Science Advances
AAAS

advances.sciencemag.org/cgi/content/full/6/35/eabc2758/DC1

Supplementary Materials for

Predicting short-range order and correlated phenomena in disordered crystalline materials

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Published 28 August 2020, *Sci. Adv.* **6**, eabc2758 (2020)
DOI: 10.1126/sciadv.abc2758

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The fluorite structure in the *Cmcm* and *C222₁* space groups

The *C222₁* space group provides a description of the atomic arrangement in disordered, anion-deficient fluorite $Ho_2Zr_2O_7$ that reproduces the experimental neutron PDF well (Fig. S1). The first step for describing the fluorite structure in the *C222₁* space group of weberite-type systems is to use a same lattice. The target pseudo-tetragonal lattice is incompatible with the 3-fold axes of the *Fm-3m* space group of fluorite. Therefore, we first reduce the symmetry of the fluorite lattice to the tetragonal subgroup G1 isomorphic to *F4/mmm*. The index of G1 in *Fm-3m* is 3, and there will be three elements in the equivalence class of G1 obtained by applying two of the lost symmetry operators: $4_y : \bar{z}, y, x$ and $4z : \bar{y}, x, z$. Then we can apply the following lattice transformation to s pace group G_1:

$$P_{F\rightarrow WT} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & \bar{1} & 1 \end{pmatrix}$$

This lattice transformation has the effect of generating supplementary elements in the translation part of the group that now consists of 16 vectors while the point group operations are kept unchanged.

The second step of the process involves a proper choice of the symmetry elements of the space group compatible with the desired final symmetry. To this purpose we can chose the following symmetry elements as generators: E: x,y,z; C: +1/2,+1/2,0; i: $\bar{x}, \bar{y}, \bar{z}$; 2_x: $x, \bar{y}, \bar{z}$ +1/2; 2_y: $\bar{x}, y, \bar{z}$.

The equivalence class of the subgroup *Cmcm* consists of 16 cosets (Table S2). They represent the 16 possible variants of symmetry *Cmcm* differing either by translations or by 90° rotations. Overall, also considering the 3 cosets of the initial transformation there are 48 variants of type *Cmcm* in the equivalence class. note that this choice of generators produces an origin shift of (0 0 1⁄4). Also, the further loss of the inversion centre ($i : \bar{x}, \bar{y}, \bar{z}$) leads to the subgroup *C222₁* (and to

an equivalence class containing 96 variants, the further 48 obtained by the product of the cosets of *Cmcm* and the inversion (*i*).The atomic positions of the fluorite structure in the standard *Cmcm* space group (resorbing the origin shift) are summarized in Table S3 and in Table S4 respectively.

In the weberite-type structure, as Y_3TaO_7, M1 is occupied by the B-type of cation, M2 and M3 by A-type cations. When averaging over variants, the effect of operator t_6 is for instance to average sites M1 and M2 while t_3 averages for instance M1 and M3. All the 48 (96) symmetry operators used to form the cosets are required to insure a cubic average of the generic orthorhombic structure. The coset operators also average the anions and the vacant sites.

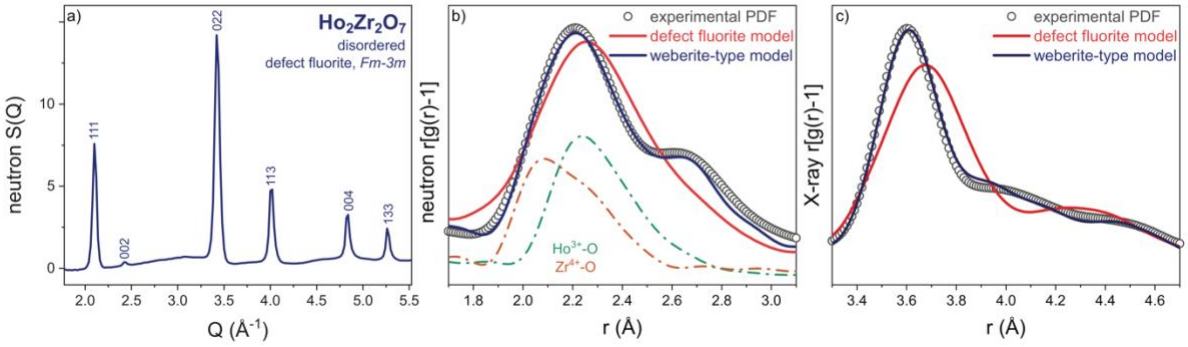

Fig. S1. Neutron total scattering data collected from the disordered, anion-deficient fluorite $Ho_2Zr_2O_7$. (A) Neutron total scattering structure function of $Ho_2Zr_2O_7$. Bragg peaks are indexed with the disordered, anion-deficient fluorite structure. Experimental (*B*) neutron and (*C*) X-ray PDFs of $Ho_2Zr_2O_7$ (black circles) compared with the disordered, anion-deficient fluorite model (red) and weberite-type ($C222_1$) model (blue). Partial PDFs (PDFs of only specific pairs of atom types) extracted from the weberite-type model are shown as dashed lines below the total PDFs.

symmetry	**$Ho_2Ti_2O_7$ (meV)**	**$Ho_2Zr_2O_7$ (meV)**
Isometric, *Fd-3m*	-192.565	-198.240
Monoclinic, *$C2_1/m$*	-191.993	-198.811

Table S1. The DFT calculations (PBE-GGA) in simple constrained symmetries confirm the improved stability of the ideal pyrochlore structure for $Ho_2Ti_2O_7$ while the calculations show that the weberite-type atomic arrangement is the stable structure for $Ho_2Zr_2O_7$.

Representative of the coset		**Cosets of *Cmcm***
$\{E\|t_1\}$	x,y,z	G_1
$\{E\|t_2\}$	$+(0,0,1/2)$	$\{E\|t_2\}\otimes G_1$
$\{E\|t_3\}$	$+(1/4,1/4,1/4)$	$\{E\|t_3\}\otimes G_1$
$\{E\|t_4\}$	$+(1/2,1/2,1/2)$	$\{E\|t_4\}\otimes G_1$
$\{E\|t_5\}$	$+(1/4,3/4,3/4)$	$\{E\|t_5\}\otimes G_1$
$\{E\|t_6\}$	$+(1/2,0,1/2)$	$\{E\|t_6\}\otimes G_1$
$\{E\|t_7\}$	$+(3/4,3/4,1/4)$	$\{E\|t_7\}\otimes G_1$
$\{E\|t_8\}$	$+(3/4,3/4,3/4)$	$\{E\|t_8\}\otimes G_1$
4_{x1}	$\boldsymbol{x,\bar{z},y}$	$4_{x1}\otimes G_1$
4_{x2}	$\boldsymbol{\frac{1}{4}+x,\bar{z}+\frac{3}{4},\frac{1}{4}+y}$	$4_{x2}\otimes G_1$
4_{x3}	$\boldsymbol{x,\bar{z}+\frac{1}{2},\frac{1}{2}+y}$	$4_{x3}\otimes G_1$
4_{1x}	$\boldsymbol{\frac{1}{4}+x,\bar{z}+\frac{1}{4},\frac{3}{4}+y}$	$4_{1x}\otimes G_1$
4_{2x1}	$\boldsymbol{\frac{1}{2}+x,\bar{z}+\frac{1}{2},\frac{1}{2}+y}$	$4_{2x1}\otimes G_1$
4_{2x2}	$\boldsymbol{\frac{1}{2}+x,\bar{z}+\frac{1}{2},y}$	$4_{2x2}\otimes G_1$
4_{3x1}	$\boldsymbol{\frac{3}{4}+x,\bar{z}+\frac{3}{4},\frac{1}{4}+y}$	$4_{3x1}\otimes G_1$
4_{3x2}	$\boldsymbol{\frac{3}{4}+x,\bar{z}+\frac{3}{4},\frac{3}{4}+y}$	$4_{3x2}\otimes G_1$

Table S2. The 16 cosets of the equivalence class of the subgroup *Cmcm*.

Atom	***x***	***y***	***z***	**Wyckoff Equipoint**
M1	0	0	1/4	4*c*
M2	1/2	0	3/4	4*c*
M3	1/4	1/4	1/2	8*d*
O1	3/8	1/4	3/4	8*g*
O2	7/8	3/4	1/4	8*g*
O3	1/8	0	1/2	*8e*
O4	5/8	0	0	8e

Table S3. Fluorite crystal structure in the *Cmcm* space group ($b'=c'=a_F\sqrt{\mathbf{2}}, a'=2a_F$).

Atom	***x***	***y***	***z***	**Wyckoff Equipoint**
M1	0	0	1/4	4*b*
M2	1/2	0	3/4	4*b*
M3	1/4	1/4	1/2	8*c*
O1	3/8	1/4	3/4	8*c*
O2	7/8	3/4	1/4	8*c*
O3a	1/8	0	1/2	4*a*
O3b	$\bar{\mathbf{1}}\mathbf{/8}$	0	$\bar{\mathbf{1}}\mathbf{/2}$	4*a*
O4a	5/8	0	0	4*a*
O4b	$\bar{\mathbf{5}}\mathbf{/8}$	0	0	4*a*

Table S4. Fluorite crystal structure in the *C*222$_1$ space group (b'=c'=$a_F\sqrt{\mathbf{2}}$,a'=2a_F).