

Thermosalience revealed on the atomic scale; Rapid synchrotron techniques uncover molecular motion preceding crystal jumping

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Descriptions of videos

Video 1: A group of single crystals being cooled from $\sim 20\text{ }^{\circ}\text{C}$ to $\sim -10\text{ }^{\circ}\text{C}$

Video 2: Large single crystal cracking during cooling from $\sim 20\text{ }^{\circ}\text{C}$ to $\sim -10\text{ }^{\circ}\text{C}$

Video 3: A second batch of single crystals showing large jumps whilst being cooled from $\sim 20\text{ }^{\circ}\text{C}$ to $\sim -10\text{ }^{\circ}\text{C}$

Video 4: A third batch of single crystals showing kinesis and rotation during cooling from $\sim 20\text{ }^{\circ}\text{C}$ to $\sim -10\text{ }^{\circ}\text{C}$

Video 5: Changes in the monoclinic angle of a single crystal when viewed down the crystallographic *b* axis during cooling. Scale bar = $100\text{ }\mu\text{m}$

Video 6: The interface between HT and LT forms propagating along the crystallographic *c* axis when viewing a single crystal down the crystallographic *a* axis during cooling. Scale bar = $200\text{ }\mu\text{m}$

Video 7: Cracking of a single crystal during cooling (HT to LT phase) followed by reclosing of the crack

Video 8: Movement of the crystal as shown in Video 7 during heating (LT to HT phase); note the crack is present but the crystal morphology remains relatively unchanged

Video 9: Reversible temperature dependent changes in thermal displacement ellipsoids and molecular arrangements during heating and cooling. Each frame represents a complete structural determination as collected from a single-crystal on the MX1 beamline.

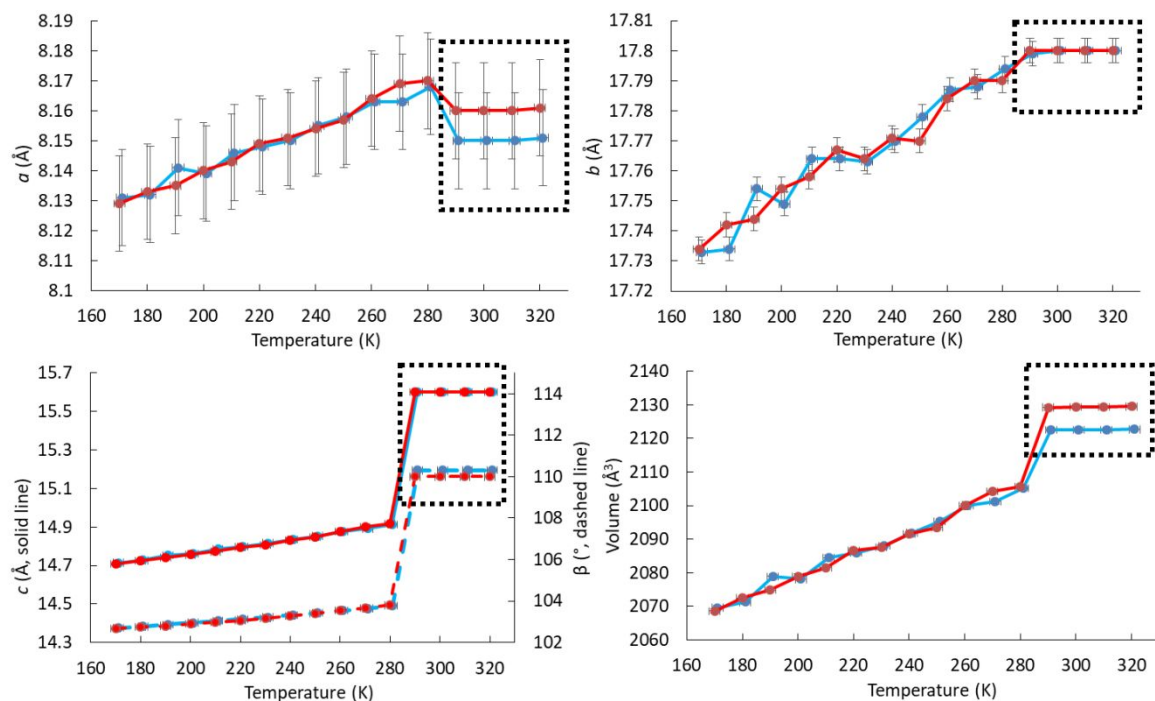


Figure S1: Summary of cell changes and parameters (obtained from VT synchrotron single-crystal X-ray diffraction). Data for the HT structure is highlighted in the dotted box.

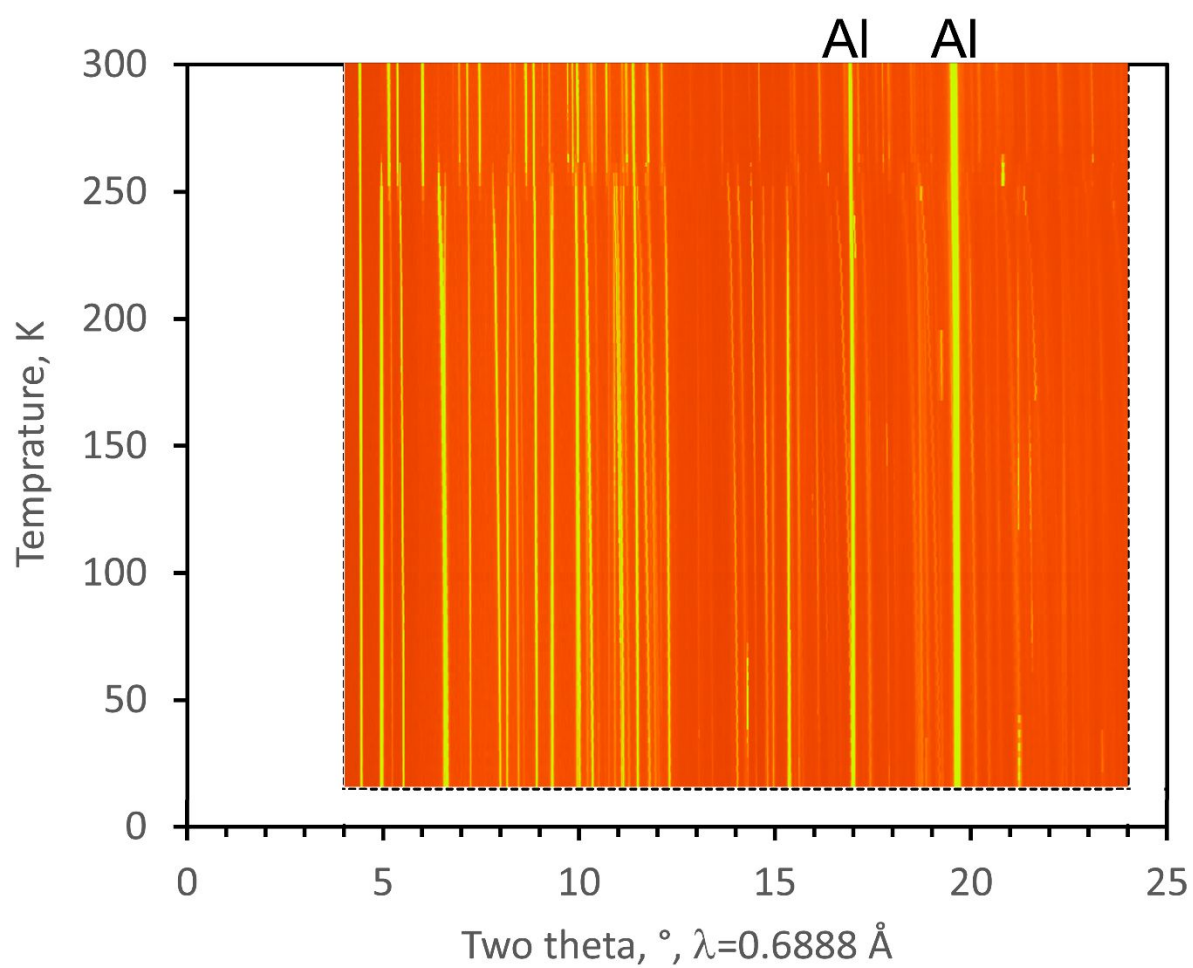


Figure S2. Pseudo-Guinier plot showing transformation of high-temperature structure to low-temperature form at about 260 K. No further structural changes were observed from the low-temperature form. The Al peaks are from the metal capillary used.

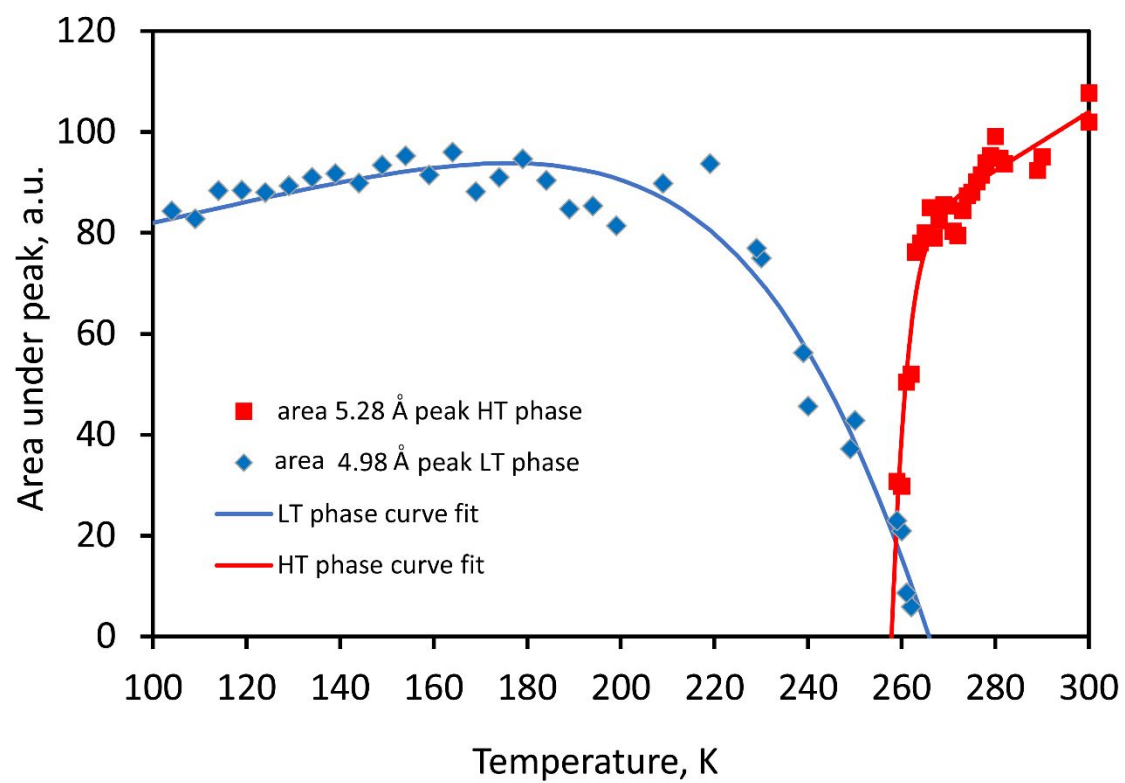


Figure S3. Areas under the representative peaks for the two phases, showing a phase transition at about 260 K. The data are from an *in situ* synchrotron experiment.

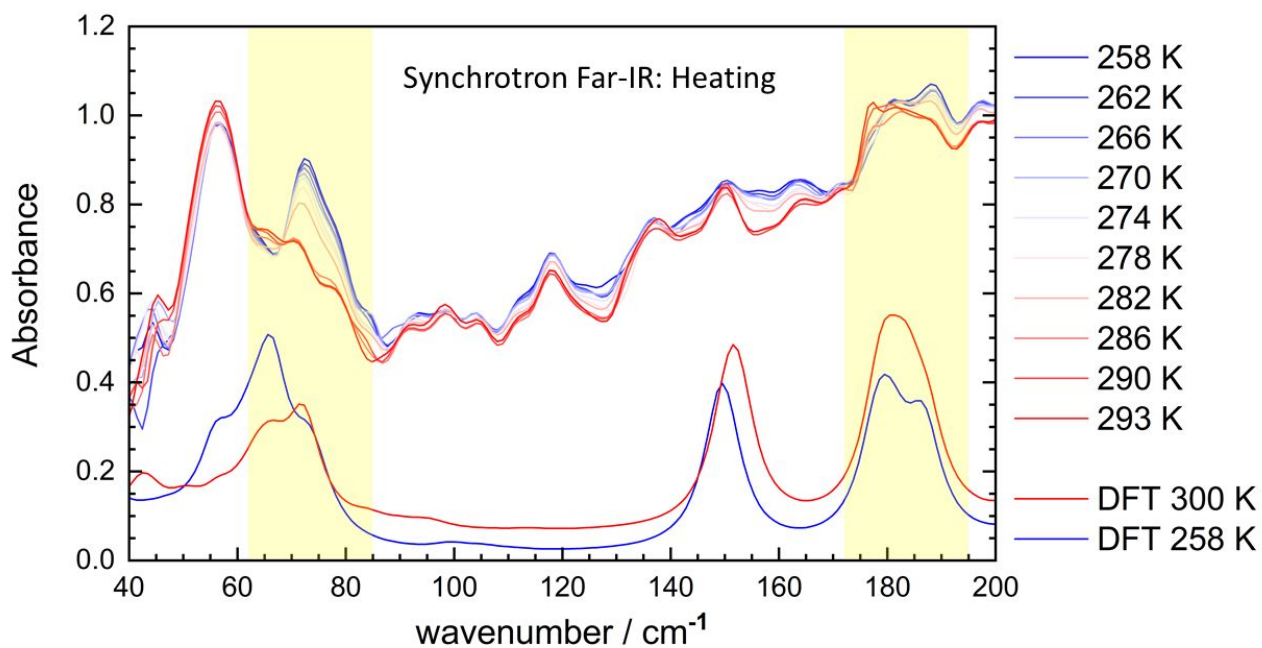


Figure S4. Synchrotron THz spectrum of NiDIP upon heating from -15 to +20 °C. C17 p-DFT frequencies calculated for the -16 (blue) and 27 °C (red) structures at the B3LYP-D3/6-311G(d) level. Regions displaying temperature dependent frequency shifts of coupled OOP and IP NiS₄/DIP torsion vibrational modes are shaded in yellow.

Table S1. Nature of the Far-IR active vibrational modes for Ni(DIPDTC)₂ assigned by p-DFT.

Synchrotron far-IR / cm^{-1}	C17 -16 °C / cm^{-1}	C17 +27 °C / cm^{-1}	Symmetry	Mode(s) ^a	Character
56 / 72	65	71	B _u	29/38	OOP&IP NiS ₄ /DIP torsion
118					
150	151	153	A _u	71	OOP NiS ₄ /DIP torsion
177 / 188	179 / 186	182	A _u /B _u	82/87/88	OOP&IP NiS ₄ /DIP torsion
216	214	225	A _u	91	IP NiS ₄ /DIP torsion
270	-	-	-	-	-
291 / 300	289 / 295	289 / 298	B _u	137/140	S-Ni-S rock/ C-C-C deformation
357	352	346 / 365	A _u /B _u	159/161/ 163/165	Ni-S stretch Some DIP deformation coupling for 163
400	399	398	B _u	173/176	C-C-C sym DIP deformation
474	464	469	B _u	183/189	C-C-C sym DIP deformation
527	515	518 / 522	B _u	197/202	C-C-C sym DIP deformation
584	578	575 / 581	A _u /B _u	205/210	C-C-C sym DIP deformation
611	607	613	A _u /B _u	217/218	C-N-C asymm DIP deformation
799	788	790	A _u /B _u	221/224	C-N-C sym DIP deformation
845	833	835	B _u	231/236	C-N-C asymm DIP deformation

These predictions confirm that many of the fundamental low frequency modes ($\nu < 500 \text{ cm}^{-1}$) are associated with NiS₄ in-plane (IP) and out-of-plane (OOP) deformations coupled to hindered rotation and torsion of the di-isopropyl groups (Table S1).

FTIR spectroscopy and DFT

Far-IR spectroscopy was performed at the Terahertz and Far-Infrared beamline at the Australian Synchrotron. A closed loop pulsed tube cryostat (Cryo Industries) was installed on the beamline Bruker IFS125 FTIR spectrometer. For each variable temperature experiment, ~ 2.5 mg of powdered Ni(DIPDTC)₂ was homogenized in paraffin wax and pressed into a pellet of 7 mm diameter. The measurements were collected under a partial helium atmosphere between room temperature and -270 °C. The 20-300 cm⁻¹ spectral region was accessed using the synchrotron edge-radiation source, a 75 micron Mylar beamsplitter, and a liquid-He cooled bolometer detector. Spectra were recorded at 4 cm⁻¹ resolution.

Periodic density functional theory (p-DFT) was performed on Ni(DIPDTC)₂ by using the Crystal17 (C17) program.¹ This code has been previously used to calculate solid-state vibrational frequencies for various molecular crystals, including those of astrophysical interest^{2, 3} where harmonic frequencies and IR intensities proved of sufficient accuracy to replicate vibrational spectra. For the present work, the hybrid B3LYP functional is selected, coupled with triple- ζ quality 6-311(d)G basis sets to describe H, C, N and S atoms.⁴ The all electron 86-411(41d)G basis set was used to describe the Ni atoms.⁵ Important for crystal systems displaying long-range interactions, such as the van der Waals forces between Ni(DIPDTC) molecules in the title crystal, D3 dispersion terms were included for all calculations.⁶ As recommended for the selected basis sets, Coulomb and Hartree-Fock exchange integrals were truncated to 10⁻⁷, 10⁻⁷, 10⁻⁷, 10⁻⁹, 10⁻³⁰ hartree. Energy convergence was performed to the thresholds (gradient RMS: 8 × 10⁻⁴ eV; displacement RMS: 8 × 10⁻⁴ eV) required for accurate calculation of harmonic frequencies.

The starting geometry for periodic-DFT calculations requires the symmetry-reduced unit cell as defined by lattice parameters, space group symmetry, and fractional atomic coordinates. These parameters were directly transcribed from crystallographic data tabled for the Ni(DIPDTC)₂ crystal at -16 (CCDC 2120590) and 27 °C (CCDC 2122302) where the respective geometric parameters (bond lengths and bond angles) converge to the LT and HT forms after the iterative energy and structure optimization procedure. Here, all symmetry-reduced atoms were relaxed within the monoclinic (*P*₂₁/*c*) cell that was observed at all temperatures. The respective -16 and 27 °C unit cell lattice parameters (*a*, *b*, *c*, and β) were fixed to the experiment values to prevent the system converging to the same minimum on the potential energy surface. Subsequent harmonic frequency calculations confirm both structures as valid local minimum (stationary point with zero imaginary frequencies). Finally, the IR spectra were simulated to provide a further means to characterize the samples via spectroscopy. Here a scaling factor of 0.965 is applied to calculated frequencies to align with experimental peaks, consistent with our chosen level-of-theory. Note that the simulated IR spectrum represents the crystal system at 0 K, where only fundamental transitions are populated. At the temperatures involved in this study one would expect higher order transitions (overtones and hot bands) to be non-negligible. These transitions amount to distort and broaden absorption bands, particularly in the low-frequency far-IR region. However, for our qualitative assessment of vibrational modes associated with the order-disorder transition, the harmonic level at 0 K is sufficient to assign spectral features from experiment and identify internal displacements coupled to structural alteration of the crystal.

Laboratory single crystal data collection at -16 °C

A green block-shaped crystal was selected under the polarizing microscope (Leica M165Z), mounted on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurements were carried out on a Bruker D8 Quest Single Crystal diffractometer with Photon II detector at -16 °C by using I μ S 3.0 Microfocus Source with Mo-K α radiation ($\lambda = 0.710723$ Å). The single crystal, mounted on the goniometer using cryo loops for intensity measurements, was coated with paraffin oil and then quickly transferred to the cold stream using an Oxford Cryo stream 800 attachment. Symmetry related absorption corrections using the program SADABS were applied and the data were corrected for Lorentz and polarisation effects using Bruker APEX3 software.⁷ The structure was solved by ShelxT (intrinsic phasing) and the full-matrix least-square refinement was carried out using Shelxl in Olex2.⁸⁻¹⁰ The non-hydrogen atoms were refined anisotropically. The molecular graphic was generated using program Olex2.

Automated MX Data reduction and processing

The automated variable temperature processing steps are:

1. Run xds2sad on XDS_ASCII.HKL_hsymm_noscale to prepare files for sadabs.
2. Moderate absorption correction is performed with SADABS (Bruker, 2007).
3. XPREP (Bruker, 2009) is run using the sadabs .hkl output file and inputting the unit cell extracted from sadabs .abs output file.
4. Xprep output instruction file is copied and updated with structure factors from reference results files (between lines starting with SFAC and HLK4). Two refinements are performed per dataset for warm and cool references.
5. Instruction file is updated with the dataset collection temperature in degrees Celsius.
6. Shelxl refinement performed with default settings.
7. Weighting in the instructions file is updated from shelxl results file.
8. Repeat steps 5 and 6 until _refine_ls_shift/su_max from shelxl output .cif has converged.

CIF files were then automatically updated with the appropriate experimental details with a custom Python script.

Post refinement analysis was performed with a python jupyter notebook that graphs harvested unit cell parameters against temperature. All code is available at the Australian Synchrotron and through correspondence with jason.price@ansto.gov.au.

A precession image of the crystal mid-way through transition was produced from MX2 diffraction data using CrysAlisPro. Increases in the temperature-dependent coefficients of thermal displacement were obtained as the values of the slope from linear regression between temperature and equivalent isotropic displacement parameters for each atom across 12 structures during heat from – 103 °C to 7 °C.

Cryogenic synchrotron powder X-ray diffraction

Powder X-ray diffraction at cryogenic temperatures was performed on the Powder Diffraction beamline at the Australian Synchrotron. Samples were loaded into a 0.2 mm (internal diameter) aluminium capillary with a 0.05 mm wall thickness, and housed within a closed loop cryostat. The temperature was cooled at a rate of 6 °C min⁻¹ in the high-vacuum atmosphere of the cryostat between room temperature at -260 °C. The X-ray wavelength was 0.6888 Å (confirmed by refinement on a LaB₆ standard). The diffraction results were merged using software developed in-house.

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