Experimental Report

Proposal: **6-03-428** **Council:** 10/2012

Title: Dynamical aspects of alloys with negative thermal expansion.

This proposal is continuation of: 6-03-411

Researh Area: Materials

Main proposer: **GASPARD Jean-Pierre**

Experimental Team: RATY Jean Yves
GASPARD Jean-Pierre
COULET Marie Vanessa
HIPPERT Francoise

Local Contact: JOHNSON Mark Robert

Samples: Se.5Te.5

Instrument	Req. Days	All. Days	From	To
IN6	4	3	29/04/2013	02/05/2013

Abstract:

Study of the temperature evolution of the dynamical properties S(q,omega) of the Selenium-Tellurium alloy (Se.5Te.5) that shows a negative thermal expansion (NTE) and a liquid-liquid continuous transition between 568 C and 858 C. We will focus on the vibrational density of states, particularly the evolution of the its high energy stretching modes around 25 meV, which are sensitive to the Peierls distortion amplitude. The latter is reduced with temperature and is accompanied by a softening of the vibrational (stretching) modes with an increase of the vibrational entropy. This proposal is a continuation of a series of successful measurements made on SexTe(1-x) alloys in the Te rich side.

_____EXPERIMENTAL REPORT_____

EXPERIMENT N° 6-03-428 INSTRUMENT IN6

DATES OF EXPERIMENT 29/04/2013 to 02/05/2013

TITLE **Dynamical aspects of alloys with negative thermal expansion**

EXPERIMENTAL TEAM (names and affiliation)
JP. Gaspard, University of Liège (B)
JY. Raty, University of Liège (B)
F. Hippert, LNCMI, Grenoble
M. Johnson, ILL

LOCAL CONTACTS: M. Johnson and M. Koza, ILL

Date of report : 8/5/2013

In a limited temperature range (about 100-200 K), a negative thermal expansion (NTE) is observed in covalent liquids with a low coordination number in the vicinity of the melting temperature. Most of them are Te based alloys (e. g. Te, $GeTe_6$, As_2Te_3 [1,2]). The low coordination of covalent structures, and their NTE, is related to the Peierls distortion, a symmetry breaking mechanism, as it has been shown by neutron diffraction, neutron inelastic scattering (NIS), theoretical modelling and *ab initio* molecular dynamics. In a previous experiment [6-03-411], we studied on IN6 the dynamics of $Se_{1-x}Te_x$ liquid alloys as a function of temperature. The addition of Se to Te moves the NTE domain to the temperature range where the liquid is at thermodynamic equilibrium for x>.23 [3]. For x =0.5 the NTE occurs between 560°C and 860 °C whereas M_{elting} = 350°C. This final experiment on the $Se_{.5}Te_{.5}$ alloy aimed at doing quantitative analysis of the temperature evolution of the dynamical properties.

The reactor started on 29/04/2013 at around 12 am and ran at a power between 51 and 53 MW. The wavelength was set to 4.14 Å. The sample was confined in a quartz tube of internal/external diameters of 8/10 mm, sealed under vacuum. The quartz tubes are surrounded by a thin cylinder of Nb (thickness= .1 mm) that allows positioning the sample and holding the thermocouples. The furnace was a cylinder of vanadium (thickness = .1 mm). The temperature was measured and monitored by two thermocouples located just above the upper part of the neutron beam.

The stoichiometric compound $Se_{.5}Te_{.5}$ sample has been measured at seven temperatures

- 360, 460, 560, 660, 760, 860 and 960°C with a counting time of 6 hours except the lowest temperature (360°C, 3 hours).
- An empty quartz tube of the same diameter has been measured at three temperatures T = 460, 660 and 860°C during 6 hours in order to have a valuable statistics. Interpolated values were taken for the intermediates temperatures and extrapolated for the two extreme temperatures. We checked that the interpolation error (i. e. the departure from linearity) is smaller than 2% in relative units.

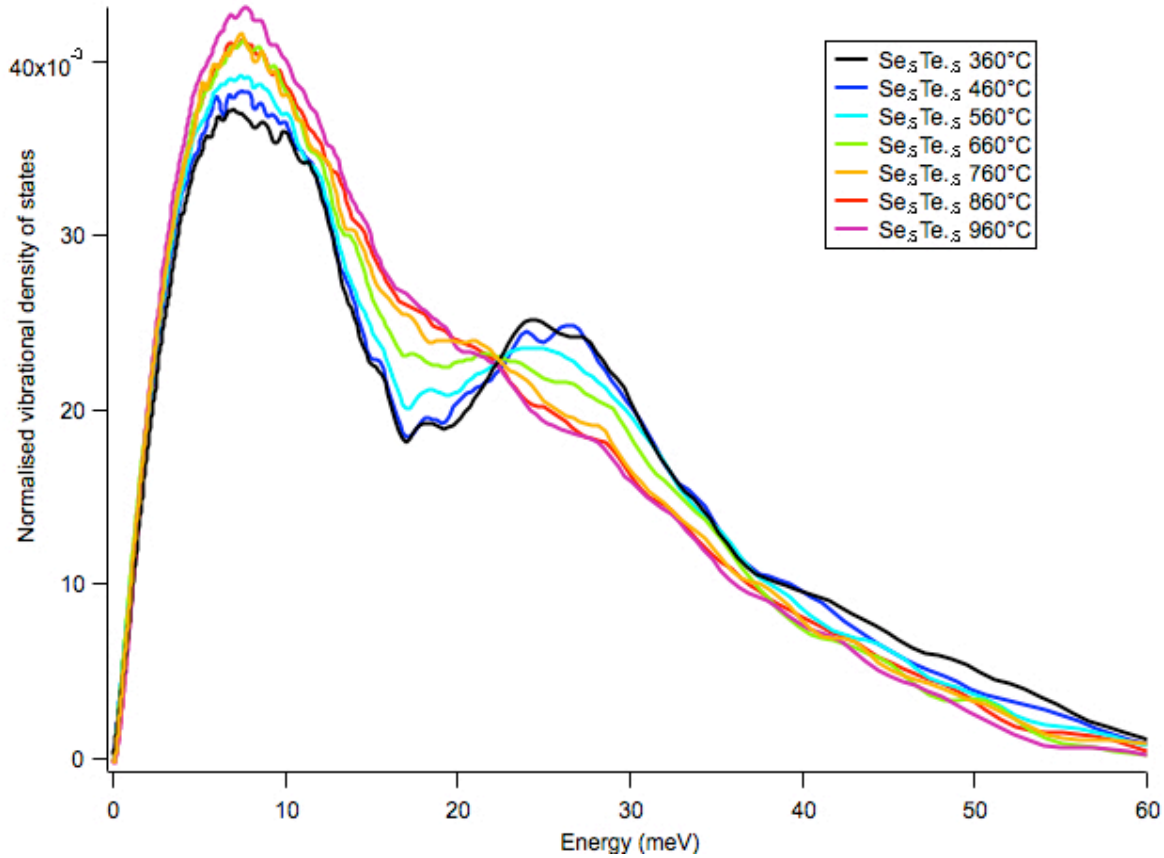

Fig. 1 Evolution of the normalised vibrational densities of states of $Se_{.5}Te_{.5}$ with temperature. The signal of the empty quartz container has been subtracted taking into account transmission.

The experiment went on normally but the slow cooling down of the furnace (about 3 hours) results in a loss of beamtime.

We observed a red shift of the vibrational spectra in the region where the NTE occurs, i. e. the high energy peak around 25 meV is shifted down to lower energies as a consequence of the elongation of the shortest bond lengths. The effect is sensible in the temperature range 460°C – 760°C. A similar behaviour was observed for the other compositions of $Se_{1-x}Te_x$ and for other covalent Te-based alloys ($GeTe_x$ and As_2Te_3) showing the universality of the behaviour. *Ab initio* molecular dynamics simulations of the $Se_{.5}Te_{.5}$ are underway.

References.

[1] C. Otjacques *et al.*, PRL 103, 245901 (2009)

[2] C. Otjacques *et al.*, Phys. Rev. B 82, 054202 (2010), report TEST-1783 and ILL Annual Report 2010, Scientific Highlights, pp. 70-71.

[3] H. Thurn and J. Ruska, J. Non Cryst. Sol., 22, 331 (1976)