ANOMALOUS PRESSURE DEPENDENCE OF ACOUSTIC PHONONS OF $AgGaSe_2$ INVESTIGATED BY INELASTIC NEUTRON SCATTERING TO 4.3 GPa

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Silver gallium diselenide $AgGaSe_2$ belongs to the semiconductor family A^{I}-B^{III}-X_2^{VI} (where A = Cu, Ag, B = Al, Ga, In, and X = S, Se, Te) that adopts the tetragonal chalcopyrite structure. X-ray diffraction studies [1] have shown that the chalcopyrite structure undergoes a quasi second-order phase transition at ~2.6 GPa to an α-phase which is stable up to ~ 6 GPa, where a first-order transition to a orthorhombic phase occurs. The structures of the α phase is not yet clearly identified, but single crystal x-ray work [2,3] on $AgGaS_2$ indicates that the α-phase is a monoclinic distortion of the chalcopyrite structure with space group symmetry Cc, and the same appears to be the case for $AgGaSe_2$ [4]. We have investigated the frequency variations of the TA phonon and low-energy optical phonon modes across this phase transition by inelastic neutron scattering to 4.3 GPa using the Paris-Edinburgh cell, at the 1T triple-axis spectrometer of the LLB [4,5]. The results reveal an exceptionally large pressure-induced phonon softening which suggest that the structural phase transition at 2.6 GPa is an instability due to a soft acoustic phonon associated with the elastic coefficient C_{44}.

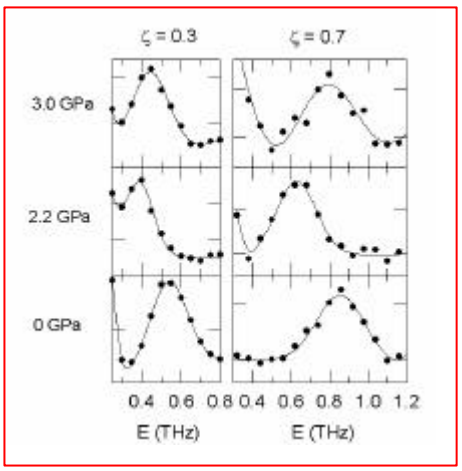

Figure 1. Constant-Q scans of the transverse acoustic phonons along the [001] direction in $AgGaSe_2$ at different pressures.

Figure 1 shows typical scans at constant reduced wave vectors (00ξ) with ξ=0.3 and ξ=0.7 across the TA[001] branch for different pressures: P = 0, 2.2 (in the chalcopyrite phase) and P=3.0 GPa (in the α phase). A strong shift to lower frequencies is observed for the TA frequencies in the chalcopyrite phase. Above ~ 2.6 GPa, however, the phonon frequencies show in general a normal behaviour with a positive pressure coefficient. Figure 2 shows the corresponding frequency variations. The softening is strong at the Γ-point and for small wave-vectors (ξ=0.3), with Grüneisen parameters as low as -10. The shifts are less pronounced for intermediate wave-vectors (ξ=0.4 to 0.7) and become again important at the boundary of the Brillouin zone.

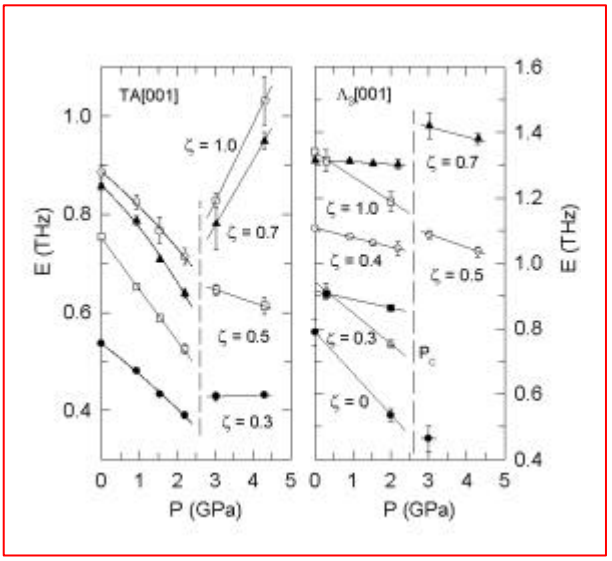

Figure 2. Frequency variations of the TA phonon (left) and the optical phonon Λ_3 (right) for different q-values along the [001] direction as a function of pressure

In Figure 3 we show the variation of the elastic coefficient C_{44} which is associated to the slope of the investigated TA[001] and TA[100] branches at Γ. The value of C_{44} decreases by ~ 50% from 24.6

GPa at atmospheric pressure to 12.8 GPa at 2.2 GPa. These results have been confirmed recently by ultrasonic measurements to 0.8 GPa, which are also shown in Fig. 3. Extrapolation of these data shows indeed that C_{44} attains very low values in the vicinity of 3 GPa.

The behaviour of TA phonons under pressure discovered here is exceptional in several aspects: the Grüneisen parameters are larger than in *any other* tetrahedral semiconductor investigated so far, the mode softening seems to be directly related to the symmetry of the high pressure phase, and finally, $AgGaSe_2$ is the first and only example of a semiconductor where the phonon dispersion could be studied in a high-pressure phase.

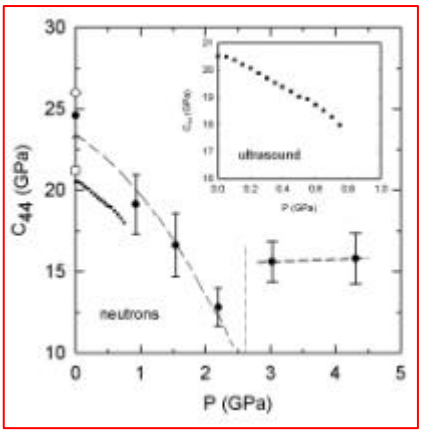

Figure 3. Pressure dependence of elastic coefficient C_{44} determined from the neutron data (large dots) and by ultrasonic measurements to 0.8 GPa. The square and the diamond correspond to ambient pressure results from measurements and ab initio calculations, respectively.

References

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