Experimental report

22/12/2021

Proposal: **7-01-552**

Council: 4/2021

Title: Anharmonic lattice dynamics in thermoelectric PbTe under high pressure

Research area: Physics

This proposal is a continuation of 7-01-468

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Samples: PbTe

Instrument	Requested days	Allocated days	From	To
IN8	6	6	21/09/2021	27/09/2021

Abstract:

Thermoelectric materials such as PbTe are interesting for energy applications as they can transform heat into useful electricity. Here, we propose to finish our investigation of the anomalous lattice dynamics of PbTe under high pressure. Our previous experiment at ILL shows a non-monotonic pressure dependence of phonon properties around p = 2.5 GPa and generally reduced phonon linewidth at high pressures. Results at additional pressure values are needed to confirm the non-monotonic pressure dependence of the phonon properties indicated by the current data. Comparison of the anticipated results with molecular dynamics simulations for the lattice dynamics will provide a detailed understanding of the intriguing lattice dynamical properties of PbTe, and, pave the path for the designs of new high-performance thermoelectric materials requiring a low lattice contribution to the thermal conductivity.

Experimental report

Anharmonic lattice dynamics in thermoelectric PbTe under high pressure

Abstract:
Thermoelectric materials such as PbTe are interesting for energy applications as they hold promise in transforming low-grade heat into electricity. Here, we propose to finish our investigation of the anomalous lattice dynamics of PbTe under high pressure. Our previous experiment at ILL shows a non-monotonic pressure dependence of optical phonon properties around P = 2.5 GPa and generally reduced phonon linewidth at high pressures. Results at additional pressure values and acoustic phonon properties are needed to cross-check the non-monotonic pressure dependence of the phonon properties indicated by the current data. Comparison of the anticipated results with molecular dynamics simulations for the lattice dynamics will provide a detailed understanding of the intriguing lattice dynamical properties of PbTe, and pave the path for the designs of new high-performance thermoelectric materials requiring a low lattice contribution to the thermal conductivity.

Thermoelectric materials (TE) are interesting for energy applications as they can transform heat into useful electricity. The energy transformation efficiency of a thermoelectric material is mainly determined by the figure of merit from materials aspects, $zT = \sigma S^2 T/(\kappa_L + \kappa_E)$, where κ_L and κ_E denote the lattice and electronic thermal conductivity, respectively; σ represents the electrical conductivity, S is the Seebeck coefficient, and T is the absolute temperature [1]. Generally speaking, a large power factor ($PF = \sigma S^2$) and a low lattice thermal conductivity κ_L are prerequisites for high zT values, thereby having a potential for practical applications [2]. The mainstream excellent TE material, PbTe, is currently the most promising and attractive TE material due to its intriguing electronic properties and thermal conductivity [3]. A recent inelastic neutron scattering experiment has revealed the extremely low lattice thermal conductivity driven by its giant anharmonic behavior [4].

In addition to Inelastic Neutron Scattering experiments at Laboratoire Leon Brillouin (LLB) and quantitative molecular simulations on PbTe at ambient pressure done by some of us [5], our previous high-pressure investigation on optical phonon modes also indicates the anomalous pressure dependence anharmonic properties. Here, we continue to complete our investigation on the anharmonic lattice dynamics in PbTe at high pressure. We used the thermal triple-axis spectrometer (TAS)

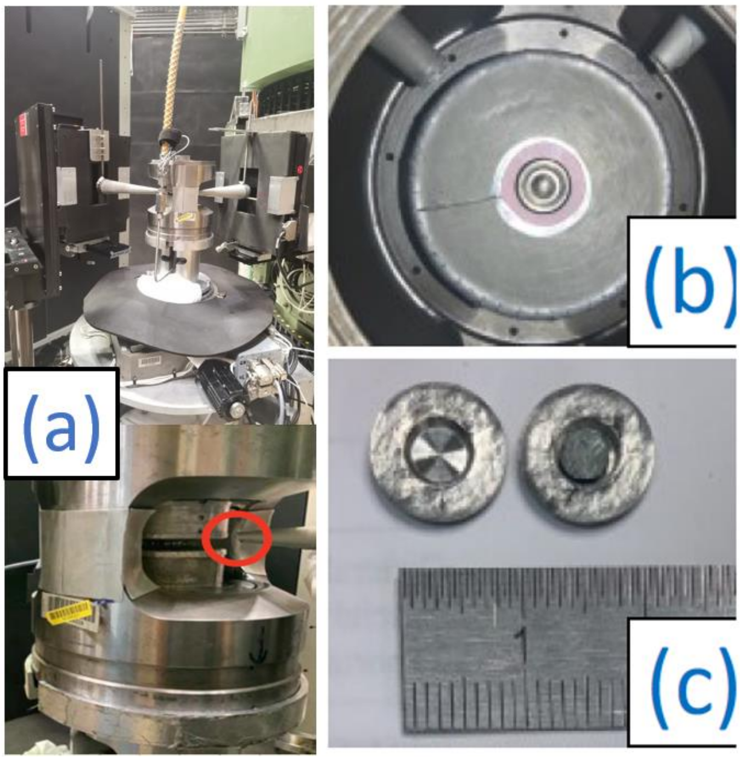

Fig. 1. Inelastic Neutron Scattering experiment set up at IN8, ILL. (a) geometry with two cones (incident beam; scattering beam) and two anvils (on/below the sample shell), high pressure oil pumped through steel pipe. (b) folded encapsulating gaskets, within which is full of alcohol liquid. (c) PbTe sample and gaskets.

IN8 at the Institute Laue Langevin (ILL) to study the phonon properties of TO (Transverse Optical) and TA (Transverse Acoustic) modes at several different hydrostatic pressures (0, 1.3, 2.0, 3.1, 4 and 5.15 GPa), along with acoustic phonon dispersion at 5.15 GPa. We did not measure phonon properties at even higher pressures because there is a phase transition at around 6 GPa for PbTe [6-7]. The measurements were performed using PG002 monochromator and PG002 analyzer, with a constant final energy of 14.7 meV. To improve the momentum resolution and suppress the experimental background, we used collimators 40'-40'-30'-30'.

As shown in Fig. 1a, both incident and scattered beams were constrained by two cadmium cones to minimize the background scattering from the pressure cell surrounding the sample and suppress air scattering. PbTe sample was cut into several pieces of discs with the same diameter of 4 mm and height of 1.2 mm (Fig. 1(c)). A single crystal PbTe (NaCl-type crystal structure) from last experiment, was pre-aligned in the 110-001 scattering plane to within 0.5° to avoid the need to tilt the pressure cell. A pair of encapsulating gaskets were used and one piece of PbTe disc was then loaded into the gasket, the inside of which was full of deuterated 4:1 methanol-ethanol liquid (Fig. 1(c)). In general, the sample was completely immersed in the liquid. The gaskets were then folded and put in between the two anvils with the upper one fixed (Figs. 1(a) and (b)).

Different pressures were applied to the sample by use of an industrial oil press and the alcohol liquid as pressure transmitting medium, which connected with a high-pressure pump apparatus (not shown). In this experiment, we reused the sample #2 for pressure-dependent experiments, which was recovered undamaged after the last experiment (experimental report of Proposal #7-01-468). Releasing pressure is difficult because of the pressure hysteresis effect. Therefore, we loaded the pressure cell with sample #2 and started increasing the pressures, i.e., 1.3, 2.0, 3.1, 4 and 5.15 GPa. On the basis of the well-established relationship between pressure to lattice constant for PbTe [8], we determined the pressure values deduced from the lattice constants by elastic longitudinal scans through (004) and (113) Bragg reflexes.

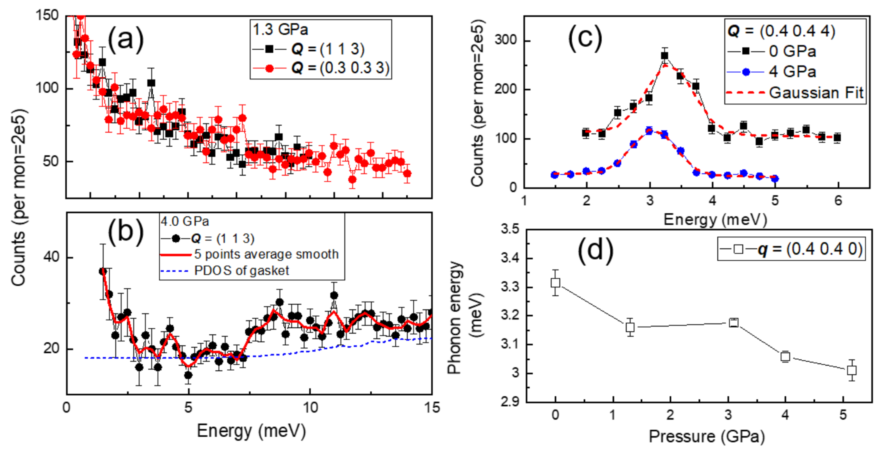

Fig. 2. Profile of the energy scans at zone center Q = (1,1,3) at (a) 1.3 and (b) 4 GPa. The red solid line in (b) is 5 points average smooth line, and the blue scatter line is projected density of states (PDOS) of the gasket. (c) Profile of the energy scans at zone center Q = (0.4,0.4,4) at 0 and 4 GPa. The red lines are Gaussian fit lines. (d) The pressure-dependent phonon energy position is determined by Gaussian fit. Data for different pressures are combined by the scans with different monitor values.

Again, we mainly focused on our energy scans at wave vectors **Q** = (1,1,3) since TO phonon is the best measured at this zone center. We repeated our optical energy scans and combined the raw data (per monitor = 200000 counts, ~ 10 minutes) for high statistics. To properly exact the phonon energy position and phonon width at **Q** = (1,1,3), we also performed energy scans at **Q** = (0.3, 0.3, 3) for comparison. As shown in Figs. 2(a)-(b), we only show the raw data of energy scans of optical phonon mode at 1.3 and 4.0 GPa for comparison. Unfortunately, we still cannot determine the phonon peak at low pressure (1.3 GPa) since the weak optical phonon modes might be covered by the strong background from current experimental setup. It is noted that we observed a broad “phonon peak” at **Q** = (1,1,3) in our last high-pressure experiment (Proposal

#7-01-468), however, we still can not exclude the origin of this peak from "empty cell" since the absence of background measurement in the last experiment. By increasing pressure to 4.0 GPa, we then observed a totally different profile with decreased counting intensity for optical phonon energy scans compared to low pressure (Fig. 2(b)), which suggests our variable pressure-dependent background based on our experimental setup. Compared to the PDOS of gasket at 300 K, we might have a phonon mode around 8-10 meV by using 5 points average smooth method. In all, it is rather challenging to conduct high-pressure INS experiments because of the surprising behavior of the background. Moreover, it is also suggested that pressure-dependent INS measurements are feasible for further high pressures experiments (above 4 GPa), since the intensity of background is largely suppressed with increasing pressure. For a comparison, we also measured the transverse acoustic (TA) phonon modes at **q** = (0.4,0.4,0) in the (004) zone. As the raw data shown in Fig. 2(c), we observe the visible TA phonon peaks and softening phonon mode under high pressure. On the basis of Gaussian fit function (as displayed in Fig. 2(d)), we derived the anomalous TA phonon modes under pressure along with almost constant phonon width (not shown in Fig. 2(d)). We further need to more experimental analysis and theoretical calculation for revealing this intriguing phonon property in PbTe. Finally, we also performed the TA phonon dispersion along [HH0] in the (004) zone under 5.15 GPa. As shown in Fig. 3, we compare our high-pressure INS TA phonon dispersion at 5.15 GPa from Thermal-TAS with the ambient pressure results from time of flight (TOF) [4], which again suggests the anomalous phonon softening behavior under pressure. We need to check the ambient-pressure TA phonon dispersion in Thermal-TAS instrument for our sample in case of the presence of energy shift between TAS and TOF instrument.

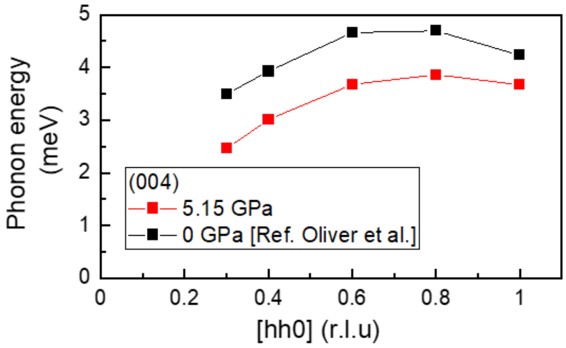

Fig. 3. TA phonon dispersion along [HH0] in the (004) zone center at 5.15 GPa. The ambient-pressure TA phonon dispersion results are taken from reference (4) for comparison.

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