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# Investigating surface dynamics with inelastic x-ray scattering

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## Abstract

A brief overview of application of the grazing incidence inelastic x-ray scattering experimental method will be presented. Inelastic x-ray scattering in grazing incidence conditions provides a new tool for selectively studying both surface and bulk lattice dynamics in a single experiment. It is possible to study acoustic and optical surface phonon modes currently with a 3 meV resolution over a wide range of momentum space and make a direct comparison between surface and bulk dispersion. In particular the case of 2H-NbSe<sub>2</sub> will be discussed. For this material a Kohn anomaly has been previously reported. Our data demonstrate that the softening of the Kohn anomaly at the 2H-NbSe<sub>2</sub> surface is significantly greater than that reported for the bulk. This is an indication of a relaxation in the topmost layers of the crystal.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Dynamics at surfaces are, by their very nature, both fascinating and notoriously difficult to access. Apart from the careful preparation required, in addition many surface techniques require ultra high vacuum and detectors that can cope with very low count rates. In spite of these complications there are many well established surface techniques such as: electron loss spectroscopy photoemission, low energy electron diffraction, scanning tunnelling microscopy, helium scattering and x-ray reflectivity. This paper will deal with the recent development of the inelastic x-ray scattering experimental method extended to investigate surface and bulk properties of a material in one experiment. In particular a study of the layered material 2H-NbSe<sub>2</sub> will be discussed. 2H-NbSe<sub>2</sub> is a member of the transition metal dichalcogenide family consisting of a layered hexagonal structure where the Nb atoms are sandwiched between Se atoms and van der Waals forces result in a low coupling constant between layers. Due to this quasi two-dimensional behaviour many interesting properties are observed in this material, ranging from superconductivity to charge density waves (CDW). A CDW transition is a metal to insulator transition occurring due to an electron density modulation with modulation wavelength  $\lambda = \pi/k_f$  [1].

The dynamics of CDW is a topic of critical importance for understanding electron–phonon interaction. Comprehensive reviews are given by Thorne [2] and Grunner [3] among others.

The presence of satellite peaks resulting from the CDW modulation was predicted by Overhauser [4] and observed by electron diffraction in 2H-TaSe<sub>2</sub> [5]. Using neutron scattering it was also possible to observe the superstructure in both bulk 2H-NbSe<sub>2</sub> and TaSe<sub>2</sub>, and since the intensity of the superstructure peak is proportional to the order parameter for the phase transition it was also possible to determine transition temperatures at 33.3 K and 122.3 K, respectively [6]. The experiment showed that 2H-NbSe<sub>2</sub> undergoes an incommensurate CDW transition at 33.3 K and remains incommensurate down to 5 K where the superconducting transition occurs. The 2H-TaSe<sub>2</sub> CDW transition is also incommensurate but is followed by a commensurate transition at 90 K.

Not only was the structure investigated by elastic neutron scattering experiments, but in addition the dynamics of the transition were probed via inelastic neutron scattering. Moncton *et al* observed strong Kohn anomalies at room temperature in the case of both 2H-NbSe<sub>2</sub> and 2H-TaSe<sub>2</sub>. For the two systems they observed  $\Sigma_1$  phonon-like displacements and although they did not measure mode softening directly

in 2H-NbSe<sub>2</sub>, it was measured for 2H-TaSe<sub>2</sub>. Detailed discussions of the Kohn anomaly may be found elsewhere in this volume [7]. In a later neutron scattering experiment Ayache and co-workers [8] investigated the softening of the longitudinal  $\Sigma_1$  phonon mode at the charge density wave satellite reflection in 2H-NbSe<sub>2</sub>. They observed two modes at room temperature, the longitudinal acoustic  $\Sigma_1\omega_2$  mode and the  $\Sigma_1\omega_1$  optical mode. The  $\omega_2$  acoustic mode was found to be at about 25 meV at room temperature softening was observed from about 100 K and appeared to be complete at 32 K within the experimental accuracy, indicating that 2H-NbSe<sub>2</sub> undergoes a second order transition at this temperature. In Raman studies softening of a low energy peak was observed and the electron–phonon coupling constant was determined to be 0.17 [9].

The above studies have concentrated on the bulk structure and dynamics of 2H-NbSe<sub>2</sub> but there have been many successful surface studies. The CDW superstructure at the surface has been observed in real space by scanning tunnelling microscopy [10] where the CDW modulation was clearly observed. The surface dynamics of NbSe<sub>2</sub> have been studied using He scattering [11]. Data collected at 160 K showed signs of softening compared to bulk neutron data collected at room temperature, consistent with a Kohn anomaly. In a grazing incidence x-ray diffraction where it was possible to carry out a direct comparison between the surface and bulk position of the surface CDW satellite peak, the authors reported that the CDW satellite was observed at the same position, on the surface as in the bulk, indicating that there is no relaxation of the in-plane lattice constant for 2H-NbSe<sub>2</sub> at the CDW phase transition [12]. This study indicated that the CDW transition occurred at a higher temperature at the surface than in the bulk. In fact it was this study that reopened the study of the dynamics at the NbSe<sub>2</sub> surface.

## 2. Grazing incidence inelastic x-ray scattering experiment (GI-IXS)

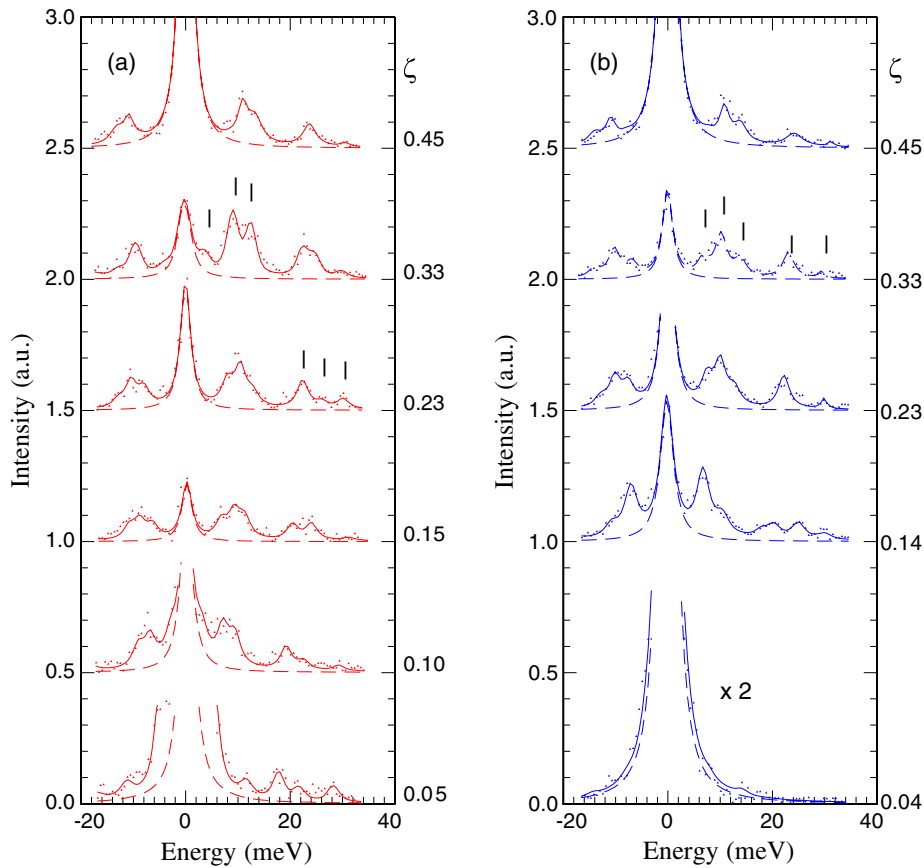
In the following an inelastic x-ray scattering experiment carried out under grazing incidence conditions is presented giving access to the dynamics of the system both at the surface and in the bulk [13]. First let us discuss the inelastic scattering technique. In the 1950s pioneering work of Walker [14] exploited diffuse scattering to obtain a dispersion curve for aluminium and so determined force constants. The technique of inelastic x-ray scattering (IXS) was first shown to be feasible in the late 1980s [15]. Hofmann has since shown that the method may also be performed on a laboratory source [16]. IXS is complementary to the long established inelastic neutron scattering (INS) techniques. Inelastic x-ray scattering has been proven to be particularly useful for cases where samples themselves are too small or the sample environment is unsuitable for neutron work. IXS can also overcome the kinematic limitations of INS when studying disordered systems at low momentum transfers or with a high speed of sound [17]. A comprehensive review may be found in [18]. Inelastic x-ray scattering directly measures the dynamical structure factor  $S(Q, E)$  with momentum transfer

$Q$  energy  $E$  and dynamic structure factor  $S$ . The study of phonon excitations in condensed matter, which have energies in the meV region, requires a relative energy resolution of at least  $\Delta E/E \approx 10^{-7}$  for x-rays. This is very demanding and requires a special set up. The high energy resolution may be obtained using a backscattering monochromator and analyser crystals also in backscattering condition. Typically, high-order  $hhh$  reflections of a Si(111) monochromator are used.

If grazing angles of incidence and exit are chosen, it is possible to keep the momentum transfer almost parallel to the surface and thus we can investigate the in-plane dynamics as we would structure in a classical grazing incidence x-ray diffraction experiment. If these angles are kept below or in the region of the angle of total external reflection we can also limit the penetration depth of the x-rays in the sample and so obtain dynamical information on the first few atomic layers. Since for x-rays the refractive index  $n < 1$ , Bragg scattering occurs under total external diffraction conditions if the angle of incidence of the incoming x-ray beam is held beneath the critical angle  $\alpha_c$  [19]. At this energy  $\alpha_c$  for 2H-NbSe<sub>2</sub> is 0.154°. By varying the angle of incidence above and below the critical angle of total external reflection the surface and bulk dynamics may be selectively investigated. Therefore, it is possible to compare surface and bulk dynamics in a single experiment.

The experiment discussed here was carried out on beam line ID28 at the European synchrotron radiation facility (ESRF). The Si(999) reflection was chosen for the backscattering monochromator delivering an incident beam of 17.798 keV and the Si analyser crystals were also set to the same reflection so that a resolution of 3 meV was obtained. The beamline is capable of delivering a higher resolution but this would have reduced the flux too much for this experiment. Data were collected with the standard analyser opening of  $20 \times 60 \text{ mm}^2$  (horizontal  $\times$  vertical). The beamline delivers an incident beam of  $250 \mu\text{m} \times 60 \mu\text{m}$  which was reduced to  $12 \mu\text{m}$  vertically to match the footprint to the sample size. The grazing incidence geometry was achieved by introducing a Pt mirror to act as a beam deflector. The sample was mounted on the beamline 4 circle diffractometer and the combination of deflector and sample tilt allowed the measurements to be carried out under grazing incident conditions. The angle of incidence was set equal to the exit angle and varied about  $\alpha_c$ .

The iodine vapour transport grown 2H-NbSe<sub>2</sub> sample [20] had dimensions of  $8 \times 4 \times 1 \text{ mm}^3$ . The sample was of extremely high quality, optically flat over its surface and with a low mosaic spread of  $0.0045 \pm 0.0001^\circ$  FWHM for the (002) reflection. The sample was introduced to vacuum after cleaving with adhesive tape in air. The (00 $l$ ) surface was horizontal to facilitate scattering along this plane in the horizontal detector plane. The sample was aligned at the surface (200) reflection. In order to benefit from the enhancement in transmission close to the critical angle while varying penetration depth incidence and exit angles of  $\alpha_c \pm 0.03^\circ$  were chosen. At incident angles below the critical the penetration depth was about 4 nm one should bear in mind that the decay is exponential so that the contribution for the top layers is far greater than from the deeper ones. Above the



**Figure 1.** NbSe<sub>2</sub> GI-IXS spectrum collected in surface sensitive setting (a) and bulk sensitive (b). The symbols represent the collected data. The solid line is the fit result and the dashed line show the contribution of the elastic component. The  $\xi$  positions are given on the right hand side of each graph. The fitted components are indicated by black markers.

critical angle bulk sensitivity is obtained with a penetration of about 100 nm at  $\alpha_c + 0.03^\circ$ . In this way it is possible to change from surface to bulk geometry without realigning or re-preparing the sample so that a direct comparison of the surface/bulk behaviour under the same experimental conditions may be obtained.

### 3. Results and discussion

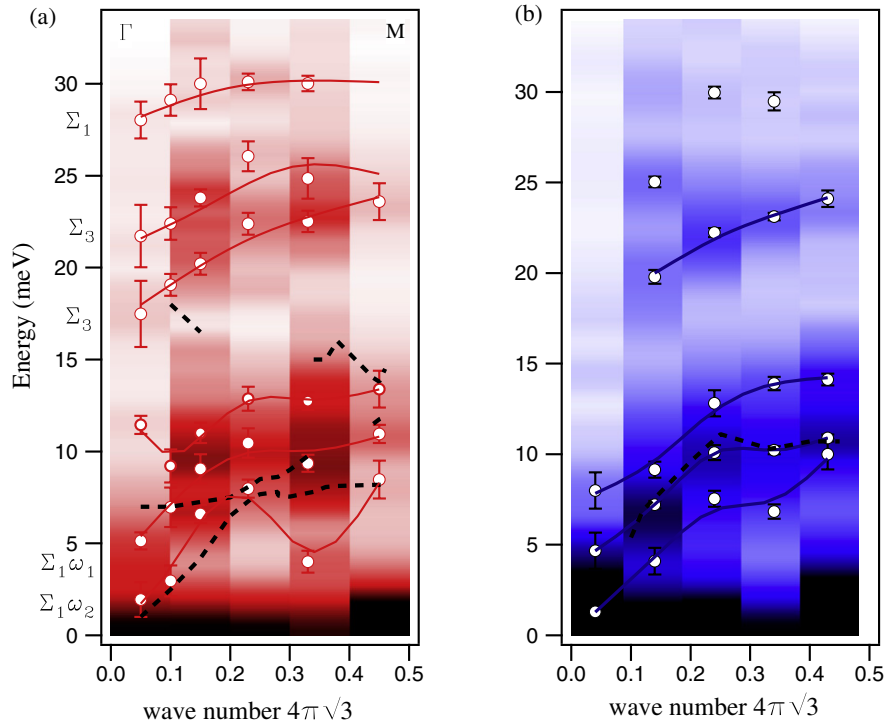
Data were collected at room temperature. From the surface (200) reflection, constant- $Q$  scans were recorded along the  $(\xi, 0, 0)$  direction from  $\xi = 0.05$  to  $0.45$  over the energy range  $-18$  to  $+34$  meV in order to record the Stokes and anti-Stokes component. Each data point took 180 s. In some cases two scans have been added. Typical energy scans are shown in figure 1 taken in both surface and bulk geometry. The data consist of a strong elastic component and inelastic components due to acoustic and optic modes. The elastic component is present at all  $Q$  values measured. This is likely to be due to a contribution from a bulk lattice reflection close to the  $(5/3, 0, 0)$  surface CDW satellite reflection position observed during alignment. Though an intense elastic component is normally associated with sample disorder, for this sample it is unlikely to be the case since a FWHM of the surface in-plane rocking scan of the Bragg reflection of  $0.005^\circ$  was measured during the experiment. The background count rate is less than

$1 \times 10^3$  counts  $s^{-1}$ . Though it is possible to clearly see the evolution of peaks as we move out through the Brillouin zone, the data close to Bragg position are resolution limited due to experimental resolution making it difficult to separate the low energy optic modes from the acoustic mode.

Fitting was carried out using the MINUIT package<sup>3</sup>. With a damped harmonic oscillator model allowing a convolution with the energy resolution profile which in this case is modelled by a Lorentz profile. The elastic peak of the NbSe<sub>2</sub> sample was determined to be  $2.6 \pm 0.2$  meV by fitting. This value was fixed for all spectra. In total six modes were observed for both the surface and bulk data, one acoustic and five optic modes. At low energies three modes are present, one acoustic and two optic and at higher energies there are three more optic modes observed. The predominantly longitudinal  $\Sigma_1$  modes are intense. In addition small contributions from some of the  $\Sigma_3$  branches, predominantly of transverse nature, are also visible. The results of the fitting discussed in detail in [13] are shown in figure 1.

In order to help with the visualization of the dispersion curve the data have been plotted in a 2-dimensional plot in figure 2. To facilitate plotting the data have been interpolated along the energy axis. We adopt previous assignment [6, 21] for the modes. For both the surface and bulk configurations

<sup>3</sup> MINUIT, D516-CERN, Computer 7600, Interim Program Library.



**Figure 2.** A two-dimensional plot of NbSe<sub>2</sub> GI-IXS data collected at room temperature collected in surface sensitive setting (a) and bulk sensitive (b) is shown to give an impression of the dispersion curve. Wavenumber  $\xi$  is given in units  $4\pi\sqrt{3}a$ . The peak positions as found by the fitting procedure described in the text are superimposed. White is the lowest and black is the highest intensity. The intensity at 0 meV is due to the elastic component. Raw data have been interpolated in order to present in this form. For comparison, data from [11] (dotted black line in (a)) and from [6] (dotted black line in (b)) are shown.

the dispersion is generally similar with both showing evidence of softening typical of a Kohn anomaly. There are, however, differences at  $\xi = 0.33$ , the position of the Kohn anomaly. While at  $\xi = 0.23$  the energy of the  $\Sigma_1\omega_2$  acoustic mode agrees with in the error bars for surface and bulk, at  $\xi = 0.33$ , the position of the anomaly, the energy of this mode is far lower in the surface sensitive case.

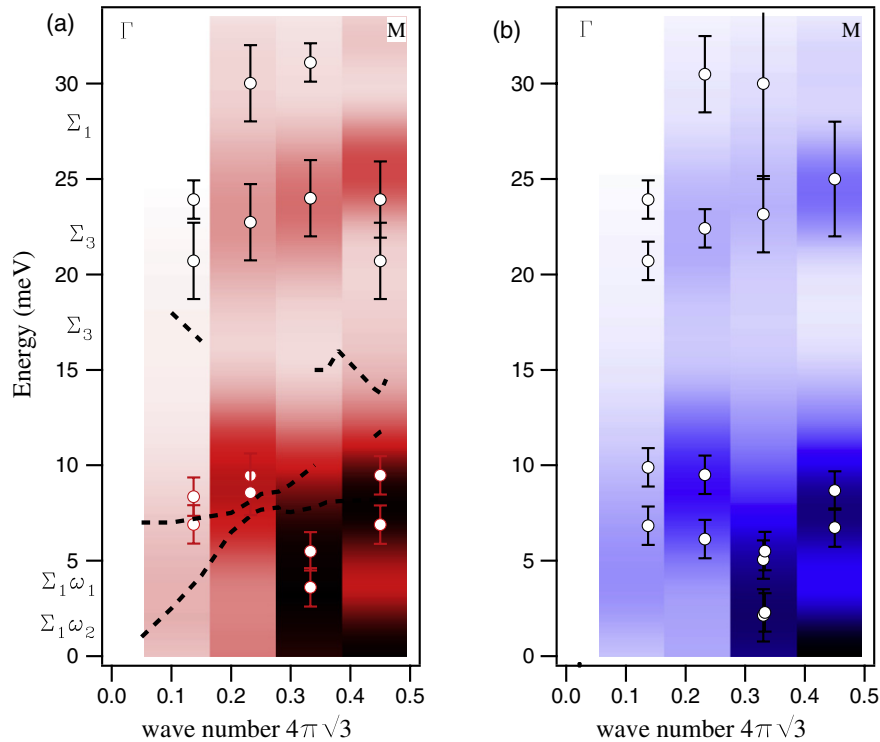
Compared to previous studies [6, 8] we have collected a considerably more extensive data set. The  $\Sigma_1\omega_1$  and  $\omega_2$  branches are resolved at the surface as well as in the bulk as previously only reported for bulk experiments [8]. In addition three optic bands at energies above 17 meV have been seen. These are in good agreement with theory [22, 23]. For both surface and bulk modes observed at 18, 22 and 28 meV in at  $\xi = 0.05$  the surface agree with previous Raman studies [9]. The lowest of these modes beginning at about 18 meV in both surface and bulk has been also seen with He scattering at 160 K [11]. The He data reports a surface Raleigh mode, s1, at similar values to the  $\Sigma_1\omega_2$  acoustic mode. Since the He data were collected at a lower temperature and two modes were resolved as opposed to three in the GI-IXS it is difficult to compare the data sets directly. Both show modes associated with the bulk  $\Sigma_1$  and  $\Sigma_3$  branches. The  $\omega_1$  and  $\omega_2$  branches are not resolved in the He data which reported less dramatic softening than observed in this experiment. The conclusion of the He scattering experiment was that there is a contraction of the van der Waals gap between the topmost two layers. Our data do not support this thesis and the enhanced softening of

the longitudinal acoustic mode rather indicates a relaxation is present.

Data collected at 100 K are shown in figure 3. The spectra are as expected less intense and the softening is now very similar for both surface and bulk. There is evidence of softening in the three low energy modes. For both surface and bulk there is softening not only at at  $\xi = 0.33$  position but also at 0.45. It is difficult to separate the low energy  $\Sigma_1$  and  $\Sigma_3$  branches. The optic branches above 20 meV are still present and now show evidence of softening. At low energy both  $\Sigma_1$  and  $\Sigma_3$  branches show significant softening in both surface and bulk. This is evidence that both the modes are involved in the transition.

#### 4. Conclusion

In conclusion, with this experiment it has been shown that GI-IXS is a good technique for investigating surface properties. The ability to study surface and bulk inelastic excitations over a wide momentum range in a single experiment provides exciting possibilities for the study of surface dynamics as illustrated in the case of NbSe<sub>2</sub>. The ability to move easily between surface and bulk geometry has real potential for the field of phase transitions where there are many open questions about the surface bulk relationship. For temperature-dependent effects where even small temperature offsets can hinder the fixing of critical temperature and so the determination of critical exponents GI-IXS provides a way to be sure that the



**Figure 3.** A 2-dimensional plot of NbSe<sub>2</sub> GI-IXS data collected at 100 K collected in surface sensitive setting (a) and bulk sensitive (b) is shown to give an impression of the dispersion curve. Wavenumber  $\xi$  is given in units  $4\pi/\sqrt{3}a$ . The peak positions as found by the fitting procedure described in the text are superimposed. White is the lowest and black is the highest intensity. The intensity at 0 meV is due to the elastic component. The raw data have been interpolated in order to present in this form. The dotted black line is the data from [11] shown for comparison.

same temperature is used for both the surface and the bulk measurements. In addition it will be possible to compare coupling constants directly.

The penetration depth of the order to 4 nm is naturally a drawback especially in the case of sub monolayer or lower coverage adsorbate experiments. However, due to the exponential decay it may still be possible to carry out such experiments when more intensity is available by using subtraction techniques to remove bulk signatures.

In the case of NbSe<sub>2</sub> we have observed acoustic and optic modes over the first Brillouin zone varying the depth sensitivity from 4 to 100 nm. The data agree well with previous experiments and extend to a new degree of detail. For both bulk and surface a Kohn anomaly is observed generally agreeing with previous studies. The surface case shows indications of increased softening as compared to the bulk and is evidence of a top layer relaxation. Temperature-dependent data currently under analysis will help to verify this prediction and allow a quantitative comparison of the surface and bulk electron-phonon coupling constant. At 100 K further softening is observed in both cases. The difference between surface and bulk behaviour appears to lessen at the CDW transition temperature is approached.

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