Pressure-induced reversal of Peierls-like distortions elicits the amorphous-amorphous transition in GeTe and GeSe

While polymorphism is a well-known concept in crystalline states, disordered systems such as liquid and amorphous materials may also show two or more states with distinct structure and physical properties within the same chemical composition [1]. The transition between the two liquid states is called liquid-liquid transition (LLT), and the solid-state counterpart is instead called a polyamorphic transition or amorphous-amorphous transition (AAT). A wide range of materials shows the phenomena of LLT and AAT. They were first identified in water and subsequently found in the other systems such as silicon, silica, germanium, tellurium, metallic glasses, and even some molecular liquids [2].

Phase-change materials (PCMs) are one of the best candidates for applications in future non-volatile memory and neuromorphic computing devices. Since the structural and kinetic properties of the amorphous and liquid states are of crucial importance for optimizing the switching speed and data retention abilities, their atomic-scale structure has attracted attention both in fundamental and applicational contexts. Recent studies identified a LLT in some PCMs, using femtosecond diffractions based on X-ray free electron laser (XFEL) in combination with *ab initio* simulations [3]. They revealed that the LLT is characterized by a distortion of the local structural environment, called Peierls-like distortion (PLD), which appears in the supercooled liquid state during quenching, eventually being stabilized in the amorphous state. Figure 1(a) schematically shows the PLD. While liquid PCMs typically show undistorted octahedral-like coordination (OLC), the PLD modifies it by introducing alternating long and short bonds. The LLT is associated with the opening of a pseudo-bandgap around the Fermi level, indicating that the LLT is also associated with a metal-to-semiconductor transition. However, it was unclear whether there is any polyamorphism in the amorphous phase of PCMs, and if it exists, how it is related to the LLTs.

To elucidate this important question, we performed *in situ* high-pressure X-ray scattering experiment at SPring-8 **BL05XU** [4] on a prototypical PCM, amorphous GeTe, and on amorphous GeSe. Both compounds are isoelectronic *p*-bonded systems, but GeSe exhibits stronger covalent bonding than GeTe. We loaded the sample pellets on the Paris-Edinburgh (PE) press for high-pressure experiment up to 10 GPa (Fig. 1(b)). The unique capabilities of BL05XU are available to study the pressure-induced AAT, while the short-lived LLT (in the order of nanoseconds) necessitates the use of an XFEL [3]. The combination of the high-energy (100.1239 keV) pink beam and the PE press with the horizontal aperture about 120° allowed us to access a maximum momentum transfer $Q_{max} = 28$ Å^{-1}, providing high-resolution pair distribution functions (Fig. 2(a)). The experimental throughput was kept high throughout the beamtime, which enabled us to successfully collect 17 datasets in 6 shifts with no significant interruption, taking advantage of the high-flux pink beam and the stable operation of SPring-8.

Since the weak alteration of the long-and-short bonds of the PLD has nearly a double period to the OLC, it manifests itself as a small “pre-peak” in the low-Q range. The inset of Fig. 2(a) shows the pre-peak of GeSe. With increasing pressure, the pre-peak becomes smaller. GeTe shows similar behavior. Pressure suppresses the PLD and transforms it into the OLC, suggesting a pressure-induced AAT. This is the reverse behavior to the LLT in the previous study [3], where the PLD emerged during cooling.

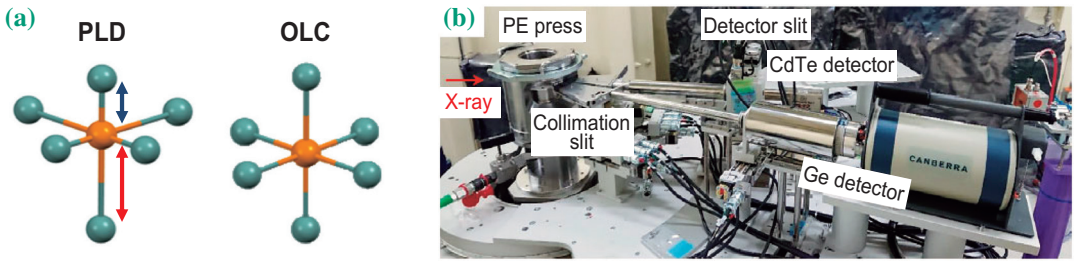

Fig. 1. **(a)** The schematic representation of the Peierls-like distortion and the octahedral-like coordination. **(b)** The setup of high-pressure X-ray scattering experiment at BL05XU [4].

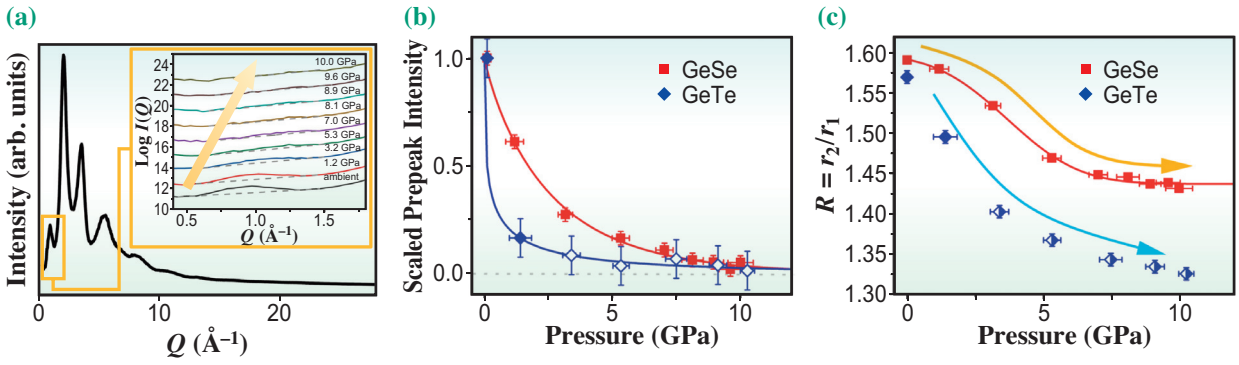

Fig. 2. **(a)** The diffraction profile $I(Q)$ of GeSe. The inset shows the pre-peak. **(b)** The pressure dependence of the pre-peak intensity. **(c)** The pressure dependence of the peak position ratio r_2/r_1 of the pair distribution functions.

Figure 2(b) shows the pressure dependence of the pre-peak intensity. It becomes negligible around 9.0 GPa in GeSe, while it vanishes at lower pressure of 3.4 GPa in GeTe.

Figure 2(c) shows the pressure dependence of the ratio of the 1st and the 2nd peak positions r_2/r_1, obtained from the pair distribution functions. The ratio decreases with increasing pressure in contrast to the rise of r_2/r_1 in the LLT. We estimate the transition pressure P_{aa} of the AAT as P_{aa} = 3.7 ± 0.4 GPa for GeSe, and P_{aa} = 1.8 ± 0.4 GPa for GeTe. The correlation between P_{aa} and the vanishing pressure of the pre-peaks indicates that the suppression of the PLD is the underlying mechanism of the AAT.

To obtain atomic-level insight on the transition mechanism, we performed molecular dynamics simulations of amorphous GeTe using a machine-learned neural-network potential, as well as *ab initio* molecular dynamics simulations of amorphous GeSe. The simulations reproduce the pressure-induced suppression of the PLD, and the suppression occurs at lower pressure in GeTe than in GeSe, in agreement with the experiment. Furthermore, the electronic density of states shows a notable rise around the Fermi level, as opposed to the opening of the pseudo-bandgap reported in the LLT.

Our results demonstrate that the pressure-induced AAT can be understood as suppressing the PLD, which is essentially the reverse mechanism to the temperature-dependent LLT in the supercooled liquid state induced by quenching [5]. Figure 3 shows the directions of the AAT and the LLT on the P–T phase diagram. The two results indicate a transition line with a negative slope. The phase diagram also suggests that we can vary the degree of the PLD by adjusting temperature and pressure, which is potentially useful to tune the properties of PCM-based functional devices.

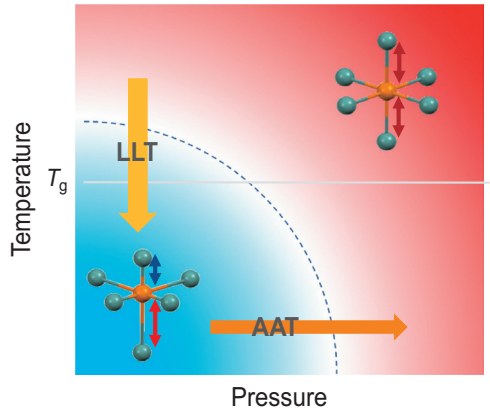

Fig. 3. The schematic of the P–T phase diagram of the PCMs. The directions of the LLT and the AAT indicate the existence of a transition line with a negative slope.

Tomoki Fujita[a,*], Yoshio Kono[b] and Riccardo Mazzarello[c]

[a] Department of Chemistry, Aarhus University, Denmark
[b] Department of Physics and Astronomy, Kwansei Gakuin University
[c] Department of Physics, Sapienza University of Rome, Italy

*Email: tofu@chem.au.dk

References

[1] C. A. Angell: Science **267** (1995) 1924.
[2] H. Tanaka: J. Chem. Phys. **153** (2020) 130901.
[3] P. Zalden *et al.*: Science **364** (2019) 1062.
[4] Y. Kono: SPring-8/SACLA Research Frontier 2022 (2023) 52.
[5] *T. Fujita, Y. Chen, Y. Kono, S. Takahashi, H. Kasai, D. Campi, M. Bernasconi, K. Ohara, H. Yumoto, T. Koyama, H. Yamazaki, Y. Senba, H. Ohashi, I. Inoue, Y. Hayashi, M. Yabashi, E. Nishibori, R. Mazzarello and S. Wei: Nat. Commun.* ***14*** *(2023) 7851.*