The REME Phases

II. What's Possible?

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Dedicated to Professor *Jack D. Dunitz*, who likes the choices that structure offers us – here are some for him!

In the second contribution on the REME phases, we enumerate the distinct networks resulting from the stacking in an eclipsed fashion of graphitic and puckered layers. Specifically, we derive all the distinct hypothetical lattices for up to $N = 7$ layers per unit cell for planar (graphitic) sheets, and up to $N = 10$ for slightly puckered layers. For the networks with slightly puckered layers, there can be only an even number of layers/unit cell, N. Additionally, we formulate an empirical rule for network stability: the structure should have either a mirror plane or a twin operation (mirror plane, followed by a color change) bisecting it half-way up the stacking axis. Using these simple principles, from the original multitude of 2^{N-1} structures for a given N, we are able to significantly narrow down the number of potential combinations. Thus, for $N = 2$, we find two nets, for $N = 4$, one, for $N = 6$, two, for $N = 8$, there are no such viable arrangements, and for $N = 10$, we exclude all but two distinct lattices. We sketch further guidelines to continue the enumeration for higher Ns. We also propose an 'overlapping' *Aufbau*, by which more-complex structures are derived from the smaller, basic ones. In the last part, we analyze the eclipsed stacking of diamond-type layers; the resulting networks are analogous (in sequencing) to those determined for slightly puckered sheets. The networks formed from staggered diamond-type layers are briefly discussed in the context of the related SiC polytypes.

1. Introduction. – The previous paper in this series introduced the structural richness of these compounds. Here, we ask the question: given that many exquisitely complex structures are known, do the ones identified so far cover the entire range of potential isomers?

In REME compounds, the RE sublattice interacts with the rest of the framework in primarily an ionic way. In thinking about the bonding, we then concentrate on the remaining anionic part, $[ME]^{n-}$, where n is the formal oxidation state of RE. As we have seen, these remnant $[ME]^{n-}$ assemblies are constructed from 2-D slabs. They are then arranged (physically connected by bonds) along the third axis in various patterns. We are concerned with the full range of lattices or graphs (be them hypothetical or real) emerging from this family. In subsequent papers, we will explore the electronics and relative energetics of the potential structures.

The building blocks are three types of slabs, present in the phases already known:

a) Planar, graphitic layers (hexagonal, h-REME), where atoms are three-connected, and there are only M−E bonds (see **1**). These sheets are arranged eclipsed with respect to each other.
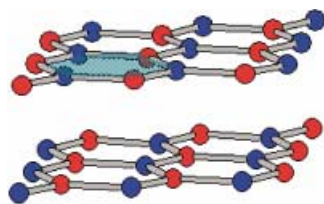
1

b) Slightly puckered layers, in which three *adjacent* atoms of a hexagon go 'up' with respect to a median plane, and are able to form three bonds with a layer above, while three other atoms go 'down', potentially generating three bonds with the layer beneath. The pattern is shown schematically in a structure detail, in **2**. In the multitude of known structures of this type, the dihedral angle within the hexagon shown below in green varies from 8° to 27°, with typical values grouped roughly in three intervals: (8° – 12°), (16° – 18°), and (24° – 27°). The last is characteristic for those networks with only two layers per unit cell and alternating M−E bonds; the first two are found only when M−M and E−E bonds are present in the structure. These layers are present in the prototypical TiNiSi structure, or the more-complex EuAuSn, described in the previous paper. The $[ME]^{n-}$ sublattices are then, in principle, four-connected nets with M−E intralayer bonds, and M−E or M−M and E−E interlayer contacts. They are in general orthorhombic (o-REMEs), and are stacked in an eclipsed way.
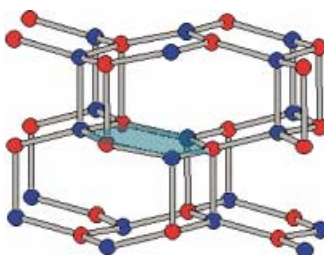
2

c) Puckered layers with still greater distortions (close to classical 'chair' hexagons) which, when stacked, form diamond-type structures by linking three *alternate* atoms of the six-membered ring upward, and the other three downward. The choices are either simple diamond, **3** (forgetting for the moment the M, E difference), with staggered chair-conformation hexagons along the stacking direction, or hexagonal diamond, **4**, forming eclipsed boat-hexagons along the same axis. The dihedral angle within the hexagon, shown below in green, varies from 40° to 45°, when the lattice is of wurtzite type, and is *ca.* 60° for those with blende-type arrangements. This is the series that includes the cubic, c-REMEs. In both of these cases, there are exclusively M−E bonds (when M and E are distinct).

3   **4**
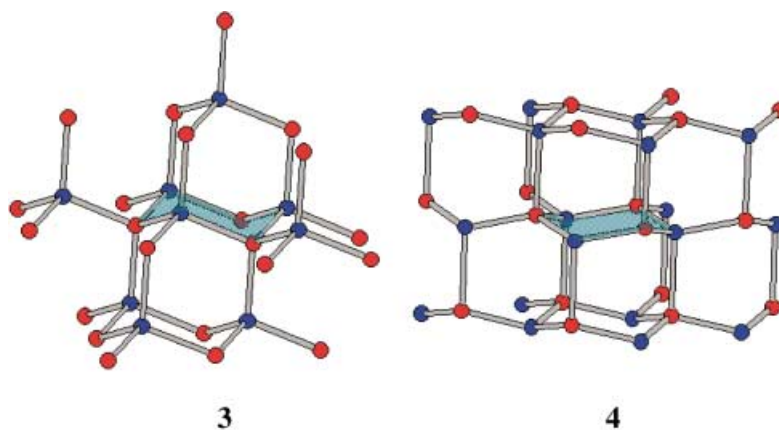
Whereas, for planar or diamond-like layers, coloring choices occur in binary compounds, such as AlB_2 (flat sheets), or ZnS – blende or wurtzite (diamond-type slabs), the particular coloring of the *b* type, found in slightly puckered layered structures is special for the ternary REME phases.

Let us explore the possible unit cells by examining in turn the structures arising from these various building blocks.

General Constraints. – The fundamental ideas used in constructing these frameworks are based on the coloring principles embedded in graph theory. In this part, the 'networks' are assumed to be just graphs, and wherever M and E are specified, we imply only two different (distinct) atomic points. These representations (graphs) do not contain any metric (or a minimal one, like puckering – really an angular metric), nor carry any electronic connotation. For this reason, we will not discuss (at the outset) any bond distances or angles.

Mathematically, the problem at hand is: having $i\mathbf{A}$ and $j\mathbf{B}$ layers, such that $i + j = N$ (N is the total number of layers in the unit cell), how many *distinct* networks are formed from the superposition of such slabs? Each layer is two-dimensional and formed from hexagons with M–E contacts only. For the planar and slightly puckered layers (the REME structures), we will further impose a restriction to the eclipsing of slabs (as they are stacked), motivated by the observed structures. In the diamond-like puckered layered arrangements, we will discuss both eclipsed and staggered situations.

We assume that the distance between layers is irrelevant (or equal), since we treat this question, to begin with, as *a graphical enumeration problem*. The starting maximum number of such arrangements (or permutations) for all the above-considered series is 2^{N-1}, but, as we will see, the real number of choices will be diminished upon adding further conditions.

Planar Layers. – In this case, the building blocks are two slabs of ME stoichiometry, which we call **A** and **B**, shown in *Fig. 1*. These are derived from an uncolored graphitic two-dimensional array. The relationship between **A** and **B** is that, by exchanging M and E positions in **A**, one obtains **B**. These two layers are equivalent, *when there is only one*
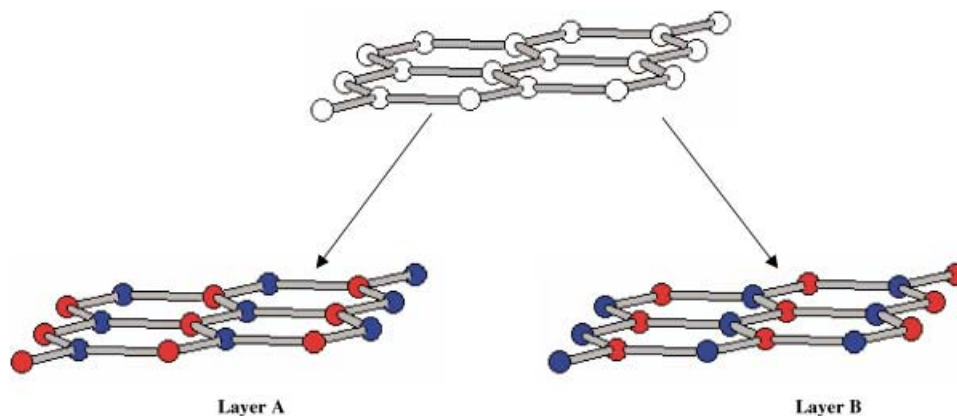
Fig. 1. *Types of planar layers and their derivation*

layer per unit cell. A distinction between them is needed to study the real lattices shaped by the superposition of more layers, for the stacking may make them nonequivalent.

We proceed with a discussion of the $N = 1, 2, 3$ cases, and then give the summary results for some higher N values.

a) For $N = 1$, there is, of course, a single network containing only **A**'s (or **B**'s). We will denote it as $(\mathbf{A})\mathbf{A}\ldots$, where the repeat group is placed in parentheses. The stacking in our drawings is 'vertical' (along y), but it is easier to express it in writing in horizontal, 'linear' fashion. $(\mathbf{B})\mathbf{B}\ldots$ is *identical* to the net specified, and related to $(\mathbf{A})\mathbf{A}\ldots$ by a translation or rotation of the whole three-dimensional lattice.

b) For $N = 2$, there is just a unique distinct network: $(\mathbf{AB})\mathbf{AB}\ldots \equiv (\mathbf{BA})\mathbf{BA}\ldots$; $(\mathbf{AA})\mathbf{AA}\ldots$ is identical to $(\mathbf{A})\mathbf{A}\ldots$ (assuming equal spacing; 'pairing distortions' would introduce a distinction), and the same is true for $(\mathbf{BB})\mathbf{BB}\ldots$, reducible to $(\mathbf{B})\mathbf{B}\ldots$ In general, this last consideration eliminates all the cases where $i = N$ and $j = 0$, or $j = 0$ and $i = N$. Layers **A** and **B** are not distinct if isolated, but are related by a symmetry operation, as noted above – a translation in the xz plane, or a rotation by $30°$ (rotation axis perpendicular to the center of the hexagon). When the slabs are stacked, the **A/B** distinction comes to the fore.

c) For $N = 3$, $i = 2$ and $j = 1$, there is a single selection, $(\mathbf{AAB})\mathbf{AAB}\ldots$, identical (given our assumptions of equidistant stacking) to $(\mathbf{ABA})\mathbf{ABA}\ldots$ This is also equivalent to $(\mathbf{BAA})\mathbf{BAA}\ldots$

In general, a total exchange between **A**'s and **B**'s is a 'symmetry operation' of these lattices.

For $i = 1$ and $j = 2$, $(\mathbf{BBA})\mathbf{BBA}\ldots \equiv (\mathbf{BAB})\mathbf{BAB}\ldots$ In $(\mathbf{BBA})\mathbf{BBA}\ldots$, when one exchanges **A** for **B**, $(\mathbf{AAB})\mathbf{AAB}\ldots$ is obtained, but we have already counted this system. Hence, $(\mathbf{BBA})\mathbf{BBA}\ldots \equiv (\mathbf{BAB})\mathbf{BAB}\ldots \equiv (\mathbf{AAB})\mathbf{AAB}\ldots \equiv (\mathbf{ABA})\mathbf{ABA}\ldots$ are not distinct. Thus, for $N = 3$, there is only one distinct network, $(\mathbf{AAB})\mathbf{AAB}\ldots$

We summarize in *Table 1* the resulting distinct possibilities for $N = 1 – 7$. The symmetries of the system greatly reduce the number of possibilities. Sometimes they are subtle. Thus, at first sight, for $N = 6$, $(\mathbf{AABABB})\ldots$ might appear to differ from $(\mathbf{AABBAB})\ldots$ But a two-fold rotation around an axis perpendicular to propagation

Table 1. *The Number of Distinct Networks Generated by Stacking Planar Layers*

N (No. of layers per unit cell)	Possible networks	No. of distinct theoretical networks
1	(**A**)**A**... ≡ (**B**)**B**...	1
2	(**AB**)**AB**...	1
3	(**AAB**)**AAB**...	1
4	(**AAAB**)**AAAB**... (**AABB**)**AABB**...	2
5	(**AAAAB**)**AAAAB**... (**AAABB**)**AAABB**... (**AABAB**)**AABAB**...	3
6	(**AAAAAB**)**AAAAAB**... (**AAAABB**)**AAAABB**... (**AAABAB**)**AAABAB**... (**AAABBB**)**AAABBB**... (**AABBAB**)**AABBAB**...	5
7	(**AAAAAAB**)**AAAAAAB**... (**AAAAABB**)**AAAAABB**... (**AAAABAB**)**AAAABAB**... (**AAABAAB**)**AAABAAB**... (**AAAABBB**)**AAAABBB**... (**AAABABB**)**AAABABB**... (**AABAABB**)**AABAABB**... (**AABABAB**)**AABABAB**...	8

line, at the asterisk in (**AABABB**)**AA*BABB**... converts it to ...**BBAB*AABBA-BAA**..., which is (**AABBAB**)...

It is evident that the number of possible arrangements (polytypes) is much smaller than 2^{N-1}. The problem at hand, the enumeration of all the distinct unit cells, has been solved by *Balaban* and *Artemi* [1], and, subsequently, by *Kaspi* [2]. All compounds characterized so far have only $N = 1$ or 2 layers per unit cell.

Slightly Puckered REME Slabs. – The ground rule (a mild metric) in this case is that [ME]$^{n-}$ nets are formed from puckered layers, with three atoms going up and three going down, stacked in an eclipsed way as described earlier in the paper. The stacking can lead to M−E connections only, or an assortment of M−E, M−M, and E−E bonds between layers, as we described in some detail in the first paper in this series. From the graphic theoretical perspective, we are not yet concerned whether M−M interlayer bonds are actually formed; E−E and M−M merely represent two edges of a rectangle (belonging to a ladder fragment). The type of chemical bond formed between layers is going to be the subject of our attention in a subsequent paper. In *Fig. 2* are illustrated the major fragments of this architecture. We have chosen this rather complicated six-layered structure in order to unambiguously illustrate the occurrence of a number of different such building blocks. Note the four-, six-, and eight-membered rings, and the distinctive 'ladders' of four-membered rings.
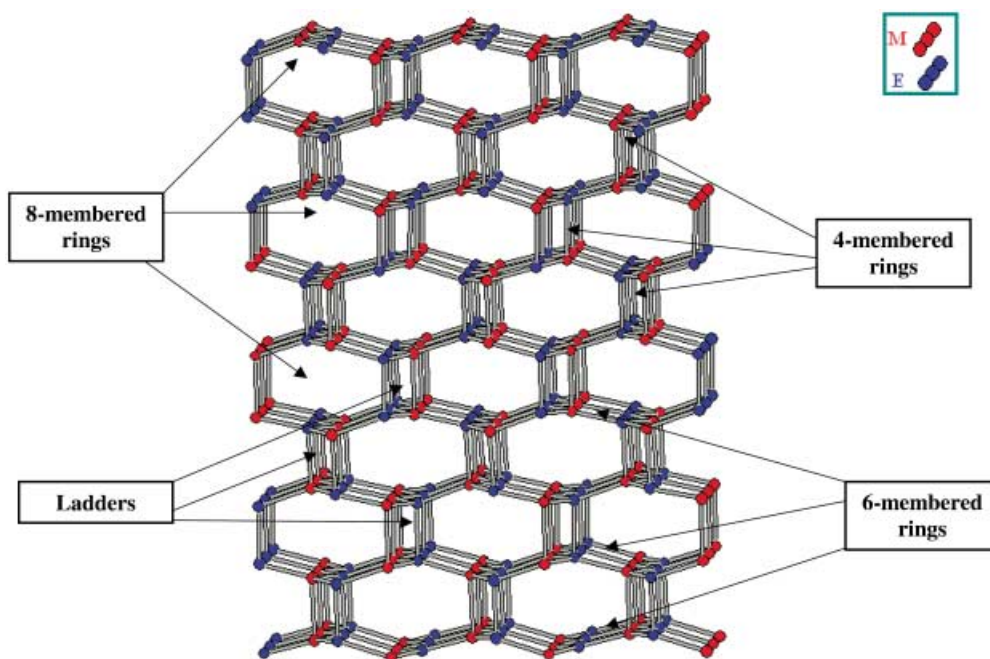
Fig. 2. *Fundamental building blocks of RE M E compounds*

Next, we begin a general analysis of the possible stacking modes. At the left side of *Fig. 3*, there are two distinct (with respect to stacking) layers, still uncolored. The obvious relation between **a** and **b** is that they are 'mirror' images of each other. Alternatively, **a** translated by $1/2(x+z)$ (if the stacking direction is y) gives **b**.
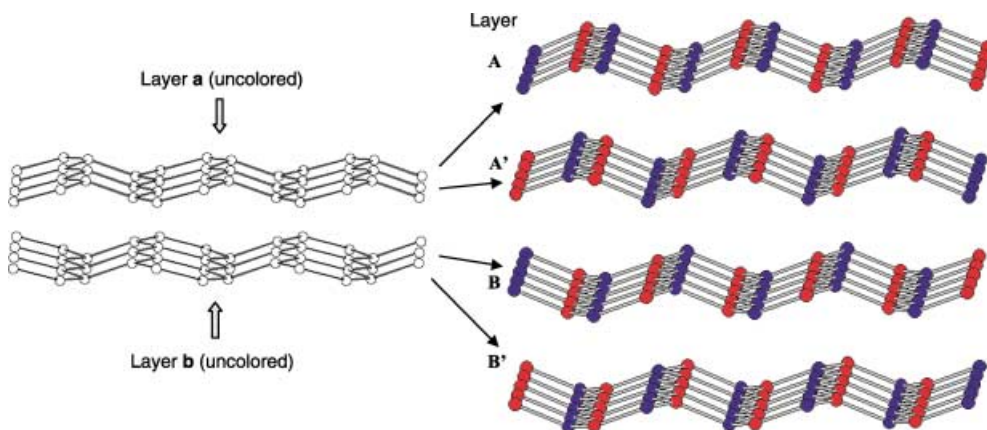

Fig. 3. *Types of slightly puckered layers*

When one restricts oneself (as we do) to exclusively M−E bonds, there are just two ways to place into **a** the two atoms M and E. In this fashion arise the two distinct layers, **A** and **A′**, parallel to each other, with the 'colors' (M, E) switched. Similarly, from **b** are formed **B** and **B′**, linked through a similar color correlation. Since **A** and **A′** have the same origin, they would be identical if they were isolated single layers. However, they are distinct when further layers are added to the unit cell.

We now apply a necessary metrical constraint. Two parallel layers, such as **A** and **A′** (and, respectively, **B** and **B′**), cannot be stacked on top of each other. If they were, they would then generate (were they to approach a bonding distance) only four-membered rings along the stacking direction, instead of four- and eight-membered cycles, the characteristic feature of the o-REME-type compounds, as discussed above[1]). Therefore, **A** (or **A′**) can sit only on top or beneath **B** or **B′**; **B** (or **B′**) can be 'connected' only to **A** or **A′**.

Bond Notations. – As noted in the first paper in this series, there are alternative and complementary descriptions of the REME structures in terms of interlayer bonds (**A** = **a**lternating or heteroatomic, M−E; **H** = **h**omoatomic, M−M and E−E) or layers (**A**, **B** *etc.*). Both notations prove worthwhile; the layer notation makes the connection with the traditional **ABC** layering notation, whereas the bonding notation facilitates the visualization of the particularities of the stacking sequences. For example, the succession **AB** generates **H1** bonds, from **BA** results **H1′**, and so on. All the correlations are shown below in the *Scheme* and detailed in *Fig. 4*.

Scheme. *The Relationship between Bond Types and Layers*
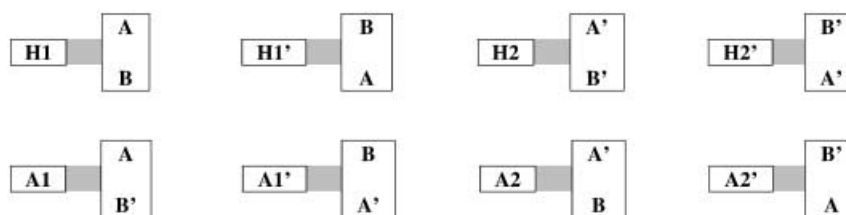
The major symmetry relations between layers are, as they should be, reflected in the bond notations. Therefore, an **H1** bond is linked to **H1′** through a translation by $1/2(x + z)$, as one A is related to B. **H1** is related to **H2** by a color change, as A is correlated to A′. The same reasoning applies to the alternating bonds (**A1**, **A1′**, **A2**, **A2′**).

The utility of this notation – seemingly complex at this point – will become apparent shortly. It turns out to be an effective and convenient way to highlight the fundamental units of o-REME assemblies.

Back to generating the lattices, there is a neat way to illustrate graphically the viable interlayer connections, namely that an **A**, **A′** layer may associate with **B** or **B′** exclusively, and **B**, **B′** with **A** or **A′** only. This is presented in *Fig. 5*. All possible unit cells

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[1]) Such four-membered rings occur in the interesting $CaAl_2Si_2$ structure and its derivatives, but are not the subject of our discussion here, considering that many fewer (less than 4%) members of the REME type adopt this arrangement.
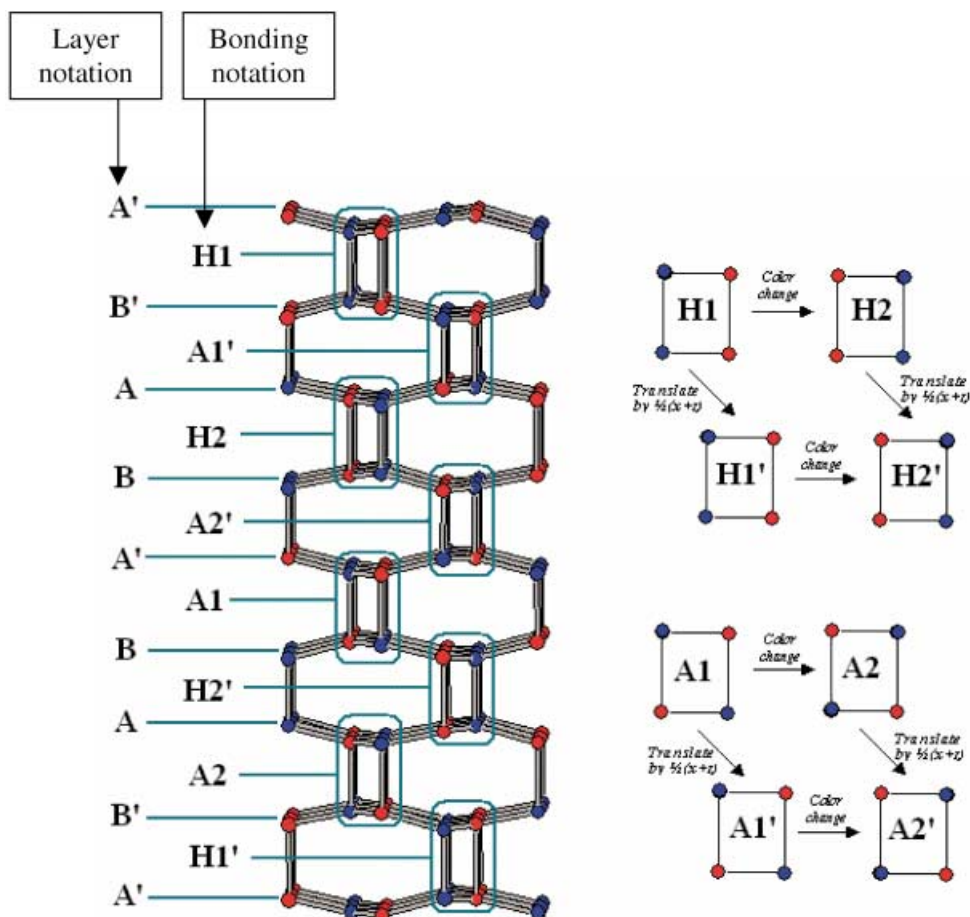
Fig. 4. *Layer* (most left) *and bonding notations.* On the right hand side are shown the only possible four-membered rings and the symmetry operations relating them.

(for a given N) are distinct descending paths in this pattern. They start from A in layer 1, and return to A in the $(N+1)$th layer below. *We chose to start all enumerations with* **A**, *but one could have as well begun with* **A′**, **B**, *or* **B′**, *and obtained the same set of structures.*

One conclusion follows immediately: there cannot exist any unit cell with an odd N. In this construction, A occurs only in every second row; thus, it takes an even number of steps to go from one **A** to another **A**.

With the help of *Fig. 5*, we are ready to enumerate the possible distinct networks or unit cells.

Using the obvious rules for layers, graphically made explicit in *Fig. 5*, one obtains for:

a) $N=2$, two possible networks:

Fig. 5. *The possible routes for connecting slightly puckered layers are those descending along diagonals in this graph* (a few diagonals are emphasized in green), *starting with an A layer for* n = 1.

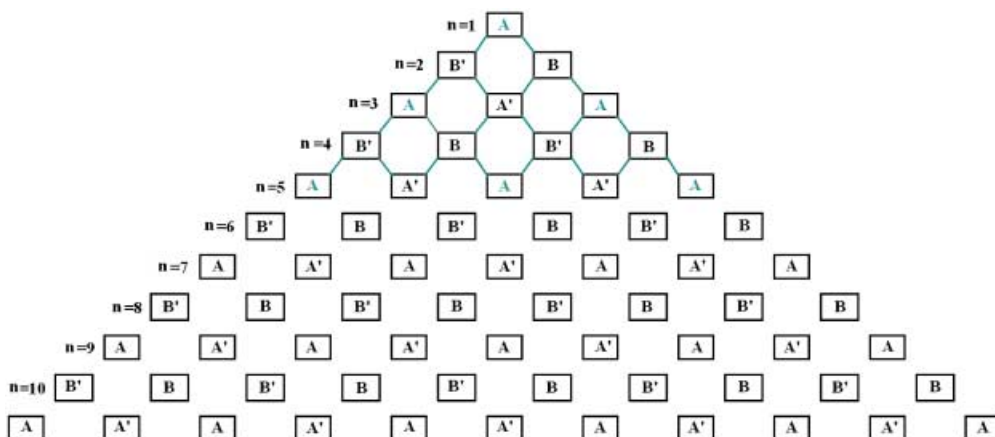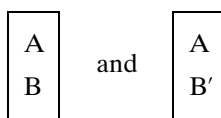Or to put it into a 'horizontal' format: (**AB**)**AB**... and (**AB′**)**AB′**... The notation is an obvious derivative of that used for planar hexagonal layers. Both of these structures are realized and are shown in *Fig. 6*. Note that one contains **H** bonds only (**2-1**), and the other **A** type bonds (**2-2**).

In *Table 2*, we have given a so called 'contracted bond notation', which means that one sums up all the blocks from the bond notations, for example a **H1 H1′** fragment is equivalent to a 2 **H1** block, and **H2 H2′** is a 2 **H2**, and an **A1A2′** is a 2**A**(**12′**). Therefore, in this notation, recurring **H1**, **H2**, or **A** groups will be 'packed' together. The numbers in parentheses for **A**'s depict the original order of the **A** units.

b) $N = 4$, the algorithmic pattern of *Fig. 5* generates the eight combinations ('walks' from an **A** in the first row of *Fig. 5* to any of the **A**'s in the fifth row, highlighted in green). We exclude those combinations that can be reduced to a lower ($N = 2$, in this

Table 2. *Possible Networks for* N = 2

N-Serial No.[a])	Layering notation	Bond notation	Contracted bond notation[b])	Observed[c]) (reference)
2-1	**A**	**H1**	(**H1**) + (**H1′**) |^{mirror plane}	✓[3]
	B	**H1′**		
2-2	**A**	**A1**	(**A1**) + (**A2′**) |^{twin operation}	✓[4]
	B′	**A2′**		

[a]) The notation we use is *N*-serial number; thus, for instance, **2-2** is the second arrangement for $N = 2$ layers per unit cell. [b]) Notation is explained in text. [c]) A check mark (✓) indicates that the structure has been observed. The literature reference is given. If the structure does not exist, then we indicate the possible reason for its absence.
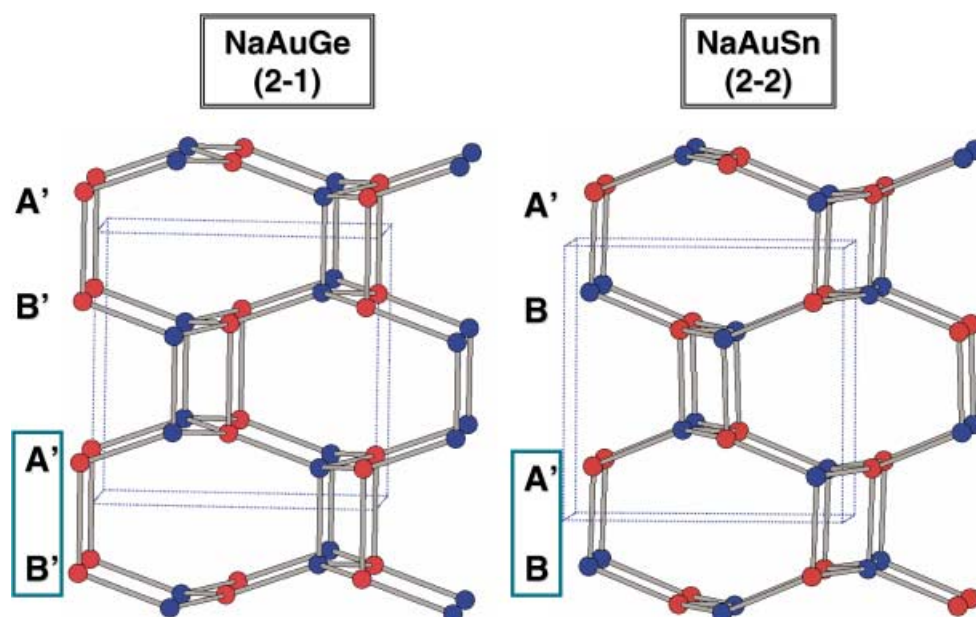
Fig. 6. *Observed networks for* N = 2; *typical compounds are NaAuGe* (**2-1**) *at left, and NaAuSn* (**2-2**) *at right*

case) number of layers/cell, or those that repeat themselves. This criterion eliminates lattices such as (**ABAB**)**ABAB**... ≡ (**AB**)**AB**..., and (**AB′AB′**)**AB′AB′**... ≡ (**A-B′**)**AB′**... Besides, sequences such as (**ABAB′**)**ABAB′**... or (**AB′AB**)**AB′AB**... are identical. There remain only two distinct arrangements, as listed in *Table 3*; the structure of the one choice realized so far is given in *Fig. 7*.

c) For *N* = 6, we found six distinct arrangements listed in *Table 4*.

d) When *N* = 8, there are 16 prospective networks, according the assumptions we made previously, listed in *Table 5*.

e) For *N* = 10, there are 53 different structures conforming to the rules set out in text.

The only arrays (graphs) found among the compounds observed to date (to our knowledge) are in fact just a few (7), summarized in *Table 7*. We have shown them using both layer and bond notation. The 'contracted' bonding notation lists the major

Table 3. *Possible Networks for* N = 4

N-Serial No.	Layering notation	Bond notation	Contracted bond notation	Observed [reference]
4-1	**A**	**H1**	(**H1** + **A1′**) + (**H2** + **A2′**) |[twin operation]	✓[5]
	B	**A1′**		
	A′	**H2**		
	B′	**A2′**		
4-2	**A**	**H1**	**H1** + **H1′** + **A1** + **A2′** = 2 **H1** + 2 **A(12′)**	No sym.
	B	**H1′**		
	A	**A1**		
	B′	**A2′**		
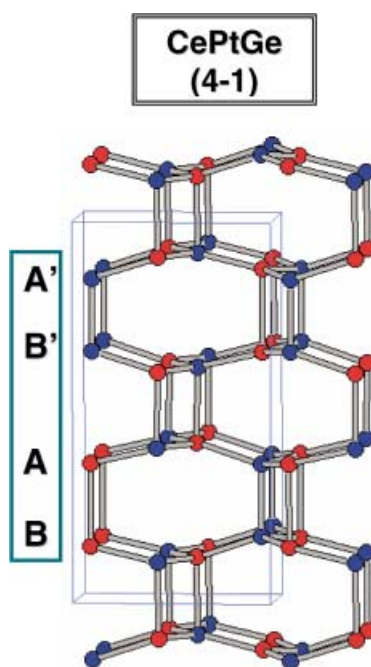
Fig. 7. *The one network observed for* N = *4; one realization is CePtGe* (**4-1**)

blocks: **H1**, **H2**, and **A**'s all added together. The reason for this bonding notation will soon become clear.

Further Constraints on REME Lattices: An Empirical Rule. – Quite empirically, we find that seven observed (out of 79 total for $N \leq 10$) arrangements are selected by the following two rules.

a) There are *no blocks with more than two units alike* (no more than 2 **H1** = **H1 H1′**, 2 **H2** = **H2 H2′**, or 2 **A**'s of any kind = **A1A2′**, or **A2A1′**).

b) At $N/2$, there must be either a mirror plane or the twin operation: mirroring, followed by a color change. The mirror plane is illustrated in *Fig. 8*, on the left side, and the twin operation is at its right. A mirror plane, as was discussed above, is equivalent to a translation by half of a unit cell in the $1/2(x + z)$ direction. The color change could also be seen as either a rotation by 180°, if the rotation vector is set to be perpendicular to any bond, or simpler, by interchanging the two colors. The permutational consequences of mirroring and color change were given earlier; they are summarized in compact form in *Fig. 9*.

The immediate consequence of this last condition is that the viable networks must contain in the same lattice at least one **H1** or one **H2** (primed or not) units (it seems that it is not necessary to have both blocks; one appears to suffice). This conclusion is easily deduced when one looks at *Fig. 9*. Essentially, it means that applying a mirror operation to layer **A**, one obtains **B**; hence, the resulting (**AB**)... sequence contains the required **H1** bond. If instead, a twin operation is applied to **A**, then **B′** follows. This

Table 4. *Possible Networks for* N = 6

N-Serial No.	Layering notation	Bond notation	Contracted bond notation	Observed [reference]
6-1	A	H1	2**H1** + 2**A**(**12**) + 2**H1**	No sym.
	B	H1′		
	A	A1		
	B′	A2′		
	A	H1		
	B	H1′		
6-2	A	H1	2 **H1** + 4 **A**(**12′12′**)	4 A
	B	H1′		
	A	A1		
	B′	A2′		
	A	A1		
	B′	A2′		
6-3	A	H1	3 **H1** + **A1′** + **H2** + **A2′**	3 H1
	B	A1′		
	A′	H2		
	B′	A2′		
	A	H1		
	B	H1′		
6-4	A	H1	[**H1** + 2 **A**(**1′2**)] + [**H1** + 2 **A**(**12′**)] ∣ [mirror plane]	✓ [6]
	B	A1′		
	A′	A2		
	B	H1′		
	A	A1		
	B′	A2′		
6-5	A	H1	**H1** + **A1′** + **H2** + 3 **A**(**2′12′**)	3 A
	B	A1′		
	A′	H2		
	B′	A2′		
	A	A1		
	B′	A2′		
6-6	A	H1	(2 **H1** + **A1′**) + (2 **H2** + **A2**) ∣ [twin operation]	✓ [7]
	B	A1′		
	A′	H2		
	B′	H2′		
	A′	A2		
	B	H1′		

(**AB′**) . . . combination has an alternating (**A**) bond. If we go on using this unit (which doesn't have yet the desired **H** bond), and apply to it a mirror operation, the outcome is (**AB′A′B**) . . ., which has an **H2** block, or else, when twinning is the preferred operation, then (**AB′AB′**) . . . arises. This last progression is redundant to (**AB′**) . . ., hence, we can eliminate it. If one continues this rationalization, one is led to the necessity of having at least an **H** block (be it **H1** or **H2**). This last 'constraint' is, in fact, the logical consequence of having at least one of the two prerequisite symmetry operations in the unit cell.

Table 5. *Possible Networks for* N = 8

N-Serial No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Layering notation	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′
	B	B′	B	B	B′	B′	B′	B′	B′	B	B	B′	B′	B′	B′	B′
	A	A	A′	A	A′	A	A	A	A	A′	A′	A′	A′	A′	A	A
	B	B	B	B′	B	B′	B	B	B	B	B	B′	B	B	B′	B′
	A	A	A	A	A	A	A′	A	A	A′	A	A	A′	A	A	A
	B	B	B	B	B	B	B	B′	B	B	B′	B	B	B′	B′	B
	A	A	A	A	A	A	A	A	A′	A	A	A	A	A	A	A′
	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
Bond notation	A2	H2	A2	A2	H2	H2	H2	H2	H2	A2	A2	H2	H2	H2	H2	H2
	H1′	A2′	A1′	H1′	H2′	A2′	A2′	A2′	A2′	A1′	A1′	H2′	H2′	H2′	A2′	A2′
	H1	H1	A2	A1	A2	A1	H1	H1	H1	A2	A2	H2	A2	A2	A1	A1
	H1′	H1′	H1′	A2′	H1′	A2′	A1′	H1′	H1′	A1′	H1′	A2′	A1′	H1′	A2′	A2′
	H1	H1	H1	H1	H1	H1	A2	A1	H1	A2	A1	H1	A2	A1	A1	H1
	H1′	H1′	H1′	H1′	H1′	H1′	H1′	A2′	A1′	H1′	A2′	H1′	H1′	A2′	A2′	A1′
	H1	H1	H1	H1	H1	H1	H1	A2	H1	H1	H1	H1	H1	H1	H1	H1
	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′
Contracted bond notation	6 H1 + 2 A(12)	5 H1 + A1′ + H2 + A2′	4 H1 + 4 A(1′21′2)	3 H1 + 2 A(12) + H1 + 2 A(12′)	4 H1 + A1′ + 2 H2 + A2	3 H1 + A1′ + H2 + 3 A(2′12′)	2 H1 + A1′ + H2 + A2′ + H1 + 2 A(12)	2 H1 + 2 A(12′) + H1 + A1′ + H2 + A2′	3 H1 + 3 A(1′21′) + H2 + A2′	2 H1 + 6 A(121′21′2)	H1 + 2 A(12) + H1 + 4 A(1′21′2)	3 H1 + A1′ + 3 H2 + A2′	2 H1 + A1′ + 2 H2 + 3 A(21′2)	H1 + 2 A(12′) + H1 + A1′ + 2 H2 + A2	H1 + A1′ + H2 + 5 A(2′121′2)	H1 + A1′ + H1 + A1′ + H2 + 3 A(2′12′)
Obs. (ref.)	6 H1	5 H1	4 H1	3 H1	4 H1	3 H1	No sym.	No sym.	3 H1	6 A	4 A	3 H1	3 A	No sym.	5 A	3 A

Table 6. *Possible Networks for* N = *10*

N-Serial No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Layering notation	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′
	B	B′	B	B	B	B	B′	B′	B′	B′	B′	B′	B′	B	B	B	B	B
	A	A	A′	A	A	A	A′	A	A	A	A	A	A	A′	A′	A′	A′	A′
	B	B	B	B′	B	B	B	B′	B	B	B	B	B	B	B	B	B	B
	A	A	A	A	A′	A	A	A	A′	A	A	A	A	A′	A	A	A	A′
	B	B	B	B	B	B′	B	B	B	B′	B	B	B	B	B′	B	B	B
	A	A	A	A	A	A	A	A	A	A	A′	A	A	A	A	A′	A	A′
	B	B	B	B	B	B	B	B	B	B	B	B′	B	B	B	B	B′	B
	A	A	A	A	A	A	A	A	A	A	A	A	A′	A	A	A	A	A
	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
Bond notation	A2	H2	A2	A2	A2	A2	H2	H2	H2	H2	H2	H2	H2	A2	A2	A2	A2	A2
	H1′	A2′	A1′	H1′	H1′	H1′	H2′	A2′	A2′	A2′	A2′	A2′	A2′	A1′	A1′	A1′	A1′	H1′
	H1	H1	A2	A1	H1	H1	A2	A1	H1	H1	H1	H1	H1	A2	A2	A2	A2	A1
	H1′	H1′	H1′	A2′	A1′	H1′	H1′	A2′	A1′	H1′	H1′	H1′	H1′	A1′	H1′	H1′	H1′	A2′
	H1	H1	H1	H1	A2	A1	H1	H1	A2	A1	H1	H1	H1	A2	A1	H1	H1	H1
	H1′	H1′	H1′	H1′	H1′	A2′	H1′	H1′	H1′	A2′	A1′	H1′	H1′	H1′	A2′	A1′	H1′	A1′
	H1	H1	H1	H1	H1	H1	H1	H1	H1	H1	A2	A1	H1	H1	H1	A2	A1	A2
	H1′	H1′	H1′	H1′	H1′	H1′	H1′	H1′	H1′	H1′	H1′	A2′	A1′	H1′	H1′	H1′	A2′	H1′
	H1	H1	H1	H1	H1	H1	H1	H1	H1	H1	H1	A2	H1	H1	H1	H1	H1	H1
	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′
Contracted bond notation	8 H1 + 2 A(1′2)	7 H1 + A1′ + H2 + A2′	6 H1 + 4 A(1′2I′2)	5 H1 + 2 A(1′2) + H1 + 2 A(1′2)	4 H1 + 2 A(1′2) + 2 H1 + 2 A(1′2)	3 H1 + 2 A(1′2) + 3 H1 + 2 A(1′2)	6 H1 + A1′ + 2 H2 + A2	5 H1 + A1′ + H2 + 3 A(2′1′2)	4 H1 + A1′ + H2 + A2 + H1 + 2 A(1′2)	3 H1 + A1′ + H2 + A2 + 2 H1 + 2 A(1′2)	3 H1 + 2 A(1′2) + 2 H1 + A1′ + H2 + A2′	4 H1 + 2 A(1′2) + H1 + A1′ + H2 + A2′	5 H1 + 3 A(1′2I′) + H2 + A2′	4 H1 + 6 A(1′2I′2)	3 H1 + 4 A(1′2I′2) + H1 + 2 A(1′2)	2 H1 + 2 A(1′2) + 2 H1 + 4 A(1′2I′2)	3 H1 + 2 A(1′2) + H1 + 4 A(1′2I′2)	2 H1 + 2 A(1′2) + H1 + 2 A(1′2′)
Obs. (ref.)	8 H1	7 H1	6 H1	5 H1	4 H1	3 H1	6 H1	5 H1	4 H1	3 H1	3 H1	4 H1	5 H1	4 H1	3 H1	4 A	3 H1	No sym.

Table 6 (cont.)

N-Serial No.	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39
Layering notation	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′
	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B	B	B′
	A′	A′	A′	A′	A′	A′	A	A	A	A	A	A	A	A	A	A	A	A	A′	A′	A
	B′	B	B	B	B	B	B′	B	B′	B′	B′	B′	B	B	B	B	B	B	B	B	B
	A	A′	A	A	A	A	A′	A′	A	A	A	A	A′	A′	A′	A	A	A	A′	A′	A
	B	B	B′	B	B	B	B	B′	B′	B	B	B	B	B	B	B′	B′	B	B	B	B′
	A	A	A	A′	A	A	A	A	A	A′	A	A	A′	A	A	A	A	A′	A′	A	A′
	B	B	B	B	B′	B	B	B	B	B	B′	B	B	B′	B	B′	B	B	B	B′	B
	A	A	A	A	A	A′	A	A	A	A	A	A′	A	A	A′	A	A′	A′	A	A	A
	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B	B
Bond notation	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	A2	A2	H2
	H2′	H2′	H2′	H2′	H2′	H2′	A2′	A2′	A2′	A2′	A2′	A2′	A2′	A2′	A2′	A2′	A2′	A2′	A1′	A1′	A2′
	H2	A2	A2	A2	A2	A2	A1	H1	A1	A1	A1	A1	H1	H1	H1	H1	H1	H1	A2	A2	H1
	A2′	A1′	H1′	H1′	H1′	H1′	H2′	A1′	A2′	A2′	A2′	A2′	A1′	A1′	A1′	H1′	H1′	H1′	A1′	A1′	H1′
	H1	A2	A1	H1	H1	A2	H2	A1	H1	H1	H1	H1	A2	A2	A2	A1	A1	A1	H1	H1	H2
	H1′	H1′	A2′	A1′	H1′	H1′	A2′	A2′	A1′	H1′	H1′	A1′	H1′	A2′	A1′	A2′	A2′	A1′	A1′	A1′	H2′
	H1	H1	H1	A2	A1	H1	H1	H1	H1	A2	A1	H1	A2	A1	H1	A1	H1	A2	A2	A1	A2
	H1′	H1′	H1′	A2′	A1′	H1′	H1′	H1′	H1′	A2′	A1′	H1′	A2′	A1′	A1′	A2′	A1′	H1′	A2′	A1′	H1′
	H1	H1	H1	H1	H1	A2	H1	H1	H1	H1	H1	A2	H1	A2	H1	A2	H1	A2	H1	H1	H1
	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′
Contracted bond notation	5 H1 + A1′ + 3 H2 + A2′	4 H1 + A1′ + 2 H2 + 3 A(21′2)	3 H1 + A1′ + 2 H2 + A2 + H1 + 2 A(12′)	2 H1 + 2 A(12) + 2 H1 + A1′ + 2 H2 + A2	3 H1 + 2 A(12′) + H1 + A1′ + 2 H2 + A2	4 H1 + 3 A(1′21′2) + 2 H2 + A2	4 H1 + A1′ + H2 + A2′ + H2 + A2	3 H1 + A1′ + H2 + A2′ + H1 + A1′ + H2 + A2′	3 H1 + A1′ + H2 + 5 A(2′12′12′)	2 H1 + A1′ + H2 + 3 A(2′12′) + H1 + 2 A(12)	2 H1 + 2 A(12′) + H1 + A1′ + H2 + 3 A(2′12′)	3 H1 + 3 A(1′21′) + H2 + 3 A(2′12′)	2 H1 + A1′ + H2 + A2′ + H1 + 3 A(1′21′)	H1 + 2 A(12) + H1 + A1′ + H2 + 2 A(12′)	2 H1 + 3 A(1′21′) + H2 + A2′ + H1 + 2 A(12)	2 H1 + 4 A(12′12) + H1 + A1′ + H2 + A2′	2 H1 + 2 A(12′) + H1 + 3 A(1′21′) + H2 + A2′	3 H1 + 5 A(1′21′21′) + H2 + A2′	2 H1 + 8 A(1′21′21′2)	H1 + 2 A(12′) + H1 + 6 A(1′21′21′2)	(2 H1 + A1′ + H2 + A2′) + (2 H1 + A1 + H2 + A2) | mirror plane
Obs. (ref.)	5 H1	4 H1	3 H1	No sym.	3 H1	4 H1	4 H1	3 H1	3 H1	3 A	3 A	3 H1	3 A	No sym.	3 A	4 A	3 A	3 H1	8 A	6 A	✓ [8]

Table 6 (cont.)

N-Serial No.	40	41	42	43	44	45	46	47	48	49	50	51	52	53
Layering notation	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′	A′
	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B′	B
	A′	A′	A′	A′	A′	A′	A′	A′	A	A	A	A	A	A′
	B′	B′	B′	B	B	B	B	B	B′	B′	B	B	B′	B
	A′	A	A	A	A′	A′	A′	A	A′	A′	A′	A′	A	A′
	B	B′	B	B′	B	B	B	B′	B	B	B′	B	B	B
	A	A	A′	A′	A′	A	A	A	A′	A	A	A′	A′	A′
	B	B	B	B	B	B′	B	B′	B	B′	B′	B	B	B
	A	A	A	A	A	A	A′	A	A	A	A′	A′	A′	A′
	B	B	B	B	B	B	B	B	B	B	B	B	B	B
Bond notation	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	H2	A2
	H2′	H2′	H2′	H2′	H2′	H2′	H2′	H2′	A2′	A2′	A2′	A2′	A2′	A1′
	H2	H2	H2	A2	A2	A2	A2	A2	A1	A1	H1	H1	A1	A2
	H2′	A2′	A2′	H1′	A1′	A1′	A1′	H1′	H2′	H2′	A1′	A1′	A2′	A1′
	A2	A1	H1	A1	A2	A2	A2	A1	A2	A2	H2	A2	H1	A2
	H1′	A2′	A1′	H2′	A1′	H1′	H1′	A2′	A1′	H1′	A2′	A1′	A1′	A1′
	H1	H1	A2	A2	A2	A1	H1	A1	A2	A1	A1	A2	A2	A2
	H1′	H1′	H1′	H1′	H1′	A2′	A1′	A2′	H1′	A2′	A2′	A1′	A1′	A1′
	H1	H1	H1	H1	H1	H1	A2	H1	H1	H1	H1	A2	A2	A2
	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′	A1′
Contracted bond notation	4 H1 + A1′ + 4 H2 + A2	3 H1 + A1′ + 3 H2 + 3 A(2′2′)	2 H1 + A1′ + 3 H2 + A2′ + H1 + 2 A(1′2)	2 H1 + A1′ + 2 H2 + A2 + H1 + A1 + H2 + A2	2 H1 + A1′ + 2 H2 + 5 A(2′2′2)	H1 + 2 A(12′) + H1 + A1′ + 2 H2 + 3 A(2′2)	2 H1 + 3 A(1′21′) + 2 H2 + 3 A(2′2)	H1 + A1′ + 2 H2 + A2 + H1 + 4 A(12′2′)	2 H1 + A1′ + H2 + 2 A(2′1) + H2 + 3 A(2′12)	(H1 + 2 A(12′) + H1 + A1′) + (H2 + 2 A(2′1) + H2 + A2) |[twin operation]	H1 + A1′ + H2 + A2′ + H1 + A1′ + H2 + 3 A(2′12′)	H1 + 7 A(1′2′21′21′) + H2 + A2′	H1 + 5 A(1′21′21′) + H2 + 3 A(2′12′)	10 A(1′2′21′21′21′2)
Obs. (ref.)	4 H1	3 H1	3 H2	No sym.	5 A	3 A	3 A	4 A	3 A	✓ [7]	3 A	7 A	5 A	10 A

Table 7. *Existing Networks*

N-Serial No.	Layering notation		Bond notation		Contracted bond notation	Ref.
2-1	**A**		**H1**		$2\,\mathbf{H1} = (\mathbf{H1}) + (\mathbf{H1'})\,|^{\text{ mirror plane}}$	[3]
	B		**H1'**			
2-2	**A**		**A1**		$2\,\mathbf{A(12')} = (\mathbf{A1}) + (\mathbf{A2'})\,|^{\text{ twin operation}}$	[4]
	B'		**A2'**			
4-1	**A**		**H1**		$(\mathbf{H1} + \mathbf{A1'}) + (\mathbf{H2} + \mathbf{A2'})\,|^{\text{ twin operation}}$	[5]
	B		**A1'**			
	A'		**H2**			
	B'		**A2'**			
6-4	**A**		**H1**		$[\mathbf{H1} + 2\,\mathbf{A(1'2)}] + [\mathbf{H1} + 2\,\mathbf{A(12')}]\,|^{\text{ mirror plane}}$	[6]
	B		**A1'**			
	A'		**A2**			
	B		**H1'**			
	A		**A1**			
	B'		**A2'**			
6-6	**A**		**H1**		$(2\,\mathbf{H1} + \mathbf{A1'}) + (2\,\mathbf{H2} + \mathbf{A2})\,|^{\text{ twin operation}}$	[7]
	B		**A1'**			
	A'		**H2**			
	B'		**H2'**			
	A'		**A2**			
	B		**H1'**			

None for $N = 8$

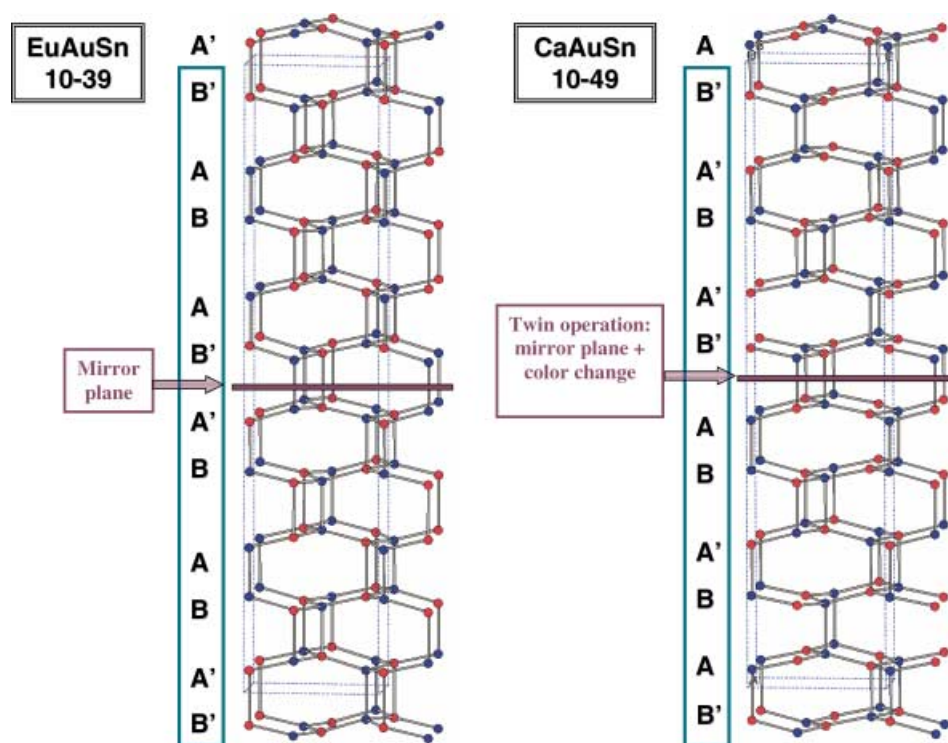| **10-39**	**A'**	**B'**	**H2**	**A1**	$(\mathbf{H2} + \mathbf{A2'} + 2\,\mathbf{H1} + \mathbf{A1}) + (\mathbf{H2'} + \mathbf{A2} + 2\,\mathbf{H1} + \mathbf{A1'})\,|^{\text{ mirror plane}} \equiv$	[8]
	B'	**A**	**A2'**	**H2'**	$(\mathbf{A1} + 2\,\mathbf{H2} + \mathbf{A2'} + \mathbf{H1}) + (\mathbf{A1'} + 2\,\mathbf{H2} + \mathbf{A2} + \mathbf{H1'})\,|^{\text{ mirror plane}}$	
	A	**B**	**H1**	**H2**		
	B	**A**	**H1'**	**A2'**		
	A $\equiv$	**B'**	**A1** $\equiv$	**H1**		
	B'	**A'**	**H2'**	**A1'**		
	A'	**B**	**A2**	**H2**		
	B	**A**	**H1'**	**H2'**		
	A	**B**	**H1**	**A2**		
	B	**A'**	**A1'**	**H1'**		
10-49	**A'**	**B'**	**H2**	**H1**	$[\mathbf{H2} + 2\,\mathbf{A(2'1)} + \mathbf{H2'} + \mathbf{A2}] + [\mathbf{H1'} + 2\,\mathbf{A(12')} + \mathbf{H1} + \mathbf{A1'}]\,|^{\text{ twin operation}}$	[7]
	B'	**A'**	**A2'**	**A1'**	$\equiv \mathbf{H1} + 2\,\mathbf{A(1'2)} + \mathbf{H1'} + \mathbf{A1}] + [\mathbf{H2'} + 2\,\mathbf{A(21')} + \mathbf{H2} + \mathbf{A2'}\,]\,|^{\text{ twin operation}}$	
	A	**B**	**A1**	**A2**		
	B'	**A'**	**H2'**	**H1'**		
	A' $\equiv$	**B'**	**A2** $\equiv$	**A1**		
	B	**A**	**H1'**	**H2'**		
	A	**B**	**A1**	**A2**		
	B'	**A'**	**A2'**	**A1'**		
	A	**B**	**H1**	**H2**		
	B	**A**	**A1'**	**A2'**		

Fig. 8. *Mirror plane and twin operations emphasized with the burgundy thick line*

In the last column in *Tables 2–6* ('Observed'), we put a check mark for those structures that are permitted by the above rules, or else note the 'disobeyed' empirical conventions, presumably leading to their nonexistence. By 'no sym.' we mean that there is no mirror plane or twinning operation at the middle of the unit cell, and by $n\mathbf{H1}$, $n\mathbf{H2}$, $n\mathbf{A}(..)$, we simply suggest that the first rule is violated, and there are more of the two consecutive blocks of the same kind in the sequence. Of course, we cannot be sure that every phase has been synthesized. However, it is quite remarkable, we submit, that two simple rules 'eliminate' all 16 combinations otherwise (without these two assumptions) possible for $N = 8$, and 51 of the 53 $N = 10$ arrangements.

Blocks and Twinning: Another View of What is Possible. – The empirical regularity points to viewing these assemblies from yet a different perspective. Thus, it appears that for $N = 6$ and $N = 10$, the networks could be 'decomposed' in two interesting ways: in the first, they may be conceived by simply linking basic units, or 'blocks', made up of two or four layers. The second construction principle involves overlaying, for example for $N = 6$ (**6-6**), of two blocks of $N = 4$ (**4-1**), but, in order to fulfill all the layer linkage constraints (no **B** can be stacked on top of **B**, or **A** over **A**), we must eliminate the repeating slabs. See *Figs. 10* ($N = 6$, structure **6-4**) and *11* ($N = 6$, structure **6-6**), where we present two possible decompositions for each of these networks. One is derived
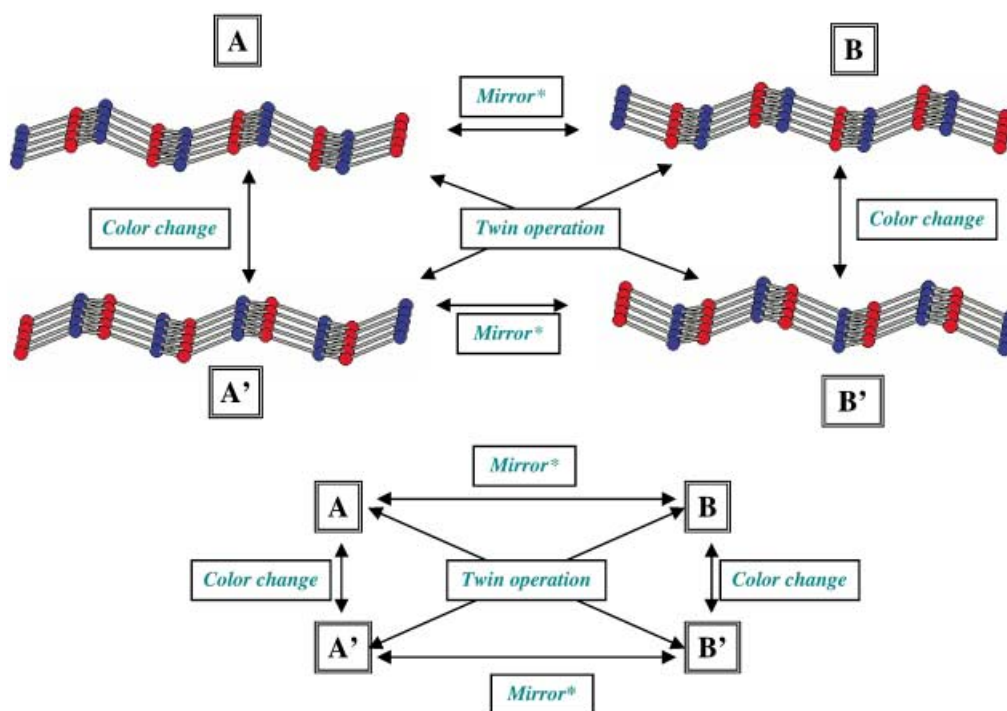
Fig. 9. *Mirror, color change, and twin operations that transform the layers* (A, A′, B, B′). Below is presented a scheme with these conversions. * Note that a mirror operation is equivalent to a translation along $1/2\,(x + z)$, if y is the stacking direction.

from the 'combination' of two existing **4-1** unit cells, which, as stipulated above, must skip the redundant layer at their ending points, where the layer would repeat. The same composition is possible if one uses instead two **4-2** networks, even though this lattice by itself is not a possibility (given that it has no mirror or twin operation within it). In *Figs. 12* ($N = 10$, **10-39** and **10-49**) and *13*, we give the breakdown into **6-4** and **6-6** cells for the two distinct and existing cases of $N = 10$. It is impressive that these networks could be seen as being entirely built up from the basic ones, **2-1**, **2-2**, and **4-1**. Or, from a different perspective, that they could be constructed from the 'preceding' network in the series of real compounds (see *Table 7*).

More generally, it appears that, for a sufficiently large N (greater than 6), a REME lattice could be derived from two $(N/2 + 1)$ lattices, in which the top and middle repeated layers are considered just once.

Following this algorithm, one could deduce the next viable network, not yet discovered. This is one having $N = 12$ layers/unit cell, which should formally come from two $N = 7$ layered structures. Or, following a different approach, by starting from a viable $N = 6$ unit cell and then applying either a mirror or a twin operation to it. The first scheme is impossible, because there is no self-standing network with an odd number of atoms. We are left with the second *Aufbau* for these assemblies. If we start from **6-4** (**AB′ABA′B**)... and apply the mirror operation, we then get (**AB′ABA′**
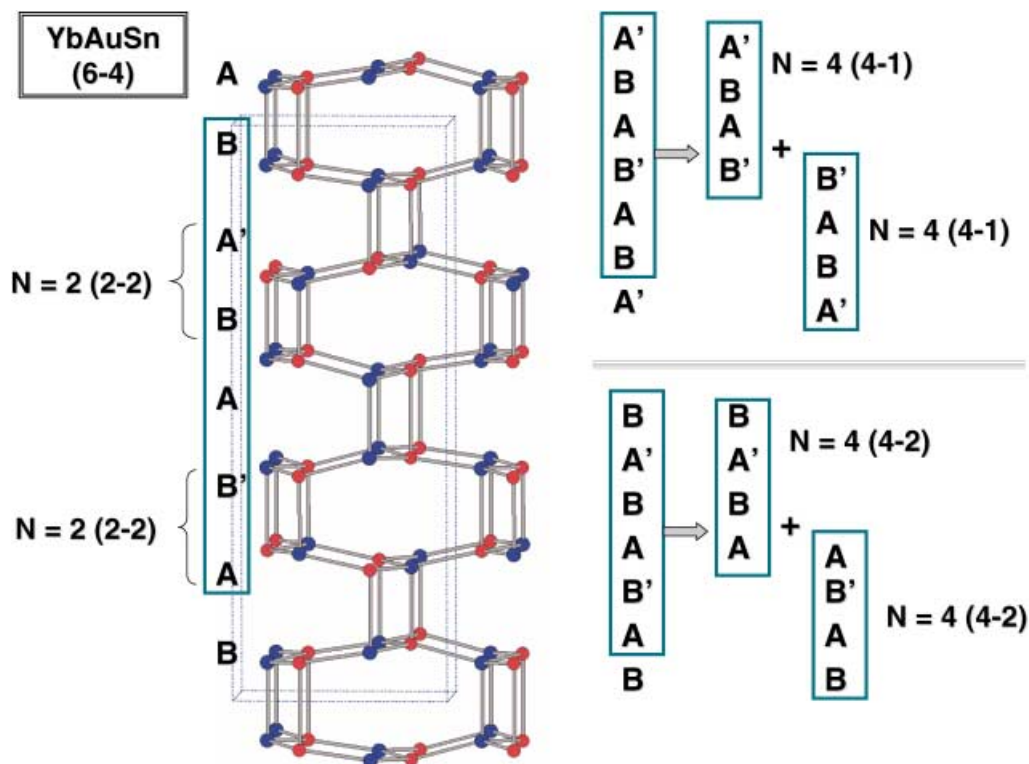
Fig. 10. *The first possible lattice for* N = 6 (YbAuGe, **6-4**), *and its decomposition into smaller units*

BAB′ABA′B) . . . If we perform a twin operation, then (**AB′ABA′BA′B′AB′AB′**) . . . is reached. The first combination seems a valid choice, having a median mirror plane and no more than two similar uninterrupted blocks, whereas the second has 3 **A** successive units, making it unlikely. Starting now from **6-6**, (**ABAB′A′B′**) . . . and applying the mirror operation, one gets: (**ABAB′A′B′A′B′A′BAB**) . . ., which has 5 **H2** blocks, and, thus, is very implausible. The twin operation affords (**ABAB′A′B′ABAB′A′B′**) . . ., which is redundant to the original **6-6**, (**ABAB′A′B′**) . . . Without doing any further permutations, we can then ascertain that, if a unit cell with $N = 12$ is discovered, then the (**AB′ABA′BAB′ABA′B**) . . . form would be a promising candidate for its structure.

Continuing our logic, an $N = 14$ unit should be formed from two $N = 8$ blocks, by subtracting the two repeating layers, as prescribed earlier for $N = 6$ or 10. Given that there is no $N = 8$ potential network, or any straightforward candidate that by twinning might develop into a viable $N = 14$ lattice obeying the previously discussed assumptions, one might then consider its formation from two $N/2 = 14/2 = 7$ layered unit cells, with a mirror or twin operation. This too is unlikely, considering that an autonomous unit with an odd N cannot exit. There are obviously possibilities of having this lattice formed from even smaller pieces, such as three $N = 4$ units, or an $N = 6$ and two $N = 4$, where one would eliminate four redundant slabs.
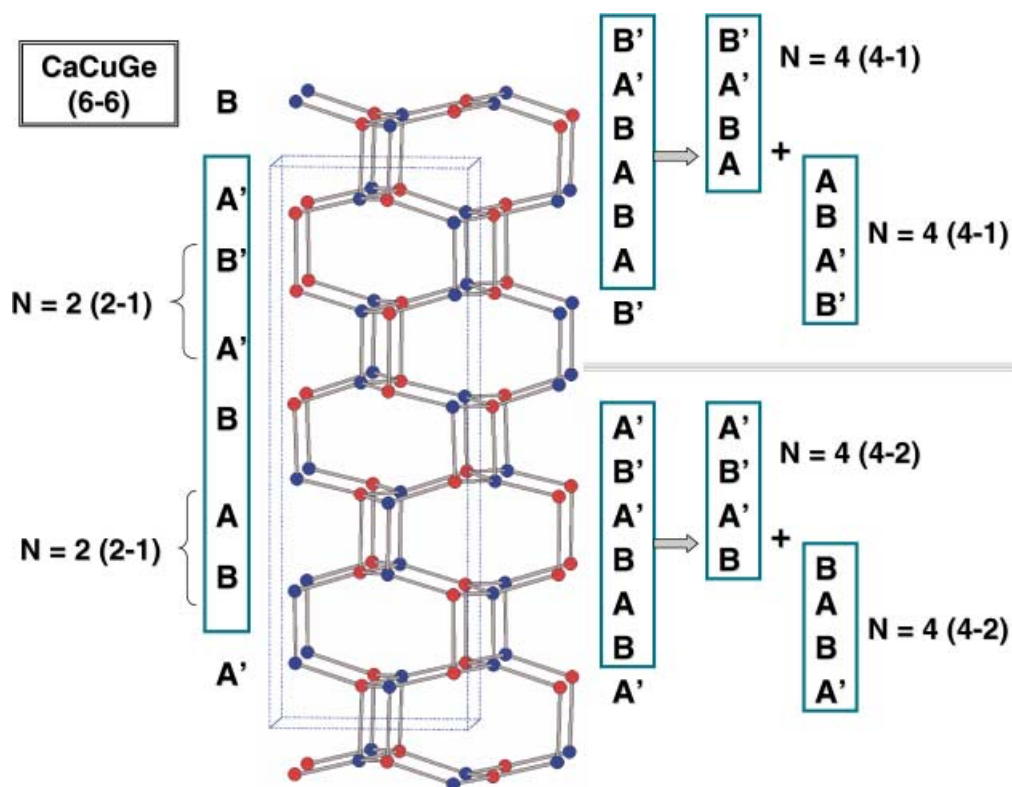
Fig. 11. *The second possible lattice for* N = 6 (CaCuGe, **6-6**), *and its decomposition into smaller units*

We will not continue our enumeration, but the empirical principles illustrated above should provide sufficient guidance in searching for possible distinct arrangements when *N* is large.

A consequence derived from the fact that there cannot exist any unit cell with *N* odd, is that if there exist such layered structures with an odd *N*, then, inevitably, at least one or more of its layers must be seriously distorted from its original conformation. This is indeed the case for a rare number of layered phases that have three layers/unit cell and crystallize in the space group *P*-6*m*2 (see Entry 9 in Table 2, Appendix, of previous paper). In order for those lattices to have an odd number of slabs/unit cell, one of the slabs is 'planarized', and the other two are distorted more toward the hexagonal diamond conformation, as if to 'compensate' for the deformation of the first 'graphitic', layer. However, as we detailed in our previous paper, there are no observed structures with an odd number of layers and all slabs puckered in a 'three adjacent 'up' and three adjacent down' way.

In the following papers in this series, we will put this discussion in a chemical context and explore the electronic preferences in the smallest unit cells, by analyzing when a certain structure is created as a function of the identity of M and E.
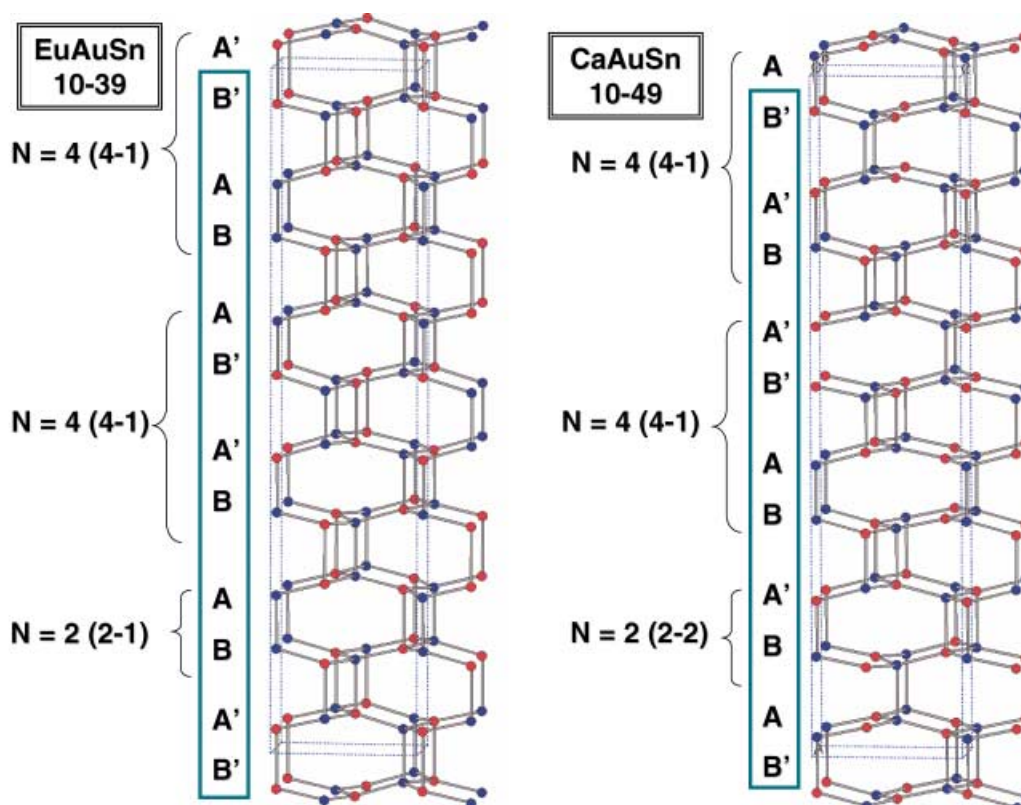
Fig. 12. *The two valid networks for* N = 10. On the left is EuAuSn (**10-39**), and on the right is CaAuSn (**10-49**).

Diamond-Like Structures. – For hexagons in a chair-like conformation (three atoms alternately go up from a median plane to form bonds to the next slab, and the other three go down), there are two distinct layers, which we will again call **a** and **b**. They are illustrated in *Fig. 14*.

The mirror image of **a** is **b**, and this relation holds as well for the colored 2-D lattices they generate. The connection between **a** and **A** (or **A′**), is evident from *Fig. 14*. To get **A′** one has only to 'switch' the M and E atoms from their sites in **A**. **B** and **B′** are derived from **b** in the same way. In stacking in the third direction, no connections (forming six-membered rings) can occur between **a** and **a**, or **b** and **b**, as they are parallel to each other. Again, such **a-a**, **b-b** layering would give rise only to four-membered rings, as in the AlSi layers in CaAl$_2$Si$_2$ structure [9–13].

If **a** comes on top of **b**, then, in the stacking direction are formed 'boat' hexagons, and the layers are *eclipsed*. The lattice resulting will, thus, belong to the hexagonal diamond (lonsdaleite) type when uncolored, and to the *wurtzite* type when colored (see *Fig. 15*, left). The layering possibilities are easily seen to be identical with what we worked out above for the slightly puckered hexagonal slabs. However, the only assemblies experimentally determined so far are (**AB′**)**AB′**... (Entry 7 in Table 2,
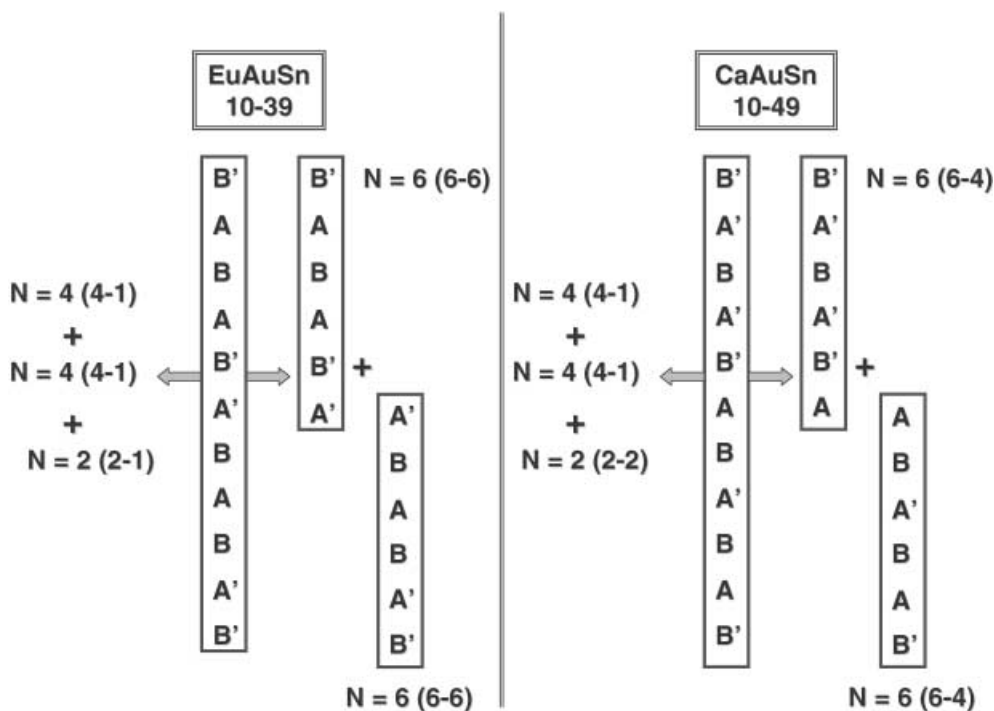
Fig. 13. *The decomposition into smaller units for* N = 10

Appendix, in the preceding article) and (**AB**)**AB**... (Entry 9 in Table 2, Appendix, in the preceding article) lattices.

When **a** is on top of **a**, or **b** of **b**, and one adds a translation within the $(x + z)$ plane, then 'chair' hexagons are formed along the third axis (y in this case), as may be seen in *Fig. 15*, right. Overall the structure is then the diamond one when uncolored, or *zinc-blende* when M and E are introduced. The slabs are in this instance *staggered*.

One can also have combinations of staggered and eclipsed layerings progressing in the third dimension.

Perhaps richest in examples of polytypes and closest to $[ME]^{n-}$ networks is SiC chemistry. The material has commercial applications; as a result, there are numerous studies of SiC, and many notations have been introduced in order to create a unified understanding of their variety. No fewer than 70 hexagonal, one cubic, and 170 rhombohedral lattices have been experimentally identified, with unit cell lengths ranging along the stacking direction from 4 to more than 1500 Å. The **ABC** notation, in SiC chemistry, is parallel to the one employed here [14–21]. In our way of thinking, these structures have only one kind of layer, which is translated within the unit cell in the plane perpendicular to the stacking direction, at one-fourth, one-half, and three-quarters of the stacking axis. The net result is that, within one such unit cell along the stacking axis, there are three such translationally dissimilar slabs, and all together give rise to staggering in these lattices. Therefore, in SiC, the coloring, were it to be called
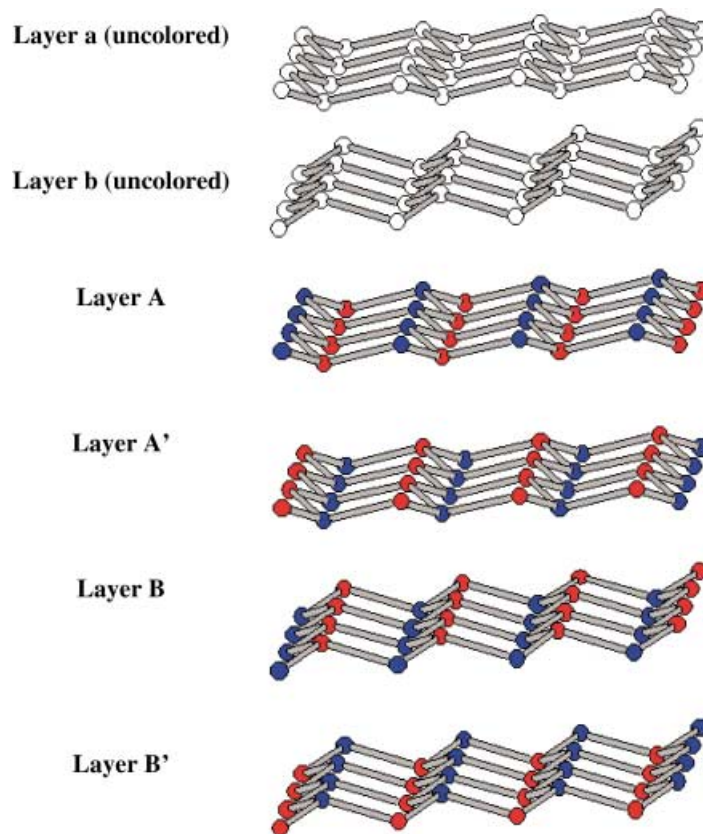
Layer a (uncolored)

Layer b (uncolored)

Layer A

Layer A'

Layer B

Layer B'

Fig. 14. *Types of 'diamond-like' puckered layers*

that, would be with one color since there is a single distinct layer available. It seems that studies on SiC are typically concerned with describing the structures experimentally observed; there appears to be little consideration of the full range of potential structures.

The most familiar SiC structures are the cubic zinc-blende type, β-SiC (3C in the *Ramsdell* notation [17], where 3 designates the number of layers per unit cell and C cubic symmetry), with the layers staggered, and wurtzite α-SiC (2 H, for 2 layers and hexagonal symmetry), having the slabs eclipsed in the 3rd dimension. The blende form has in the **ABC** notation the layer sequence (**ABC**)**ABC**..., and wurtzite (**AB**)**AB**... Interestingly, the pure 2 H polytype has not been found yet. Other common units are 4 H, with the order (**ABCB**)**ABCB**..., and 6 H, (**ABCACB**)**ABCACB**... When the layers are at different heights in the crystal, rhombohedral symmetry is generated; nevertheless, such lattices still can be described in the hexagonal system. The smallest rhombohedral variant is 15R, with the unit cell: (**ABCACBCABACABCB**)... The other polytypes are combinations of cubic and hexagonal stacking sequences.
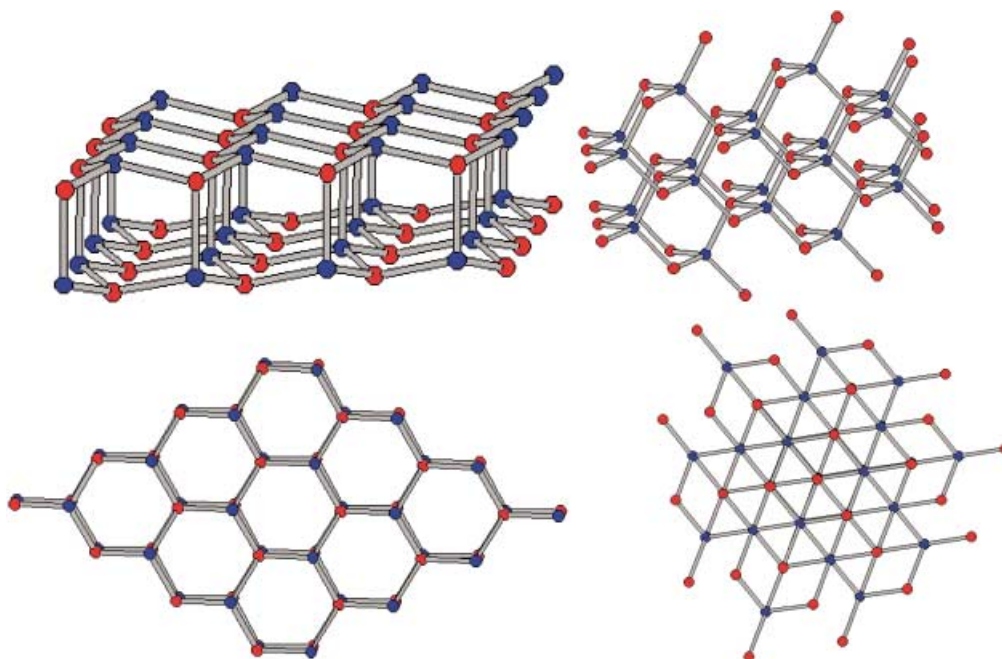
Fig. 15. *Left: a cut from the hexagonal diamond network, showing the eclipsed stacking, and boat-shaped rings along* y. *Right: zinc blende, a 'staggered' stacking, forming chairs along* y.

Since these cases are thoroughly explored in the SiC literature, we only mention them here and make the connection between the **ABC** notation from SiC surveys and ours. In general, the REME phases avoid the multitude of SiC polytypes [22–27]. Why this is so remains to be explained.

Conclusions. – We have derived several algorithms for enumerating and selecting as likely the theoretically distinct unit cells, consisting of graphitic, slightly puckered or puckered diamondoid layers, stacked in an eclipsed way along the third direction. The first two cases we have explored in detail, and for the third we inferred the effects.

When the stacked slabs are two-dimensionally planar, we have enumerated all the potential unit cells up to $N = 7$. Only the $N = 1$ and 2 cases are known. For the networks with puckered layers, we first concluded that there must be only an even number, N, of layers/unit cell. Moreover, we found an empirical rule, stating that any potentially realizable network must have either a mirror plane or a twin operation (mirror plane, followed by a color change), dissecting it half way 'up' the unit cell. Using these simple principles, from an original multitude of 2^{N-1} structures, we were able to significantly narrow down the number of possible combinations. Thus, for $N = 2$, we found two distinct nets, for $N = 4$, one, for $N = 6$, two, for $N = 8$ no viable arrangements, and, for $N = 10$, we excluded all but two distinct lattices, which in fact are those observed. We have sketched further guidelines, to continue the enumeration for higher N's.

In addition, we proposed an 'overlapping' *Aufbau*, by which more-complex structures are derived from the smaller, basic ones. In the last part of this article, we analyzed the eclipsed stacking of diamond-type layers, and concluded that resulting networks are analogous (in sequencing) to those determined for slightly puckered sheets. The arrangements formed from staggered diamond-type layers were briefly discussed in the context of the related SiC polytypes.

In the following paper in this series, we will approach the electronic puzzles that arise in the case of slightly puckered structures, and argue in favor of electronic effects deciding over a layering or another.

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