Experimental report

09/02/2016

Proposal: 7-02-158 **Council:** 4/2015

Title: Phonon softening at the structuralphase transition in thermoelectricmaterial SnSe

Research area: Physics

This proposal is a new proposal

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Experimental team: Tapan CHATTERJI

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Samples: SnSe

Instrument	Requested days	Allocated days	From	To
IN8	7	4	02/12/2015	07/12/2015

Abstract:

The narrow band-gap IV-VI semiconductors have attracted renewed interest due to their various interesting properties viz. phase-change properties, thermoelectricity, topological effects etc. Recently ultralow thermal conductivity and high thermoelectric figure of merit have been found in SnSe single crystals that may find use in waste thermal energy conversion to useful electrical energy. This has motivated us to study the phonon and soft mode dynamics close to the high temperature structural phase transition temperature in SnSe. This study will help us how ultralow thermal conductivity and high thermoelectric figure of merit have been found in SnSe is related with the anharmonicity and soft mode dynamics. We request 7 days of neutron beam time on the triple-axis spectrometer IN8 for the proposed experiment.

Phonon softening at the structural phase transition in thermoelectric material SnSe

Introduction:

The narrow band-gap IV-VI semiconductors have attracted renewed interest due to their variousinteresting properties viz. phase-change properties [1], thermoelectricity [2-3], topological effects [4] etc. Recently ultralow thermal conductivity and high thermoelectric figure of merit have beenfound in SnSe single crystals [5]. The dimensionless figure of merit ZT (Z = figure of merit, T =absolute temperature) for this layered sample is highly anisotropic and is very large. The material shows a very high ZT = 2.6 +- 0.3 at 923 K measured on a single crystal along the b-axis. The ZT value is also very high ZT = 2.3 +- 0.3 along the c-axis but it is significantly reduced ZT = 0.8+-0.2 along the a-axis of the orthorhombic unit cell. The layered structure of SnSe is a distortedrock-salt structure and has anomalously high Gruenisen parameters caused by anharmonicity and anisotropic bonding. The exceptionally low thermal conductivity (0.23 $Wm^{-1}K^{-1}$ +- 0.03 at 923 K) in SnSe is due to anharmonicity.

A good understanding of the reasons for all these thermoelectric properties requires a complete knowledge of lattice dynamics and soft mode at the high temperature α−β phase transitions (B16 to B33 type) in SnS and SnSe at about T = 850 K. Chattopadhyay et al. [6] investigated this phase transition by single crystal neutron diffraction. This investigation indicated that the α−β phase transitions in SnS and SnSe are of second order displacive type and consist mainly of continuous movement of the Sn and S/Se atoms almost entirely along the [100] direction and suggest the softmode behavior of a zone-boundary phonon of the β−phase. We already possess some preliminary phonon dispersion data on both SnS and SnSe collected on the triple axis spectrometer at LLB reactor and also have done shell model for experimental help and more recently ab-initio DFT and phonon calculations [7]. Here we report the results of inelastic neutron scattering investigation of the soft mode in SnSe single crystal at high temperature.

From our previous investigation [7] we have the complete phonon dispersion in SnSe. In Fig. 1 we show the dispersion along (0 ζ 0).

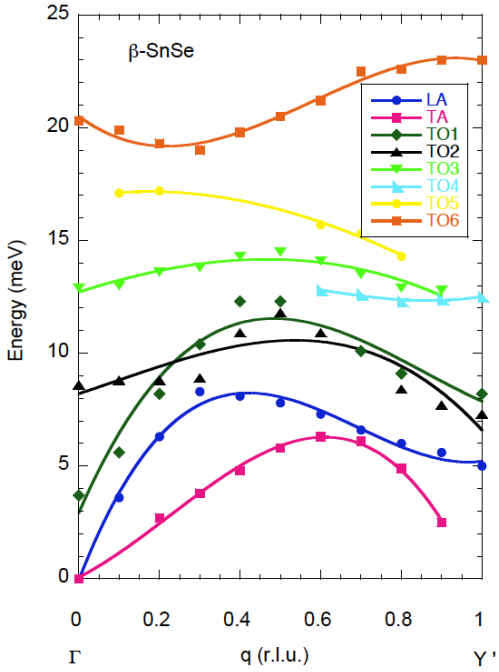

Fig. 1 - The experimental phonon dispersions in β-SnSe at T = 853 K along (0 ζ 0). The continuous curves are guides to the eye. LA, TA and TO in the legends mean logitudinal acoustic, transverse acoustic and transverse optic modes, respectively.

Experiment:

A large single crystal of SnSe was fixed to the sample stick of the ILL furnace with its [100] crystallographic axis vertical. The furnace with the SnSe crystal was placed on the triple-axis spectrometer IN8 of the Institut Laue-Langevin. The scattering plane was (0kl). At the beginning we reproduced our previous measurements of the phonon dispersion of SnSe at room temperature. We

then selected a few Q points and we did energy scans at these selected points as a function of temperature. The Q points we have studied are (0, 4, 0.5) and (0, 4, 1), (0, -0.5, 2) and (0, -1, 2). Fig. 2 shows the energy scans at Q = (0, 4, 0.5) and the temperature dependence of the corresponding phonon energy. We also measured their dispersion along (0 0 ζ) which we do not show here. There is softening of this zone-boundary phonon but the energy does not become zero. There are two phonon branches one of which with higher energy softens considerably whereas the other with lower energy practically remains constant or softens a little bit. The results are very similar for the phonons at (0, 4, 1) shown in Fig. 3. There exists only partial softening of the phonon at the phase transition. But there exist only a single phonon branch at this Q point.

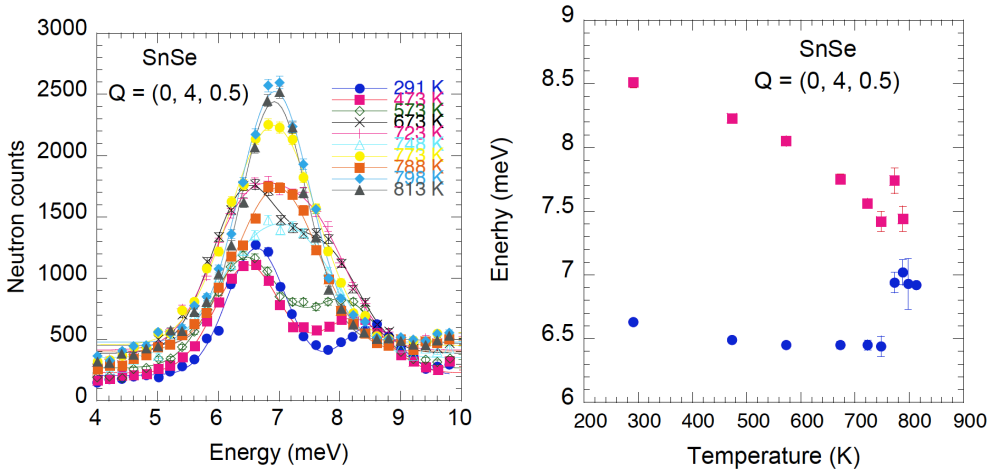

Fig. 2 – (a) Energy scans at Q = (0, 4, 0.5) at different temperatures. (b) Temperature variation of the phonon energy.

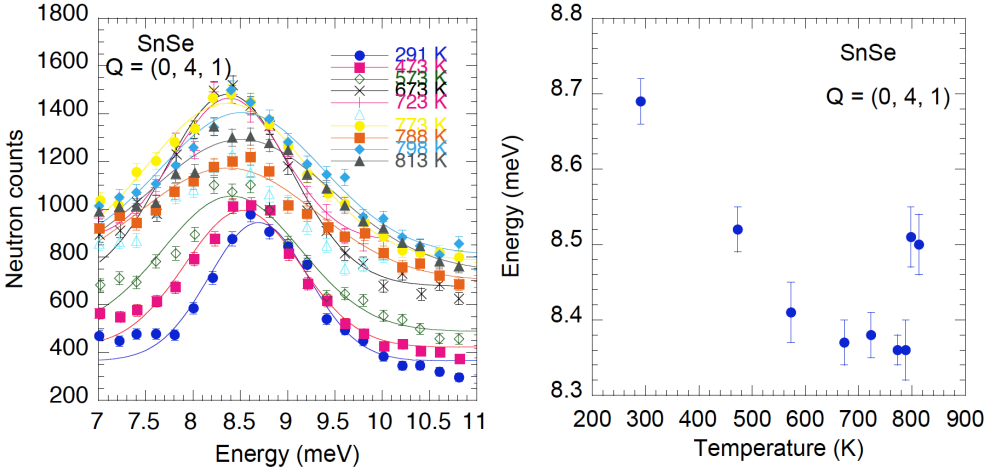

Fig. 3 – (a) Energy scans at Q = (0, 4, 1) at different temperatures. (b) Temperature variation of the corresponding phonon energy.

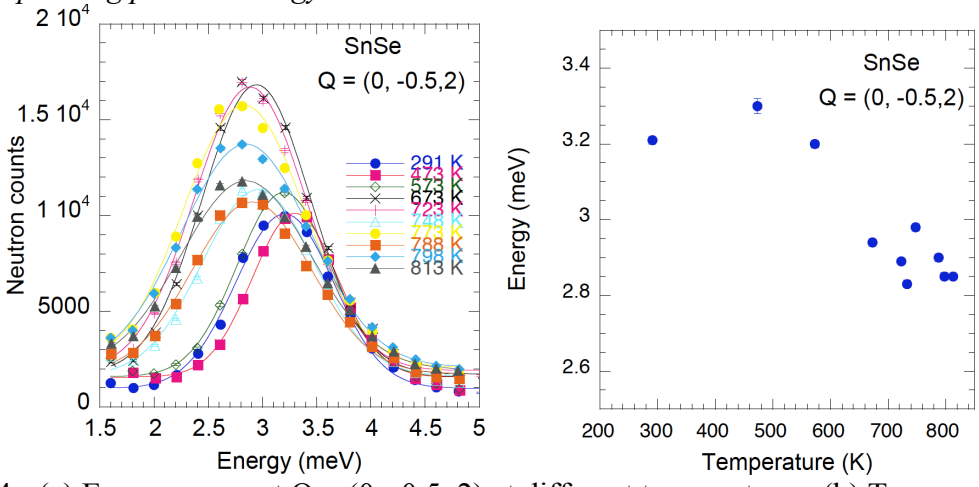

Fig. 4 - (a) Energy scans at Q = (0, -0.5, 2) at different temperatures. (b) Temperature variation of the corresponding phonon energy.

We have investigated the softening of phonon energies at the zone boundary point Q = (0, -0.5, 2)

and also at Q = (0, -1, 2) shown in Fig. 4 and 5. We have also measured their complete dispersions along (0 ζ 0) as a function of temperature, which we do not show here.

We did not have enough time to study phonon softening in SnSe for the phonons along (ζ 0 0) by using another orientation of the crystal.

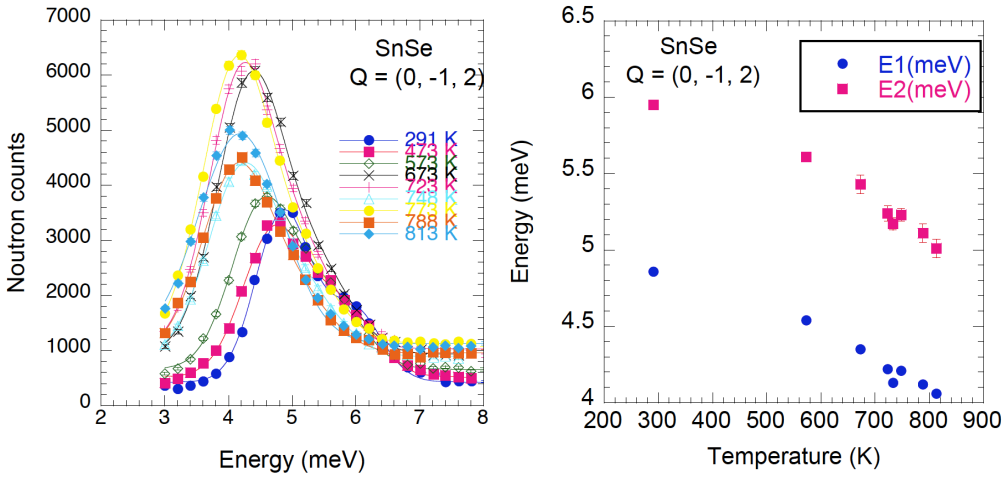

Fig. 5 - (a) Energy scans at Q = (0, -1, 2) at different temperatures. (b) Temperature variation of the corresponding phonon energy.

Future plans:

We wish to extend the present study the phonon dispersion along (ζ 0 0) and their softening as a function of temperature at the α–β structural phase transition in SnSe at T_c = 810 K.

References:

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[7] T. Chatterji et al. (unpublished)