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Supporting information for article:

Understanding Extended Homometry Based on Complementary Crystallographic Orbit Sets

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S1. Further Discussion on 1D Homometric Prototype

In chapter 3.2, a 1D homometric prototype is mentioned to help explaining the structure of layer homometric pairs. In fact, this is a special situation of the general 1D prototype discussed by Patterson and Bullough. The general prototype could be described as:

Theorem S1: For a 1D structure, if a cell can be separated by 4 parts of atoms termed as A_1, A_2, B_1 and B_2, and $A = A_1 \cup A_2$, $B = B_1 \cup B_2$. The structure after a translation of $1/4$ for A or B are termed as A' or $B^{'}$, respectively. If A_1, A_2, B_1 and B_2 have the following properties:

1. A_1 and A_2 can be related by a translation of $1/2$ in the smallest cell, *i.e.*, $\forall i \in A_1, \exists j \in A_2$, where $x_i = x_j + 1/2$, and both A_1 and A_2 do not contain a translation of $1/4$ in such a cell.

2. B_1 and B_2 can be related by a translation of $1/4$ in the smallest cell, *i.e.*, $\forall i \in B_1, \exists j \in B_2$, where $x_i = x_j + 1/4$, in such cell.

Then $A \cup B$ is enantiomorphic or homometric with $A \cup B'$ or $A^{'} \cup B$.

Proof: The structure factors of the 1D structure can be separated as the contribution of each part:

$$\begin{aligned} F_h &= \sum_{j\in A_1} f_j \exp\left(i2\pi\, hx_j\right) + \sum_{j\in A_2} f_j \exp\left(i2\pi\, hx_j\right) + \sum_{j\in B_1} f_j \exp\left(i2\pi\, hx_j\right) + \sum_{j\in B_2} f_j \exp\left(i2\pi\, hx_j\right) \\ &= \sum_{j\in A_1} f_j \exp\left(i2\pi\, hx_j\right)(1 + \exp i\pi h) + \sum_{j\in B_1} f_j \exp\left(i2\pi\, hx_j\right)\left(1 + \exp\frac{i\pi h}{2}\right) \\ &= F_{h,A} + F_{h,B} \end{aligned} \tag{S1.1}$$

The structure factors after the translation of A is:

$$F_{h,t} = F_{h,A} \cdot \exp\left(\frac{i\pi h}{2}\right) + F_{h,B} \tag{S1.2}$$

Since A has a translation of $1/2$, the translation of $1/2$ for each part (A or B) of the structure will not change the structure. Thus, the effect of translation of $1/4$ for A and B is the same, which means $A^{'} \cup B$ and $A \cup B'$ are congruent.

Considering the structure factors for A and B separately:

For A, because of the $1/2$ translation, the reflections of $h = 2n + 1$ are absent. Furthermore, since A do not contain a translation of $1/4$, the reflections of $h = 4n + 2$ are generally not absent.

$$F_{2n+1,A} = \sum_{j\in A_1} f_j \exp\left(i2\pi\, hx_j\right)(1 + \exp i\pi(2n+1)) = 0 \tag{S1.3}$$

For B, because of the $1/4$ translation, the reflections of $h = 4n + 2$ are absent.

$$F_{4n+2,B} = \sum_{j\in B_1} f_j \exp\left(i2\pi\, hx_j\right)\left(1 + \exp\frac{i\pi(4n+2)}{2}\right) = 0 \tag{S1.4}$$

According to the definition of the smallest cell, B do not contain translations of $1/2$, so the reflections of $h = 2n + 1$ for B are generally not absent.

Then let us consider the total effect of the $\frac{1}{4}$ translation of A on the whole structure factors.

For $h = 4n$, the structure factors of both A and B remain the same.

For $h = 4n + 2$, the structure factors of B is absent, and the phases of the structure factors of A change by π. The whole structure factors' amplitudes are the same while the phases change by π.

For $h = 2n + 1$, the structure factors of A is absent and the structure factors of B are unchanged. The whole structure factors are thus unchanged.

Therefore, all the intensities of structure factors of the two structures are the same. The phases of the triple structure invariants $F_{2n+1}F_{2n+1}F_{-4n-2}$ are changed by π between the two structures, which indicates the two structures are not congruent. As a result, $A \cup B$ and $A^{'} \cup B$ are enantiomorphic or homometric structures and for most situations, they are homometric. The two structures are enantiomorphic only when all the phases of structure invariants $F_{2n+1}F_{2n+1}F_{-4n-2}$ are $\pm\pi/2$, which will be discussed in detail in theorem S2.

□

The 4-atom 1D homometric prototype (structure **2a** and **2b**) discussed in the article is a special situation of this general prototype.

Theorem S2: For 1D structure $A \cup B$ and $A^{'} \cup B$ discussed in theorem S1, they are enantiomorphic structures when A, B, A_1, B_1, A_2, B_2 are centrosymmetric, and the set of centers of symmetry of B_1 and B_2 are equal to the set of centers of symmetry of A.

Proof: If $A \cup B$ and $A^{'} \cup B$ are enantiomorphic, then A and A' are enantiomorphic and B should be centrosymmetric. Since A and A' are related by translation, they should also be centrosymmetric, with 4 centers of symmetry related by $1/4$ translation in a cell. The centers of symmetry of A and A' are at:

$$t_A;\ \ t_A + \frac{1}{4};\ \ t_A + \frac{1}{2};\ \ t_A + \frac{3}{4} \quad t_A \in \left[0, \frac{1}{4}\right) \tag{S1.5}$$

Then A and A' can be related with 4 other centers of symmetry, at:

$$t + \frac{1}{8};\ \ t_A + \frac{3}{8};\ \ t_A + \frac{5}{8};\ \ t_A + \frac{7}{8} \quad t_A \in \left[0, \frac{1}{4}\right) \tag{S1.6}$$

Additionally, since A can be separated by 2 parts A_1 and A_2 related by translation of $1/2$, A_1 and A_2 should both be centrosymmetric.

Similarly, $B, B^{'}, B_1$ and B_2 are all centrosymmetric. Noting the centers of symmetry of B_1 at t_B and $t_B + \frac{1}{2}$, then the centers of symmetry of B_2 should be at $t_B + \frac{1}{4}$ and $t_B + \frac{3}{4}$ $(0 \leq t_B < \frac{1}{2})$.

Then B_1 and B_2 can be related by 2 centers of symmetry in a cell:

$$t_B + \frac{1}{8};\ t_B + \frac{5}{8} \quad t_B \in \left[0, \frac{1}{4}\right) \tag{S1.7}$$

These are also the centers of symmetry of B in a cell.

If $A \cup B$ and $A^{'} \cup B$ are enantiomorphic, A and B should not share the same center of symmetry, and there should exist same centers of symmetry connecting A and A', and connecting B_1 and B_2, *i.e.*:

$$x_B = x_A, or\ x_B = x_A + \frac{1}{4}$$

corresponding the enantiomorphic pairs respectively.

This means the centers of symmetry of B_1 and B_2 should be located at the centers of symmetry of A.

□

A typical structure to describe theorem S2 is:

$$A = \left\{0, \frac{1}{2}\right\}; A_1 = \{0\}; A_2 = \left\{\frac{1}{2}\right\};$$

$$B = \{-0.1, 0.1, 0.15, 0.35\}; B_1 = \{-0.1, 0.1\}; B_2 = \{0.15, 0.35\}$$

Then $A^{'} = \left\{\frac{1}{4}, \frac{3}{4}\right\}$ and $A \cup B$ is enantiomorphic with $A^{'} \cup B$.

S2. Further discussion on real extended homometric structures

S2.1. S2.1 Cubic homometric structures——GeI_4

As is shown in Figure S1, GeI_4 type (SnI_4 in ICSD) (Jaeger *et al.*, 1925) structure is in $Pa\bar{3}$ space group. In both structures, the I atoms are in cubic closest packing (ccp) and Ge atoms occupy 1/8 of the tetrahedral voids. All the I atoms in the original structure (**6a**, see Figure S1a) are 1-coordinated, and the I atoms in its homometric pair (**6b**, see Figure S1b) are 0,1, or 2-coordinated. With the origin chosen in Figure S1, the Ge and I atoms are in different positions. In the original structure, Ge atoms occupy the $8c$ crystallographic orbit where $x = 1/8$, and I atoms occupy $8c$ crystallographic orbit where $x = 1/4$, and a $24d$ crystallographic orbit including the point $(0, 0, 1/4)$. In its homometric pair, Ge atoms occupy the $8c$ crystallographic orbit where $x = 3/8$, and I atoms occupy $4a$, $4b$, and a $24d$ crystallographic orbit including the point $(0, 1/4, 1/4)$. In fact, all the I atoms can be taken as the same ccp lattice and they are split into multiple crystallographic orbits because of the influence of Ge.

The union set of both structures is displayed in Figure S1c, and it is in $Ia\bar{3}d$ space group with the same cell parameter a (different primitive cell). All the Ge atoms are now in $16b$ crystallographic orbit. The I atoms in $8c$ of original structure and in $4a$ and $4b$ (they can be changed to each other by different definition of origin) are now in $16a$ crystallographic orbit, and other I atoms are now in a $48f$ crystallographic orbit where $x = 1/4$. Then the two structure can be taken as the combination of 3 complementary half crystallographic orbits.

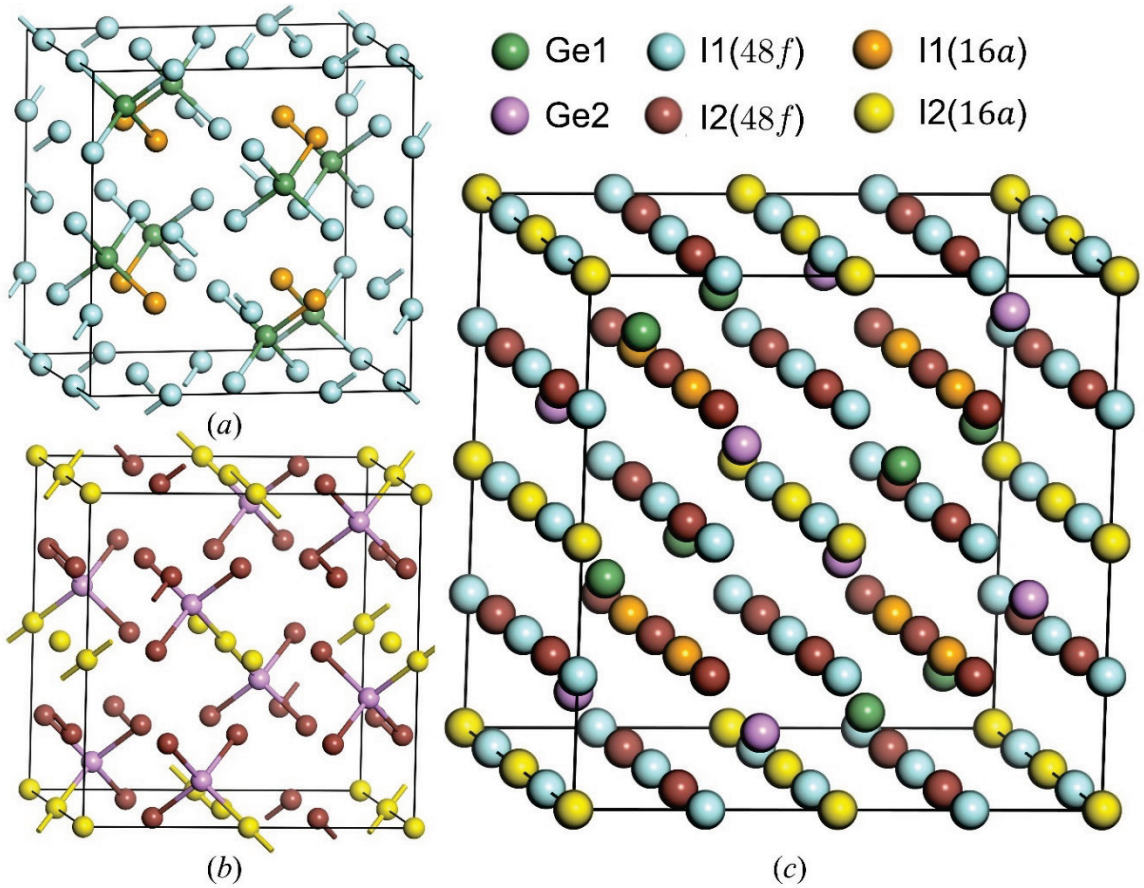

Figure S1 The cubic homometric structures of GeI_4.

S2.2. S2.2 Further discussion on weakly homometric structure $Hg(NH_3)_2Cl$

For the convenience of presentation, the weakly homometric pairs in chapter 3.2 is shown and discussed in a common cell where $a = b = c = 8.120$ Å. In fact, the two structure have different unit cells, neither of them is in the unit cell in the text. The unit cells of both structures are shown in Figure S2. The original structure (**5a**) is in $Cmmm$ space group and the parameters are $a = b = 8.120$ Å, $c = 4.060$ Å. The transition from unit cell to the common cell is $a' = a, b' = b, c' = 2c$. The weakly homometric structure (**5b**) is in $P4/mmm$ space group and the parameters are $a = b = 5.742$ Å, $c = 4.060$ Å. The transition from unit cell to the common cell is $a' = a + b, b' = a - b, c' = 2c$. Notably, the primitive cells of **5a** and **5b** is the same.

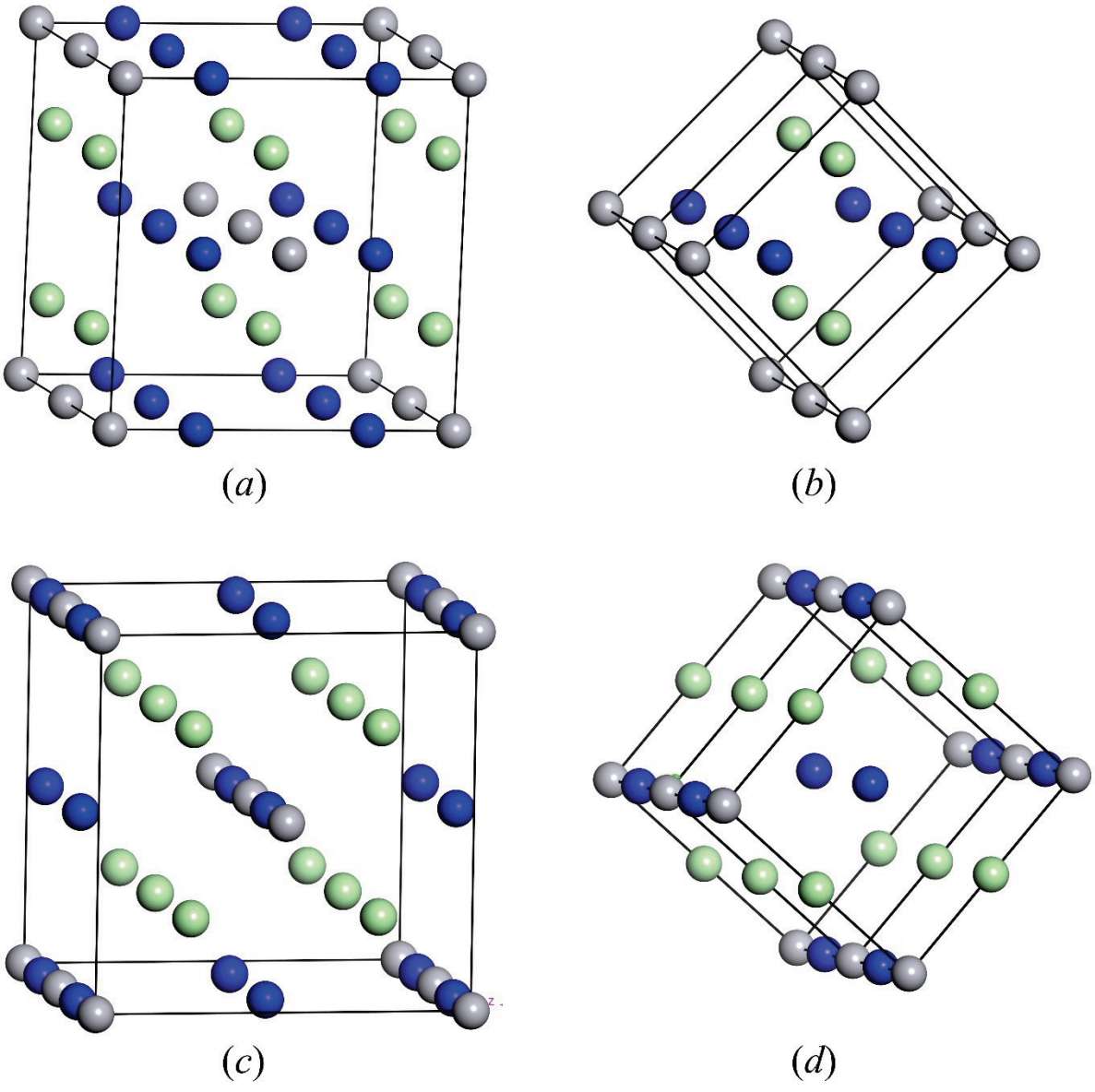

Figure S2 Common cells and primitive cells of $Hg(NH_3)_2Cl_2$ without H atoms. (*a*) The common cell and (*b*) the primitive cell of the original structure **5a**; (*c*) the common cell and (*d*) the primitive cell of the weakly homometric structure **5b**.

Since **5a** and **5b** are weakly homometric pairs, they cannot be taken as combination of multiple complementary lattice points. In the union structure, Hg atoms form a primitive cubic lattice where $a = b = c = 4.060$ Å, while Cl and N atoms form primitive tetragonal lattice where $a = b = 2.871$ Å, $c = 4.060$ Å. As is shown in Figure 4*c*, Hg atoms can be taken as the combination of two complementary set of the cubic lattice above, but Cl and N atoms cannot be taken as the combination of the lattice with the same cell although this is possible in their own period. This means the two structures are weakly homometric rather than homometric.

S3. Further discussion on deviation from the homometric position

Because of the reduction of the symmetry after the separation of the lattices or the crystallographic orbits, some parameters of fixed atom coordinates become free variables. These parameters determined by the process of refinement would not be fixed to these particular values and as a result, in ICSD database, structures analyzed in early ages are more likely to have homometric pairs than recent results. Many other structures in $SrPdF_4$, $TaSe_2$ or GeI_4 type are slightly deviated from the homometric prototypes, which are shown in Table S1~S3.

Table S1 Comparison of atomic site in different $SrPdF_4$ type (ICSD $KBrF_4$ type) structure

composition	ICSD No.	Wyckoff symbol	atom	x	y	z	reference
$SrPdF_4$[a]	108990	$4a$	Sr	0	0	0.25	(Bergerhoff *et al.*, 1983)
		$4d$	Pd	0	0.5	0	
		$16l$	F	0.173	0.673	0.125	
$BaPdF_4$	108891	$4a$	Ba	0	0	0.25	(Bergerhoff *et al.*, 1983)
		$4d$	Pd	0	0.5	0	
		$16l$	F	0.164	0.664	0.123	
$KBrF_4$	255737	$4a$	K	0	0	0.25	(Ivlev & Kraus, 2018)
		$4d$	Br	0	0.5	0	
		$16l$	F	0.65508(11)	0.15508(11)	0.37889(7)[b]	

a. The structure of $PbPdF_4$ (ICSD No.108892) reported in the same literature shares the same structure and the z parameter of $16l$ site of F atoms is also 0.125, which means it has a homometric pair.

b. The z parameter of this site is equivalent to 0.12111(7), which is deviated to the site of 0.125.

Table S1 Comparison of atomic site in different $TaSe_2$ type (ICSD TaS_2(2H) type) structure

composition	ICSD No.	Wyckoff symbol	atom	x	y	z	reference
$TaSe_2$	24314	$2b$	Ta	0	0	0.25	(Bjerkelund *et al.*, 1967)
		$4f$	Se	0.3333	0.6667	0.125(5)	
$TaSe_2$	18130	$2b$	Ta	0	0	0.25	(Brown & Beerntsen, 1965)
		$4f$	Se	0.3333	0.6667	0.118(1)	
NbS_2	603911	$2b$	Nb	0	0	0.25	(Pfalzgraf *et al.*, 1987)
		$4f$	S	0.3333	0.6667	0.125(5)	

Table S2 Comparison of atomic site in different GeI_4 type (ICSD SnI_4 type) structure

composition	ICSD No.	Wyckoff symbol	atom	x	y	z	reference
GeI_4	22399	$8c$	Ge	0.125	0.125	0.125	(Jaeger *et al.*, 1925)
		$8c$	I	0.25	0.25	0.25	
		$24d$	I	0	0	0.25	
GeI_4	67895	$8c$	Ge	0.12923(4)	0.12923(4)	0.12923(4)	(Walz *et al.*, 1993)
		$8c$	I	0.25071(3)	0.25071(3)	0.25071(3)	
		$24d$	I	0.01306(3)	0.00289(2)	0.25203(2)	
SnI_4	51571	$8c$	Sn	0.1286(1)	0.1286(1)	0.1286(1)	(Reuter & Pawlak, 2001)
		$8c$	I	0.2537(1)	0.2537(1)	0.2537(1)	
		$24d$	I	0.2550(1)	0.0078(1)	0.0001(1)	

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