Resonant and non-resonant Raman scattering in InSe and GaSe

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Two-dimensional (2D) van der Waals (vdW) crystals have recently attracted considerable attention due to their unique electronic band structure and functionalities. Among these crystals, the metal monochalcogenide III-VI compounds, InSe and GaSe, have emerged as promising 2D semiconductors due to the strong dependence of their band gap energy on the layer thickness [1].

Here, we report on non-resonant and resonant Raman scattering in InSe and GaSe crystals. The experiments are performed at different excitation wavelengths using He-Ne (λ=632.8 nm) and Ar^+ (λ=514.5 nm) lasers over a wide temperature range (5 - 350 K).

The measured Raman spectra show up to 7 peaks in both materials, which are due to first order Raman scattering processes. We attribute the 6 high-energy modes to intralayer vibrations and the low-energy mode to a shear mode of rigid interlayer vibration. The intensity of these modes is strongly affected by both the excitation energy and temperature.

In particular, we found that the resonant scattering conditions achieved in InSe and GaSe at room temperature using λ=514.5 nm and 632.8 nm can be strongly modified by varying the sample's temperature. The figure shows the temperature dependence of the intensity for the A_1-mode. Surprisingly, the measured dependences are very similar for both materials, despite their optical band gaps are different (~1.3 eV for InSe and ~2 eV for GaSe at 300 K). Firstly, the intensity grows slowly and increases by up to 2 times with increasing temperature from 5 K to 270 K. This is followed by a steep decrease for a further increase of temperature up to 350 K.

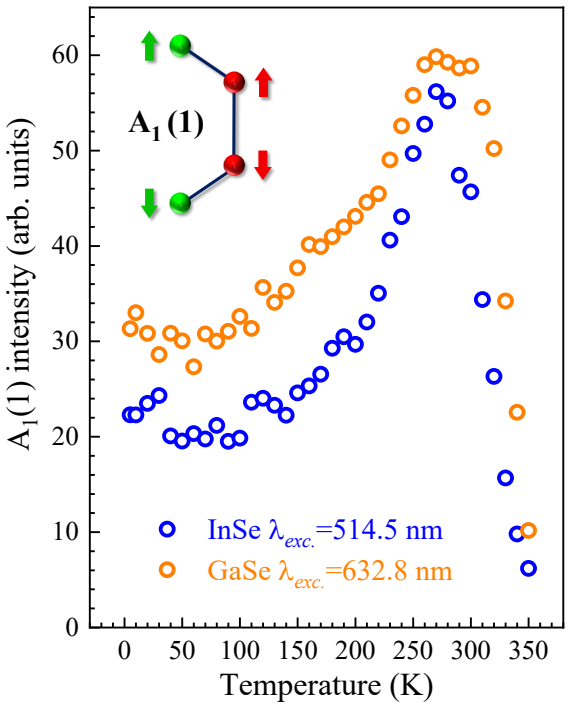

Figure Temperature dependence of the $A_1(1)$ intensity in InSe and GaSe.

These effects can be explained in terms of a temperature driven crossover from non-resonant to resonant Raman scattering. For InSe, the Raman resonance condition involves the excitation of a high-energy excitonic resonance at *E'*~2.4 eV. For GaSe, however, it involves the exciton band-edge resonance at *E*~2 eV. In both cases, the Raman resonance condition is reached when the energy difference between the laser excitation energy and the excitonic resonances is equal to the phonon energy, *e.g.*, the A_1 mode, which is known as out-going resonance conditions.

Our results demonstrate that temperature can be used both to study exciton-phonon interaction as well as the energy of high-energy excitonic transitions.

[1] G. W. Mudd, *et al.*, Sci. Rep. **6**, 39619 (2016), D. J. Terry, *et al.*, 2D Mater. **5**, 041009 (2018).