the double line in Fig. 1 and subsequent figures. By the bye, this means that the transition from the root structure [$G140, 4a+(4b+8h)$] occurs not to the [$G226, 8a+(24c)$] structure but directly to [$G221, 1a+(3c)$].

Archetype structures

In the course of stepwise movement upward the hierarchical tree, there always appears a structure without higher-symmetry aristotype. We call such structures archetype structures (Kitaev et al., 2015)). For the structures shown in Fig. 1, there is the only archetype structure (superior aristotype one), namely [G221, 1a+(3c)]. This is just the desired highest-symmetry approximation of the root structure [G140, 4a+(4b+8h)]. Summing up, disregarding impossible transitions and possible but physically identical structures, we obtain the following diagram, see Fig. 2.

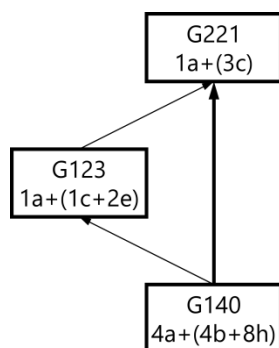


Figure 2. The concluding hierarchical tree for the [G140, 4a+(4b+8h)] structure type

The aristotype structure [G123, 1a+(1c+2e)] may either be intermediate one in the phase transition from the root structure to the archetype one or not be since there is a direct-path transition $G140 \rightarrow G221$. It depends on the "structural conditions" mentioned above and is lying outside the scope of this paper. Experimentally, not only crystals with both the root structure and archetype one have been observed (5 and more than 200, correspondingly) but also 14 crystals with such an "intermediate" structure are known.

As a similar example, we can discuss the hierarchical tree with the root structure [G204, 8c+(24g)] characteristic for 13 AX_3 crystals such as $CoAs_3$, NiP_3 , and so on. The group G204 has minimal supergroups G200 and G229, aristotype structures being [G200, 1b+(3c)] and [G229, 8c+(24h)], correspondingly, see left part of Fig. 3.

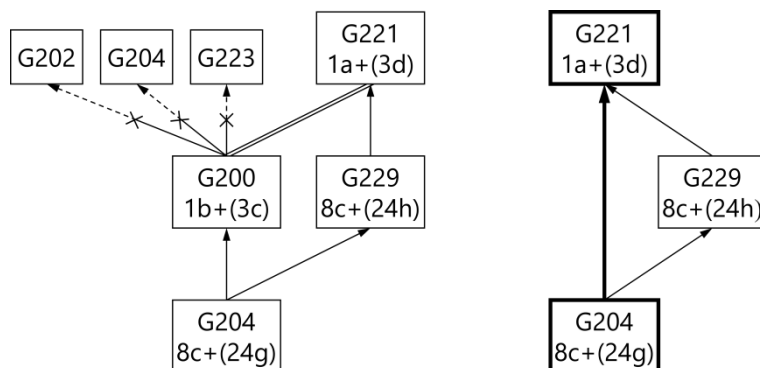


Figure 3. The hierarchical tree for the root [G204, 8c+(24g)] structure type, construction and result

At the next step of stepwise movement upward the hierarchical tree, it appears to be that the G229 group has a sole supergroup, namely G221 whereas the G200 one has four supergroups: G202, G204, G223, and the very same G221, although the correspondence between the Wyckoff positions can be established only in the latter case (the other three arrows are crossed in the figure).

Furthermore, the aristotype structure [G200, 1b+(3c)] is non-characteristic since it sets the same spatial distribution of atoms (their coordinates in a crystal) as the [G221, 1a+(3d)] archetype structure. In other words, the phase transition from the root [G204, 8c+(24g)] structure occurs not to [G200, 1b+(3c)] one but directly (without intermediate phases) to the archetype structure [G221, 1a+(3d)]. Noteworthy, the experiments have detected only the root and archetype structure, which is marked with the thick frames in right part of Fig. 3.

The hierarchical trees with multiple archetypes

The next root structure is a representative although laborious example, [G167, 6b+(18e)]. 12 crystals with such a structure are known, VF_3 , ScF_3 , and so on. There are eight minimal supergroups of the group G167, although only three of them meet the Wyckoff-position-compatibility condition, the corresponding structures are [G223, 2a+(6c)], [G226, 8b+(24c)], and [G166, 3a+(9d)]. The first of the three structures is archetype one, the second one is non-characteristic and its characteristic structure, namely the [G221, 1a+(3d)] one is also archetype structure for the third of the three intermediate structures. Graphically, it is illustrated with Fig. 4.

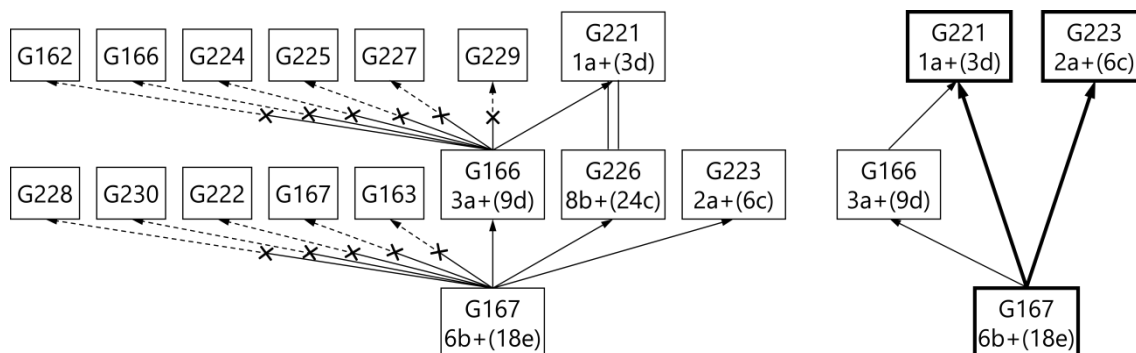


Figure 4. The hierarchical tree for the root [G167, 6b+(18e)] structure type, construction and result

The existence of the second archetype structure implies that there are two high-symmetry approximations of the initial crystal structure. Notably, experiments have detected about 70 crystals with the archetype [G223, 2a+(6c)] structure while only four with the [G221, 1a+(3d)] one. Certainly, "structural conditions" play very important role here. For a crystal with the hettotype structure [G167, 6b+(18e)], the tools of Bilbao Crystallographic Server (BCS. n.d.) are able to exclude those aristotype structures which request enormous change in the parameters of the lattice or Wyckoff Positions in the course of the phase transition, that is to say, the correct high-symmetry approximation can be chosen of the two in accordance with the lattice parameters (if known).

A similar subfamily of the AX_3 crystals has the root structure [G148, 6c+(18f)], about 40 crystals being known including FeCl_3 , BiI_3 , TiCl_3 , etc.. In this case, there are a lot of non-characteristic structures, e.g. [G200, 1a+(3c)], [G202, 8c+(24e)], [G225, 8c+(24e)], [G226, 8a+(24c)]. That is why we do not draw the complete diagram, joining those structures under the aegis of their characteristic structure [G221, 1a+(3c)]. Discarding some structures, which transitions are impossible in, and disregarding possible but physically identical structures, we obtain the following diagram in Fig. 5. Here are three archetype structures, although only just the [G221, 1a+(3c)] one having been experimentally observed.

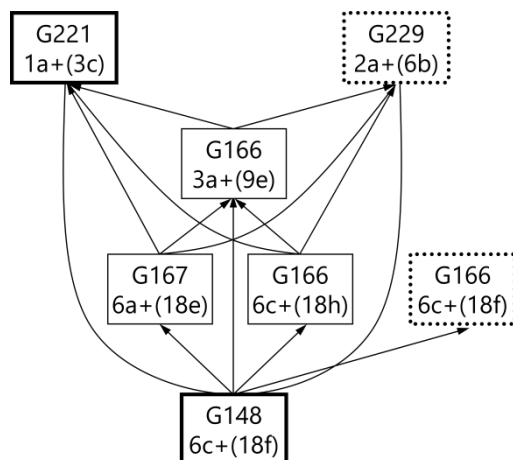


Figure 5. The hierarchical tree for the root [G148, 6c+(18f)] structure type

The "dead-end" structures

There appears a rather usual situation when side branches of the hierarchical tree, which formally include archetype structures, do not bear fruits. Here it is apparent that the lower is the symmetry of the root hettotype structure, the higher is the number of aristotype and dead-end structures.

As an example, we can consider the root structure [G59, $2a+(2b+4f)$] of the orthorhombic Ag_3Sb , Au_3Hf , Au_3In , Au_3Zr , Cu_3Ge , Cu_3Sb , Cu_3Sn , Cu_3Ti , MoNi_3 , NbNi_3 , NbPt_3 , Ni_3Sb , Ni_3Ta , Pt_3Ta . This structure is physically identical to the structures [G59, $2a+(2b+4e)$], [G59, $2b+(2a+4f)$], and [G59, $2b+(2a+4e)$]. However, only the alphabetically-second variant [G59, $2a+(2b+4f)$] can be found in the literature, what is the result of the adopted choice of the X and Y axes of real crystals.

There are seven minimal supergroups of the group G59, namely G51, G59 itself, G63, G65, G71, G129, and G137, although only two of them, G65 and G71, meet the Wyckoff-position-compatibility condition. For these two supergroups, there are huge amount of variants of atomic distributions over the Wyckoff positions, namely 32 in the case of the G65 group (they can be combined in four physically non-equivalent sets) and 72 in the case of the G71 group (two different sets). At the next steps, the number of supergroups drastically increases, although the majority of the "group/supergroup" transitions appear to be incompatible with the Wyckoff-position-compatibility condition. Finally, The hierarchical tree for the root [G59, $2a+(2b+4f)$] structure type looks as is shown in Fig. 6.

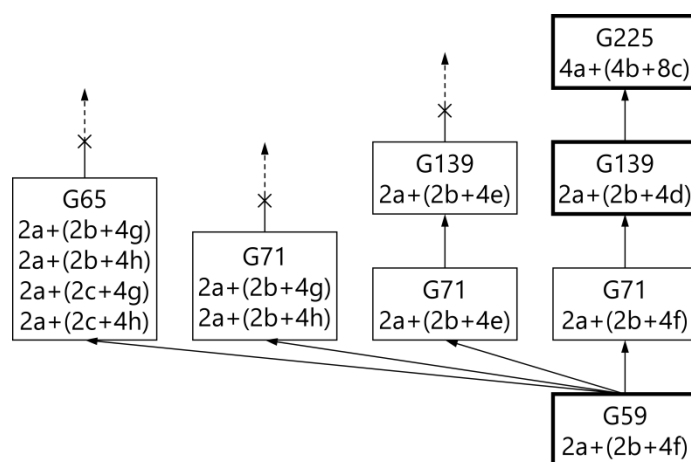


Figure. 6. The hierarchical tree for the root [G59, $2a+(2b+4f)$] structure type

It is worth to note that real crystals have been found only for the structures marked with bold frames in this figure, namely 14 above mentioned orthorhombic crystals, 16 tetragonal crystals with the structure [G139, $2a+(2b+4d)$], and about 40 cubic crystals with the structure [G225, $2a+(2b+4c)$]. The discussion of this phenomenon lies outside the scope of this paper.

The situation is even more complicated when the atoms in a crystal occupy the general (lowest-symmetry) Wyckoff positions only. For instance, 27 crystals have the Ni_3P structure [G82, $8g+(8g+8g+8g)$]. Here, the hierarchical-trees method is applicable merely formally and extremely laborious. For example, there is the necessity to consider about fifty only allowed and only non-equivalent structures and only at first step (seven of 8 supergroups should be considered), and the number of steps is four. The number of chains e.g. G82 - G - G - G - G221 is equal to 73, and there are 1400 variants of transformations with index 48 only. It is obvious that unambiguous determination of the archetype of a real crystal is questionable.

The last AX_3 crystal subfamily which we discuss here includes 30 compounds such as Be_3Nb , BaPb_3 , and so on, the root structure [G166, $(3a+6c)+(3b+6c+18h)$]. Although there are only two archetypes for this hettotype structure, they have similarly unusual form, namely [G225, $(4a+8c)+(4b+8c+24e)$] and [G225, $(4a+8c)+(4b+32f)$] with a lot of Wyckoff positions occupied. No crystal of such a kind (not speaking of exact coincidence) is known. Taking into account that, historically, there were a lot of examples when actually simple crystals had been described as complex multipositional structures but after elaboration the number of occupied Wyckoff

positions was drastically reduced, one can not but take into account the possibility of inaccuracy of the structure determination.

Conclusion

We have analyzed crystals of the AX_3 family and determined high-symmetry approximations for its subfamilies. Despite large number of the AX_3 crystals (about five hundred), the number of the cubic high-symmetry types (archetypes) appears to be restricted to four only, namely [G225, $4a+(4b+8c)$], [G223, $2a+(6c)$], [G221, $1a+(3d)$], and [G221, $1a+(3c)$]. The discussed structure types are grouped in fig. 7, the number of crystals of each type being also indicated below Wyckoff positions.

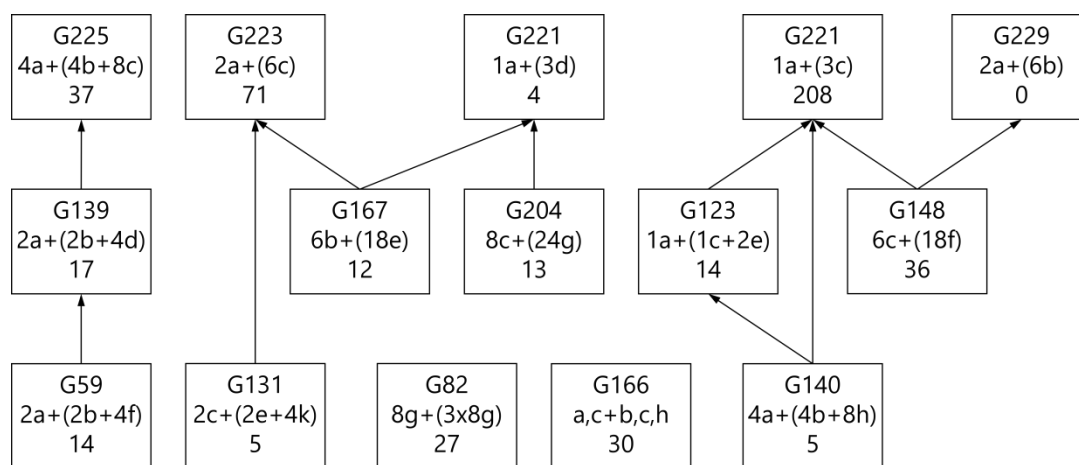


Figure 7. The retrieved high-symmetry structure types of the AX_3 family

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