Supporting Information for:

# Original network of zig-zag chains in the β polymorph of $Fe_2WO_6$: crystal structure and magnetic ordering

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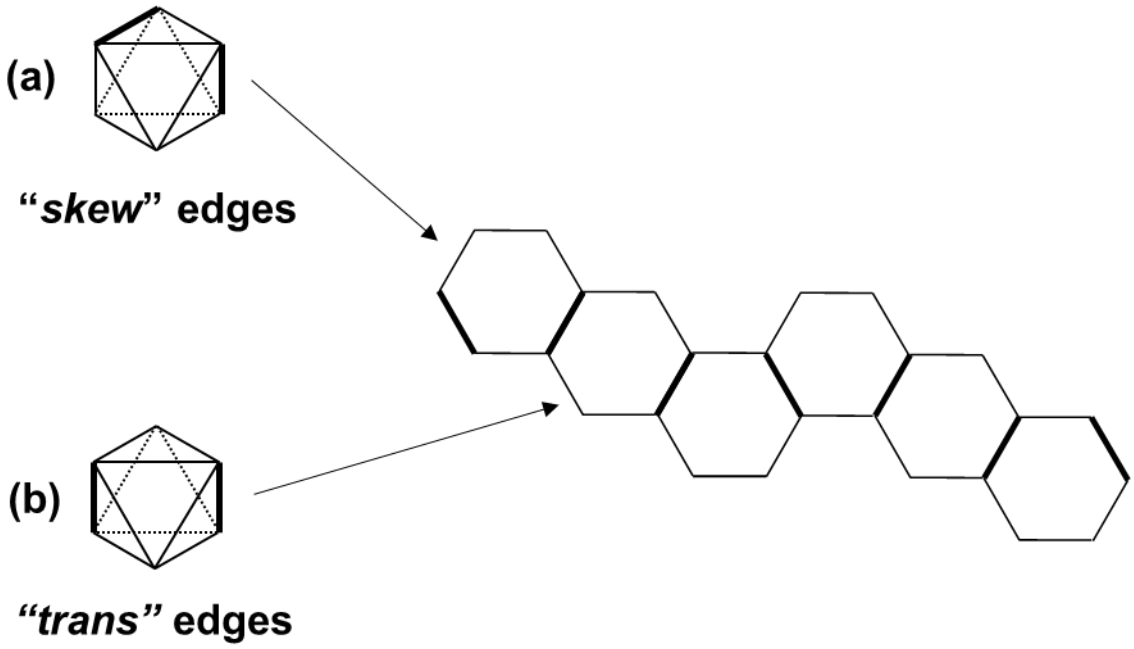


**Figure S1.** Octahedra sharing (a) "skew" and (b) "trans" edges forming a zig-zag chain of octahedra.

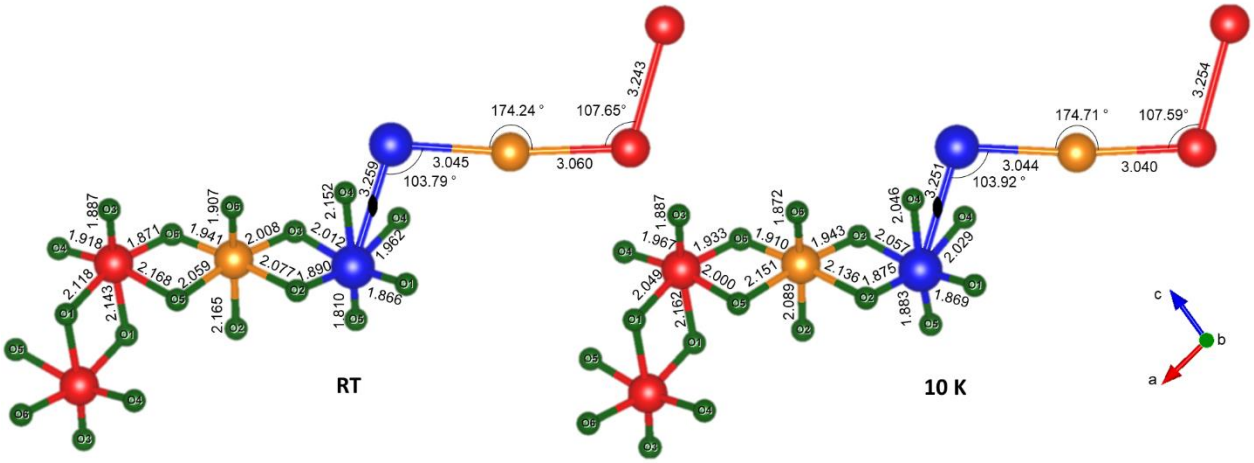


**Figure S2.** Projections along [010] to show selected interatomic distances (in Å) and angles (in degrees) in $\beta$-$Fe_2WO_6$ at room temperature and 10K. Black dots in the middle of the W-W bonds correspond to the inversion center. $WO_6$ octahedra, blue; $Fe1O_6$ octahedra, red; $Fe2O_6$ octahedra, orange.

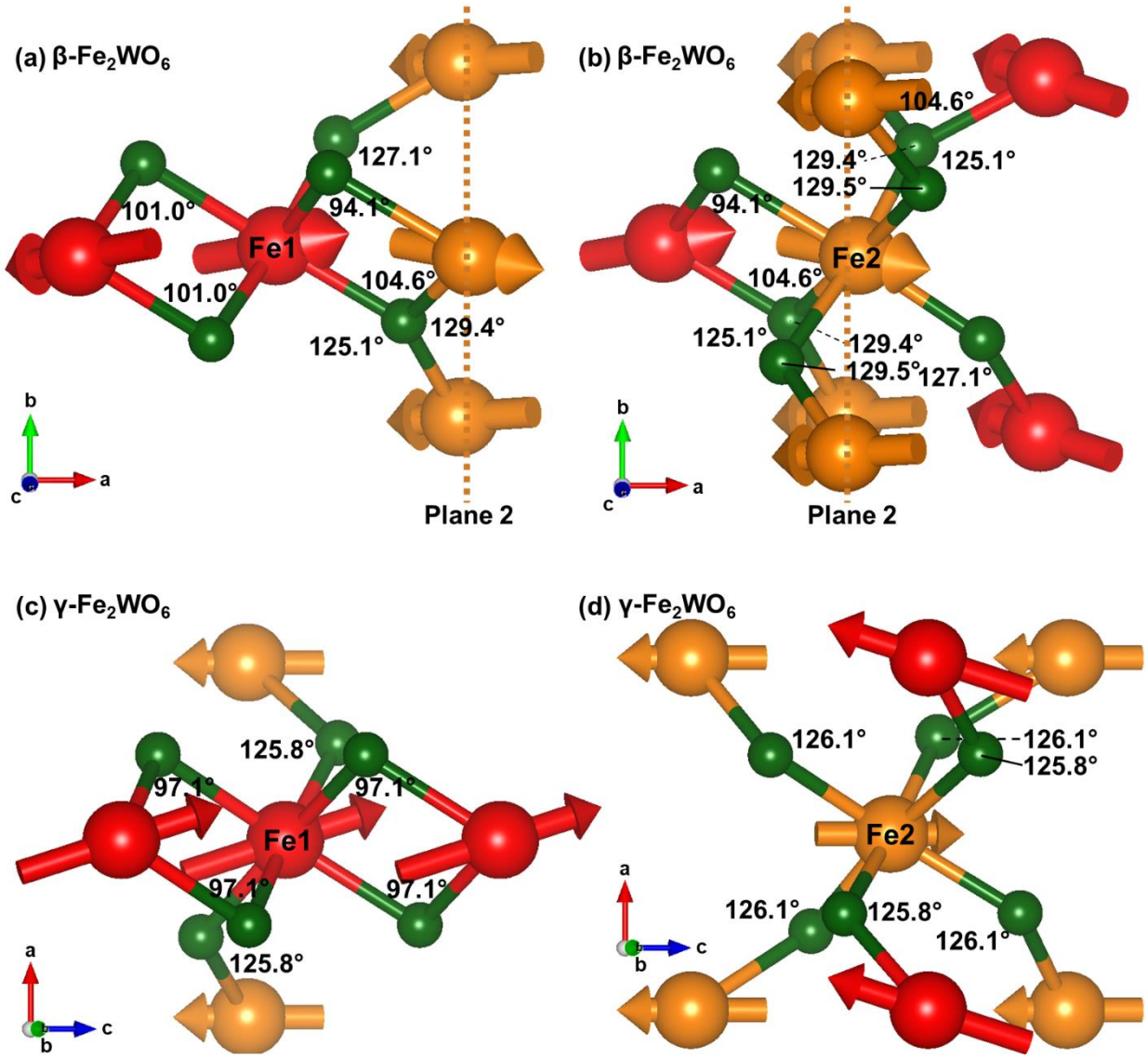


**Figure S3.** Representations of the environments and magnetic interactions of Fe1 and Fe2 in **(a,b)** *β*-$Fe_2WO_6$ and **(c,d)** γ-$Fe_2WO_6$. In β-$Fe_2WO_6$, Fe1 has 3 AFM and 1 FM interactions; Fe2 has 6 AFM and 1 FM interactions. In γ-$Fe_2WO_6$, Fe1 has 2 AFM and 2 FM interactions; Fe2 has 6 AFM interactions. Oxygen atoms are represented by dark green spheres.

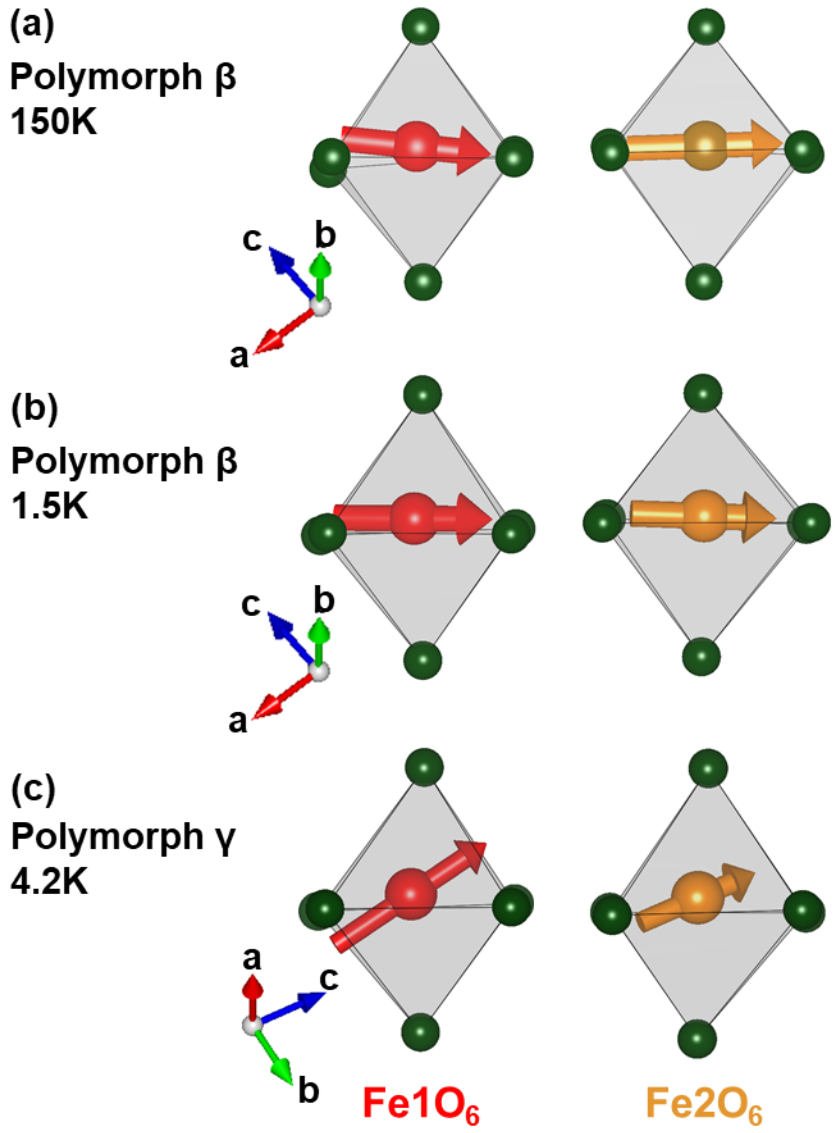


**Figure S4.** Orientations of the $Fe^{3+}$ moments in the $FeO_6$ octahedra **(a)** in $\beta$-$Fe_2WO_6$ at and above 150 K, **(b)** at 1.5 K and **(c)** in $\gamma$-$Fe_2WO_6$ at 4.2 K. The representations of individual octahedra show that the canting of the moment away from the *ac* plane in $\beta$-$Fe_2WO_6$ below 150 K corresponds to a realignment of the spin towards the basal plane of the octahedron.

| $WO_6$ | x | y | z | $Fe1O_6$ | x | y | z | $Fe2O_6$ | x | y | z |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **W1** | **0.5876** | **-0.0036** | **0.3613** | **Fe1** | **0.5853** | **-0.5085** | **-0.1451** | **Fe2** | **0.7449** | **0.0043** | **0.7708** |
| O4 | 0.4760 | -0.2190 | 0.3714 | O1 | 0.4686 | -0.2568 | -0.1315 | O3 | 0.6328 | -0.2257 | 0.6648 |
| O5 | 0.6365 | -0.2670 | 0.1789 | O4 | 0.5240 | -0.7810 | -0.3714 | O2 | 0.8110 | -0.2691 | 0.5360 |
| O3 | 0.6328 | -0.2257 | 0.6648 | O1 | 0.5314 | -0.7432 | 0.1315 | O6 | 0.8055 | -0.1995 | 1.0522 |
| O1 | 0.5314 | 0.2568 | 0.1315 | O3 | 0.6328 | -0.2257 | -0.3352 | O2 | 0.6890 | 0.2309 | 0.4640 |
| O4 | 0.5240 | 0.2190 | 0.6286 | O5 | 0.6365 | -0.2670 | 0.1789 | O6 | 0.6945 | 0.3005 | 0.9478 |
| O2 | 0.6890 | 0.2309 | 0.4640 | O6 | 0.6945 | -0.6995 | -0.0522 | O5 | 0.8635 | 0.2330 | 0.8211 |
| **Barycenter** | **0.5816** | **-0.0008** | **0.4065** | **Barycenter** | **0.5813** | **-0.4955** | **-0.0967** | **Barycenter** | **0.7494** | **0.0117** | **0.7477** |
| **Off-centering** | **0.0903 Å** | **-0.0127 Å** | **-0.2531 Å** | **Off-centering** | **0.0604 Å** | **-0.0596 Å** | **-0.2711 Å** | **Off-centering** | **-0.0677 Å** | **-0.0339 Å** | **0.1296 Å** |

**Table S1.** Atomic positions, barycenter positions and off-centering in the $MO_6$ octahedra in polymorph $\beta$ at room temperature. Off-centering is expressed in Å and calculated as the difference between the positions of the cation and the barycenter.

| $WO_6$ | x | y | z | $Fe1O_6$ | x | y | z | $Fe2O_6$ | x | y | z |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **W1** | **0.5000** | **0.1128** | **0.7500** | **Fe1** | **0.5000** | **0.4436** | **0.7500** | **Fe2** | **0.5000** | **0.7758** | **0.7500** |
| O4 | 0.2400 | 0.0409 | 0.5958 | O1 | 0.2266 | 0.3729 | 0.5692 | O3 | 0.2240 | 0.7035 | 0.5817 |
| O5 | 0.2760 | 0.2035 | 0.5817 | O4 | 0.2600 | 0.4591 | 1.0958 | O2 | 0.2734 | 0.8729 | 0.5692 |
| O3 | 0.2734 | 0.1271 | 1.0692 | O1 | 0.2600 | 0.5409 | 0.5958 | O6 | 0.2760 | 0.7965 | 1.0817 |
| O1 | 0.7600 | 0.0409 | 0.9042 | O3 | 0.7734 | 0.3729 | 0.9308 | O2 | 0.7760 | 0.7035 | 0.9183 |
| O4 | 0.7266 | 0.1271 | 0.4308 | O5 | 0.7400 | 0.4591 | 0.4042 | O6 | 0.7240 | 0.7965 | 0.4183 |
| O2 | 0.7240 | 0.2035 | 0.9183 | O6 | 0.7400 | 0.5409 | 0.9042 | O5 | 0.7266 | 0.8729 | 0.9308 |
| **Barycenter** | 0.5000 | 0.1238 | 0.7500 | **Barycenter** | 0.5000 | 0.4576 | 0.7500 | **Barycenter** | 0.5000 | 0.7910 | 0.7500 |
| **Off-centering** | **0.0000 Å** | **-0.1858 Å** | **0.0000 Å** | **Off-centering** | **0.0000 Å** | **-0.2353 Å** | **0.0000 Å** | **Off-centering** | **0.0000 Å** | **-0.2543 Å** | **0.0000 Å** |

**Table S2.** Atomic positions, barycenter positions and off-centering in the $MO_6$ octahedra in polymorph $\gamma$ at room temperature. Off-centering is expressed in Å and calculated as the difference between the positions of the cation and the barycenter.

| $WO_6$ | x | y | z | $FeO_6$ | x | y | z |
|---|---|---|---|---|---|---|---|
| **W** | **0.0000** | **0.1808** | **0.2500** | **Fe** | **0.5000** | **0.3215** | **0.7500** |
| O1 | -0.2158 | -0.1068 | 0.4167 | O1 | 0.2158 | 0.1068 | 0.5833 |
| O1 | -0.2158 | 0.1068 | -0.0833 | O2 | 0.2623 | 0.6150 | 0.5912 |
| O2 | -0.2623 | 0.3850 | 0.4088 | O2 | 0.2623 | 0.3850 | 1.0912 |
| O1 | 0.2158 | -0.1068 | 0.0833 | O1 | 0.7842 | 0.1068 | 0.9167 |
| O1 | 0.2158 | 0.1068 | 0.5833 | O2 | 0.7377 | 0.3850 | 0.4088 |
| O2 | 0.2623 | 0.3850 | 0.0912 | O2 | 0.7377 | 0.6150 | 0.9088 |
| **Barycenter** | 0.0000 | 0.1283 | 0.2500 | **Barycenter** | 0.5000 | 0.3689 | 0.7500 |
| **Off-centering** | **0.0000 Å** | **0.3001 Å** | **0.0000 Å** | **Off-centering** | **0.0000 Å** | **-0.2713 Å** | **0.0000 Å** |

**Table S3.** Atomic positions, barycenter positions and off-centering in the $MO_6$ octahedra in $FeWO_4$ at room temperature. Off-centering is expressed in Å and calculated as the difference between the positions of the cation and the barycenter.

| **β-$Fe_2WO_6$ structure at RT** | | | |
|---|---|---|---|
| Site | Formal charge q | Charge distribution Q (with Fe and W on actual positions) | Charge distribution Q (with Fe and W at barycenters) |
| W | 6 | **6.05** | **5.54** |
| Fe1 | 3 | **2.997** | **3.189** |
| Fe2 | 3 | **2.953** | **3.267** |

**Table S4.** Comparison of q, the formal charge of the cations, and Q, the value calculated for each octahedron using the implementation in the Vesta software [K. Momma and F. Izumi, J. Appl. Crystallogr. 44 (2011) 1272–1276] of the charge distribution method [M. Nespolo, G. Ferraris, R. Hoppe, J. Ceram. Process. Res. 2 (2001) 38–44]. The agreement between the formal charge and the actual structure is excellent.