	Experiment title:	Experiment number:
ESRF	Phonon dispersions in 2D semiconducting transition metal dichalcogenides WS2 and WSe2	HC-4047
Beamline: ID28	**Date of experiment**: from: 22.08.2018 to: 28.08.2018	**Date of report**: 03.05.2020
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Names and affiliations of applicants (* indicates experimentalists):

SOULIOU Sofia-Michaela* (Karlsruhe Institute of Technology, IQMT)
PAPANGELIS Kostantinos* (Aristotle University of Thessaloniki, Faculty of Physics)
PARTHENIOS John* (FORTH Institute of Chemical Engineering Sciences, Patras)
MICHAIL Antonios (FORTH Institute of Chemical Engineering Sciences, Patras)
TORNATZKY Hans* (Technische Universität Berlin, Institut für Festkörperphysik)
MAULTZSCH Janina*(Friedrich-Alexander-Universität Erlangen, Department Physik)
GILLEN Roland (Friedrich-Alexander-Universität Erlangen, Department Physik)

Report:

The purpose of the current beamtime was to determine experimentally the phonon dispersions in WS_2 and WSe_2, two important members of the family of semiconducting transition metal dichalcogenides, which exhibit technologically interesting properties when thinned down to an atomic layer [1]. Our measurements targeted the bulk counterparts of the monolayer systems, which are considered as 2D materials of weakly coupled monolayers.

The experiment was performed at the main inelastic x-ray scattering (IXS) station of the ID28 beamline at the ESRF, using the (9 9 9) reflection of the main backscattering monochromator at 17.794 keV. The x-ray beam was focused using KB mirrors and the final beam spot size on the sample was ~20 x 20 μm^2. The measured sample was a ~25 μm thick flake exfoliated from a WS_2 single crystal piece. The high quality of the crystal was verified prior to the official start of the beamtime by x-ray diffuse scattering measurements obtained at the side station of the ID28 beamline. The sample was glued on a conically shaped glass rod and placed on a standard goniometer head mount. All the measurements were performed at ambient conditions.

The IXS data were collected along the main high symmetry directions of the reciprocal space (space group $P6_3/mmc$, No. 194), i.e. the Γ-M, Γ-K, K-M and Γ-A directions, in longitudinal, transverse in-plane and transverse out-of-plane geometries. Typical IXS spectra recorded in the proximity of the (200) Bragg along the Γ-M direction are shown in Figure 1-a. The small (or even absent) quasielastic line observed in the IXS spectra verifies the high quality of the measured crystal. An overview of the experimentally determined phonon dispersions along the Γ-M direction is given in Figure 1-b (including the three main geometries). In the same figure we plot our results on the theoretical phonon dispersions calculated within the framework of density functional perturbation theory (DFPT). The agreement between the experimental and theoretical dispersion is very good, particularly for the lower energy acoustic phonon branches. Earlier ab initio calculations highlighted that the phonon dispersions in this bulk layered system resemble strongly those of the single-layer system, capturing all the main characteristics [2]. One of the differences that can be identified already at this stage is the presence of out-of-phase (shear and breathing-like) rigid layer modes in the case of the bulk system (blue arrow in Fig.1-b indicates the breathing-like rigid layer mode in the Γ-M direction). Moreover, the calculations capture the splitting of the higher energy optical phonon branches due to the weak interlayer coupling in the bulk system, which was nevertheless too small to be unambiguously observed within the working IXS experimental resolution (3 meV at the used setting).

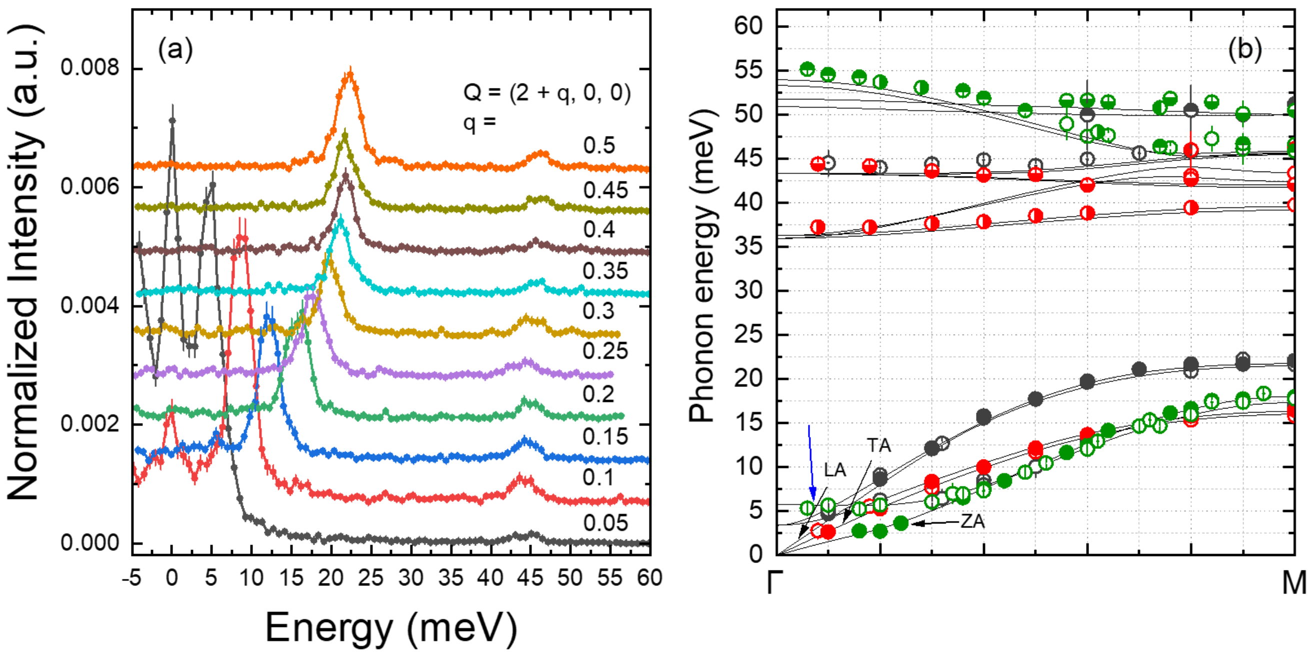

Figure 1: (a) Momentum dependence of the IXS spectra along the Γ-M direction of the reciprocal space. The spectra were taken at ambient conditions close to Γ=(2,0,0). Note that the spectrum recorded at Q = (2.05, 0, 0) has been scaled by a factor of 0.4 and that the rest of the spectra have been vertically shifted for clarity. (b) Experimental and DFPT calculated phonon dispersions along the Γ-M direction. The symbol color code corresponds to measurements taken in mostly longitudinal (grey), transverse-in-plane (red) and transverse-out-of-plane (green) geometries. The longitudinal, transverse-in-plane and transverse-out-of-plane acoustic branches are indicated with the black arrows (labelled LA, TA and ZA respectively). The blue arrow indicates the breathing-like rigid layer mode.

Although our initial plan was to measure both WS_2 and WSe_2 crystals and to make a comparative study of the two, within the time limits of this beamtime we could only complete our measurements on WS_2. This was partially due to the long measuring time required to obtain the dispersions of the high energy phonon brunches (up to 60 meV). Moreover, in order to access the phonon dispersions in all high symmetry directions of the reciprocal space, the sample had to be mounted on two different motor rotation setups. In addition, the synchrotron was operating in 16 Bunch mode at the time of the experiment and approximately one day of beamtime was lost because of a major intervention in the vacuum chamber of one of the ESRF beamlines. Future experiments will hopefully allow to measure the phonon dispersions in WSe_2 and to finalize the comparative study of the lattice dynamics in the two sibling systems.

References:

[1] S. Wu et al., Nature 520, 69 (2015)

[2] A. Molina-Sánchez and L. Wirtz, PRB 84, 155413 (2011)