ESRF	**Experiment title:** Phonon Density of States in Tellurium at High Pressures Measured by IXS	**Experiment number**: HS3576
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Shifts: 18	**Local contact(s)**: A. Bosak	*Received at ESRF:*

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Report:

Tellurium belongs to a group of elements that adopt an incommensurately modulated crystal structure at high pressure. The phase Te-III, stable in the pressure range of 8–29 GPa, has a body-centred monoclinic (bcm) structure with an incommensurate transverse modulation, where the modulation vector is parallel to the crystal *b*-axis (Fig. 1). The same structure type was also observed in the chalcogens Se and S. Recent calculations have suggested that these incommensurate phases may arise through Fermi-surface nesting via a Kohn anomaly or charge density wave [1]. In our previous experiment HS3200 we have measured phonon dispersion curves of Te-III with inelastic x-ray scattering (IXS) from a single crystal at 8.5 GPa, and have observed a pronounced phonon anomaly at wavevectors related to the incommensurate modulation vector. The accompanying first-principles calculations reproduced the anomaly, indicated a lattice dynamical instability of the unmodulated bcm parent structure and revealed surprisingly effective Fermi-surface nesting (for a simple three-dimensional metal) as the origin of the dynamical instability [2].

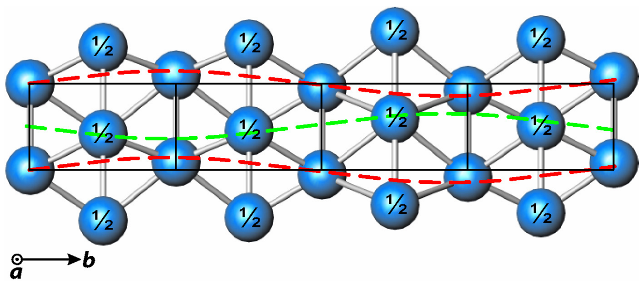

Figure 1: The incommensurately modulated crystal structure of Te-III at 8 GPa as viewed down the *a*-axis. The modulation wave (0*q*0) is shown by the dashed lines.

Obtaining a single crystal of Te-III was a major obstacle and required the screening and pressurising of many Te crystals as they usually break apart at the structural phase transitions. Single-crystal techniques were therefore not a viable option to measure the pressure dependence of the phonon spectrum within the Te-III phase and across the phase boundary at ~29 GPa into the Te-V phase (with body-centred cubic (bcc) structure). In the experiment HS3576 we therefore explored the possibility of measuring the phonon density of states (DOS) from a powder sample in a diamond anvil high-pressure cell. The method of measuring the phonon DOS with IXS has been pioneered only recently by Bosak and Krisch of ID28 and its potential demonstrated for several materials at ambient conditions [3]. It was unclear, however, whether the elastic and inelastic scattering from ~1.5-mm high diamonds on either side of a ~30-µm-thick sample in a diamond anvil pressure cell (DAC) would hamper the IXS measurements on the sample.

The present inelastic x-ray scattering experiment was performed on beamline ID28 using the Si (11,11,11) configuration, i.e., with a photon energy of 21 keV and an energy resolution of 1.5 meV. Taking advantage

of the bank of nine detectors at slightly different scattering angles, up to 18 IXS spectra covering a range of momentum transfers could be collected with only two data collections per pressure point. Most of these spectra were used for the extraction of the phonon DOS using the procedure described in [3], but a few of them had usually to be excluded because their inelastic signal was hidden by strong elastic scattering from diffraction lines.

The Te powder samples were pressurised in Merrill-Bassett-type diamond anvil cells with Boehler-Almax-type seats and anvils that offer large scattering angles without background scattering from the anvil seats. Previous structural studies indicated that Te remains relatively soft in the pressure range of interest. Even if loaded without a pressure-transmitting medium, there was usually little broadening of the diffraction lines with increasing pressure. The samples were therefore pressurised without a pressure transmitting medium for the IXS study so as to avoid any possible contamination of the IXS spectra due to scattering from the pressure medium.

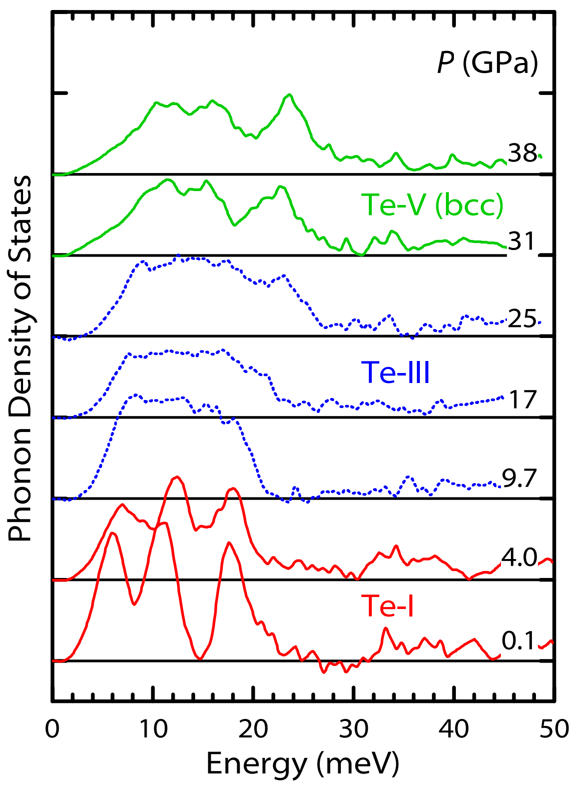

Figure 2: Phonon density of states of three phases of Te under pressure up to 38 GPa, measured by IXS.

The experiment was very successful, and Fig. 2 shows the measured evolution of the phonon DOS of Te with pressure across three phases — the ambient and low-pressure phase Te-I with trigonal chain structure, the incommensurately modulated Te-III and the bcc phase Te-V — up to 38 GPa. The phonon DOS is clearly qualitatively different for the three phases. Most notable is the lack of any fine structure in the phonon DOS of the incommensurate phase Te-III. The origin of this will be analysed on the basis of complementing first-principles lattice dynamical calculations. Possible effects of anharmonicity and finite temperatures are not easily taken into account in DFT-based calculations, but the comparison of the measured and calculated phonon DOS will allow us to assess the accuracy of these calculations. A second interesting observation is that the low-energy part of the measured phonon DOS of the bcc phase, in particular in the 31-GPa spectrum, deviates from the usual parabolic behaviour. This deviation confirms the existence of low-energy phonon anomalies as predicted theoretically by Mauri *et al.* [4] and which are reproduced in our own calculations.

The experimental results alone provide an overall picture of the changes of the lattice dynamics in Te with pressure and allow us to identify phonon anomalies such as in bcc-Te at 31 GPa. In addition to this, they are invaluable in assessing the accuracy of the accompanying phonon calculations. The incommensurate nature of the Te-III phase and the possible effects of anharmonicity and finite temperature render *ab initio* phonon calculations a significant challenge, even with state-of-the-art computational methods. Further lattice dynamical calculations of Te-I and Te-III are currently in progress and will be used to aid the interpretation of the measured phonon DOS and its pressure dependence. The overall aim of this study is to understand which of the observed phase transitions are driven by lattice dynamical instabilities. These results are expected to be directly transferable to the lower-*Z* chalcogens selenium and sulfur that adopt the same incommensurately-modulated structure as well as the bcc structure at higher pressures. Finally, this work has demonstrated the potential of using IXS to measure the vibrational density of states of sufficiently strong-scattering elements and compounds under extreme conditions well into the megabar pressure range.

References

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