Structural and optical characterization of transition metal dichalcogenide polymorphs

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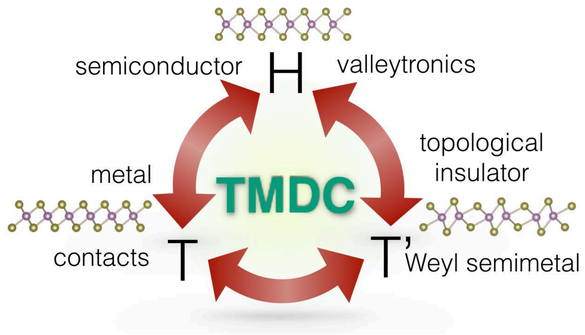
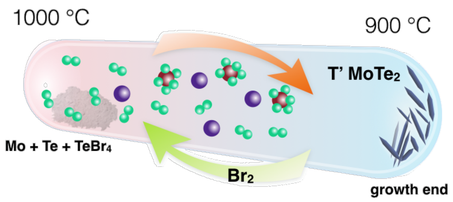
Introduction

Polymorphism of transition metal dichalcogenide (TMDC) has recently attracted great attention due to its novel physical properties. Polarization and crystal-orientation resolved micro-Raman spectroscopy provides an insightful and noninvasive tool to study the TMDC polytypes.

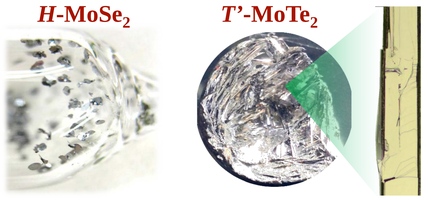


For *H*-TMDCs, we show that the scattered photons, even in monolayer *H*-TMDC, can have both helicity in `one' valley. For *T'*-TMDC, we report on the emergence of two low-wavenumber shear Raman bands in *T'*-$MoTe_2$ due to a phase transition from the monoclinic to the orthorhombic lattice, arising from inversion symmetry breaking.

Sample preparation

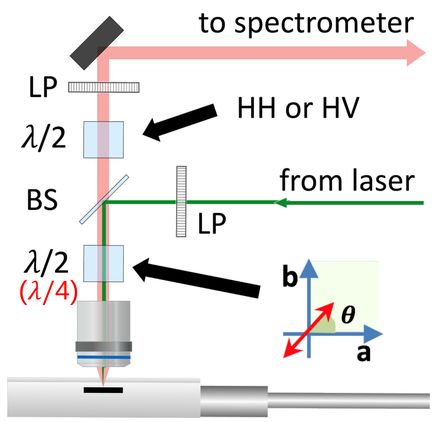


Schematic of CVT growth of *T'*-$MoTe_2$



Pictures of bulk *H*-$MoSe_2$ and *T'*-$MoTe_2$.

Experimental setup



Experimental setup of polarization and crystal orientation resolved Raman spectroscopy.

Angle-dependent Raman cross section

The polarization and crystal orientation dependent Raman intensity can be calculated with the effective Raman tensor. The following is an example showing the calculation for *m*-mode and *z*-mode in *T'*-$MoTe_2$.

$$I = A| < \epsilon_i|R^T \cdot \Re \cdot R|\epsilon_o > |^2$$

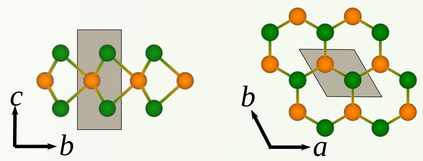
$$\mathcal{R}(A_1) = \begin{pmatrix} d & 0 & 0 \\ 0 & e & 0 \\ 0 & 0 & f \end{pmatrix}, \mathcal{R}(A_2) = \begin{pmatrix} 0 & g & 0 \\ g & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$

$$I^m_{HH}(\theta) = \left|d\cos^2\theta + e\sin^2\theta\right|^2, \quad I^z_{HH}(\theta) = |g|^2\sin^2(2\theta).$$

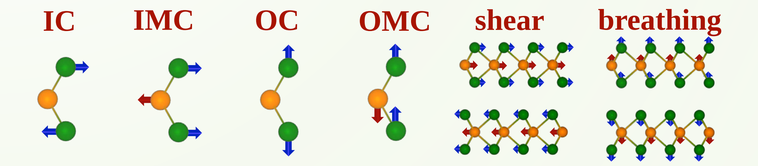
$$I^m_{HV}(\theta) = \left|\frac{d-e}{2}\right|^2 \sin^2(2\theta), \quad I^z_{HV}(\theta) = |g|^2\cos^2(2\theta).$$

H-TMDC

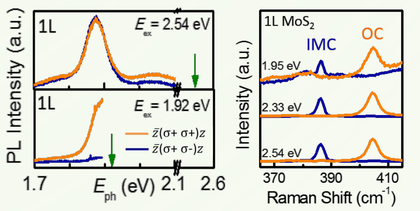
- M: transition metal
- X: chalcogen

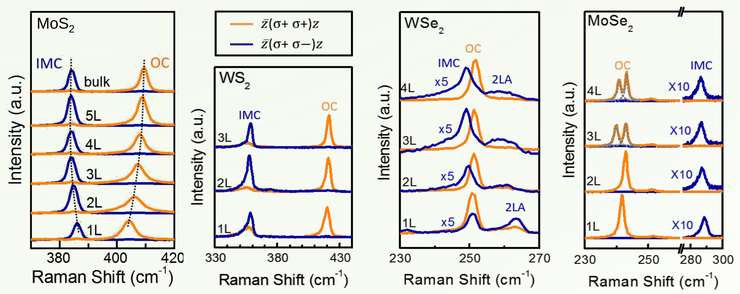


H-TMDCs have a graphite-like structure with each graphene sheet replaced with an MX_2 triatomic layer. The zone center phonons can be classified into 6 types: 4 intralayer and 2 interlayer modes.

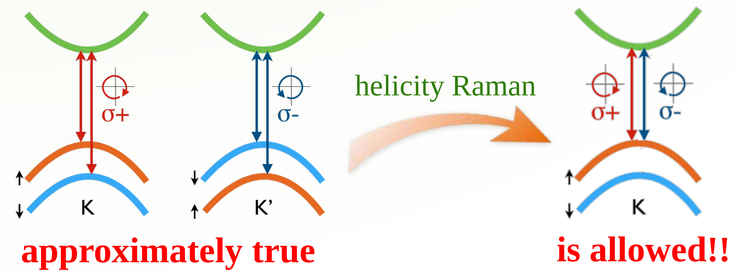


Distinct from helicity PL measurement which follows valley-photon selection rule, the helicity of Raman scattered light is sensitive to **phonon symmetry** but insensitive to **photon energy**, **number of layer** and **types of *H*-TMDC**.





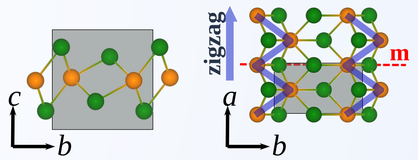
The selection rule of helicity of Raman is explained with Raman tensors calculation. Our results further show that the photon with opposite helicity can be emitted from the **SAME** valley, which indicates the valley-photon selection rule is approximately true.



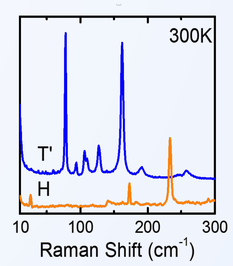
approximately true **is allowed!!**

T'-TMDC

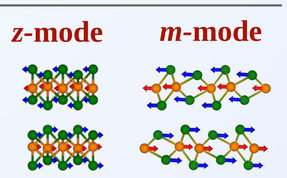
- M: transition metal
- X: chalcogen



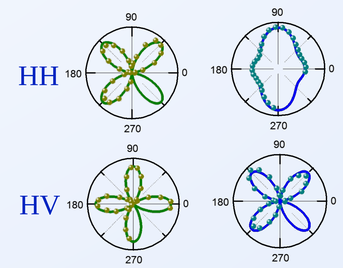
Due to strong interactions between transition metal atoms, *T'*-TMDCs form zigzag TM atomic chains (blue lines above) and exhibit distinct properties from *H*-TMDCs. The zone center phonons in *T'*-TMDCs can be classified into two categories: *zigzag* modes*(z)*, vibrating along *zigzag* chains; and mirror-modes*(m)*, vibrating in the mirror planes. (red dash line above)



For bulk *T'*-$MoTe_2$, there are totally 36 zone-center phonons, including 24 *m*-mode and 12 *z*-modes. *Z*-modes and m-modes have different symmetry, and show distinct angular dependence.



For HH configuration, *z*-modes show 4-fold symmetry; *m*-modes exhibit 2-fold symmetry. For HV configuration, both z-mode and *m*-modes display 4-fold symmetry but with their intensity maximum shifted by 45 degree.



Four new Raman modes of *T'*-$MoTe_2$ are observed when cooled down. The phase transition from T'_{mo} to T'_{or} involves inversion-symmetry-breaking which is key to the existence of Weyl fermions.