Supplementary Information (SI) for Dalton Transactions.

Electronic Supporting Information: Refining Hydrogen Positions in α-FeOOH through Combined Neutron Diffraction and Computational Techniques

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TEMPERATURE DEPENDENCE OF HYDROGEN-BOND GEOMETRY

In addition to the O2-H bond length (Fig. 2(d) in the main text), we evaluated the H$\cdots$O1 and O1$\cdots$O2 distances, and the O2-H$\cdots$O1 angle as a function of temperature (Fig. S1).

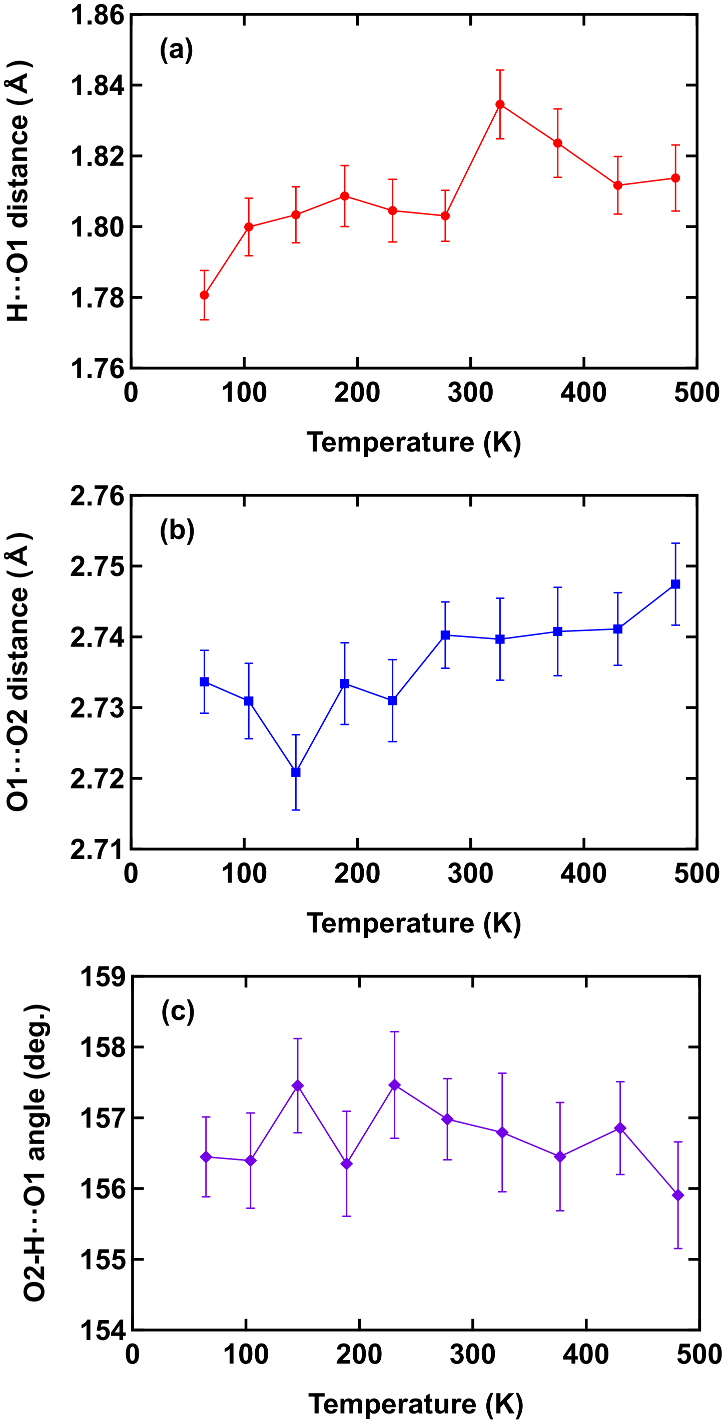

FIG. S1. Temperature dependence of (a) H$\cdots$O1 distance, (b) O1$\cdots$O2 distance, and (c) O2-H$\cdots$O1 angle.

DIFFERENCE-FOURIER MAP

We provide a difference-Fourier map (Fig. S2) generated by setting the H occupancy to zero. This type of map is commonly used to identify atomic positions missing from a structural model. In this case, the model was constructed using only Fe, O1, and O2 atoms. By calculating the structure factor, F_{calc}, from this model with observed structure factor, F_{obs}, the resulting difference map reveals residual scattering density not accounted for by the model. The observed residual density is located at the expected hydrogen positions, further supporting that the neutron refinement correctly captures the H position even in an undeuterated sample.

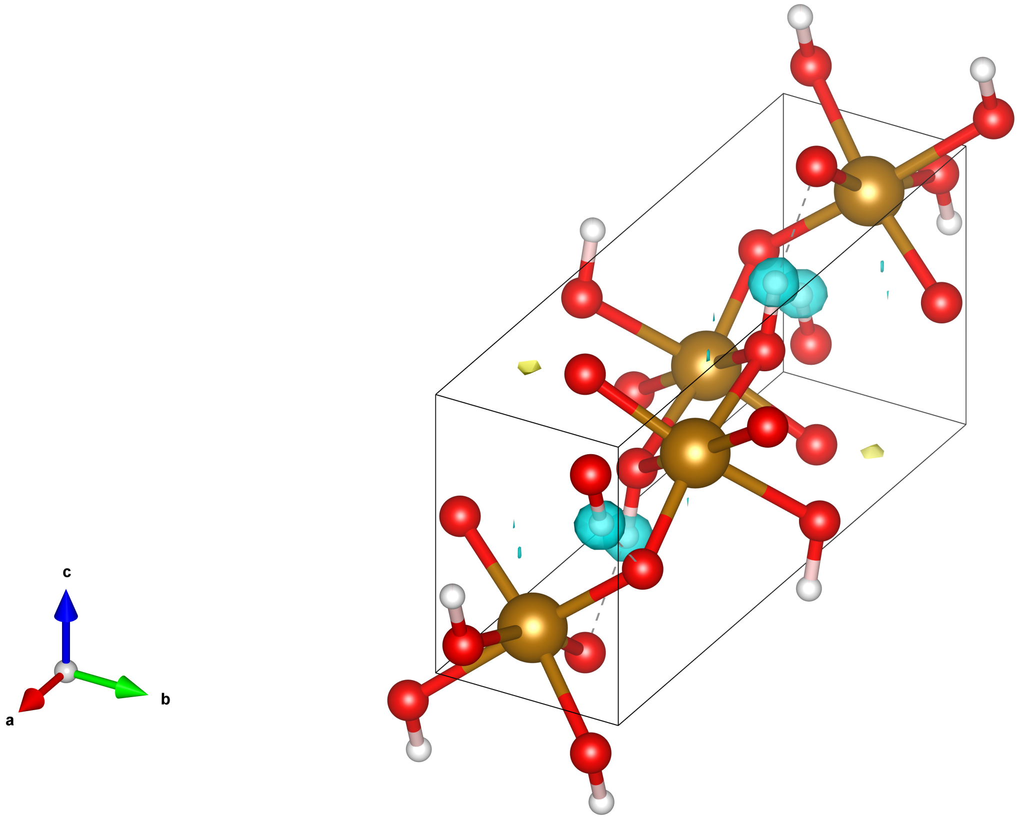

FIG. S2. Difference-Fourier map used to corroborate the refined H positions, with negative scattering length density contoured in cyan at the 0.17 fm/Å^3 level.

DEBYE-GRÜNEISEN FIT TO TEMPERATURE-DEPENDENT LATTICE PARAMETERS

The DFT+U calculated structures correspond to 0 K, whereas the neutron diffraction refinements span 64.8-485 K. To address thermal-expansion effects when comparing lattice constants, we additionally fitted the temperature dependence of a, b, and c using a Debye-Grüneisen model (Fig. S3),

$$l(T) = l_0 + AU_{\mathrm{D}}(T),\ U_{\mathrm{D}}(T) = 9Nk_{\mathrm{B}}T\left(\frac{T}{\Theta_{\mathrm{D}}}\right)^3\int_0^{\Theta_{\mathrm{D}}/T}\frac{x^3}{e^x-1}\mathrm{d}x,$$

where $l \in \{a, b, c\}$ denotes the lattice parameter, l_0 is its zero-temperature value, A is a proportionality constant describing the coupling between the lattice parameter and the phonon energy, $U_{\mathrm{D}}(T)$ is the lattice internal energy within the Debye approximation, N is the number of atoms per formula unit, k_{B} is the Boltzmann constant, and Θ_{D} is the Debye temperature. Fitting was performed and extrapolated to 0 K, obtaining $a = 9.93432$ Å, $b = 3.01191$ Å, and $c = 4.59270$ Å. These values differ from the 64.8 K parameters by approximately 5×10^{-4} Å and are marginally closer to the 0 K DFT values (especially for a and b), consistent with thermal expansion.

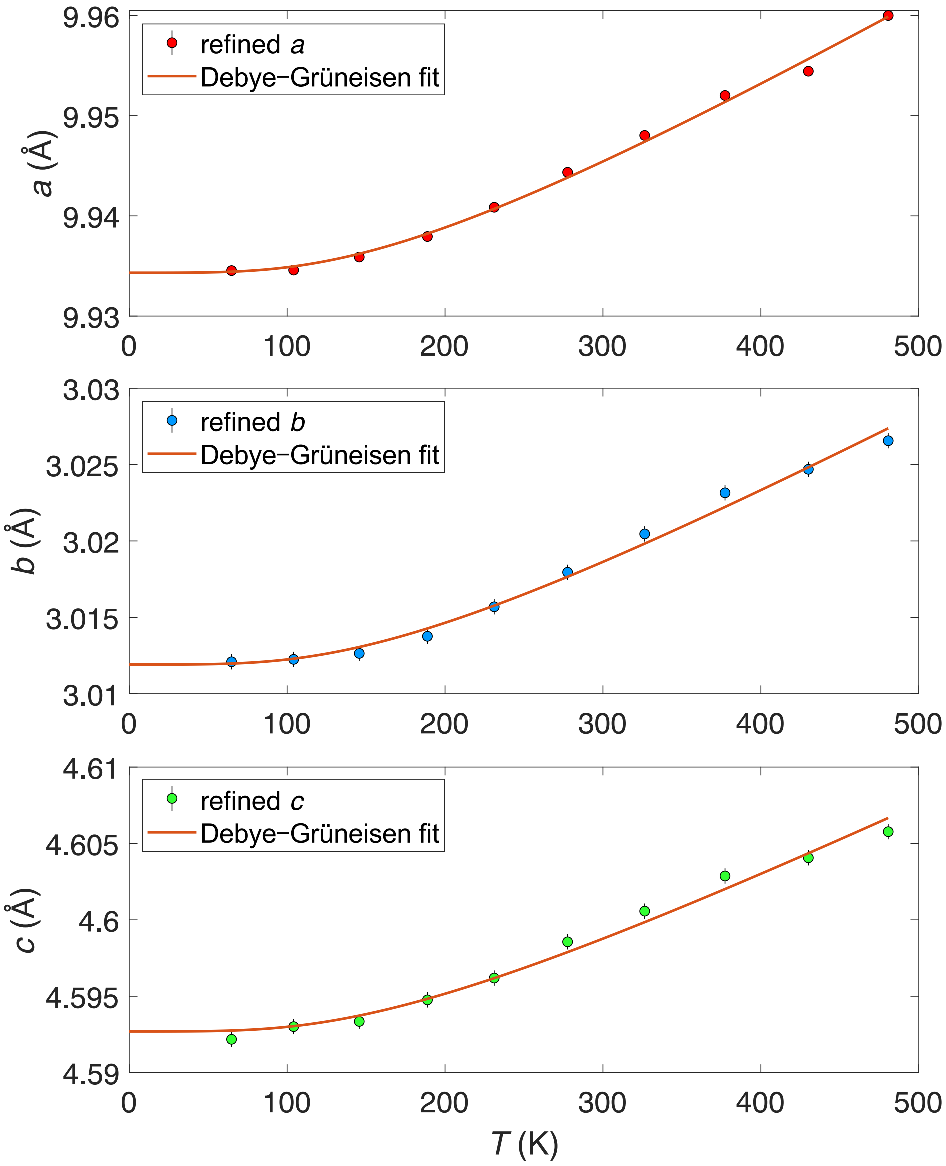

FIG. S3. Debye-Grüneisen model fits to the observed temperature dependence of the lattice parameters.