Supplementary Information (SI) for ChemComm.
This journal is © The Royal Society of Chemistry 2024

Electronic Supplementary Information accompanying "Structurally and Electronically Driven Uniaxial Negative Thermal Expansion in $BaIrO_3$"

Alexander J. Browne,[a,b] Andrew D. Fortes,[c] Andreas W. Rost[b*] and Alexandra S. Gibbs,[a,c]

[a] School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK.
[b] School of Physics and Astronomy, University of St Andrews, St Andrews, KY16 9SS, UK.
[c] ISIS Pulsed Neutron and Muon Source, STFC Rutherford Appleton Lab, Harwell Campus, Didcot, OX11 0QX, UK.

Email: a.rost@st-andrews.ac.uk

Methods:

4.5g of $BaIrO_3$ was synthesised by a solid-state reaction. Powders of $BaCO_3$ (Sigma-Aldrich, 99%; pre-dried at 650°C overnight) and ^{193}Ir (Isoflex 99.46 atom% enriched) in the stoichiometric ratio were ground together in an agate pestle and mortar then pressed into a pellet, which was heated in a covered alumina crucible. A total of seven heating steps (1000°C for 12h; 1000°C for 48h; 1050°C for 48h; 1100°C for 36h; 1150°C for 48 h; 1150°C for 18h; 1200°C for 60h) were required, with the pellet ground and re-pressed between each. Enriched ^{193}Ir was used to minimise neutron absorption.[1]

Powder neutron diffraction data were collected using the HRPD beamline,[2] ISIS Pulsed Neutron and Muon Source (data DOI 10.5286/ISIS.E.RB1910632). The sample was held in an aluminium slab can with vanadium windows. A closed cycle refrigerator was used for cooling.

Rietveld refinements were done using TOPAS Academic, V7.[3] Crystal structure diagrams were prepared using VESTA3.[4] Symmetry-mode analysis was done using ISODISTORT.[5]

The magnetic susceptibility was obtained using a Quantum Design MPMS3, measuring in an applied field of 0.1 T.

Fits to the principal lattice strains ε_{Xi}:

As discussed in the main text, lattice strains ε_{Xi} along the orthogonal principal axes X*i* were obtained using PASCal.[6] These data are plotted in Fig. 1b (using a percentage scale) and again in Fig. S1 (using an absolute scale). Using an absolute scale allows fits to determine the linear thermal expansion coefficients α_{Xi} to be made. At high temperatures, the linear relationship $\varepsilon_{Xi} \propto \alpha_{Xi} T$ is valid. To account for the slight change in gradient that occurs on crossing T_C = 184 K, two linear fits were made to each ε_{Xi}: one between 80 K and 182 K, and one between 186 K and 270 K. Data for 280-300 K

were excluded due to a discontinuity (most visible in ε_{X1}) which we believe to be an experimental artifact and not intrinsic behaviour. At very low temperatures this linear behaviour breaks down; between 10 and 60 K, all three ε_{Xi} could be fit with $\varepsilon_{Xi} \propto T^3$, as per the Debye model.

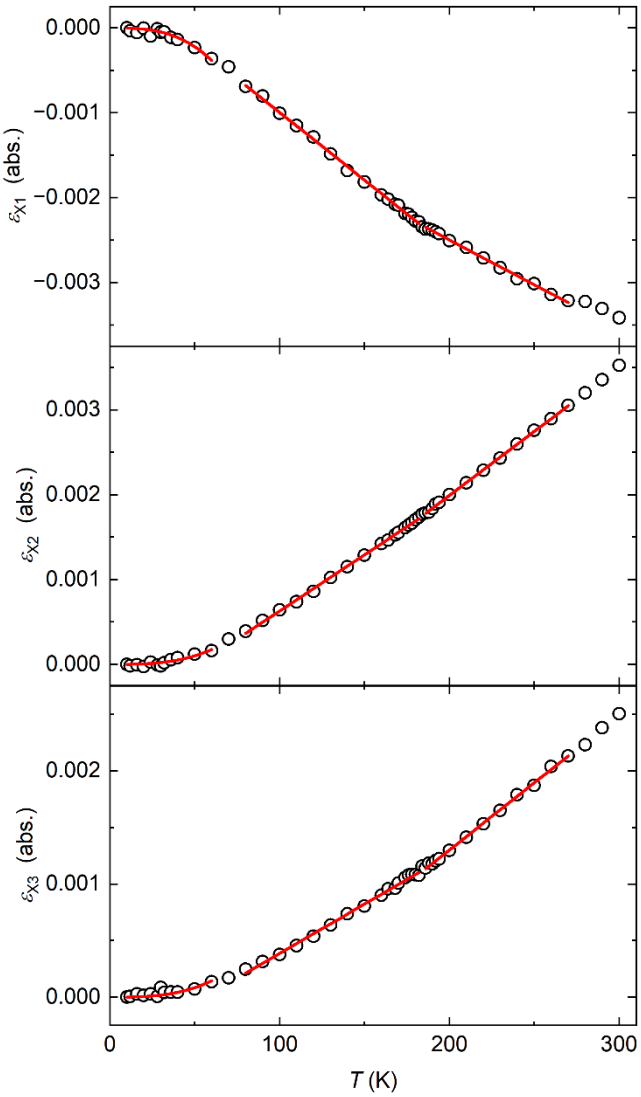

Fig. S1 Fits to the lattice strains ε_{Xi}.

Determining the volumetric thermal expansion coefficient α_V:

The volumetric thermal expansion coefficient can be defined[7] as

$$\alpha_V = \frac{1}{V_0} \times \frac{dV}{dT}$$

We show the variation of volume with temperature in Fig. 1b; an expansion of the low-temperature regime is shown in Fig. S2. Whilst V starts to increase when $T > 100$ K, it is effectively constant at lower temperatures. A linear fit between 10 K and 100 K gives $dV/dT = 1.6(2.0) \times 10^{-4}$ Å^3 K^{-1} and $V_0 = 848.43(1)$ Å^3, and together these determine the average $\alpha_V = 1.9(2.0) \times 10^{-7}$ K^{-1} in this temperature range.

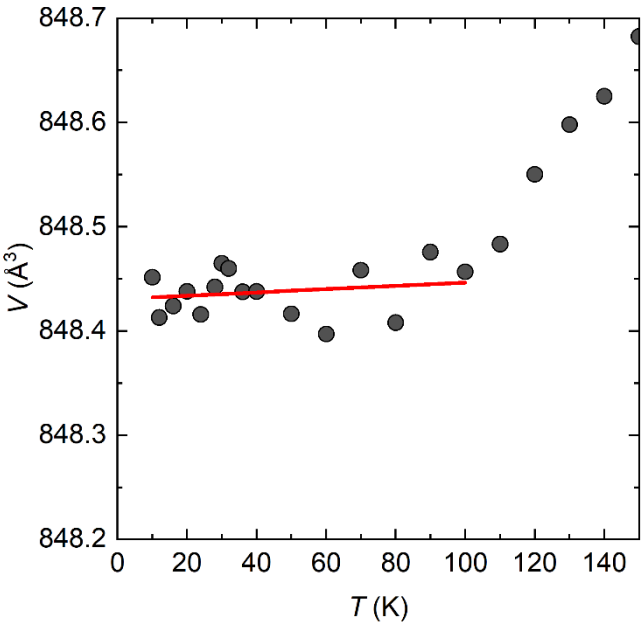

Fig. S2 The unit cell volume as a function of temperature, with a linear fit between 10 K and 100 K.

---

[1] A. C. Hannon, A. S. Gibbs and H. Takagi, *J. Appl. Cryst.*, 2018, **51**, 854-866.
[2] A. D. Fortes and A. S. Gibbs, *J. Neutron Res.*, 2020, **22**, 91-98.
[3] A. A. Coelho, *J. Appl. Cryst.*, 2018, **51**, 210-218.
[4] K. Momma and F. Izumi, *J. Appl. Cryst.*, 2011, **44**, 1272-1276.
[5] (a) H. T. Stokes, D. M. Hatch, and B. J. Campbell, ISODISTORT, ISOTROPY Software Suite, iso.byu.edu. (b) B. J. Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, *J. Appl. Cryst.*, 2016, **39**, 607-614.
[6] M. Lertkiattrakul, M. L. Evans, and M. J. Cliffe, *J. Open Source Softw.*, 2023, **8**, 5556.
[7] J. Chen, L. Hu, J. Deng and X. Xing, *Chem. Soc. Rev.*, 2015, **44**, 3522-3567.