Supplementary Information for

Electronic origin of negative thermal expansion in V_2OPO_4

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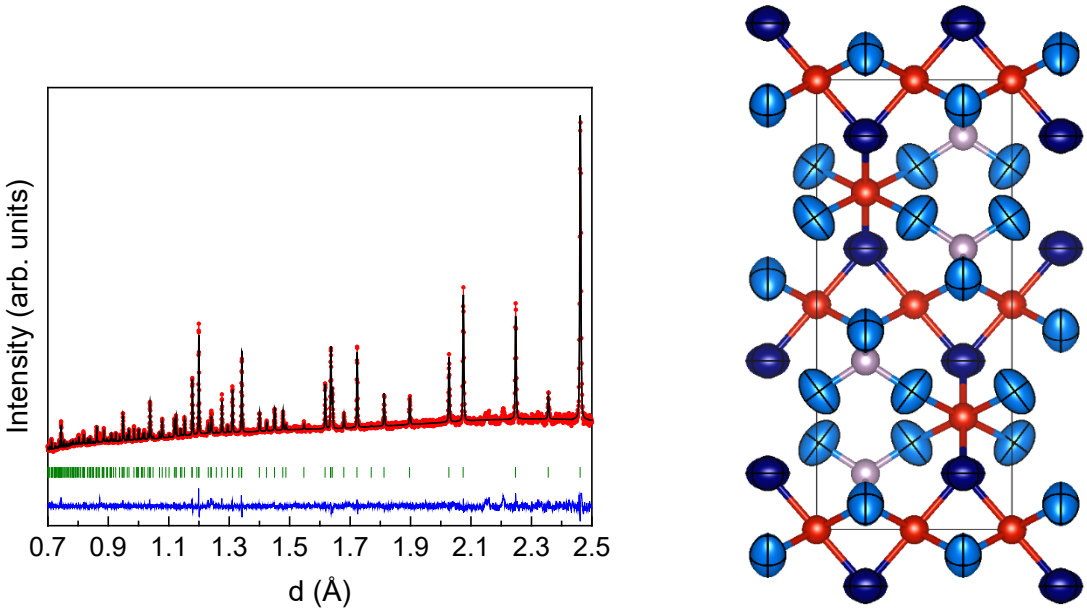


Fig. SI-1. Fitted 773 K neutron powder data and the refined tetragonal $I4_1/amd$ structure showing the anisotropic thermal ellipsoids for the oxygens (O1/O2 = light/dark blue).

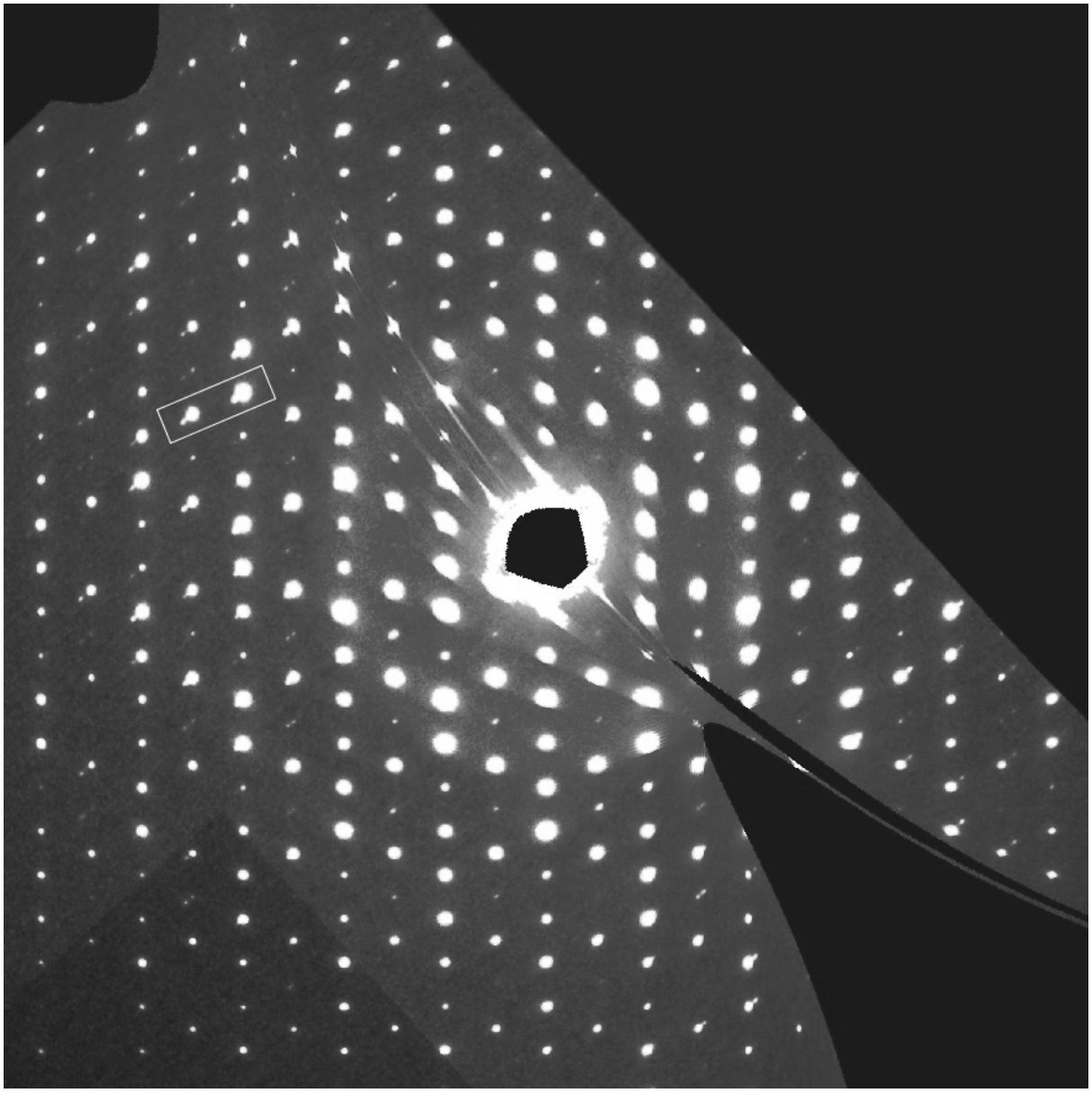
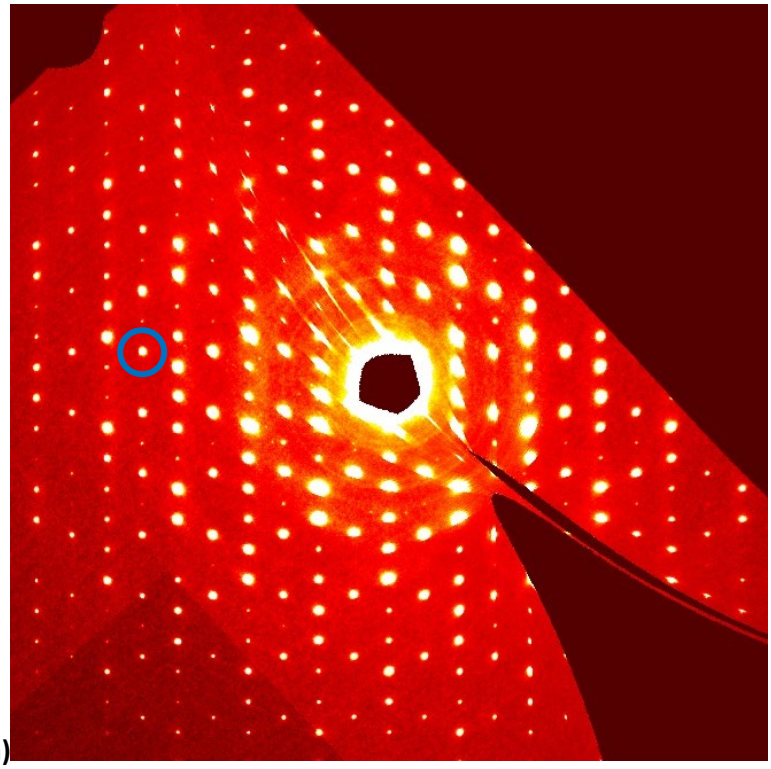


Fig. SI-2. (a) Tetragonal (h -1 l) precession images from high-resolution single crystal x-ray diffraction at 623 K integrated over (0 -0.8 0) and (0 -1.2 0). The highlighted area corresponds to the (-7 -1 6) and (-6 -1 7) reflections as shown in Fig. 4(a).

(a)



(b)

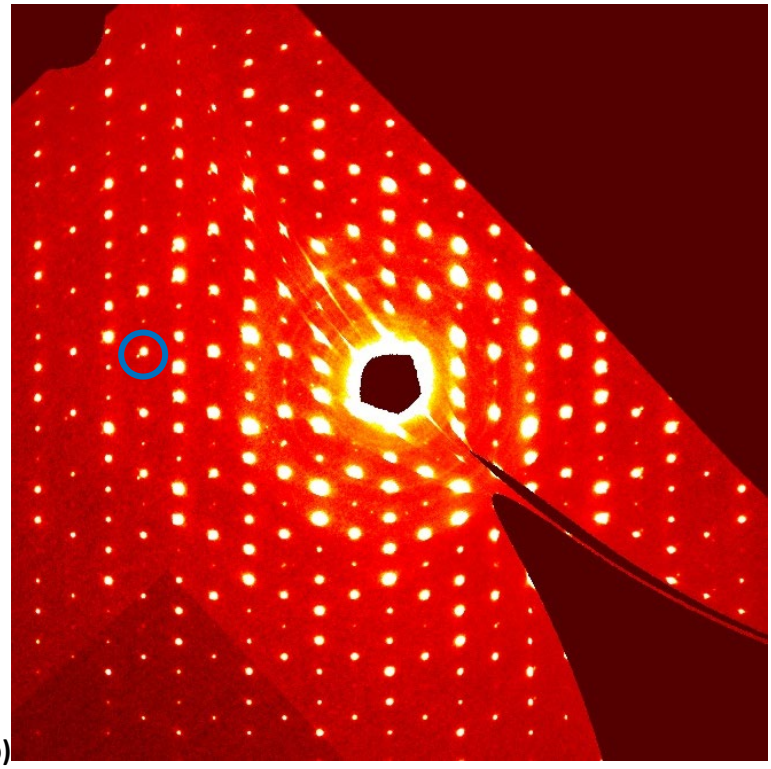


Fig. SI-3. (a) Tetragonal (h -1 l) precession images from high-resolution single crystal x-ray diffraction at (a) 773 K and (b) 673 K. These were collected during cooling from 1273 K after cycling the crystal 300 → 873 → 300 →1273 K. The emergence of additional peaks on cooling from 773 to 673 K, e.g. in circled region, demonstrates the reversibility of the reported microstructural effects.

Table SI-1. Anisotropic thermal U-parameters (Å^2) for the O sites in V_2OPO_4 from 673 to 973 K from NPD refinements.

	U11	U22	U33	U12	U13	U23	Ueq
673 K							
O1	0.0197(11)	0.0235(11)	0.0313(10)	0.00000	0.00000	-0.0085(8)	0.0248(11)
O2	0.0249(14)	0.0249(14)	0.022(2)	0.00000	0.00000	0.00000	0.0238(17)
773 K							
O1	0.0204(10)	0.0262(11)	0.0324(9)	0.00000	0.00000	-0.0106(7)	0.0263(10)
O2	0.0318(14)	0.0318(14)	0.019(2)	0.00000	0.00000	0.00000	0.0274(16)
873 K							
O1	0.0223(10)	0.0280(11)	0.0346(9)	0.00000	0.00000	-0.0113(7)	0.0283(10)
O2	0.0329(14)	0.0329(14)	0.019(2)	0.00000	0.00000	0.00000	0.0284(16)
973 K							
O1	0.0242(11)	0.0302(11)	0.0373(10)	0.00000	0.00000	-0.0123(8)	0.0305(10)
O2	0.0333(14)	0.0333(14)	0.022(2)	0.00000	0.00000	0.00000	0.0295(17)