

Liquid-liquid transition and individual atomic diffusion in GeTe systems

Ayano Chiba, Yukinobu Kawakita, Takanori Hattori, Franz Demmel
Keio University, J-PARC JAEA, ISIS RAL

It has recently been thought that the density maximum of water at 4 °C is related to a structural change of water (O. Mishima, H. E. Stanley, Decompression-induced melting of ice IV and the liquid-liquid transition in water, *Nature*, 1998, 396, 329). Similar density anomalies are known for liquid Ge-Te mixtures. Particularly, the eutectic composition Ge₁₅Te₈₅ shows the sharpest structural change as a function of temperature (C. Bergman *et al.*, Experimental investigation of the waterlike density anomaly in the liquid Ge₁₅Te₈₅ eutectic alloy, *Phys. Rev. B*, 2003, 67, 104202). We chose to measure this eutectic composition, whose low melting point (375 °C) allows us to cover the structural change region widely. By substituting isotope Ge-73 ($\sigma_{\text{inc}} = 1.5$ barn) for natural Ge, we aim to measure the self-diffusion constant D_{Ge} and its change at the structural change region, separately from the contribution of Te ($\sigma_{\text{inc}} = 0.09$ barn), by use of DQ^2 law at low Q range for quasielastic neutron scattering (QENS) spectra.

We prepared Ge₁₅Te₈₅ whose Ge was substituted by Ge-73, and encapsulated the sample in a quartz tube whose inner and outer diameters were 9 mm and 10 mm, respectively. We chose this thick sample size because the fraction of Ge is as low as 15% and thus intended incoherent scattering intensity was expected to be low. The cell was set into a furnace, which was evacuated to 10⁻³ mbar when heating, and finally down to 10⁻⁶ mbar. Measurements were done at 9 temperature points from melting temperature to 600°C, where the transition region is expected to be around 400 - 450°C.

We succeeded to detect an interesting change of D_{Ge} at the structural change region. Figure 1 (a) shows the half-width of half-maximum (HWHM) of the quasielastic peaks at varied temperatures. By

the DQ^2 law, it is seen that the diffusion largely depends on temperature below 450°C, while the temperature dependence is rather smaller for higher temperatures, higher than 450°C. Figure 1 (b) shows an Arrhenius plot of D_{Ge} . At 400 - 450°C, a clear deviation from a straight line is observed. This is the first experimental data that shows a change of the individual diffusion in the binary liquid system at liquid-liquid structural-change region.

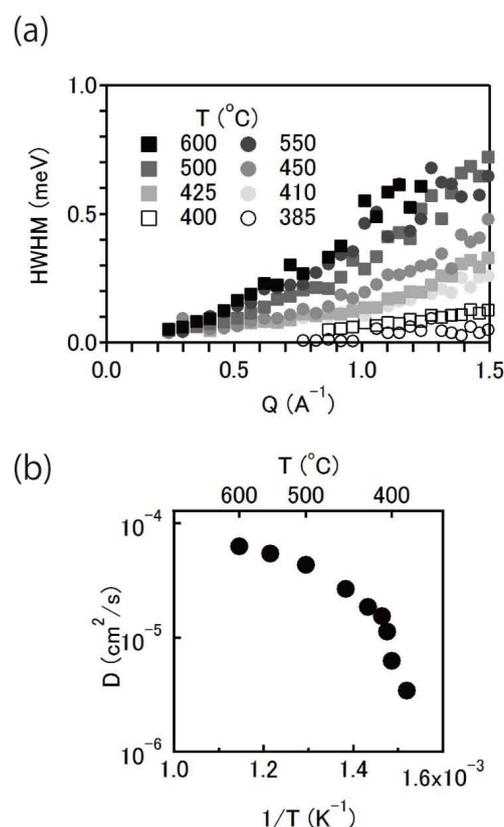


Fig. 1. Results for liquid Ge₁₅Te₈₅ : (a) HWHM of the quasielastic peaks as a function of Q at varied temperatures, and (b) Arrhenius plot of D_{Ge} .