Supporting Information to:

Synthesis and Properties of $La_{18}Fe_5Cu_4S_{26}O_8$, Containing Large Magnetic Clusters

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Structure Refinement Strategy for SC-XRD Data

1. Refining the lattice parameters.
2. Determining the symmetry of the crystal structure. (*Cmcm* is the initial guess).
3. Determining the species and isotropic thermal parameters of the ordered sections of the crystal structure (La, S, O, and the ordered Fe-positions).
4. Refine anisotropic thermal parameters of the ordered sections.
5. Determining the plausible sites in the disordered section from crystallographic consideration and electron density maps.
6. Determination of species in each site of the disordered section by trial and error. This step included a number of considerations and logical guidelines to narrow down the space of possible arrangements:
    - The total occupancy of too closely adjacent sites may not exceed 1.
    - The observed disorder is assumed to be an averaged image of different configurations.
    - The individual occupancies of each site corresponds to how often the corresponding configuration is assumed.
    - Cu+ is the species more likely to occupy trigonal planar sites compared with Fe2+.
    - The total occupancies have to add up to the correct stoichiometry.
    - The occupancy of each site must be as close to the value obtained from refining the occupancy with an isotropic thermal parameter as possible.
    - Sufficient refinement parameters.

7. Once a motif which satisfied all necessary conditions was found, the partial occupancies were fixed to the appropriate values for that motif. The partially occupied sites were refined with isotropic thermal parameters, as they are too close for anisotropic refinement to resolve properly.

8. Finally, the thermal parameters of the full structure was refined to obtain the final structure.

Additionally, the electron density of the disordered section was analyzed in lower symmetries to test whether the partial occupancies would dissappear, but lower symmetry refinements all resulted in the same disorder.

Table S1. Structural parameters for LFCSO, as refined from single-crystal X-ray data at 293 K, with additional information on the refined parameters.

Atom	Site	*x*	*y*	*z*	Occ.	U_{iso} (Å^2)
La1	8*f*	0.5	0.42836(2)	0.53727(4)	1	0.0065(1)
La2	4*c*	0.5	0.32992(2)	0.25	1	0.0053(2)
La3	16*h*	0.78807(3)	0.32055(1)	0.53350(3)	1	0.0071(1)
La4	8*g*	0.77609(4)	0.43308(2)	0.25	1	0.0070(1)
Fe1	4*c*	0	0.24876(6)	0.25	1	0.0110(4)
Fe2	8*f*	0.5	0.0102(1)	0	0.5	0.0210(5)
Fe3	16*h*	0.5681(7)	0.0952(2)	0.1944(6)	0.125	0.015(2)
Cu1	8*f*	0.5	0.0948(2)	0.1631(5)	0.25	0.026(1)
Cu2	16*h*	0.3300(5)	0.0603(2)	0.1494(5)	0.25	0.045(1)
Cu3	16*h*	0.2925(5)	0.0538(2)	0.2058(5)	0.125	0.010(1)
S1	8*f*	0	0.23198(7)	0.4868(2)	1	0.0087(4)
S2	4*c*	0.5	0.48045(9)	0.25	1	0.0086(6)
S3	8*g*	0.2356(2)	0.26844(7)	0.25	1	0.0093(4)
S4	4*c*	0.5	0.0139(1)	0.25	1	0.0107(6)
S5	4*c*	0	0.3240(1)	0.75	1	0.0100(7)
S6	8*f*	0	0.39215(8)	0.4370(2)	1	0.0163(5)
S7	8*e*	0.2465(2)	0	0	1	0.0132(5)
S8	8*g*	0.3210(2)	0.38384(8)	0.75	1	0.0215(6)
O1	16*h*	0.6535(3)	0.3770(2)	0.4046(3)	1	0.0070(9)

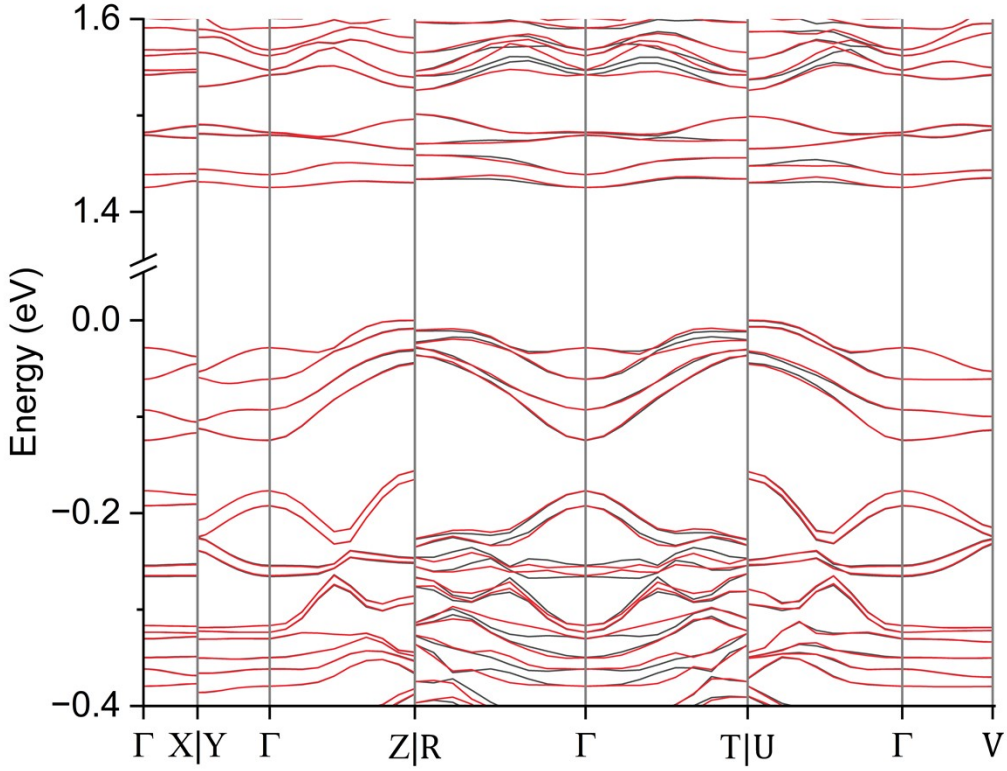

Figure S1: The band structure of LFCSO, calculated with an applied U_{eff} = 3 eV.