Supplementary Information
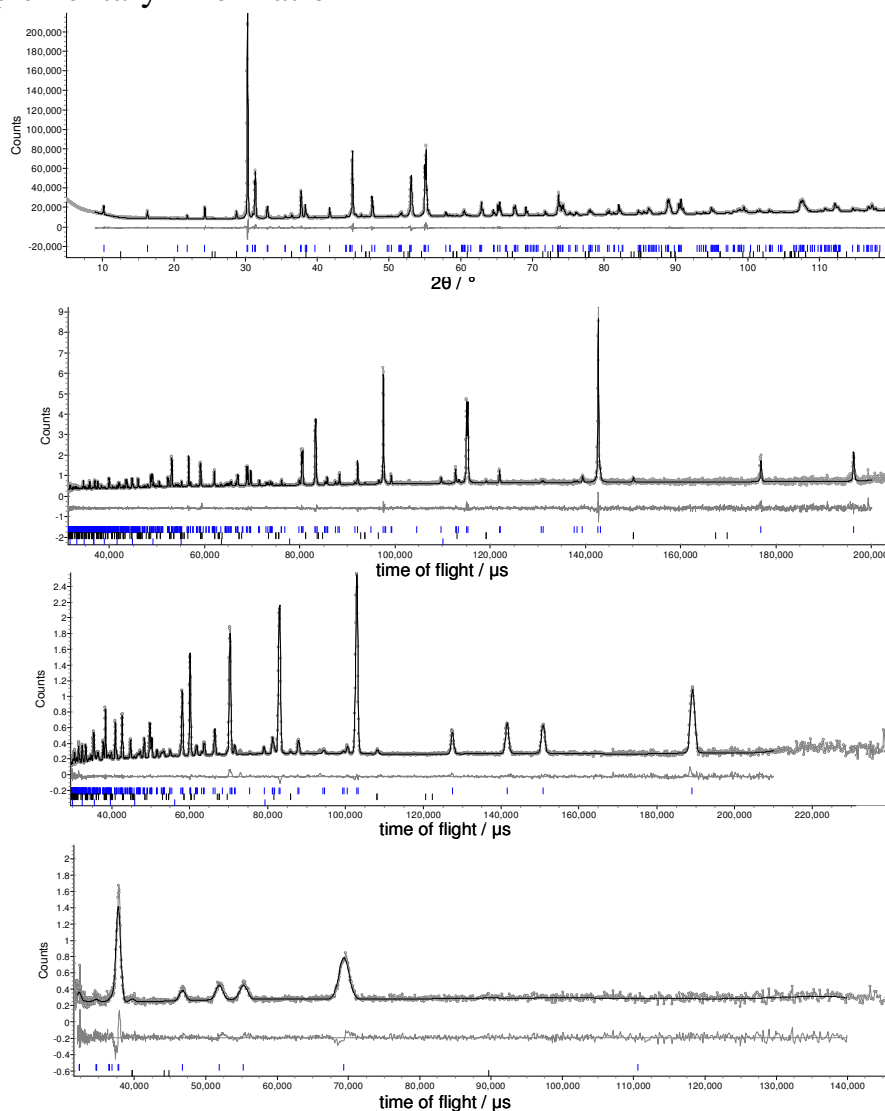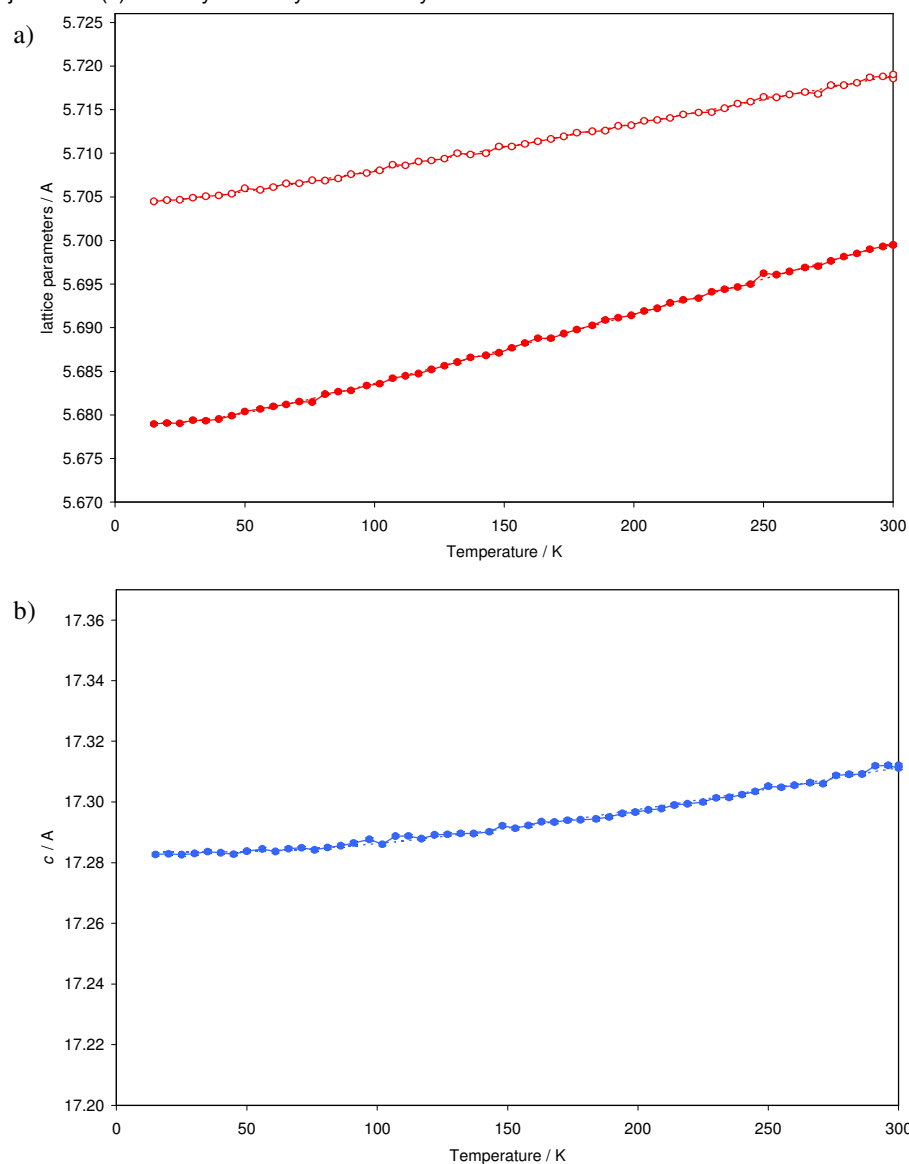

S1.   Rietveld refinement profiles from combined refinement using 295 K a) XRPD data, b) backscattered NPD data, c) 90° NPD data and d) 30° NPD data for $Ce_2O_2FeSe_2$ with observed and calculated patterns shown in grey and black, respectively; difference profile shown below in grey, peak positions shown with vertical tick marks for $Ce_2O_2FeSe_2$ (directly below profile), Ce_2O_2Se (second from top) and vanadium (bottom, NPD refinements only).
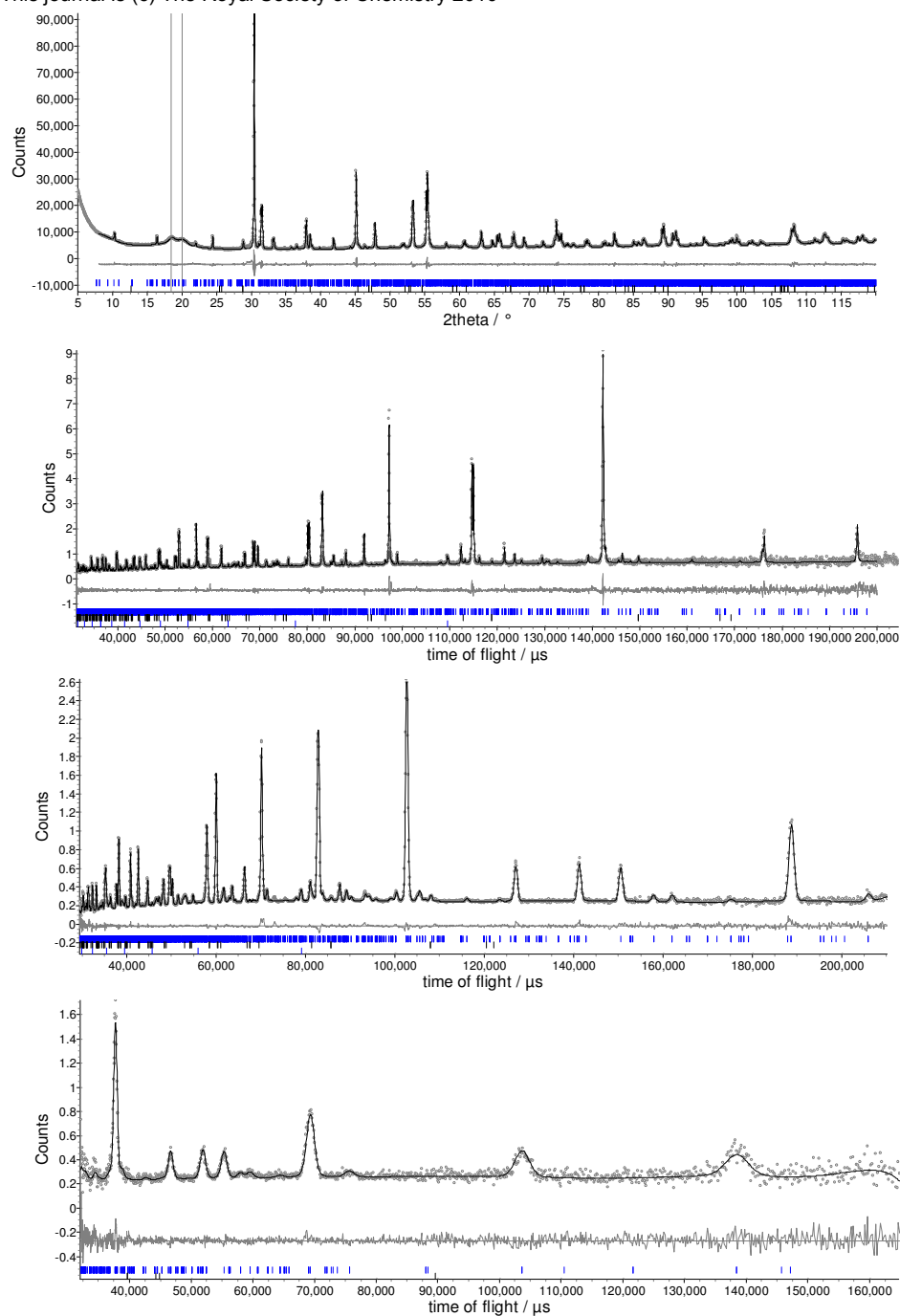
a)

b)

S2. Plots of unit cell parameters as a function of temperature determined from sequential Rietveld refinements using XRPD data a) *a* and *b* lattice parameters shown with closed and open points, respectively and b) *c* lattice parameter. Thermal expansion was modelled using
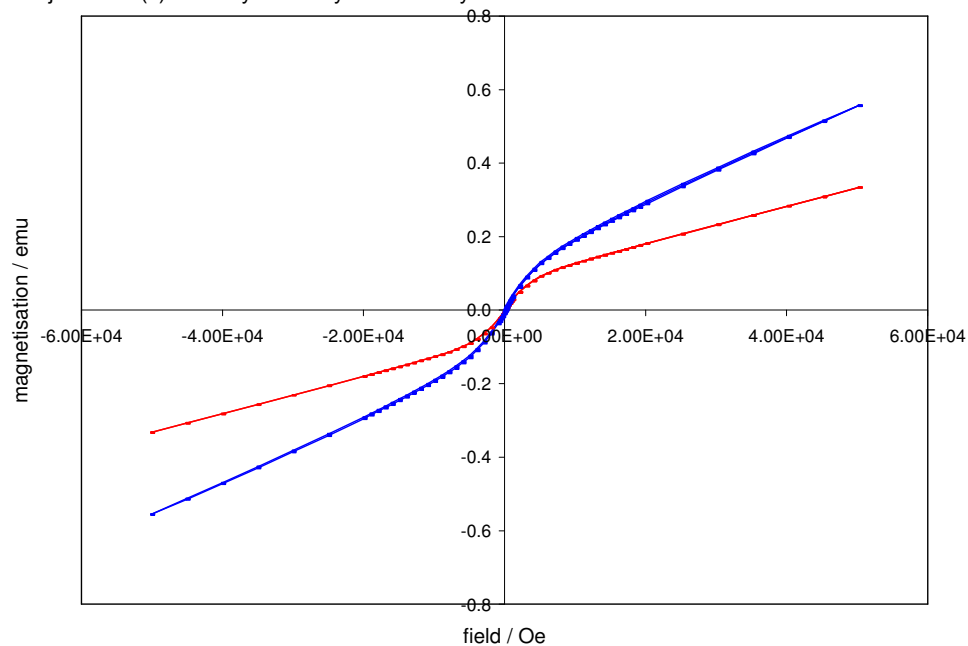
the expression: $\ln\left[\dfrac{a_T}{a_0}\right] = \dfrac{C_i\theta_i}{\exp\left(\theta_i/T\right)-1}$ where a_T is the *a* lattice parameter at temperature T,
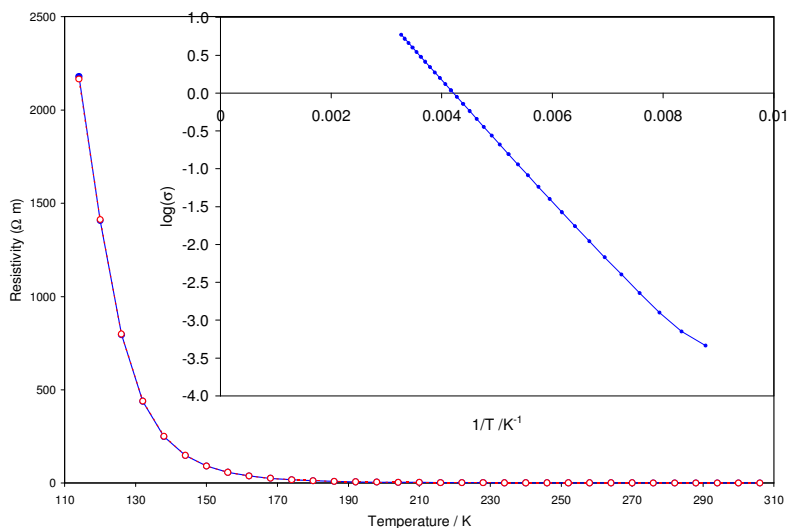
a_0 is the a lattice parameter at 0 K, C_i a constant and θ_i the Einstein temperature. Einstein temperatures are 110(4) K, 89(6) K and 280(15) K for *a*, *b* and *c*, respectively, corresponding to increases of 0.36%, 0.26%, 0.17% and 0.79% in *a*, *b*, *c* and volume, respectively.

S3.   Rietveld refinement profiles from combined refinement using 12 K a) XRPD data, b) backscattered NPD data, c) 90° NPD data and d) 30° NPD data for $Ce_2O_2FeSe_2$ with observed and calculated patterns shown in grey and black, respectively; difference profile shown below in grey, peak positions shown with vertical tick marks for $Ce_2O_2FeSe_2$ (directly below profile), Ce_2O_2Se (second from top) and vanadium (bottom, NPD refinements only).

S4.   Plots of magnetization versus field for $Ce_2O_2SeFe_2$ at 295 K (red) and 12 K (blue).

S5.   a) Electrical resistivity of $Ce_2O_2FeSe_2$ as a function of temperature and inset, Arrhenius plot of log(conductivity) versus reciprocal temperature, with data collected on cooling (blue, closed points) and on warming (red, open points).