Experimental report

05/09/2022

Proposal: **7-01-557**

Council: 4/2021

Title: Probing phonon anharmonicity of pure and doped InTe thermoelectrics with inelastic neutron scattering

Research area: Materials

This proposal is a resubmission of 7-01-538

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Samples: $In_{0.99}Na_{0.01}Te$
$In_{0.99}Pb_{0.01}Te$
$In_{0.99}Al_{0.01}Te$
InTe

Instrument	Requested days	Allocated days	From	To
PANTHER	5	3	15/05/2021	17/05/2021
			28/06/2021	30/06/2021

Abstract:

To design efficient thermoelectric materials for waste heat harvesting applications it is essential to understand the origin of low lattice thermal conductivity at the atomic level. InTe, showing a chain-like structure with In^{1+} ions loosely bound to a cage-like system, has been considered as a promising thermoelectric material due to its ultralow lattice thermal conductivity. However, the mechanism behind the ultralow thermal conductivity remains largely unclear. Using inelastic neutron scattering technique, this proposal will study phonon density of states of pure and doped InTe powdered samples. By combining with theoretical calculations, we aim to reveal the impact of rattling phonon modes induced by the loosely bound In^{1+} ions on the phonon anharmonicity and lattice thermal conductivity. The results of this project will unravel the underlying microscopic origin of the ultralow lattice thermal conductivity, which will provide insights into the design of efficient thermoelectric materials.

Experimental Report: # 7-01-557

Probing phonon anharmonicity of pure and doped InTe thermoelectrics with inelastic neutron scattering

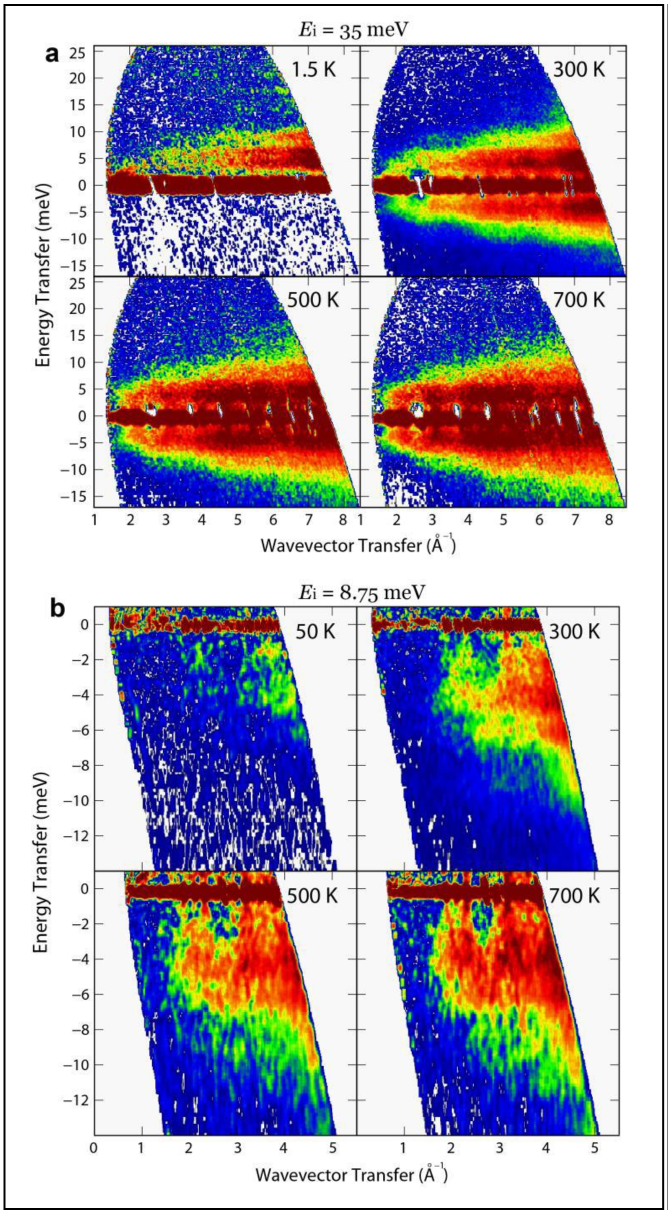
Instrument: thermal time-of-flight spectrometer PANTHER
Incident energy: 8.75 meV and 35 meV
Temperatures: 1.5, 50, 100, 200, 300, 500, 700 K with 8.75 meV, and 1.5, 300, 500, 700 K with 35 meV
Acq. time: 4, 3, 2 h (35 meV) and 6, 4, 2 h (8.75 meV) at 1.5 K, up to 300 K and in furnace, respectively
Sample Environment: standard cryostat (1.5-300 K) and high-T furnace F1 (300-700 K)
Samples: InTe and $In_{0.99}Na_{0.01}Te$ powdered material of mass ~ 6g each
Sample can: Al-foil (cryostat) and Nb-foil (furnace) cylinders of 6 mm diameter.

InTe (Space group: I4/mcm, a = 8.4450(2) and c = 7.1469(1) Å at 300 K) has recently been studied as a promising thermoelectric material due to the ultralow lattice thermal conductivity (~0.7-0.3 W/m/K at 300-700 K) despite its relatively simple crystal structure. InTe, a mixed-valent compound, is generally described by the formula In1+In3+Te2. The In3+ ions are tetrahedrally coordinated to Te2+ ions forming (InTe4/2)- chains along the c axis while the In1+ ions are weakly bound to a cage-like system of eight Te atoms with the distorted square anti-prismatic arrangement. The weakly bound In1+ ion is therefore expected to contribute to the low-frequency vibration modes, which should be particularly important for understanding the low lattice thermal conductivity of InTe. Although there are experimental studies on thermoelectric properties of pure and doped InTe, there is no systematic study so far on revealing the origin of the phonon anharmonicity and ultralow lattice thermal conductivity in InTe thermoelectrics.

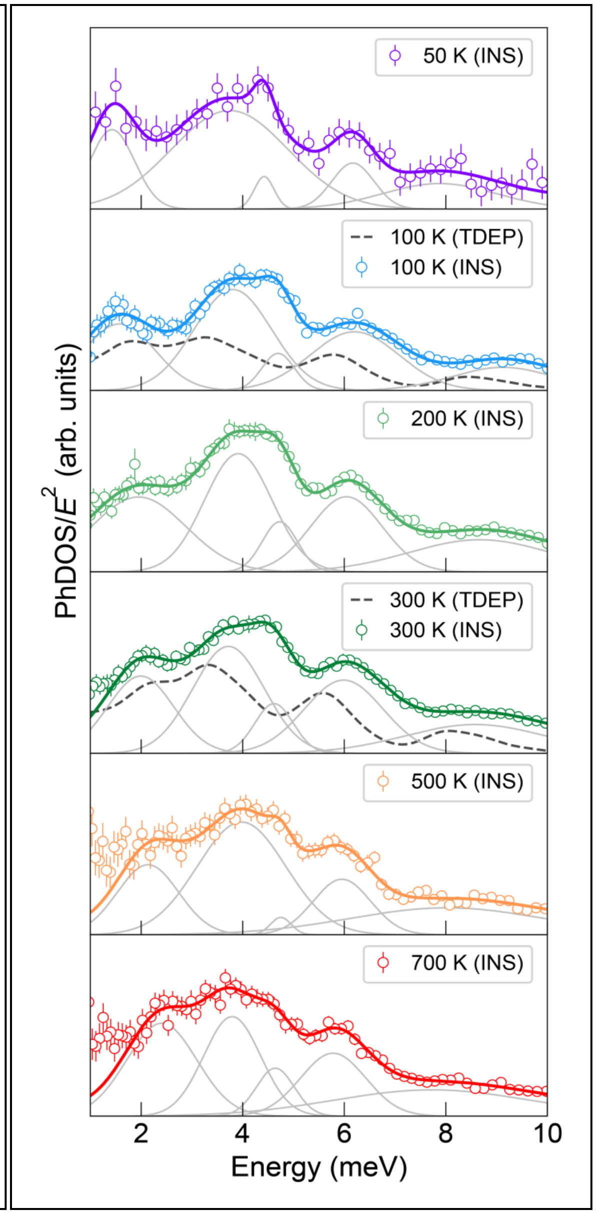
The goal of the experiment was to reveal the microscopic origin of the intrinsically low lattice thermal conductivity of InTe with inelastic neutron scattering experiments and the lattice dynamics and lattice thermal conductivity. According to the inelastic neutron experiments, we intended to achieve a better understanding of the impact of the "rattler"-like vibrational modes induced by the In1+ atoms on the phonon anharmonicity and lattice thermal conductivity. Moreover, we wished to study the temperature and doping effects on the low-lying rattling.

INS measurements were performed on the direct geometry thermal time-of-flight spectrometer PANTHER. Approximately 6 g of powdered sample material from crushed single crystalline pieces was used for the experiment. We applied an incident energy E_i of 35 meV (FWHM = 1.4 meV) to cover the full spectrum at temperatures of 1.5, 300, 500, and 700 K and a smaller E_i of 8.75 meV (FWHM = 0.3 meV) to probe the low-energy phonon modes with a higher resolution at temperatures of 1.5, 50, 100, 200, 300, 500, and 700 K. A cryostat was utilized for measurements at temperatures up to 300 K. Above 300 K measurements were carried out in a high vacuum furnace. Auxiliary data were recorded from sample cans and vanadium standard for calibration of the detectors. Data were corrected for background signals, instrument effects such as the energy dependence of the helium counter efficiencies and the self-attenuation and absorption.

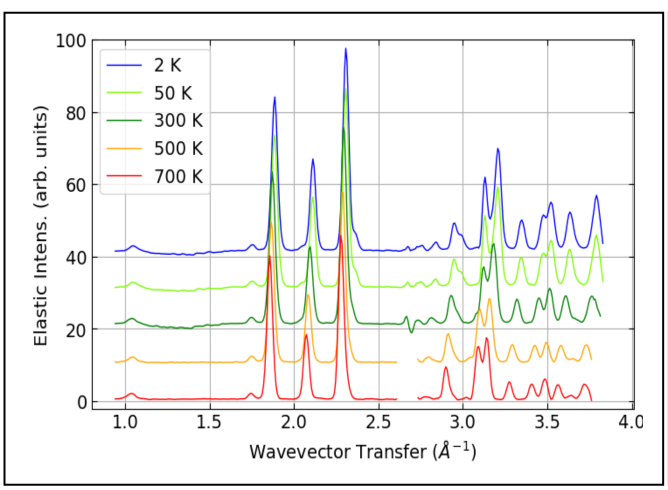
Figures: (Top left) Selected S(Q,E) contrast maps of InTe recorded with the two different setups at the indicated T. (**Top right**) Temperature dependent GDOS/E^2 results on InTe from Ei = 8.75 meV data exploited for fitting of the low energy modes and tracing of the phonon renormalization upon heating. (**Bottom left**) Elastic intensities of InTe recorded with Ei = 8.75 meV highlighting the high quality of the sample material. Voids in the data are positions of Al and Nb Bragg reflections from the sample environments. (**Bottom right**) GDOS of the two compounds at 1.5 and 300 K recorded with Ei = 35 meV.



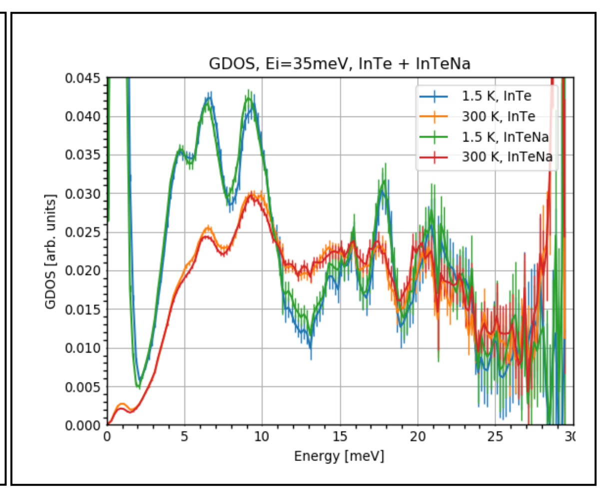
Ei = 35 meV
a
1.5 K
300 K
500 K
700 K
Energy Transfer (meV)
Wavevector Transfer (Å^{-1})
Ei = 8.75 meV
b
50 K
300 K
500 K
700 K
Energy Transfer (meV)
Wavevector Transfer (Å^{-1})



50 K (INS)
100 K (TDEP)
100 K (INS)
200 K (INS)
300 K (TDEP)
300 K (INS)
500 K (INS)
700 K (INS)
PhDOS/E^2 (arb. units)
Energy (meV)



2 K
50 K
300 K
500 K
700 K
Elastic Intens. (arb. units)
Wavevector Transfer ($Å^{-1}$)



GDOS, Ei=35meV, InTe + InTeNa
1.5 K, InTe
300 K, InTe
1.5 K, InTeNa
300 K, InTeNa
GDOS [arb. units]
Energy [meV]