Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary information: Assessing the local structure of highly defective $Ca_4Fe_9O_{17}$ combining STEM and FAULTS

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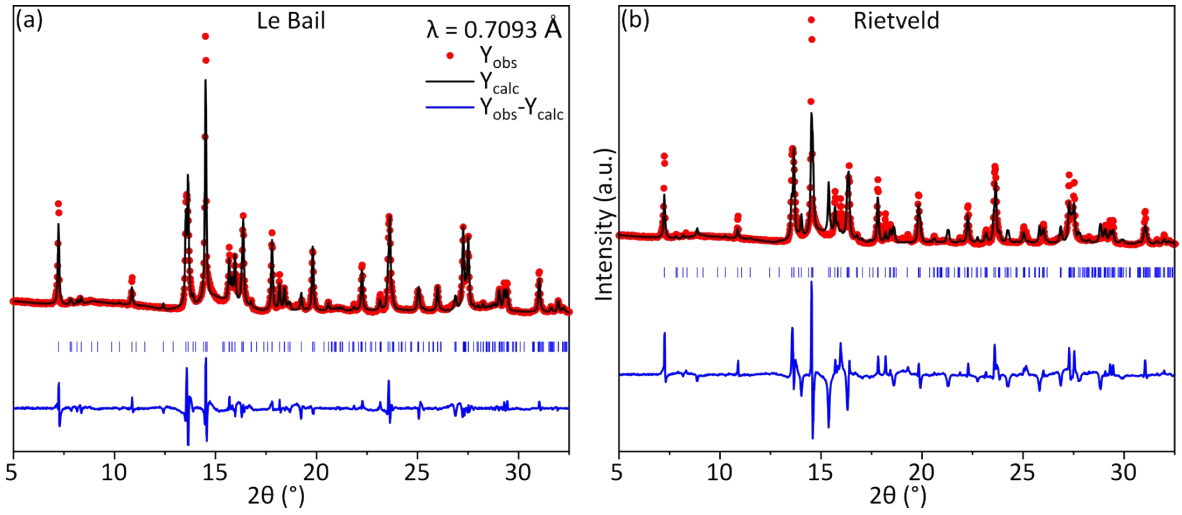

Figure S1. (a) Le Bail and (b) Rietveld refinement of $Ca_4Fe_9O_{17}$.

Creation of the layers and the stacking vectors

To optimize computational time, the unit cell was transformed into a smaller cell using the pymatgen library for Python. [1] The transformation matrix (1) has been applied to the conventional standard structure:

$$\begin{pmatrix} 0.5 & 0.5 & 0 \\ -0.5 & 0.5 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (1)$$

Secondly, the origin of the cell is shifted 0.251 in *c* so that the layer where the stacking fault occurs starts at z = 0. Finally, as the stacking direction needs to be perpendicular to the *ab* plane, *α* and *β* angles are set to 90º, the value of *c* is corrected, and atomic positions are modified accordingly. The transformation steps can be found in Figure S2. Thanks to this transformation, the unit cell has been reduced from 60 atoms to 30.

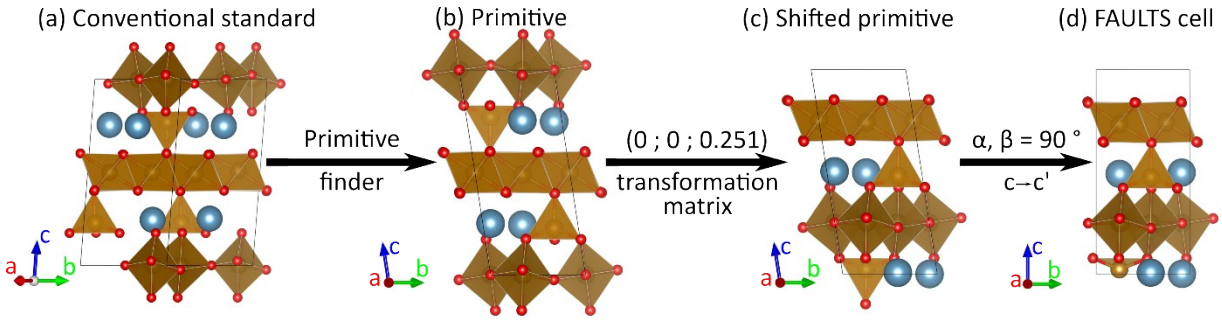

Figure S2. Steps followed from the conventional standard structure to the FAULTS cell.

Figure S3 (a) shows, marked with a red circle, that iron is located above an oxygen atom from FeO_6 octahedra. Since there are three equivalent positions, three different stacking vectors can be considered, as shown in Figure S3 (b) and indicated in table S1.

Table S1. Possible transition vectors used in the simulation and the refinement.

	x	y	z
Tr1	-1/6	-1/3	1
Tr2	-1/6	-5/6	1
Tr3	-1/6	-5/6	1

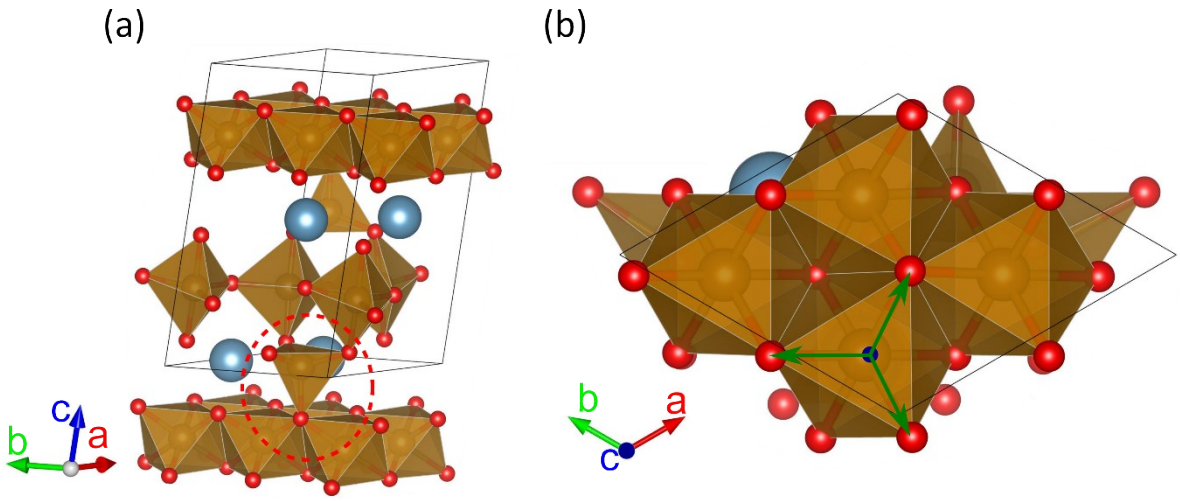

Figure S3. (a) $Ca_4Fe_9O_{17}$ structure where the zone where stacking faults may occur is marked with a red circle. (b) Green arrows show the possible transition vectors in the *xy* plane.

Table S2. Initial unit cell and atomic positions, $B_{iso,}$ and occupancies used in the FAULTS simulations of $Ca_4Fe_9O_{17}$ with a varying degree of stacking faults.

	a,b	c	gamma		
Unit cell	6.0250	11.2504	120		
Atom	x	y	z	B_{iso}	Occupancy
Ca	0.4593	0.9145	0.4961	1.00	1.00
Ca	0.1208	0.2496	0.4901	1.00	1.00
Ca	0.7875	0.5830	0.0060	1.00	1.00
Fe	0.1247	0.7495	0.7422	1.00	1.00
Fe	0.7884	0.5848	0.4740	1.00	1.00
Fe	0.1199	0.2477	0.0221	1.00	1.00
Fe	0.1181	0.9163	0.2480	1.00	1.00
Fe	0.4559	0.5777	0.2478	1.00	1.00
Fe	0.7944	0.2548	0.2482	1.00	1.00
Fe	0.6278	0.2496	0.7324	1.00	1.00
Fe	0.1277	0.2494	0.7519	1.00	1.00
Fe	0.6197	0.7495	0.7422	1.00	1.00
O	0.8003	0.5906	0.6412	1.00	1.00
O	0.9592	0.9084	0.8432	1.00	1.00
O	0.2925	0.5850	0.6475	1.00	1.00
O	0.4570	0.9139	0.8368	1.00	1.00
O	0.7936	0.0712	0.6476	1.00	1.00
O	0.4719	0.4277	0.8367	1.00	1.00
O	0.2926	0.0852	0.6445	1.00	1.00
O	0.9569	0.4137	0.8398	1.00	1.00
O	0.4381	0.9163	0.2480	1.00	1.00
O	0.5040	0.5901	0.4193	1.00	1.00
O	0.8302	0.2425	0.0768	1.00	1.00
O	0.7775	0.2870	0.4208	1.00	1.00
O	0.4068	0.5456	0.0753	1.00	1.00
O	0.0855	0.8671	0.4193	1.00	1.00
O	0.1347	0.9655	0.0768	1.00	1.00
O	0.1375	0.2509	0.2716	1.00	1.00
O	0.8028	0.5816	0.2245	1.00	1.00

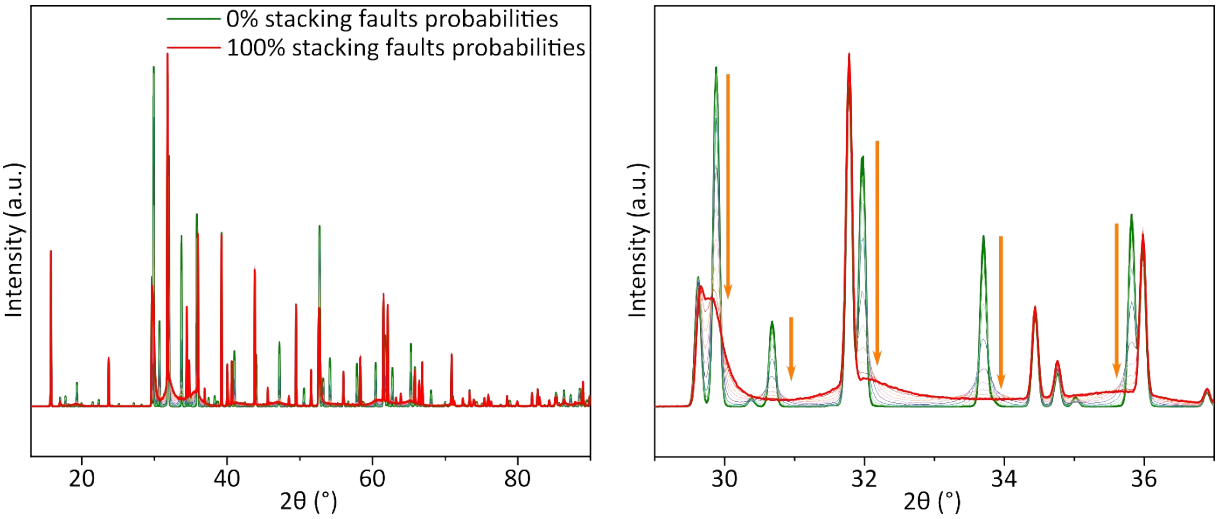

Figure S4. Simulation of diffraction pattern for the $Ca_4Fe_9O_{17}$ phase with a varying degree of stacking faults probabilities (λ = 1.54056 Å). The inset shows a zoom in the 28-40 range. The green line represents the ideal stacking with a 0% of probabilities of stacking faults, while the red line represents the structure with a 100% of stacking faults probabilities, i.e., totally random stacking vector sequence. Orange arrows mark peaks which disappear with increasing probabilities of stacking faults.

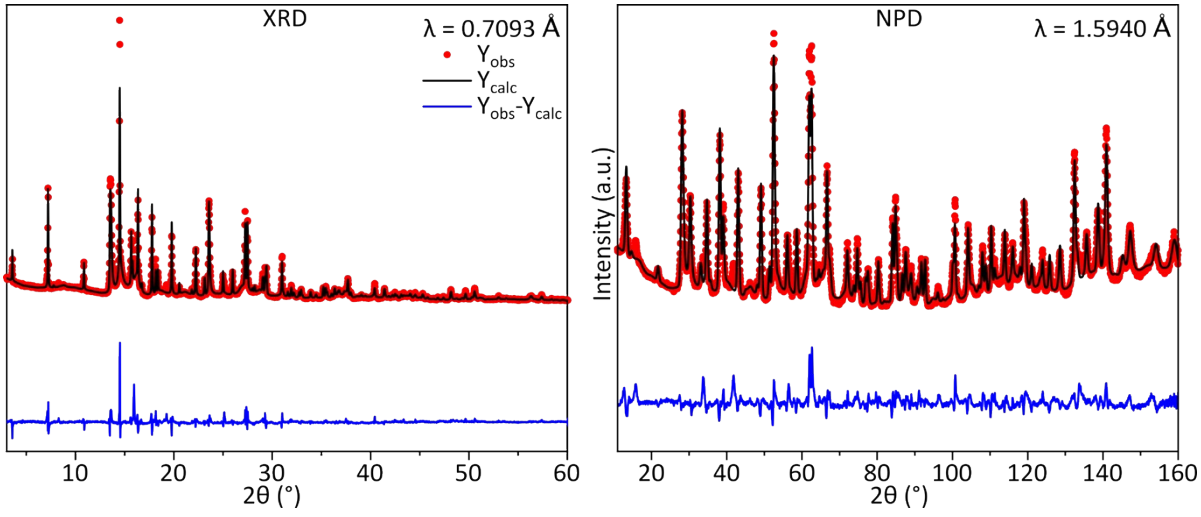

Figure S5. Full XRD and NPD refined patterns using FAULTS.

Table S3. FAULTS-refined atomic positions obtained from XRD and NPD data.

	XRD			NPD		
	x	y	z	x	y	z
Fe	0.11994	0.24810	0.02039	0.11473	0.24929	0.01849
Ca	0.45103	0.90595	0.00837	0.44350	0.92994	0.00962
Ca	0.78514	0.58042	0.00768	0.78526	0.58468	0.00672
Fe	0.11121	0.91430	0.25000	0.13583	0.90912	0.25000
Fe	0.44701	0.57674	0.25000	0.46302	0.5668	0.25000
Fe	0.78758	0.25548	0.25000	0.80408	0.24728	0.25000
Fe	0.78558	0.57851	0.47878	0.78234	0.58164	0.47829
Ca	0.45602	0.90888	0.49263	0.47041	0.91866	0.49361
Ca	0.12133	0.24588	0.49303	0.13323	0.24994	0.49359
Fe	0.61267	0.74295	0.74237	0.61511	0.74156	0.74407
Fe	0.11624	0.75003	0.74193	0.12085	0.75025	0.74585
Fe	0.61967	0.24782	0.74163	0.62013	0.24513	0.74332
Fe	0.11641	0.24707	0.76782	0.11138	0.25138	0.75998
O	0.80968	0.57694	0.62783	0.78279	0.57343	0.64281
O	0.96083	0.94362	0.85400	0.95139	0.90994	0.84763
O	0.28634	0.57940	0.66472	0.27944	0.57855	0.65087
O	0.45050	0.92389	0.83820	0.44400	0.91671	0.83167
O	0.78539	0.09204	0.66386	0.7876	0.07501	0.65324
O	0.49003	0.42876	0.85256	0.44195	0.40917	0.84597
O	0.27233	0.07319	0.67809	0.29545	0.08442	0.65121
O	0.98077	0.42093	0.84875	0.94264	0.42046	0.85011
O	0.48993	0.89685	0.25173	0.48713	0.90975	0.25746
O	0.48989	0.60250	0.42205	0.49053	0.5866	0.42431
O	0.80078	0.23328	0.08737	0.80990	0.23926	0.07285
O	0.76280	0.27222	0.41117	0.76071	0.29314	0.41632
O	0.39694	0.55547	0.07767	0.41088	0.55082	0.07497
O	0.07965	0.87443	0.41614	0.06139	0.85967	0.42373
O	0.12755	0.95508	0.08603	0.13209	0.93790	0.07523
O	0.16696	0.24331	0.26416	0.16968	0.24581	0.26028
O	0.84717	0.57261	0.24046	0.80464	0.57458	0.21548

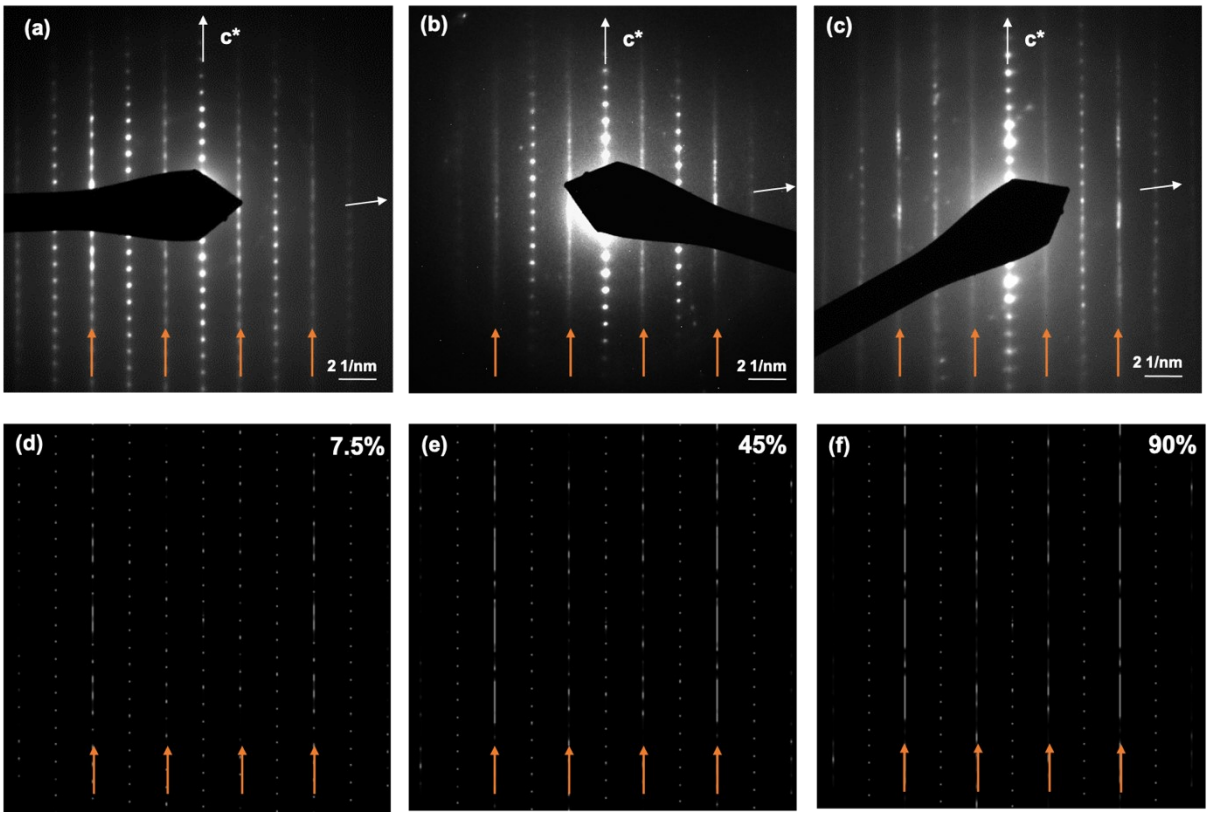

Figure S6. SAED figure a) b) and c) correspond to diffraction patterns along the [010], [110] or [1-10] axis of $Ca_4Fe_9O_{17}$ phase crystals showing different degrees of disorder. Images d), e) and f) correspond to the diffraction patterns simulated by the Faults program along the [010], [110] or [1-10] axis with degrees of disorder of 7.5%, 45% and 90% respectively.

REFERENCES

(1) Ong, S. P.; Richards, W. D.; Jain, A.; Hautier, G.; Kocher, M.; Cholia, S.; Gunter, D.; Chevrier, V. L.; Persson, K. A.; Ceder, G. Python Materials Genomics (Pymatgen): A Robust, Open-Source Python Library for Materials Analysis. *Comput. Mater. Sci.* **2013**, *68*, 314–319. https://doi.org/10.1016/j.commatsci.2012.10.028.