ESRF	**Experiment title:** Bulk and surface inelastic x-ray scattering investigation of the charge density wave material NbSe2	**Experiment number**: HS 2217
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Report:

2H-$NbSe_2$ is a quasi-two-dimensional material and displays a Peierls distortion resulting in a charge density wave (CDW) phase transition at 33.3 K. This transition has been the subject of previous neutron and X-ray studies and is observed to be of second order within experimental accuracy [1,2,3]. Using inelastic neutron scattering, Moncton *et al.* measured the room temperature bulk phonon dispersion curve for $NbSe_2$. They observed a phonon softening of the Σ_1 mode at the CDW satellite position in Q-space[1]. Ayache *et al.* have observed a complete mode softening at the CDW phase transition in the bulk [2]. 2H-$NbSe_2$ dispersion curve calculations are found in Wakabayashi *et al* [4] for the two dimensional Kohn anomaly and Motizuki *et al.* [5] who report a theoretical study of 2H-$TaSe_2$ and 2H- $NbSe_2$ lattice dynamics and phonon anomalies. Previously bulk inelastic X-ray scattering has been used to study both lattice phonon branches as well as a Kohn anomaly in CDW-systems like $K_{0.3}MoO_3$ [6,7] and $NbSe_3$ [8]. Inelastic X-ray scattering carried out at grazing incidence should provide a unique opportunity to investigate the mode softening at the surface of 2H-$NbSe_2$ and to relate it directly to that of the bulk of the same sample.

These first grazing incidence geometry phonon measurements were performed at the inelastic scattering beamline ID28 at the ESRF. A total flux of $6x10^{10}$ ph/s (at 200mA) is available with an instrumental energy resolution of 5.5 meV in a beam of 80 μm(V) x 250 μm (H). This resolution is provided by the Si 888 backscattering reflection at a photon energy of 15.816 KeV. The single crystal 2H-$NbSe_2$ sample - 1 mm thick, surface area of 4 x 8 mm^2 - was mounted with the surface normal (0,0,1) vertical in a vacuum chamber after cleaving using the sticky tape method. Grazing incidence geometry was achieved by inserting a Pt coated glass mirror before the sample to accurately deflect the primary beam downwards. Surface sensitivity was achieved by combining this deflection with the sample ϕ rotation. An incidence angle and exit angle close to the critical angle of total external reflection (0.18°) was obtained, providing a penetration depth of ~23 Å. The pre-sample slits were adjusted to 60 μm vertically in order to minimise background and edge scattering. The surface alignment was complicated by the beamline layout, originally not designed for grazing incidence geometries. Following an open slit reflectivity to determine the critical angle, the sample was oriented at α_c - 0.027°. This small change of angle was chosen so that we remained below the critical angle, but still benefited

from the enhancement in the transmission function close to α_c. In this orientation the 200 in plane surface reflection was aligned and constant-q scans on the longitudinal acoustic branch propagating along (h, 0, 0) were carried out at room temperature. h was varied over the range 1.95 to 1.6 scanning an energy range of ± 30 meV for (1.95,0,0) and (1.9,0,0) and ± 40 meV for the rest of the data. The data were collected with the standard analyser opening of 20 x 60 mm^2 (H x V) providing a q resolution of about Δq = 0.0216 $Å^{-1}$(Figure 1 a).

We also measured the bulk phonon spectra at room temperature for comparison in order to develop our understanding of the dynamics of this very interesting system Figure 1 (b) and to be more sensitive to eventual changes. For the bulk data a thin layer of the sample (~ 12 μm, transmission 60%) was cleaved onto Scotch tape and measured in transmission geometry(transmission was 60%). Due to poor bulk sample quality and resolution problems no dispersion data could be extracted.

Due to the time required for the experimental alignment in this novel application of IXS and technical problems with the cryostat we did not achieve our additional objective of investigating the temperature dependence of the mode softening in $NbSe_2$

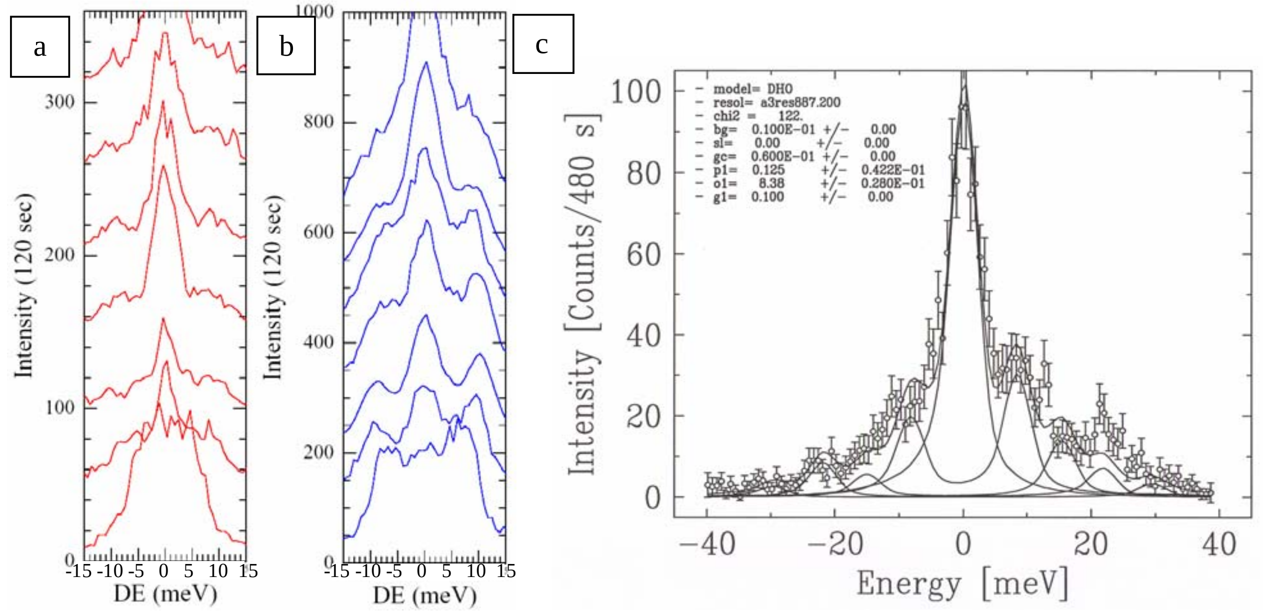

Figure 1 Surface (a) and bulk (b) IXS spectra of 2H-NbSe$_2$, measured on ID28, ESRF at 300 K . Shown is a section of the data collected along the longitudinal acoustical phonon branch in the range 1.9,0,0 to 1.5,0,0 (bulk) and 1.95,0,0 to 1.6,0,0 (surface) from bottom to top. (b) Grazing incidence IXS spectrum at h=1.67 fitted using damped harmonic oscillators.

In conclusion we have successfully obtained the first grazing incidence inelastic X-ray scattering spectra. In this experiment we showed that it is possible to probe surface behaviour of phonons with X-rays. The data have been fitted using a damped harmonic oscillator to describe the energy resolution profile. The fit of the spectrum taken at h=1.67 is shown in Figure 1c. We have observed the Σ_1 modes ω_1 and ω_2 as reported by Ayache *et al.* [2] and in addition optical bands at higher energy as predicted in the theoretical calculations of Motizuki *et al.* [5].

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