Experimental report

23/10/2024

Proposal: 7-02-227 **Council:** 10/2023

Title: Understanding orientational dynamics in barocaloric plastic crystal mixes using quasielastic and inelastic neutron scattering

Research area: Materials

This proposal is a new proposal

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Samples: Neopentyl Glycol-Pentaglycerine
Neopentyl Glycol-Pentaglycerine-Pentaerythritol
2-Bromoadamantane C10H15Br

Instrument	Requested days	Allocated days	From	To
IN16B Si 111 BATS	4	4	25/03/2024	29/03/2024
IN5	2	2	12/04/2024	14/04/2024

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. One of the most notable of these materials is neopentylglycol (NPG), where recent experiments on this material have demonstrated colossal barocaloric effects (BCE) that rival longstanding commercial refrigerants for the first time. However, notable drawbacks associated with NPG include low thermal conductivity and significant supercooling effects, where the latter results in undesirable hysteresis during phase transitions. We have recently discovered reduction of hysteresis in binary and tertiary solid solutions of NPG with other related plastic crystals. Here we wish to use quasielastic (QENS) and inelastic neutron scattering (INS) to explore the molecular reorientations in these solid solutions and better understand the underlying cause of the reduced hysteresis.

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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 that it is possible to optimise the operational conditions for in PC neopentyl glycol (NPG) solid solutions, containing pentaglycerine (PG) and pentaerythritol (PE). In this experiment we wanted to investigate microscopic origins of these calorimetry observations through mapping out the molecular dynamics of NPG solid solutions on heating and cooling using quasielastic neutron scattering and inelastic fixed-window scan experiments.

Experimental details

Powder samples of NPG (99% purity), PG (99% purity) and PE (99% purity) were purchased from Sigma-Aldrich and used as received. Solid solutions were prepared by dissolving each material in ethanol, before leaving the solvent to evaporate under ambient conditions. The resulting solid-solution 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 materials 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), inelastic intensity at 3 µeV and 9 µeV energy transfer (90 s each). 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 200 K, 230 K, 260 K, 293 K, 330 K and 350 K on both instruments, providing QENS spectra either side of the phase transition (T_0 ~ 298 K). FWS data was obtained on heating from 200 K to 350 K and then on cooling from 350 K to base temperature (~ 10 K). Data below was compared to that of pure NPG obtained in experiment 7-02-221. Data analysis for this work is in the initial stages.

Results

QENS data was fit according to models we refined from studies of pure NPG (see experimental report for 7-02-221) to make clear comparisons of the solid solution NPG. The obtained QENS data can be seen in Fig. 1. We found that, unlike in pure NPG, a second Lorentzian was required at 293 K, just before the phase transition of this material at 298 K (see Fig. 2). We obtained FWS data around the phase transition, clearly observing distinct differences between the NPG and the solid solution (Fig. 3). Fitting of activation energies and investigations around these differences is ongoing and should be prepared into a manuscript for publication in 2025.

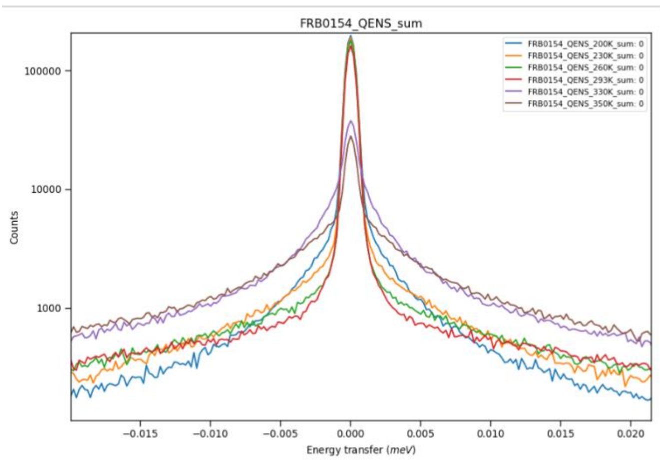

Figure 1 | QENS data obtained for NPG/PG/PE solid solution on IN16B.

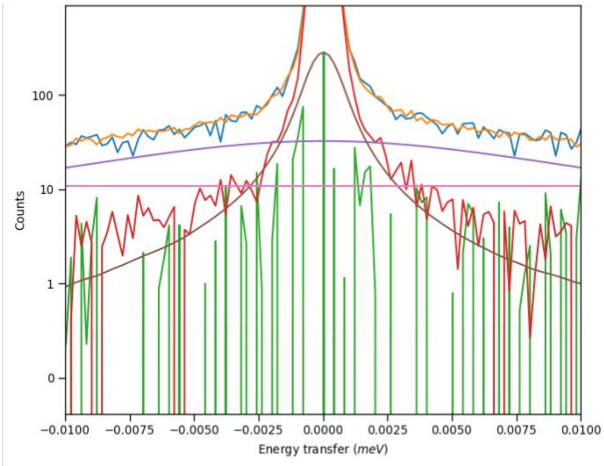

Figure 2 | QENS fitting for NPG/PG/PE solid solution at 293 K. Blue line is data, orange is the fit, brown and purple are the Lorentzians, pink is the background and green is the difference.

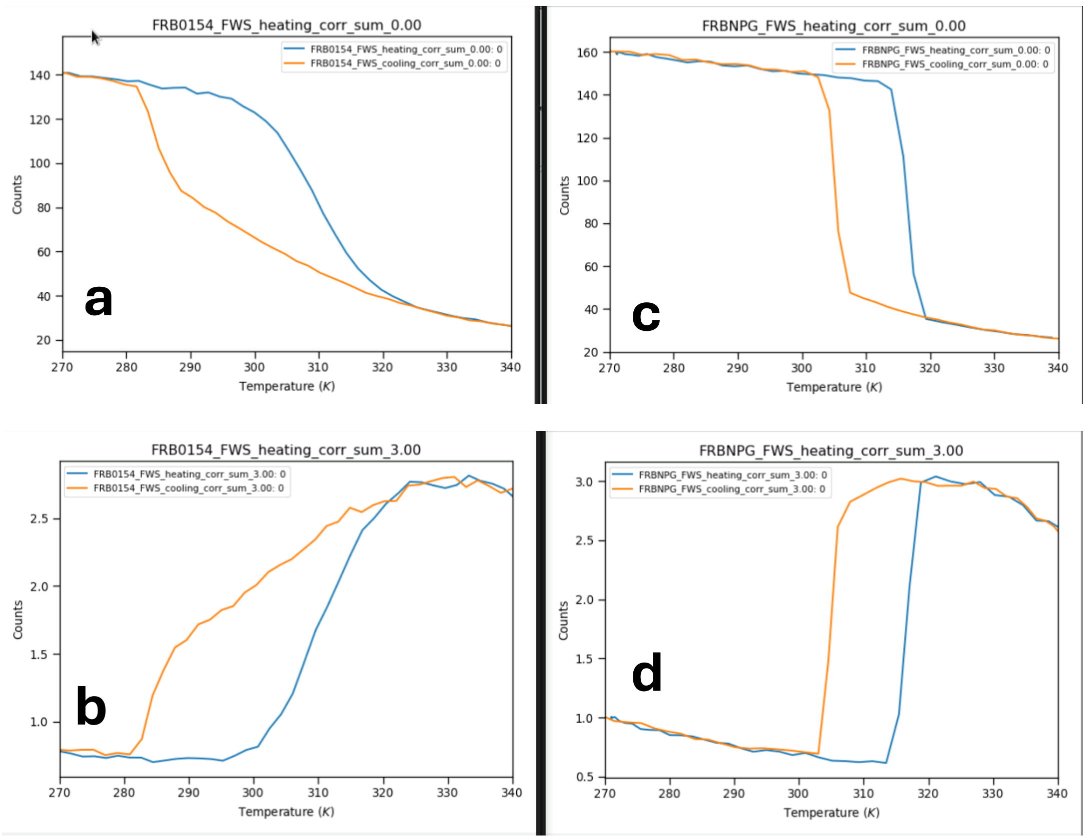

Figure 3 | FWS around the phase transition on heating and cooling. (a) EFWS, (b) IFWS of solid solution and (c) EFWS, (d) IFWS of NPG.

This preliminary work has been analysed further into figures for an upcoming publication, these figures can be seen below.

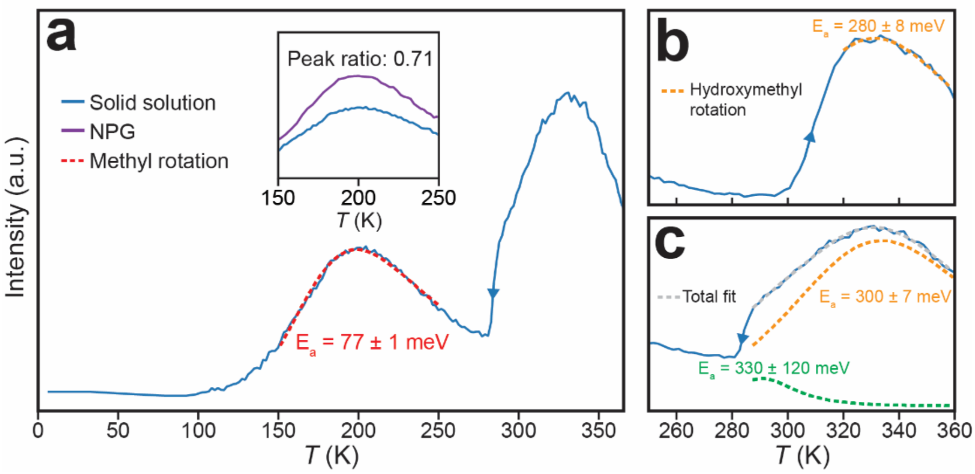

Figure 4 | (a) IFWS on cooling from 355 to 10 K showing the fit for the CH3 rotation activation energy. (b) Fit of the high temperature region above the phase transition on heating, giving an activation energy for the hydroxymethyl rotation. (c) Fit of the high temperature region above the phase transition on cooling, providing an activation for two modes in this case. Identification of these modes is underway, but the orange line is expected to be the hydroxymethyl rotation.

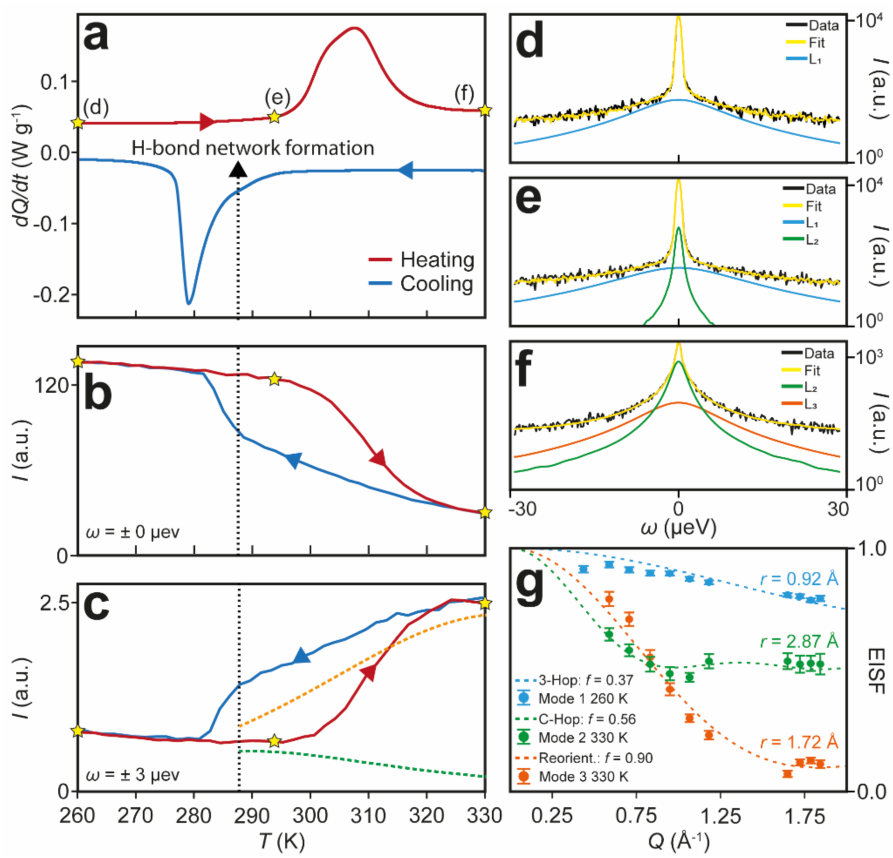

Figure 5| (a) calorimetry data on heating and cooling with stars showing the temperatures that QENS measurements were taken. (b) EFWS measurements of the phase transition region on heating and cooling. (c) IFWS measurements of the phase transition region on heating and cooling. The dashed lines are the fits of the two modes for the cooling data as obtained in Fig. 4. (d-f) QENS fits for the temperatures given by the stars in panels (a-c). (g) EISF plot and fits showing the three different modes detected (methyl rotation, hydroxymethyl rotation and molecular reorientation).