Supporting Information

Orbital Contribution to Paramagnetism and Non-Innocent Thiophosphate Anions in Layered $Li_2MP_2S_6$ where *M* = Fe, Co

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Figure S1. Solid-state synthesis setup. Stoichiometric ratios of starting reagents are ground together and placed in the graphite crucible shown above. This crucible is then sealed in a quartz ampoule.

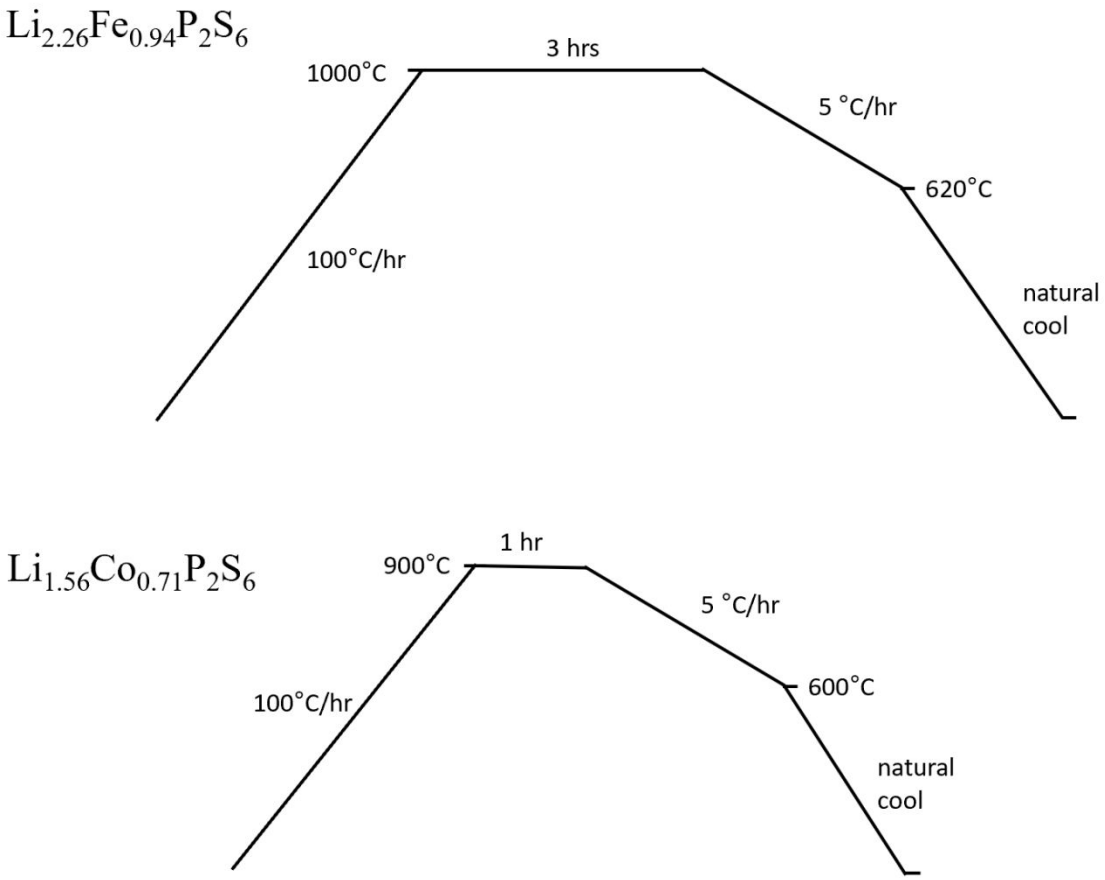

Figure S2. "Bridgman-like" single crystal heating profiles for the iron and cobalt thiophosphates.

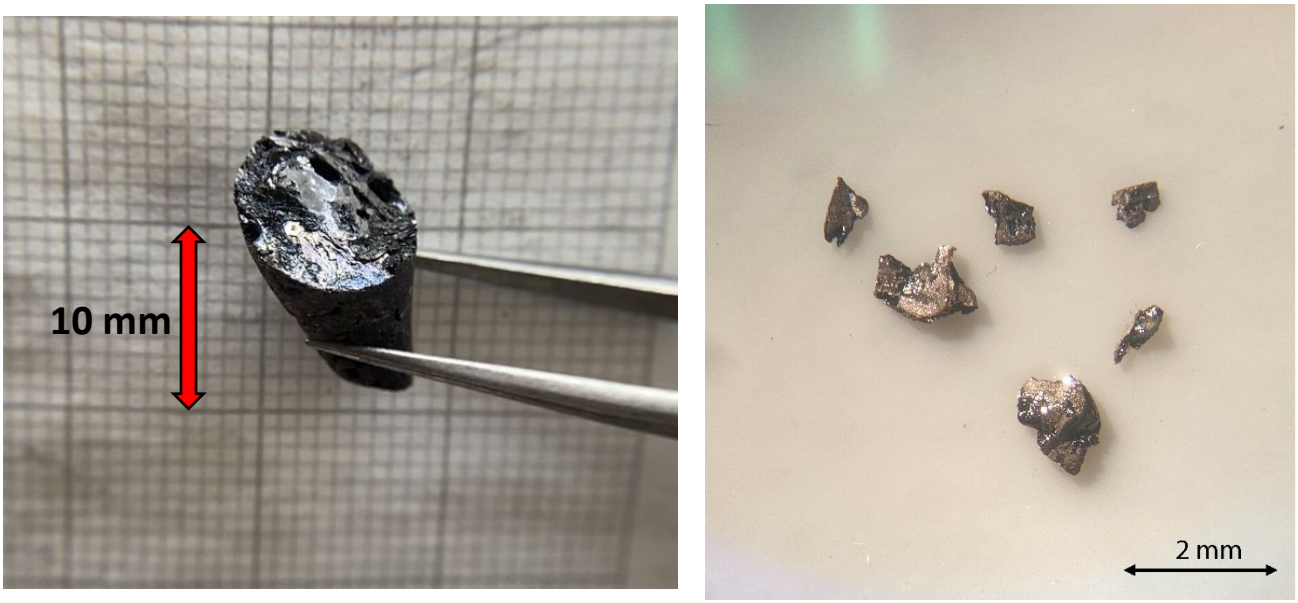

Figure S3. Example $Li_{1.56}Co_{0.71}P_2S_6$ single crystals. These crystals grow in a layered manner; when broken off from the bulk, they are about 1-4 mm long with a shiny metallic surface that degrades within seconds of contact with air.

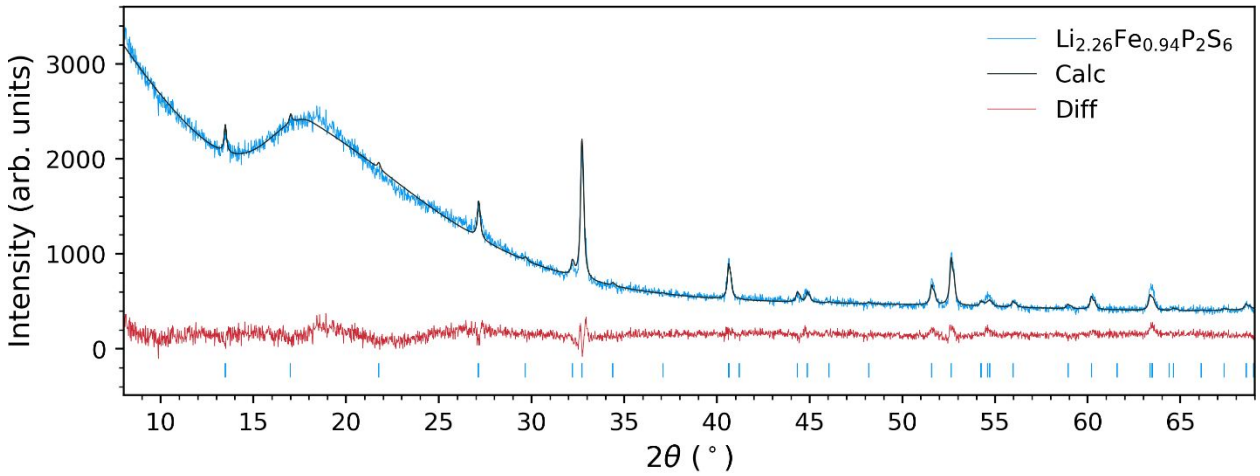

Figure S4. X-ray powder diffraction and Rietveld fit of $Li_{2.26}Fe_{0.94}P_2S_6$. The large broad peak at approximately 18° 2θ is due to Kapton tape used to minimize air exposure during experiment.

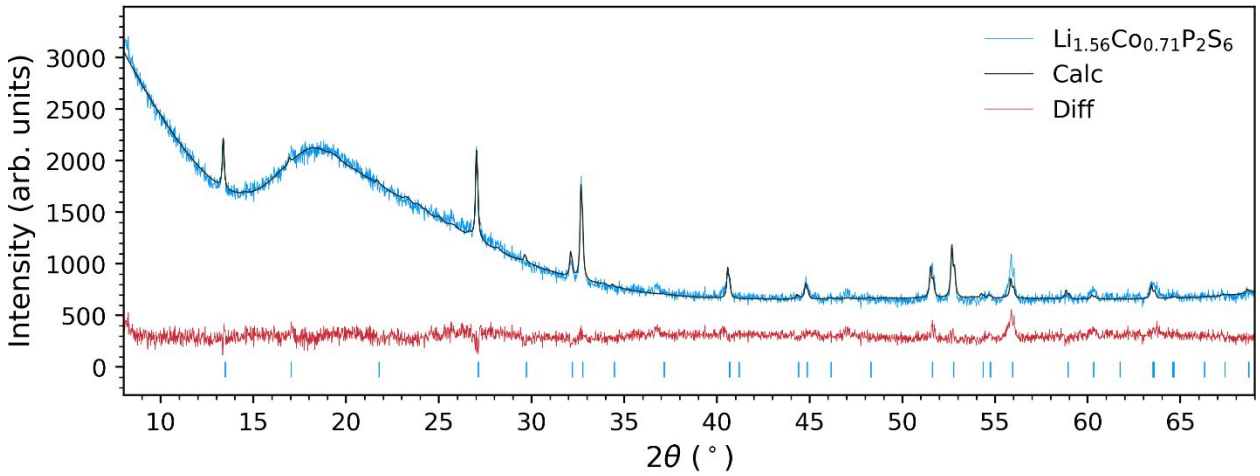

Figure S5. X-ray powder diffraction and Rietveld fit of $Li_{1.56}Co_{0.71}P_2S_6$. The large broad peak at approximately 18° 2θ is due to Kapton tape used to minimize air exposure during experiment.

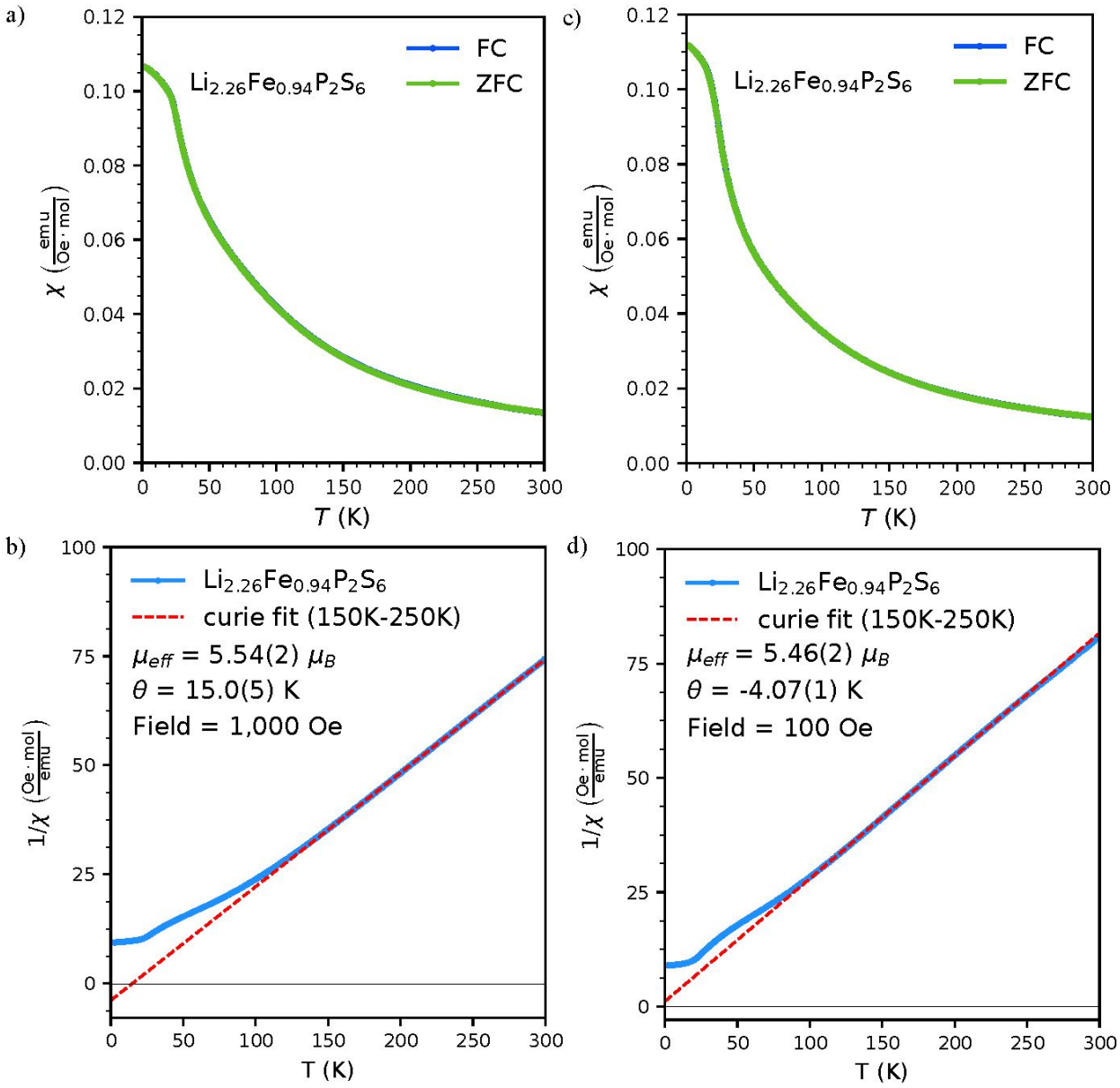

Figure S6. Field cooled (FC) and Zero-field cooled (ZFC) of $Li_{2.26}Fe_{0.94}P_2S_6$ at 1,000 Oe (a) and 100 Oe (b). Curie-Weiss fit extracts a magnetic moment of 5.54(2) μ_B for 1,000 Oe (c) and 5.46(2) μ_B for 100 Oe (d).

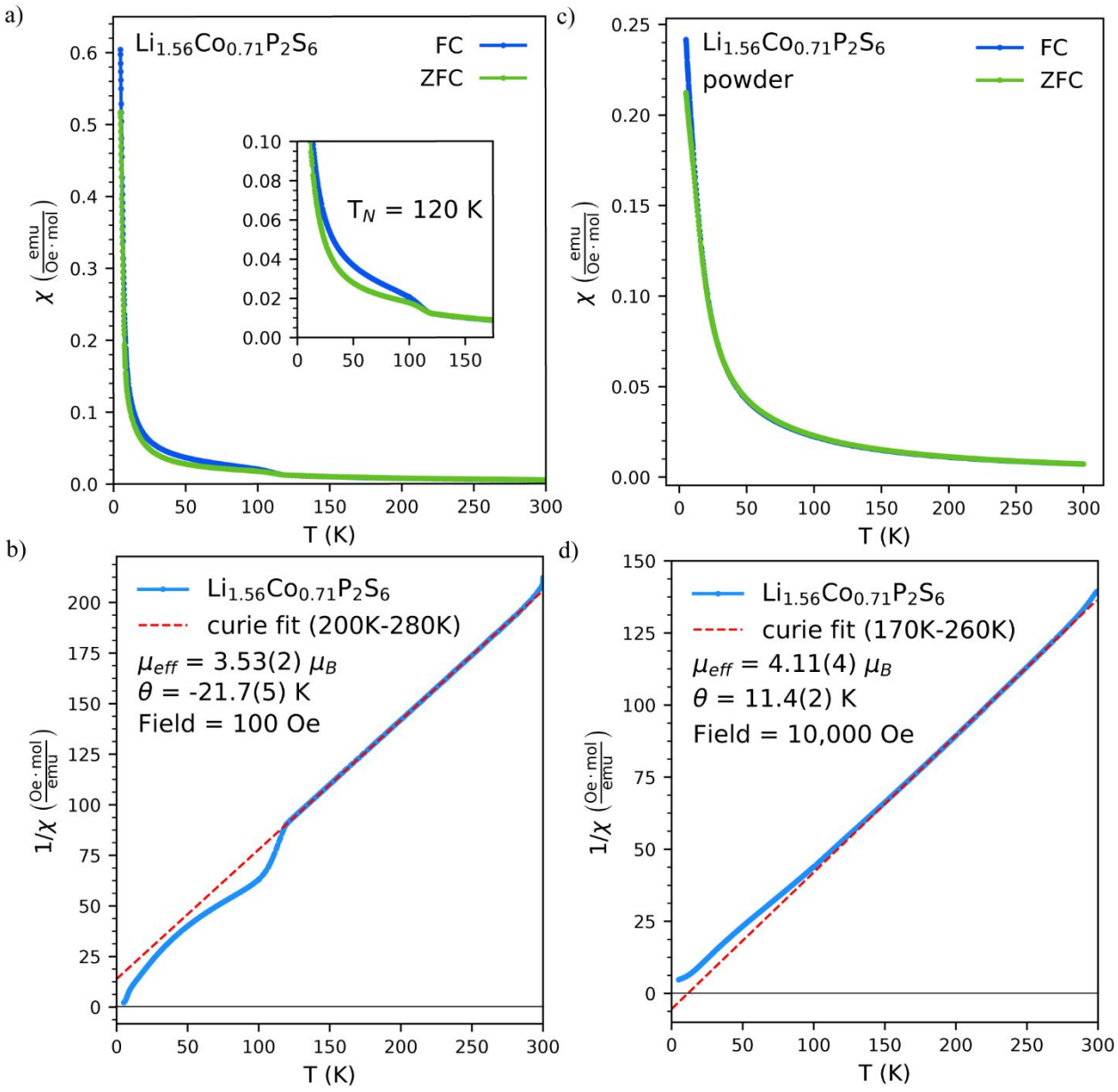

Figure S7. Field cooled (FC) and Zero-field cooled (ZFC) of $Li_{1.56}Co_{0.71}P_2S_6$ powder at 100 Oe (a) and 10,000 Oe (b), the inset shows a small deviation at 120 K. (b) Curie-Weiss fit extracts a magnetic moment of 3.53(2) μ_B (c) and 4.11(4) μ_B (d) respectfully.

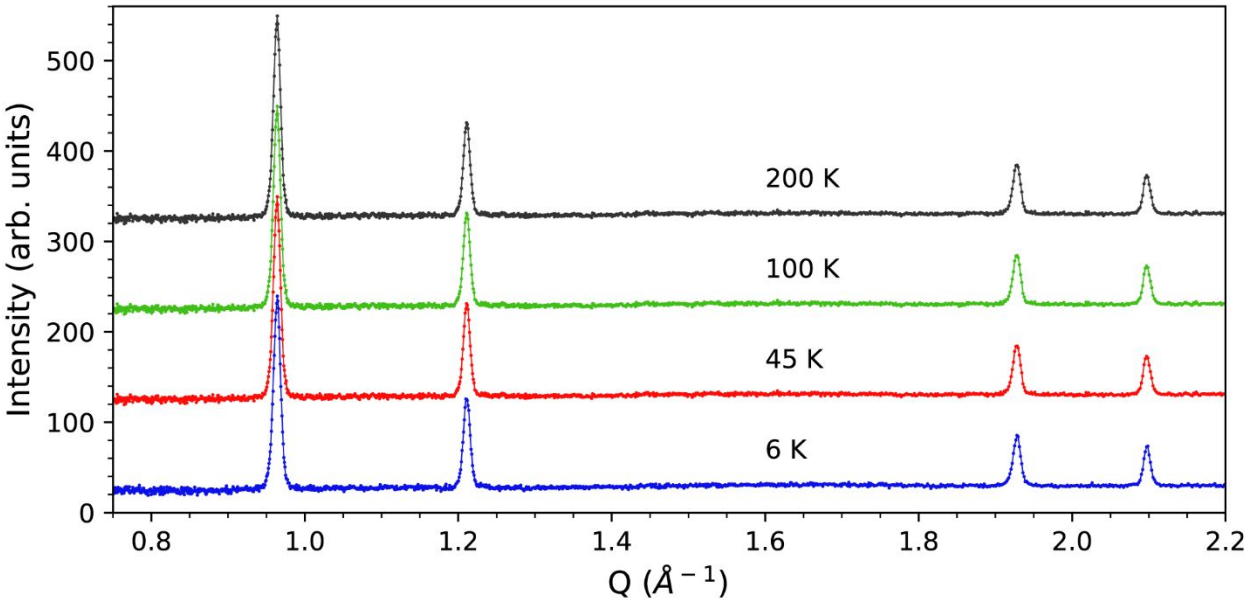

Figure S8. This is Figure 8 (neutron powder diffraction of $Li_{2.04}Fe_{1.12}P_2S_6$) zoomed in to four diffraction patterns at low Q. There is no substantial difference in the different temperature scans.

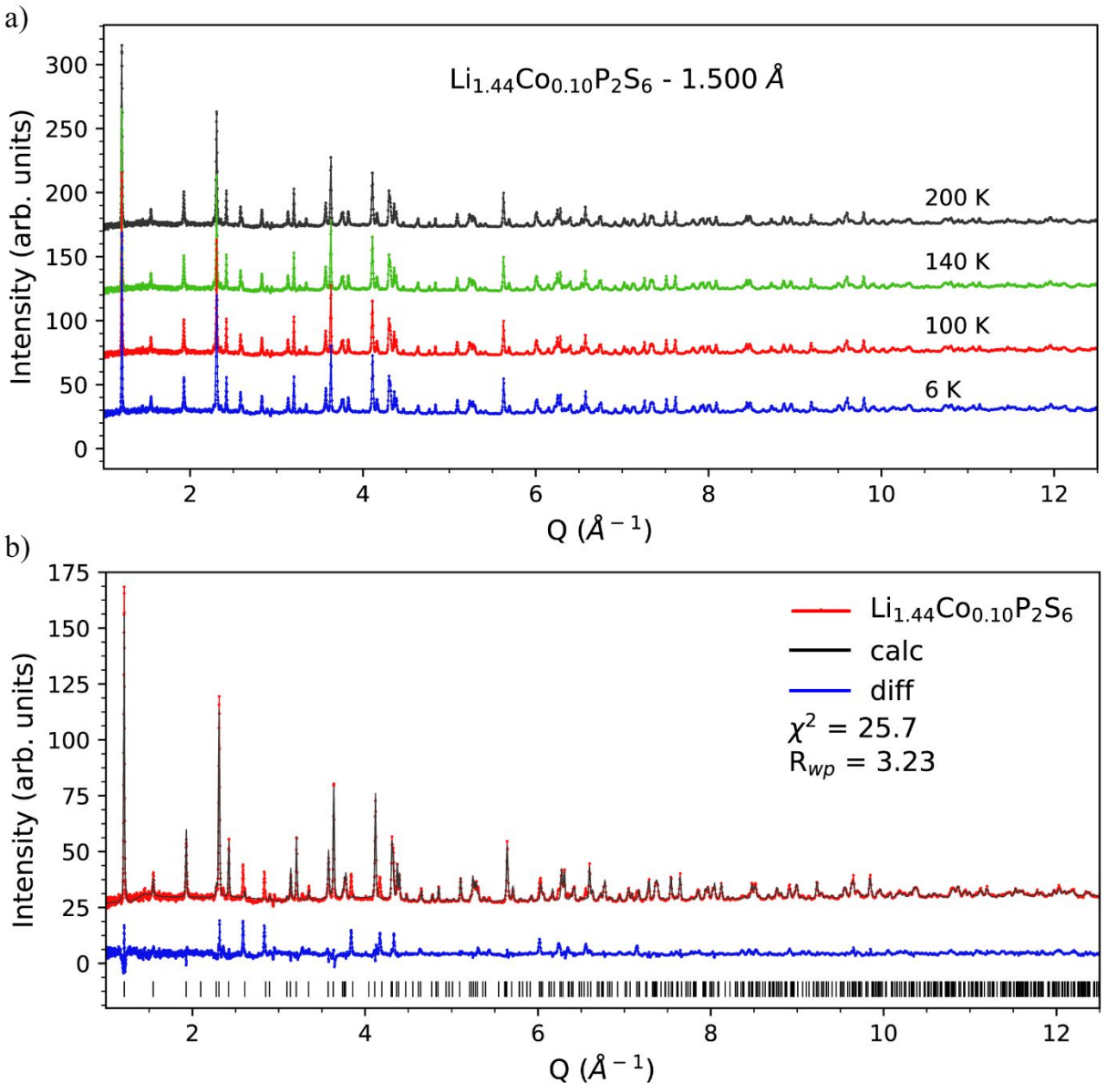

Figure S9. Neutron powder diffraction of $Li_{1.73}Co_{0.43}P_2S_6$ from the POWGEN diffractometer (SNS, ORNL). (a) All patterns look identical across the four measured temperatures suggesting no magnetic ordering. (b) Rietveld refinement demonstrates an impurity that is clearly present in this sample.