In-situ Neutron Scattering as a Grand Opportunity for Caloric Materials Research: A Case Study of Colossal Barocaloric Effects

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ABSTRACT
Caloric materials are systems that exhibit significant thermal effects at phase transitions induced by external fields. They can be used for the solid-state refrigeration through a designated cooling cycle. Current caloric materials are characteristic of small isothermal entropy changes of about 50 J kg⁻¹K⁻¹, which is one of serious obstacles to the real applications. Recently, we have discovered that plastic crystals exhibit excellent barocaloric effects with typical entropy changes higher than 400 J kg⁻¹K⁻¹ induced by a small pressure. While these findings imply the solid-state refrigeration technologies based on caloric materials would be on the horizon, the underlying microscopic scenario on such colossal barocaloric effects has be established by employing in-situ pressure dependent neutron scattering measurements, which also serves as a confirmation of the new finding from the very fundamental origin. The present study might inspire to promote the application of neutron scattering techniques in the future caloric materials research.

Keywords: caloric effect, solid-state refrigeration, plastic crystals

1. Introduction
Caloric effects are phase-transition thermal effects regulated by external fields [1]. They was initially known as magnetocaloric effect in magnetic materials with magnetic fields as the driving force about one hundred years ago [2]. In the last few decades, the caloric family has been significantly expanded with the emerging members such as the barocaloric effect in which the hydrostatic pressure serves as the stimulus. Two more members are elastocaloric effects in ferroelastics and electrocaloric effects in ferroelectrics, where the driving forces are uniaxial stress and electric fields, respectively. These four caloric effects are schematically summarized in Fig. 1. As a promising alternative to the vapor compression cycle technology that is currently in wide service, the refrigeration technologies based on solid-state caloric effects have been attracting intense attention in recent decades because of their potential higher efficiency and avoided greenhouse gas effect.

Isothermal entropy changes (ΔSᵣ) and adiabatic temperature changes (ΔTₐd) are two critical quantities for characterizing the performances of caloric materials. A caloric material with larger absolute values of ΔSᵣ and ΔTₐd allow more heat exchange with the refrigeration loading in one single thermodynamic cycle so that a higher energy conversion efficiency is expected. Consequently, the persistent efforts have been devoted to discovering new caloric materials with improved performances in last a few decades. So far, however, caloric materials are characteristic of small isothermal entropy changes of about 50 J kg⁻¹K⁻¹, which is one of serious obstacles to real applications.

Fig. 1. Schematic diagram of current four major caloric effects in solids.
Very recently, our thermodynamic measurements indicate that plastic crystals exhibit excellent barocaloric effects with typical entropy changes higher than 400 J kg\(^{-1}\)K\(^{-1}\) induced by a small pressure, ~ 50 MPa [3]. The value is almost one order of magnitude higher than that of all caloric materials reported before. For this reason, we named it as colossal barocaloric effect. More importantly, the driving pressure has been significantly lowered. While these findings imply the solid-state refrigeration technologies based on caloric materials would be on the horizon, the underlying microscopic scenario on such colossal barocaloric effects has to be established, as far as the fundamental issue is concerned. In other words, as a new phenomenon, the colossal barocaloric effects in the plastic crystals become convincing only when the origin is microscopically justified.

2. Experiment considerations

As plastic crystals are also called orientation-disordered crystals, the reorientational dynamics might play a decisive role in the colossal barocaloric effects. Thus, in-situ high-resolution inelastic neutron scattering (INS) as well as quasi-elastic neutron scattering (QENS) measurements are proposed on the representative plastic crystal neopentylglycol (NPG), whose chemical formula is \(\text{C}_5\text{H}_{12}\text{O}_2\) and IUPAC name is 2,2-dimethyl-1,3-propanediol.

The key to accomplishing the proposed experiments is the optimization of experimental conditions and minimization of the background for QENS signals. Thus, the cold neutron disk chopper spectrometer BL14 AMATERAS of J-PARC was chosen for such a study for its superior energy resolution in wide energy bands accommodated with the multi-\(E_i\) capacity [4,5]. The chopper configurations were 300 Hz (CH01), 300 Hz (CH02) with a slit width of 10 mm, and 150 Hz (CH03), which enabled the selection of \(E_i = 23.72, 5.93, 2.64\) meV with energy resolution of 0.42, 0.078, and 0.026 meV, respectively.

The required high pressure environment was generated through a clamped cell made of an Al–Zn–Mg-based alloy (Mesoalite). As shown in Fig. 2a, the cell contributes very little background except a peak located at about 1.5 Å\(^{-1}\), which spreads from the elastic line and extends to the inelastic channel. This signal is attributed to Teflon, which was used as an inner container in the pressure cell. Then, we have to consider how to select a proper pressure transmitting medium to ensure quasi-hydrostatic conditions. Given that what we are looking for is the QENS signal, a pressure transmitting medium with minimized incoherent scattering length is desirable. We considered a few options and finally we came to realize KBr would be the best one. Shown in Fig. 2b is the inelastic data of KBr contained in the pressure cell. There is quite few intensity present in this \(Q-E\) region, compared with the empty cell. A mixture of the sample and KBr powder was pelleted at a desirable loading with a hand press, using a load–pressure curve determined beforehand. The actual pressure generated in the cell was determined at the high-pressure neutron diffractometer (PLANET) [6] from the change of the lattice parameters of KBr using the equation of state [7].

The inelastic data reduction was performed using the Utsusemi suite [8]. The resulting dynamic structure function \(S(Q, E)\) were visualized in Mslice of DAVE as a function of momentum transfer \((Q)\) and energy transfer \((E)\) [9].

3. Results and discussion

The molecular configuration of NPG is characteristic of a tetrahedral motif. The five carbon atoms form a tetrahedron, in which two carbon atoms are attached to hydrogen atoms in the methyl group, whereas two others form the hydroxymethyl group. At room temperature, the NPG molecules are ordered on a monoclinic lattice with space group \(P2_1/n\) [10]. This ordered phase transforms into an face-centered-cubic lattice at \(T_i \approx 314\) K on heating under the ambient pressure.
We performed QENS measurements on NPG at selected temperatures near \( T_t \). Shown in Fig. 3a is the contour plots of \( S(Q,E) \) with \( E_i = 2.64 \) meV at 300 K under the ambient pressure. The intense stripes centered at \( E = 0 \) represent the elastic line, which contains most of the scattering intensity. It can be seen that the elastic lines dominate the spectrum at this temperature. At 325 K (Fig. 4a), just above \( T_t \), a less-intense signal spreads out from \( E = 0 \) and weakens as \( E \) increases, which corresponds to QENS originating from hydrogen atoms. The spectral fitting suggests that the hydrogen atoms in the methyl group are subjected to \( C_3 \) reorientation in both ordered and disordered phases (\( C_3 \) reorientation might be further frozen at about 60 K), while the whole molecule undergoes isotropic reorientation in the disordered phase.

Then, we move to the pressure-dependent QENS experiment that is able to directly provide insights into the microscopic dynamics of the system in response to the application of pressure. It can be seen in Fig. 3b that the QENS signal at 300 K under 286 MPa is also identical to the ambient pressure case. This suggests that the \( C_3 \) motion of methyl group is not sensitive to the application of pressure. As shown in Fig. 4b, in contrast, the QENS signal at 325 K is mostly suppressed under a pressure of 286 MPa, which indicates that free isotropic reorientation of the whole NPG molecules are hindered. Indeed, the QENS intensity is already effectively suppressed even at a lower pressure of 178 MPa. These QENS data directly verify that orientational disorder is restrained by the pressure, inducing entropy changes. The pressure suppression of orientational disorder is also manifested in phonons as phonons become much sharper at 286 MPa, which is attributed to the reduced scattering by the orientational disorder. These experimental insights unambiguously indicate that the colossal barocaloric effects of NPG can be attributed to the suppression of the extensive orientational disorder by pressure.

Fig. 3. Contour plots of \( S(Q,E) \) of the sample with KBr contained in the cell at \( E_i = 2.63 \) meV at 300 K under ambient pressure (a) and 286 MPa (b).

Fig. 4. Contour plots of \( S(Q,E) \) of the sample with KBr contained in the cell at \( E_i = 2.63 \) meV at 325 K under ambient pressure (a) and 286 MPa (b).

4. Prospects

In summary, we have directly observed the pressure suppression of molecular orientational disorder of the NPG plastic crystal, which is benefited by the fine energy resolution of the instrument and the designated high-pressure sample environments that provide very little background for the QENS signals we are interested in. While such an in-situ experiment qualitatively indicates that the colossal barocaloric effects are related to the pressure-tuned molecular orientational disorder, the quantitative investigation would be a future direction in this field. One may expect more precise QENS results allow to count the possible configurations and obtain the corresponding entropy changes, which should be comparable to the thermodynamic measurements.
The core physical issue of caloric materials is the evolutions of atomic structures and interactions as a function of driving forces including pressure, magnetic fields, electric fields, stresses as well as light illumination in multiple spatial and temporal scales. State-of-the-art characterization techniques based on large-scale facilities such as the neutron scattering are highly desirable in this case due to the powerful experimental abilities and versatile complex sample environments. In other words, the experimental techniques based on large-scale facilities provide a great opportunity for caloric materials research and we hope that our present study would inspire both the neutron scattering and caloric materials communities. A similar routine study can be performed on other caloric materials to understand the microscopic mechanisms. For example, an in-situ diffraction measurement on an elastocaloric material with a loading frame would help to unveil the structural changes as well as the regular lattice strain information induced by uniaxial stresses.

Multicaloric effect gradually becomes attractive given that application of multiple fields allows us to enhance the entropy changes and eliminate the hysteresis loss of the thermodynamic cycles [10]. As far as the multicaloric effect is concerned, the caloric materials community may have an increasing demands on more complex sample environments that can simultaneously provide at least two more driving fields, like temperature-pressure-illumination. This kind of sample environments along with the neutron scattering techniques is highly beneficial to explore the more exotic behaviors of solids in an unprecedentedly large parameter space.

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