Acta Cryst

B

STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS

Supporting information for article:

A general method for searching homometric structures

Yihan Shen, Yibin Jiang, Jianhua Lin, Cheng Wang and Junliang Sun

S1. Supporting text

S1.1. The distance homometric structure search method

For a given structure, the structure factor is given by:

$$F(hkl) = \sum_n (f_n \exp[2\pi i(hx_n + ky_n + lz_n)])$$

$$= \sum_n f_n\{\sin[2\pi(hx_n + ky_n + lz_n)] + i\cos[2\pi(hx_n + ky_n + lz_n)]\} \quad (1)$$

The intensity is proportional to $F(hkl)F^*(hkl)$, which is expressed as:

$$F(hkl)F^*(hkl) =$$

$$\sum_{m,n} f_m f_n^*\{\sin[2\pi(hx_m + ky_m + lz_m)]\sin[2\pi(hx_n + ky_n + lz_n)]$$

$$+ \cos[2\pi(hx_m + ky_m + lz_m)]\cos[2\pi(hx_n + ky_n + lz_n)]\}$$

$$= \sum_{m,n} f_m f_n^* \cos[2\pi(hx_m + ky_m + lz_m - hx_n - ky_n - lz_n)] \quad (2)$$

Divide the crystallographic orbits into 3 unions P, Q, and R. For simplicity, we use the matrix forms below for further discussion:

$$\boldsymbol{H} = \begin{bmatrix} h \\ k \\ l \end{bmatrix}, \boldsymbol{X}_m = \begin{bmatrix} x_m \\ y_m \\ z_m \end{bmatrix}$$

Suppose there are p atoms locate at the crystallographic orbits from P, q atoms for Q and r atoms for R, then total intensity can be divided into:

$$I(\boldsymbol{H}) = CF(\boldsymbol{H})F^*(\boldsymbol{H})$$

$$= \frac{1}{2}\left[I_{PP}(\boldsymbol{H}) + I_{QQ}(\boldsymbol{H}) + I_{RR}(\boldsymbol{H})\right] + I_{PQ}(\boldsymbol{H}) + I_{PR}(\boldsymbol{H}) + I_{QR}(\boldsymbol{H}) \quad (3)$$

And for any pair of (P, Q), $I_{PQ}(\boldsymbol{H})$ is defined as:

$$I_{PQ}(\boldsymbol{H}) = C \sum_{p \text{ in } P, q \text{ in } Q} \{f_p f_q^* \cos[2\pi \boldsymbol{H}^T(\boldsymbol{X}_p - \boldsymbol{X}_q)] + f_q f_p^* \cos[2\pi \boldsymbol{H}^T(\boldsymbol{X}_q - \boldsymbol{X}_p)]\}$$

$$= C \sum_{p \text{ in } P, q \text{ in } Q} \{(f_p f_q^* + f_q f_p^*) \cos[2\pi \boldsymbol{H}^T(\boldsymbol{X}_p - \boldsymbol{X}_q)]\} \quad (4)$$

where C is a constant. $I_{PQ}(\boldsymbol{H})$ is the term of intensity generated by atom pairs with one from union P and the other from union Q.

Suppose that there are two symmetry operations $\boldsymbol{A}$ and $\boldsymbol{B}$ which belong to the point group of the crystal's reciprocal lattice. The position of $\boldsymbol{A}$ and $\boldsymbol{B}$ are $\boldsymbol{X}_A$ and $\boldsymbol{X}_B$. P remains unchanged under $\boldsymbol{A}$ and

Q remains unchanged under $\boldsymbol{B}$. R will be changed under $\boldsymbol{A}$ or $\boldsymbol{B}$, but $\boldsymbol{A}$R and $\boldsymbol{B}$R are identical. Union $\boldsymbol{A}$R=$\boldsymbol{B}$R=R', consider a structure containing P, Q and R', $I_{R'R'}(\boldsymbol{H})$ has the following form:

$$I_{R'R'}(\boldsymbol{H}) = 2C \sum_{r_1',r_2' \ in \ R'} f_{r_1} f_{r_2}^* \cos[2\pi \boldsymbol{H}^T (\boldsymbol{X}_{r_1'} - \boldsymbol{X}_{r_2'})]$$

$$= 2C \sum_{r_1,r_2 \ in \ R} f_{r_1} f_{r_2}^* \cos[2\pi \boldsymbol{H}^T (\boldsymbol{A}(\boldsymbol{X}_{r_1} - \boldsymbol{X}_A) + \boldsymbol{X}_A - \boldsymbol{A}(\boldsymbol{X}_{r_2} - \boldsymbol{X}_A) - \boldsymbol{X}_A)]$$

$$= 2C \sum_{r_1,r_2 \ in \ R} f_{r_1} f_{r_2}^* \cos[2\pi \boldsymbol{H}^T \boldsymbol{A}(\boldsymbol{X}_{r_1} - \boldsymbol{X}_{r_2})]$$

$$= 2C \sum_{r_1,r_2 \ in \ R} f_{r_1} f_{r_2}^* \cos[2\pi (\boldsymbol{A}^T \boldsymbol{H})^T (\boldsymbol{X}_{r_1} - \boldsymbol{X}_{r_2})]$$

$$= I_{RR}(\boldsymbol{A}^T \boldsymbol{H}) \tag{5}$$

$I_{PR'}(\boldsymbol{H})$ can be written as:

$$I_{PR'}(\boldsymbol{H}) = C \sum_{p \ in \ P, r' \ in \ R'} \{(f_p f_{r'}^* + f_{r'} f_p^*)\cos[2\pi \boldsymbol{H}^T (\boldsymbol{X}_p - \boldsymbol{X}_{r'})]\} \tag{6}$$

$$= C \sum_{p \ in \ P, r \ in \ R} \{(f_p f_{r'}^* + f_{r'} f_p^*)\cos[2\pi \boldsymbol{H}^T (\boldsymbol{X}_p - \boldsymbol{A}(\boldsymbol{X}_r - \boldsymbol{X}_A) - \boldsymbol{X}_A)]\} \tag{7}$$

As $\boldsymbol{A}P = P$, for all p in P there is one and only one p' that makes $\boldsymbol{X}_{p'} = \boldsymbol{A}(\boldsymbol{X}_p - \boldsymbol{X}_A) + \boldsymbol{X}_A$. So we can reformulate Eq. 7 as follows:

$$I_{PR'}(\boldsymbol{H}) = C \sum_{p \ in \ P, r \ in \ R} \{(f_p f_{r'}^* + f_{r'} f_p^*)\cos[2\pi \boldsymbol{H}^T (\boldsymbol{A}(\boldsymbol{X}_p - \boldsymbol{X}_A) + \boldsymbol{X}_A - \boldsymbol{A}(\boldsymbol{X}_r - \boldsymbol{X}_A) - \boldsymbol{X}_A)]\}$$
$$= I_{PR}(\boldsymbol{A}^T \boldsymbol{H}) \tag{8}$$

Similarly, considering $\boldsymbol{B}Q = Q$, $I_{QR'}(\boldsymbol{H})$ has

$$I_{QR'}(\boldsymbol{H}) = I_{QR}(\boldsymbol{B}^T \boldsymbol{H}) \tag{9}$$

As $\boldsymbol{A}$ and $\boldsymbol{B}$ are point group operations, $\boldsymbol{A}^T \boldsymbol{H}$, $\boldsymbol{B}^T \boldsymbol{H}$ and $\boldsymbol{H}$ have the same distance to the origin. Thus, they will contribute to the same peak in PXRD, and the summation of all contributions for certain reflection will be the same according to Eq. 3. So, the original structure containing unions P, Q, R and the structure containing unions P, Q, R' are identical in PXRD.

S1.2. Extended discussion of diffraction equality of NaNbO$_3$(Str. 1a&b)

The correlation of the reflections between the two structures can be explained by dividing each structure into two substructures. One substructure which is the same in two structures contains Na and O in the space group of $I2_12_12_1$; the other contains Nb in $C222_1$, which can be related by an inversion center at (0,0,0.125) from Str. 1a to Str. 1b. As the Na and O substructure and the Nb substructure have

different symmetries, the coordination environment of Nb atoms may change after the inversion center operation. For the reflections *h k 2n* which corresponds to the reflections from the averaged structure with half c-axis, the intensities and phases are equal since the average structure of Str. 1a and Str. 1b are the same. For the reflections *h k 2n*+1, as the Na and O substructure are body-centered, it only contributes the intensity to those reflections with h+k=2n+1 where h+k+l=2n. The Nb substructure has a C-center which only contributes the intensity to those reflections with h+k=2n. So when l=2n+1, the Na and O substructure and Nb substructure contribute to different reflections and will not affect each other. Moreover, as Nb substructure only contains one type of element, only phases will change during the inversion center operation even with considering of resonant scattering. Consequently, the intensity of reflections with l=2n+1 of Str. 1a and Str. 1b are the same.

S2. Supporting tables

Table S1   List of homometric structures found by the program mentioned in the text.

ICSD No.	Composition	Note	ICSD No.	Composition	Note
1381	$Cu_{16}O_{14.15}$	$I4_1/amd$	52289	Cr_7C_3	$P6_3mc$ to $Cmc2_1$
4141	$Eu_2Sn_2O_7$	$Fd\bar{3}m$	53191	$CrNb_4Se_8$	$P6_3/mmc$
9965	V_2C	$Pbcn$	76432	$NaNbO_3$	$P222_1$ to $P2_12_12_1$
15958	$Hg(NH_3)_2Cl_2$	weakly; $Cmmm$ to $P4/mmm$; H not determined	77675	Cu_4O_3	$I4_1/amd$
18126	HgI_2	$I4_1/amd$	85824	FeH	$P6_3/mmc$
22073	$PtCl_4$	$Pa\bar{3}$	100566	Cu_4O_3	$I4_1/amd$
22177	V_8C_7	weakly; $P4_332$ to $C2/m$	108192	V_2C	$Pbcn$
22399	GeI_4	$Pa\bar{3}$	108594	$Mn_{0.25}TaS_2$	$P6_3/mmc$
24314	$TaSe_2$	$P6_3/mmc$	108990	$SrPdF_4$	$I4/mcm$
24317	$TaSe_2$	$P6_3/mmc$	109091	Li_5GaO_4	$P4_122$
26888	$Bi_{1.5}Cd_{0.5}O_{2.75}$	$Ia\bar{3}d$	153979	$Ge_{1.00009}V_{0.5495}$	weakly; $I4/mmm$ to $Cmcm$; V not determined
27035	D_2S	$Pa\bar{3}$	171908	Cu_2FeS_2	weakly; $F\bar{4}3m$ to $R3m$
27680	$CaUO_3$	$Ia\bar{3}$	171910	Cu_2FeS_2	weakly; $F\bar{4}3m$ to $R3m$
28387	Ta_2O	weakly; $I\bar{4}3m$ to Cm	607870	AlGdGe	weakly; $I4_1/amd$ to $C2/m$
29311	$FeNiS_2$	weakly; $Fm\bar{3}m$ to $R\bar{3}m$	645370	$NbSe_2$	$P6_3/mmc$
31625	UCl_6	$P\bar{3}m1$	651092	TaS_2	$P6_3/mmc$
37226	TeI_4	$I4_1/amd$ to $Imma$	655978	Mn_2Y	weakly; $I4_1/amd$ to $C2/m$

42433	$V_2D_{0.85}$	weakly; $I4_1/amd$ to $C2/m$
51540	$Cr_{0.35}Mo_{0.65}$	$I4/mmm$ to $I4_1/amd$
51542	$Cr_{0.16}Mo_{0.84}$	$I4/mmm$ to $I4_1/amd$

S3. Supporting figures
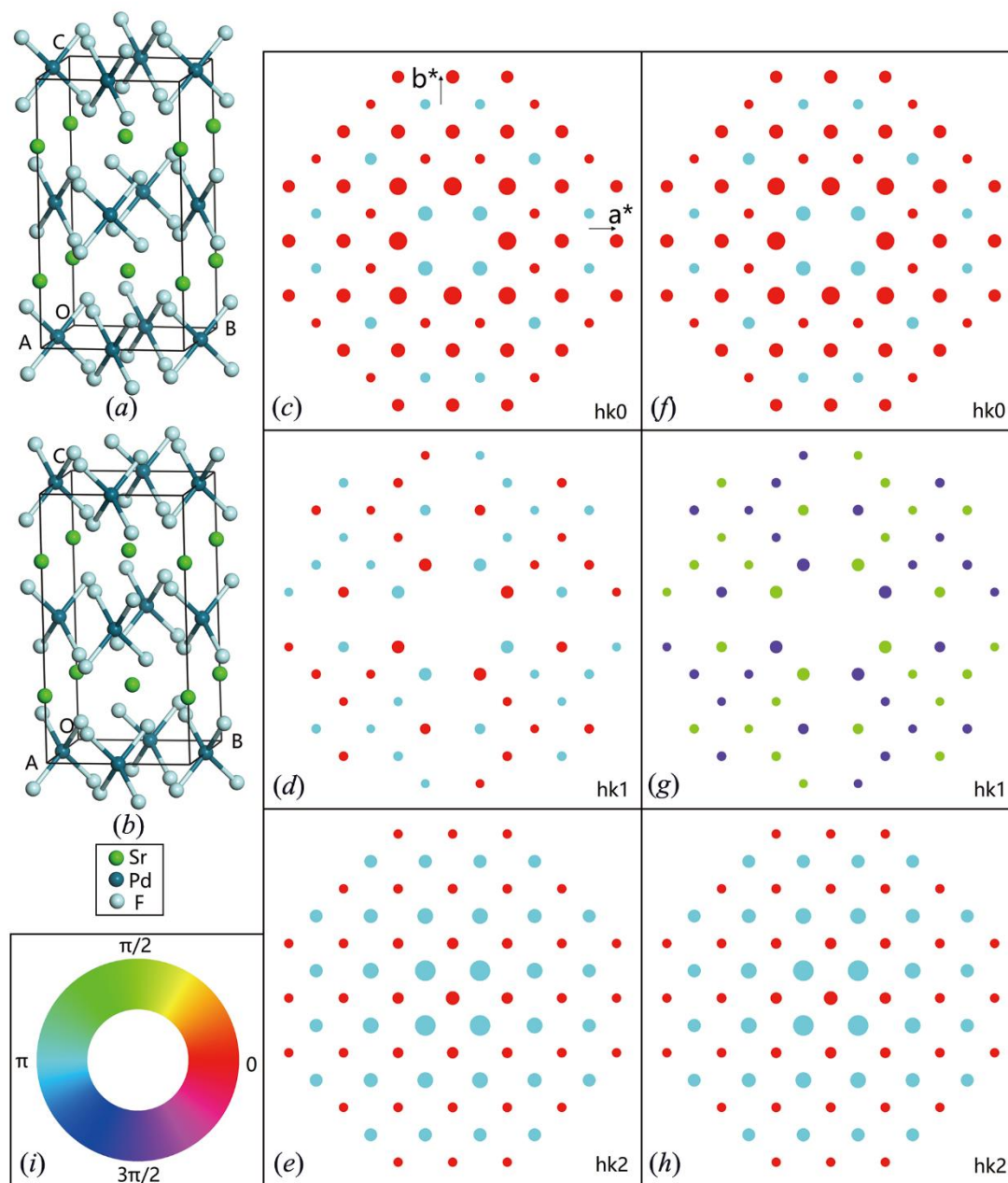
Figure S1

Structures and diffraction equality of $SrPdF_4$ (Str. 2a&b). (a) Original structure of $SrPdF_4$ (Str. 2a); (b) The homometric structure of Str. 2a (Str. 2b). (c)(d)(e) Structure factors of Str. 2a. (f)(g)(h) Structure factors of Str. 2b. (i) Correspondence of phase angle and color in figure (c)~(h). For the reflections with $l=2n$, Str. 2a and Str. 2b are equal in both intensities and phases. For the reflections with $l=2n+1$, Str. 2a and Str. 2b are equal in intensities, but different in phases.

The difference between two structures is that the F-substructure is shifted by one quarter of the unit cell along the c-axis, so similar to Str. 1a and Str. 1b, the structure factor correlation between two structures can be explained by dividing each structure into two substructures. One substructure contains Sr and Pd atoms in $P4/mmm$ symmetry with $\frac{1}{\sqrt{2}}$ of the a-axis and half of the c-axis and the other contains F in $I4/mcm$ symmetry.

For the reflections $h\ k\ 2n+1$, as the c-axis of the Sr/Pd substructure is half of original cell, it doesn't contribute any intensities to these reflections, i.e. only the F-substructure contributes to $h\ k\ 2n+1$ reflections, so these reflections have equal intensities but different phases between two structures due to the shift of one quarter of the unit cell for the F-substructure.

For the reflections $h\ k\ 4n$, as the translation vector of the F part is $\frac{1}{4}c$, the translation operation will not affect the reflections $h\ k\ 4n$, so these reflections will have same intensities and phases in both structures.

For the reflections $h\ k\ 4n+2$, the F-substructure doesn't contribute to these reflections, because the $h\ k$ $4n+2$ reflections of the F-substructure are same as $h\ k\ 2n+1$ reflections in a folded structure with half of the c-axis and the folded structure contains two same layers at z=0.25 and z=0.75, causing the extinction of these reflections. As only Sr and Pd part contributes to $h\ k\ 4n+2$ reflections, these reflections have same intensities and phases in both structures.

Although both structures are centrosymmetric, as the inversion center of Str. 2b is not at the origin of the cell, there are reflections with phases other than 0 and π.
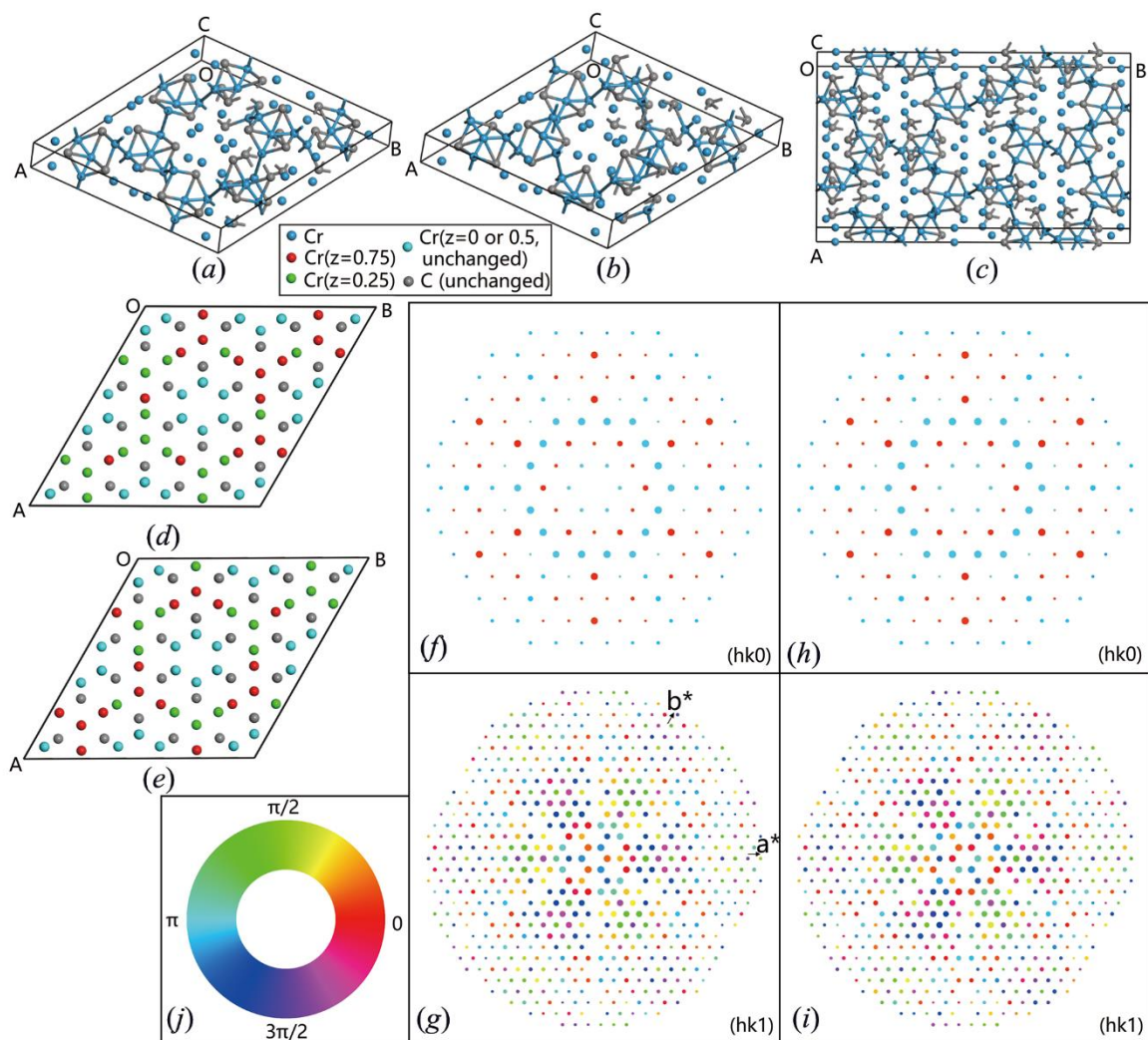
Figure S2

Structures of Cr_7C_3 (Str. 5a&b). (a) Original structure of Cr_7C_3 (Str. 5a, No.52289 in ICSD); (b) The homometric structure of Cr_7C_3 (Str. 5b). (c) The orthorhombic cell of Str. 5b. (d) Str. 5a along the c-axis; (e) Str. 5b along the c-axis. Blue and black spheres are Cr and C atoms respectively in (a), (b) and (c). Green and red spheres are Cr atoms with c=0.25 and 0.75 respectively, and cyan spheres are Cr atoms with c=0 or 0.5, in (d) and (e). (f)(g) Structure factors of Str. 5a. (h)(i) Structure factors of Str. 5b. (j) Correspondence of phase angle and color in figure (f)~(i). The phases for the hk1 reflections in Str. 5a have a 3-fold axis, while those of Str. 5b do not.

Note that if resonant scattering is considered, Str. 5a and Str. 5b can be distinguished by their slightly different intensities of Friedel's pairs. For example, the symmetry correlated reflections 101, 011, $\bar{1}$11, $\bar{1}$01, 0$\bar{1}$1, 1$\bar{1}$1 have higher intensities than their Friedel's pairs in Str. 5a, but in Str. 5b, 10$\bar{1}$, 01$\bar{1}$, $\bar{1}$11, $\bar{1}$0$\bar{1}$, 0$\bar{1}\bar{1}$, 1$\bar{1}$1 reflections have higher intensities than others.