Experimental report

13/09/2024

Proposal: **7-02-221**

Council: 4/2023

Title: Understanding orientational dynamics in novel barocaloric hybrid composites using quasielastic and inelastic neutron scattering

Research area: Materials

This proposal is a new proposal

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Local contacts: Markus APPEL

Samples: neopentyl glycol composite
neopentyl glycol

Instrument	Requested days	Allocated days	From	To
IN5	2	2	04/09/2023	06/09/2023
IN16B Si 111 BATS	4	4	10/12/2023	12/12/2023

Abstract:

Plastic crystals are amongst some of the most promising phase change materials for use in solid-state energy storage and heating/cooling technologies. This is primarily due to a substantial latent heat accompanying their first-order solid-solid phase transitions involving freezing of molecular reorientations. However, notable drawbacks associated with these materials include low thermal conductivity and significant supercooling effects, where the latter results in undesirable hysteresis during phase transitions. We have recently demonstrated that the supercooling of the plastic crystal neopentyl glycol (NPG) can be significantly reduced by forming novel hybrid composites. We wish to use quasielastic (QENS) and inelastic neutron scattering (INS) to explore the molecular reorientations in these composites and better understand the underlying cause of the reduced supercooling.

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Experiment Objectives

Barocaloric (BC) plastic crystals (PC) are emerging as viable, sustainable alternatives to harmful vapour refrigerants in heating and cooling technologies such as heat-pumps and refrigerators. However, these materials display significant hysteresis effects, that ultimately limits their immediate technological suitability. We have recently demonstrated, using high-pressure calorimetry, x-ray diffraction and real-space imaging, that it is possible to reduce thermal hysteresis in the archetypical PC neopentyl glycol (NPG) through the formation of NPG nanocomposites. In this experiment we wanted to investigate microscopic origins of thermal hysteresis reduction through mapping out the molecular dynamics of NPG and its composites on heating and cooling using quasielastic neutron scattering and inelastic fixed-window scan experiments.

Experimental details

Powder samples of NPG (99% purity) were purchased from Sigma-Aldrich and used as received. Composites were prepared by dissolving NPG in ethanol, adding the nanopowder and ultra-sonicating for 1 hr before leaving the solvent to evaporate under ambient conditions. The resulting composite powder was taken to ILL to be loaded into measurement cans. We combined experiments on both IN5 and IN16B to fully explore the quasi-elastic signals in our NPG composites with a large overall dynamic range. On IN5 a wavelength of 6 Å was used, yielding a FWHM energy resolution of 60 μeV, dynamic range of ± 1.3 meV and *Q*-range of 0.10 to 1.89 Å^{-1} in this experiment. IN16B was used in standard configuration with strained Si11 Doppler monochromator and analysers had a FWHM energy resolution of 0.75 μeV, dynamic range of ± 0.028 meV and *Q*-range of 0.19 to 1.89 Å^{-1}. QENS measurements were obtained using scan times of 2 hrs on IN16B and 30 mins on IN5. FWS measurements were performed during a temperature ramp of approximately 0.5 K min^{-1} with alternating acquisitions of elastic (90 s) and inelastic intensity at 3 μeV energy transfer (90 s). Approximately 0.5g of sample was loaded into an aluminium can for measurements on both IN16B and IN5. Empty can and vanadium standard measurements were acquired and used to correct the NPG data.

QENS data was obtained at temperatures of 250 K, 280 K, 300 K, 320 K, 330 K and 350 K on both instruments, providing 3 QENS spectra either side of the phase transition (T_0 = 314 K). FWS data was obtained on heating from 250 K to 350 K and then on cooling from 350 K to base temperature (~ 10 K).

Results

1 QENS of NPG

Corrected QENS data from both instruments was rebinned in *Q* (0.19 to 1.89 Å^{-1}) to provide consistent spectra for fitting across the full dynamic range provided by IN5 and IN16B. This data was fitted with a resolution function (from a 2 K scan) convoluted with a delta function and a number of Lorentzians and a flat background (see Fig. 1). From previous QENS studies and theory on NPG[1,2], we expected one rotational mode below T_0 and three modes above. However, due to the dynamic range limitations of each instrument we were only able to detect two modes above T_0 on each instrument, though by combining both instruments we detect all three modes (see Fig. 2). Mode characterisation was done by calculating the EISF(*Q*) and fitting the data with

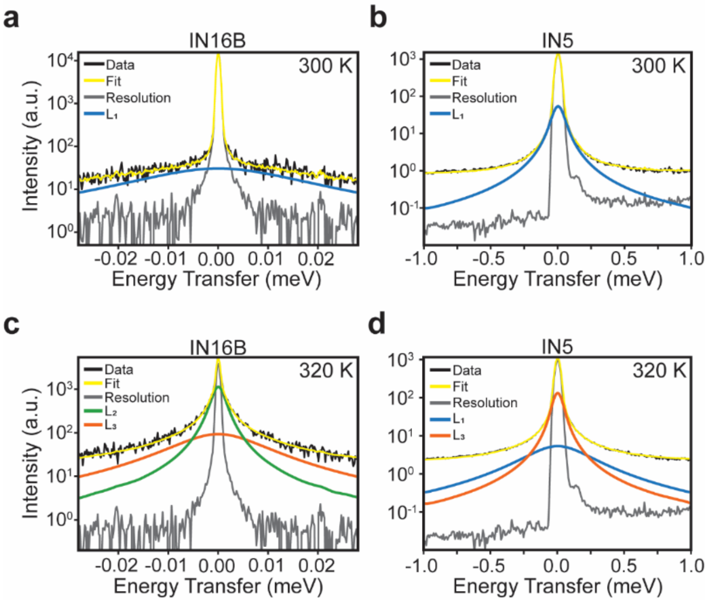

Figure 1 | Representative QENS data fits for Q = 0.83 Å^{-1}. (**a,b**) Example fits for IN16B and IN5 QENS data below the phase transition (300 K). Here, only a single Lorenztian is included in the model. (**c,d**) Example fits above the phase transition (320 K). In this case, two Lorenztians are required to fit the data.

known geometric models for molecular reorientation[3]. This data and the corresponding molecular schematics can be seen in Fig. 3. We further found that by including a fractional parameter in the EISF fitting, we were able to observe an increase in the fraction associated with the molecule reorientation mode as a function of temperature (Fig. 3c). This has implications for explaining an outstanding discrepancy between calculated and theoretical entropy change in NPG. A manuscript containing this data is currently awaiting to be submitted to Nature Communications.

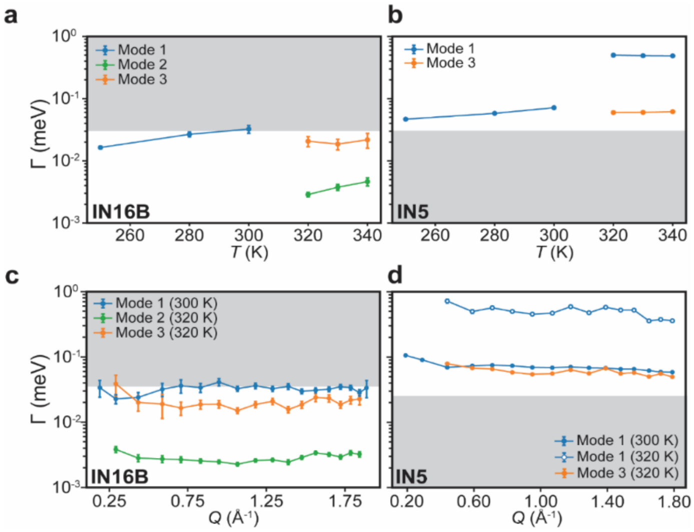

Figure 2 | *T*- and *Q*-dependence of mode frequencies. (**a,b**) *Γ*(*T*) for each of the observed modes, from the Lorentzian fits across the two instruments. (**c,d**) *Γ*(*Q*) for each of the observed modes at temperatures just below (300 K) and above (320 K) the phase transition.

2 QENS & FWS of NPG composites

We performed the same analysis on the composites as above, with the exception that we found two Lorentzians were required to fit the data at 280 K and 300 K, rather than one as in pure NPG. Furthermore, the IFWS comparison between NPG and the composites indicated increased quasielastic signal on approach o the phase transition compared to pure NPG. Note that we have not included figures for this analysis due to an ongoing patent application. The experimental report will be updated to show this data once the application process has concluded. This data is still being analysed but we aim to submit this work in a separate manuscript by the end of 2024.

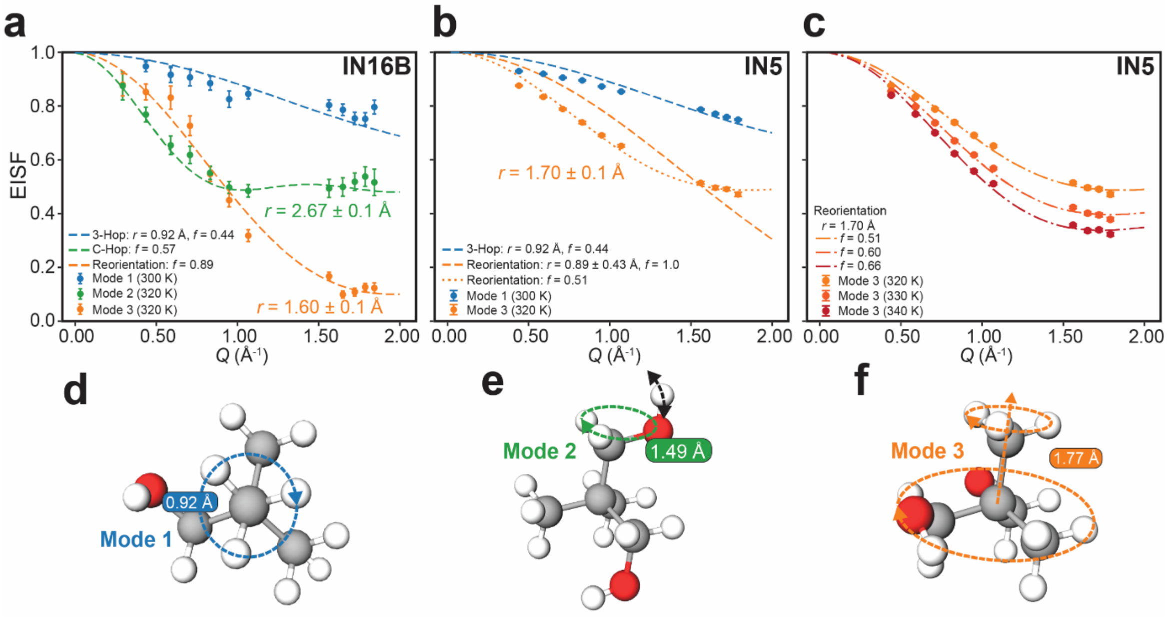

Figure 3 | Fitting of EISF(*Q*) and identification each of the observed modes. (**a,b**) Summary of EISF fitting for T = 300 K, 320 K to data collected from **(a)** IN16B and **(b)** IN5. (**c**) *T*-dependence of the reorientation mode fraction fitted to IN5 data. (**d-f**) Schematics of the NPG molecule, indicating the geometric origin for the radii of rotation obtained from fits in (**a,b**).

1 Li et al., Nature 567, 506 (2019).

2 Li et al., Nat Commun 11, 1 (2020).

3 Bee, *Quasielastic Neutron Scattering, Principles and Applications in Solid State Chemistry, Biology and Materials Science* (Adam Hilger, 1988).