ESRF	**Experiment title:** Bulk and surface inelastic x-ray scattering investigation of the charge density wave material $NbSe_2$	**Experiment number**: HS 2605
Beamline: ID28	**Date of experiment**: from: 12 February 2005 to: 24 February 2005	**Date of report**: 24.02.04
Shifts: 30	**Local contact(s)**: Dr. Jorge Serrano	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Bridget M. Murphy*, Martin Müller*, Jochim Stettner* (Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, Leibnizstraße 19, 24098 Kiel, Germany)

Herwig Requardt* (ESRF)

Werner Press (Institut Laue-Langevin, BP 156 - 38042 Grenoble Cedex 9, France.)

Report:

The layered transition metal dichalcogenides exhibit fascinating properties due to their van der Waals bonded layered structure: superconducting behaviour, nonlinear and anisotropic electrical properties, very large dielectric constants, charge density wave (CDW) instabilities and a wealth of dynamical features [1]. $NbSe_2$ is a member of this group of materials. As a result of its layer-like structure $NbSe_2$ displays almost two-dimensional behaviour, exhibiting a CDW and superconductivity [2 3 4]. The single crystal investigated in this work is predominantly of the 2H-polytype.

2H-$NbSe_2$ 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 [5,6,7]. 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[5]. Ayache *et al*. have observed a complete mode softening at the CDW phase transition in the bulk [6]. 2H-$NbSe_2$ dispersion curve calculations are found in Wakabayashi *et al* [8] for the two dimensional Kohn anomaly and Motizuki *et al*. [9] 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 $K_{0.3}MoO_3$ [10,11] and $NbSe_3$ [12]. 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.

This recent experiment(February 2005) was a follow up to our pilot grazing incidence geometry phonon measurements performed at the inelastic scattering beamline ID28 at the ESRF[13,14]. A total flux of $2.70 \cdot 10^{10}$ ph/s (at 200mA) is available with an instrumental energy resolution of 3.0 meV in a beam of 15 μm(V) x .300 μm (H). This resolution is provided by the Si 999 backscattering reflection at a photon energy of 17.794 KeV. The single crystal 2H-$NbSe_2$ sample - 1 mm thick, surface area of 4 x 8 mm^2 - was mounted with the (0001) surface 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 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 (0.154°) was obtained, providing a penetration depth of ~40 Å. The pre-sample slits were adjusted to 15 μm vertically in order to minimise background and edge scattering. Following surface alignment, the sample was oriented at α_c - 0.03° for surface sensitive measurements and α_c + 0.03° for bulk measurements.. These small changes of angle were chosen so that we had surface or bulk sensitivity, but still benefited from the enhancement in the transmission function close to α_c. The (200) in-plane surface reflection was aligned and constant-q scans on the longitudinal acoustic branch propagating along $\langle \xi, 0, 0 \rangle$ were preformed. ξ was varied over the range 1.95 to 1.6 scanning an energy range of -18 to +30 meV. The data were collected with a standard analyser opening of 20 x 60 mm^2 (H x V) providing a q resolution of about Δq = 0.0216 Å^{-1}. In addition we measured dispersion curves at 100 K, 65 K and 40K for ξ values varied between1.86 to 1.55.

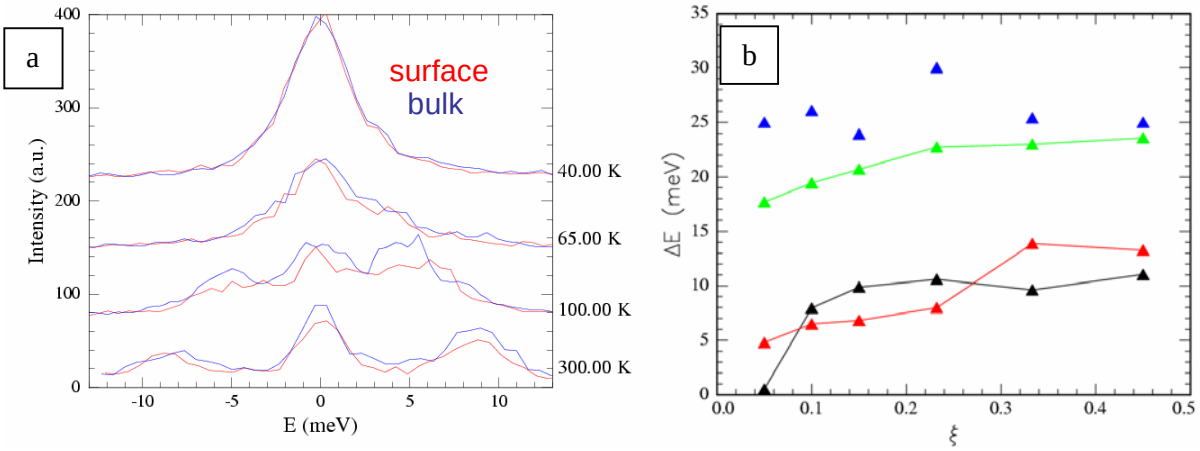

Figure 1(a) Temperature dependent surface and bulk IXS spectra of 2H-$NbSe_2$ at the CDW satellite position ξ=1.67 measured on ID28, ESRF showing a consistent energy offset between surface and bulk.(b) Room temperature surface dispersion curve of $NbSe_2$ showing evidence of phonon softening even at room temperature.

In conclusion we have successfully obtained surface and bulk sensitive data from a single $NbSe_2$ sample using grazing incidence inelastic X-ray scattering. We have observed phonon softening at the surface and in the bulk of $NbSe_2$ .We have observed the Σ_1 modes ω_1 and ω_2 as reported by Ayache *et al.* [6] and in addition optical bands at higher energy as predicted in the theoretical calculations of Motizuki *et al.* [9]. There is evidence that though the behaviour at the surface is similar to that of the bulk there is some evidence of an energy offset at a range of temperatures.

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