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Observation of an ideal excitonic insulator in bulk MoS_2 at high pressure

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The scope of the first experiment carried out in February 2022 was to test a single crystal of MoS_2 at different pressures at room temperature, in order to check the sample quality, as well as to compare the measured phonon branches with the ab-initio theoretical calculations, performed in the absence of excitonic effects. Excitons are expected to soften (and interact with phonons) at lower temperature, driving the transition to the excitonic insulator.

Experimental details

The single crystal of MoS_2 was cut by laser ablation, inserted in a diamond anvil cell (see Fig. 1) with the c-axis perpendicular to anvil's cullets, and filled with helium gas as transmitting medium. Ruby fluorescence method was used to monitor the pressure during the experiment. We have undertaken inelastic X-ray scattering at ID28 main station using an energy resolution of ΔE=3 meV with "Si(999) and the KB focusing setup. The anvil cell was inserted in a rotation stage, in order to have more degree of freedom to investigate a large region of the reciprocal space.

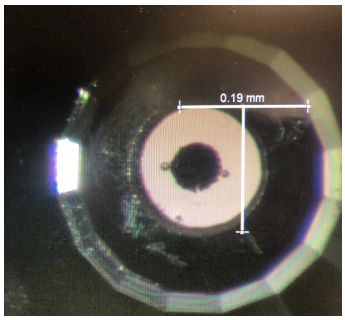

Fig.1: MoS_2 single crystal mounted inside the diamond anvil cell.

Different pressures were applied: 0.42 GPa, 11.47 GPa, 20.88 GPa and 32.83 GPa. The choice of the intermediate pressures was motivated by the investigation of the coexistence of $2H_c$ and $2H_a$ phases, observed by diffraction techniques.
Data were collected along all main crystallographic directions available in the experimental geometry, with all 9 analyzers used to compare with theoretical calculations from first principles.
Importantly, the halves of the diamond anvil cells were not pre-aligned, hence some reciprocal lattice directions were affected by the presence of diamond Bragg tails, especially at high pressure. Therefore, in the next planned experiment at low temperature we will pre-orient the two diamond halves and then check the orientation of the crystal by means of elastic diffraction.

Computational methods

The experimental IXS spectra have been compared with the dynamical structure factor $S(\mathbf{Q},E)$, computed using the theoretical treatment proposed in Refs. [1,2]. In practical calculations, we have approximated the Dirac delta with a Lorentzian function characterized by a full half width maximum of 3.0 meV, to mimic the finite experimental resolution. The atomic form factors for Molybdenum and Sulphur have been modeled using the parametrization provided by the International Tables for Crystallography.
Electronic and vibrational properties have been evaluated at the DFT level, as implemented in the Quantum Espresso package [3], using PBE [4] approximation for the exchange correlation potential together with a plane wave basis set, while the electron–ion interaction has been modeled through norm-conserving pseudopotentials produced with the code ONCVPSP [5]. In ground state calculations, kinetic energy cut-off for wavefunctions has been fixed to 90 Ry and the Brillouin zone has been sampled using a 16 x 16 x 4 Monkhorst-Pack grid. The atomic positions and unit cell parameters under external pressure have been computed by relaxing the crystal up to when forces acting on atoms were smaller than 2.5 X 10^{-4} eV/A0. Following the results of Ref. [6], we have included the effect of Van der Waals interaction between layers (through Grimme-D3 parametrization [7]) only at small pressure values, below 5.0 GPa. Vibrational properties have been evaluated within Density Functional Perturbation Theory (DFPT), starting from ground state charge density: dynamical matrices have been explicitly computed on a 8 x 8 x 4 grid and then evaluated ondenser grids by Fourier interpolation.

Data analysis

IXS spectra were collected at different pressures at room temperature. A complete set of scans was collected along the Γ-A, Γ-K, K-M and Γ-M directions, with the phonon intensities measured by all the 9 analysers that are placed in the horizontal scattering plane.

Figure 2 shows the phonon spectra collected at different pressures along selected reciprocal lattice directions. The experimental data are compared with ab-initio calculations.

The ab-initio calculations based on the $2H_c$ crystallographic structure show a good agreement with the observed phonon groups from low pressure up to 11.47 GPa , in agreement with previous experimental work [8]. A small hardening (about 1-2 meV) is observed in the measured phonon branches w.r.t these calculations. At 20.88 GPa the two sets of calculations, which are respectively based on the $2H_a$ and $2H_c$ structure, do not match separately the experimental data, which likely points to the coexistence of the two phases. This possible mixing of $2H_a$ and $2H_c$ phases leads to the systematic absence of some phonon groups. The absence / partial observation of some phonon branches might hint to the mixing between in-plane and out-of-plane phonon polarizations, as previously observed also at ambient pressure for some specific phonon frequencies [8]. The interpretation of the observed mixing effect is beyond the scope of our proposal.

At higher pressure (32.88 GPa) phase $2H_a$ becomes stable, as confirmed by the excellent agreement with the ab-initio predictions. The overall theoretical results will be used as a guide line to disentangle the interaction with the excitonic branch, which we expect to become visible at lower temperature.

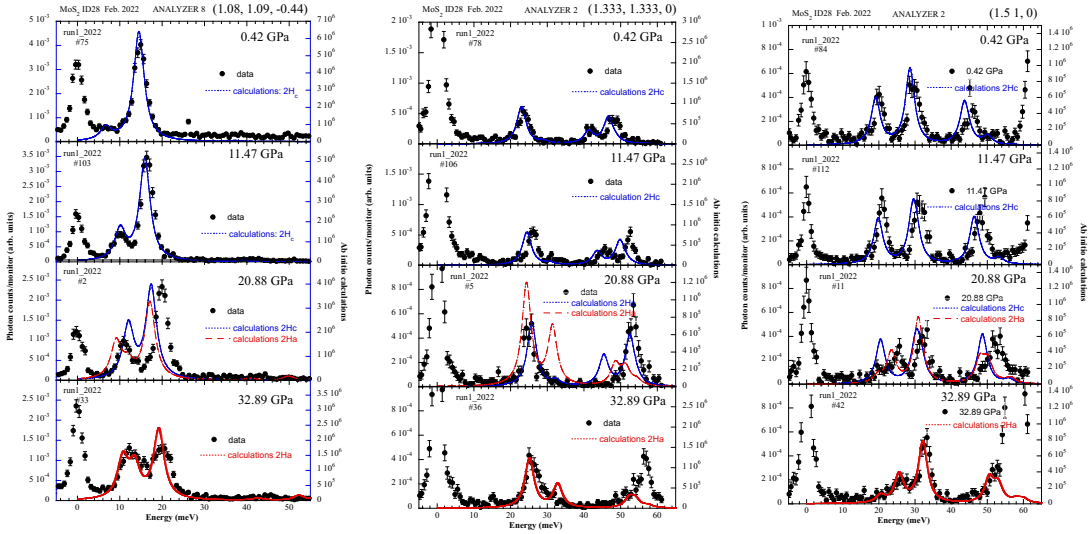

Fig. 2 Comparison between IXS scans and ab-initio calculations for a selected set of reciprocal lattice points **Q** *at different pressures P. Left panels:* **Q** = (1.08, 1.09, -0.44). *Center panels:* **Q** = (1.33, 1.33, 0). *Right panels:* **Q** = (1.5, 1, 0). *From top to bottom panels: P = 0.44, 11.47, 20.88, 32.89 GPa. The blue (red) lines represent the ab-initio calculations for the $2H_c$ ($2H_a$) phase. A spurious peak due to the Bragg tails of diamond anvil is visible at higher energy.*

In conclusion, the reported experimental results show the feasibility of the experiment on MoS_2 from ambient conditions up to 33 GPa, which was our objective. At such high pressure, we expect MoS_2 to develop at low temperature an exciton that interacts with the lowest optic and acoustic phonon branches in the range of 20-30 meV. This will be the target of our next experiment.

References:

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