Experimental report

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Title: anharmonic lattice dynamics under pressure in PbTe

Research area: Materials

This proposal is a new proposal

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Samples: PbTe

Instrument	Requested days	Allocated days	From	To
IN8	10	8	24/09/2019	01/10/2019

Abstract:

Understanding the influence of anharmonic interaction on lattice-dynamical properties is the key to engineer/design new high-performance thermoelectric materials requiring a low lattice contribution to the thermal conductivity. Here, we propose to investigate the unusual lattice dynamics in seminal thermoelectric PbTe under high pressure. Quantitative molecular simulations by some of us explain the observed anomalous properties at ambient pressure with strong anharmonic influences. Our measurements as a function of pressures up to 6 GPa and a corresponding analysis based on our model will (1) scrutinize the assignment to anharmonic processes, (2) provide a more complete understanding of the intriguing lattice dynamical properties of PbTe, and (3) pave the path for the designs of new high-performance thermoelectric materials.

Anharmonic lattice dynamics under pressure in PbTe

Thermoelectric materials are interesting for energy applications as they can transform heat into useful electricity, otherwise lost to the environment[1]. The energy transformation efficiency of a thermoelectric material is determined by the figure of merit, $ZT=\sigma S^2T/\kappa$, where σ is electrical conductivity, S Seebeck coefficient, T absolute temperature and κ thermal conductivity. An efficient thermoelectric material must have a low thermal conductivity. Thermal conductivity comprises electrical conductivity (κ_E) and lattice conductivity (κ_L). Understanding phonon anharmonic lattice dynamics is important for both fundamental and practical application reasons to improve thermoelectric efficiency by suppressing the lattice thermal conductivity (κ_L). Low thermal conductivity compound, PbTe, is currently among the most efficient thermoelectric material[2]. Recent inelastic neutron scattering experiments revealed strongly anharmonic behaviors in phonon scattering which were proposed to play an important role in producing the extremely low lattice thermal conductivity[3].

Both Inelastic Neutron Scattering experiments at Laboratoire Leon Brillouin (LLB) and quantitative molecular simulations on PbTe[4] by some of us explain the observed anomalous properties at ambient pressure with strong anharmonic influences. Here, we report on our investigation of the anharmonic lattice dynamics in PbTe at high pressures. We used the thermal triple axis spectrometer IN8 at the Institute Laue Langevin (ILL) to study the phonon properties of TO (Transverse Optical) modes at several different hydrostatic pressures (0, 1.3, 2.55, 3.7 and 5.3 GPa). We didn't measure phonon properties at even higher pressures because there is a phase transition at around 6 GPa for PbTe[5,6]. The measurements were performed using PG002 monochromator and Si111 analyzer, with a constant final energy of 14.7 meV. To improve the momentum resolution and suppress the experimental background, we used collimators 30'-40'-40'-30'.

As shown in Fig. 1a, both incident and scattered beam were constrained by two cones to minimize the background scattering from the pressure cell surrounding the sample. A single crystal PbTe (NaCl crystal structure) was pre-aligned in the 110-001 scattering plane to within 0.5° to avoid the need to tilt the pressure cell. PbTe sample was cut into several pieces of discs with the same diameter of 4 mm and height of 1.2 mm. 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. 1c). 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. 1a and 1b). 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 Fig. 1). We used three samples cut from the same large PbTe single crystal. One is for ambient pressure and the other two are for high pressures. We first did energy scans at ambient pressure (sample #1) and 3.7 GPa (sample #2) to see whether there is a difference between each other. In the experiment, scans can only be done at constant or increasing pressure. Releasing pressure is difficult because of the pressure hysteresis effect. Therefore, we reloaded the cell with sample #3 and restarted increasing the pressures, i.e. 1.3, 2.55 and 5.3 GPa. The crystals were recovered undamaged after the experiments. The equation of state for PbTe is well

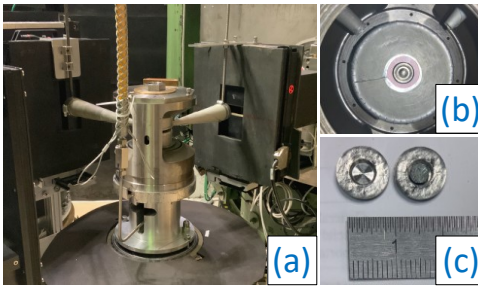

Fig. 1. Inelastic Neutron Scattering experiment setup at IN8, ILL. a, geometry with two cones (incident beam; scattered beam) and two anvils (on/below the sample shell), high pressure oil pumped through steel pipe. **b**, folded encapsulating gaskets, within which is full of alcohol liquid. **c**, PbTe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

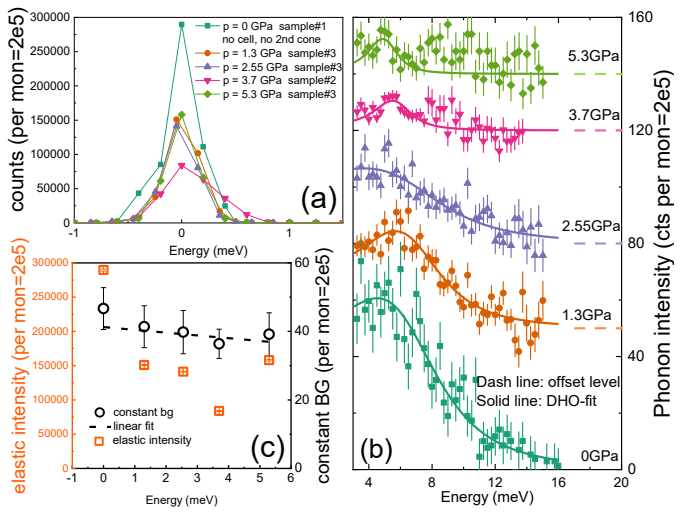

Fig. 2. Profile of the energy scans at the zone center Q = (1,1,3) at different pressures (a, b) and variation of the constant background and elastic intensity (c). Data for different pressures are combined by the scans with different monitor values. For the interesting energy range (i.e. 3-7 meV) at P = 3.7 and 5.3 GPa, the scans were done with a high statistic. Error bars are from the counting statistics. Data in **b** is shown in E > 3meV after subtracting the constant background. The solid lines in **b** are DHO-fit lines. The dash lines in **c** are linear fits to get the fitting constant background.

known[7]. Hence, the pressure values were deduced from the changes in the elastic constants determined from longitudinal scans through the (220) and (004) Bragg reflexes.

We performed most of our energy scans at wave vector **Q** = (1,1,3) since the TO phonon is best measured at this zone center point. The data were subsequently combined (per monitor = 200000 counts, ~ 480 seconds) at the specific **Q**-point and the final raw data sets are shown in Fig. 2. Both elastic intensity and constant background varied at different pressures (see in Figs. 2a and 2c). To estimate the constant background, we averaged the intensity at high energy range from 13 to 16 meV. It slightly decreases with pressure. This is likely due to the two anvils approaching each other with increasing pressure. Both anvils are covered to a large extend by cadmium in order to suppress background scattering (except for the position of the sample gasket). The obtained values were approximated by a line (Fig. 2c), which was used for the background value at the respective pressures in the data analysis. Constant background subtracted data is shown in Fig. 2b. For the elastic intensity at zero energy, they are nearly the same at the fixed setting, i.e. 1.3, 2.55 and 5.3 GPa with sample #3, while changed at different settings, i.e. 0 (sample #1) and 3.7 GPa (sample #2). The elastic signal was approximated by two Gaussian functions centered at zero energy ($FWHM_1$= 0.4 meV, $FWHM_2$= 2.5 meV) and the results show that the elastic signal is close to zero (< 5 counts per monitor) when energy transfer is over 3 meV. Therefore, we analysed only the data for E > 3 meV (Fig. 2b).

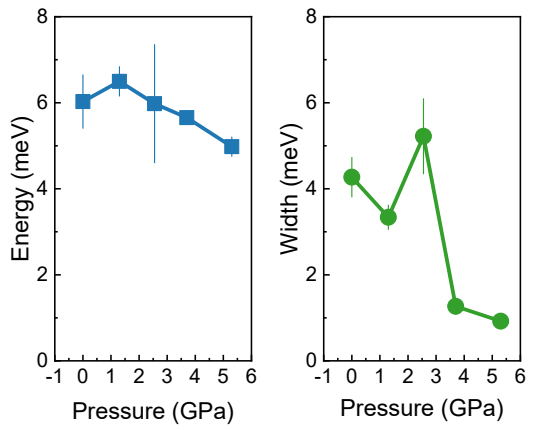

Fig. 3. TO phonon energy position and linewidth at different pressures. Phonon energy position and linewidth are determined by the DHO fit.

The phonon peak at ambient pressure is broad at the zone center **Q** = (1,1,3). The data was approximated with a Damped Harmonic Oscillator (DHO) function convoluted with the experimental resolution. Here, the energy resolution determined from a vanadium scan is 0.9 meV. The lines in Fig. 2b are the DHO fitting results. Overall the phonon peak becomes sharp and its intensity decreases with pressure. A notable exception is the results for P = 2.55 GPa. Here, the phonon softens and broadens compared to the results obtained at P = 1.3 GPa before it sharpens significantly at P ≥ 3.7 GPa. The former observation can be understood in comparison to earlier results for transverse acoustic (TA) phonon under pressure[8] and ultrasound data for similar rocksalt structure SnTe[7] reporting a softening after an initial hardening in the pressure

range $0 \leq P \leq 1.5$ GPa. For P = 3.7 and 5.3 GPa, the broad phonon scattering is replaced by a sharp peak at $E \approx 5$ meV. We invested a day of beam time to obtain high statistics in this energy range at P = 3.7 GPa and the feature is further corroborated by the data taken at 5.3 GPa. Both data sets indicate another broad feature at higher energies. This broad peak may be background scattering from the cell, which was hidden by the broad phonon intensity at lower pressures. But we do not know since we did not do any "empty-cell" measurements.

The determined TO phonon energy position and linewidth from DHO fits are shown in Fig. 3. The phonon energy position is generally similar to our neutron scattering data at ambient pressure and room temperature at LLB. Phonon energy initially hardens and then softens with the pressure, and shows a pronounced nonlinearity in the energy shifts. Overall, the phonon linewidth decreases at high pressures.

References

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