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Report:

Abstract *2H-NbSe2 is a van der Waals bonded layered structure, which undergoes a charge density wave transition. We have investigated the charge density wave transition in NbSe2 using grazing incidence X-ray diffraction on ID1 at the ESRF. The evolution of the satellite reflection has been observed above and below the critical angle of total external reflection in order to carry out a direct comparison between the surface and bulk behaviour. We successfully isolated the surface charge density wave structure on a high quality single crystal. The central finding is that the behaviour of the surface charge density wave satellite differs from that in the bulk: At the surface, the charge density wave transition occurs at a higher temperature than in the bulk; also, the transition appears to be continuous. It is likely that we observe the unusual case defined as a "surface transition".*

Transition metal dichalcogenides have a van der Waals bonded layered structure resulting in interesting properties such as charge density wave (CDW) instabilities [1,2,3]. CDWs are thought to result from Fermi surface nesting [4]. This study is focused at understanding the surface behaviour of the CDW transition in NbSe2, a hexagonal layered structure, space group P63/mmc, with lattice constants a=3.443 Å and c=12.547 Å [5]. In NbSe2 CDW occur below 33.3 K forming a hexagonal superstructure [1,2,3].
The single crystal 2H-NbSe2 sample, prepared by Bell labs, had an area of 4 x 8 mm^2 and thickness of 3 mm [6]. This GID experiment was carried on ID1 at 10.4 keV. The sample was cleaved in air and then mounted, under a Be dome, on the cold finger of a closed-cycle Helium cryostat mounted on the diffractometer. In the temperature range 15 to 50 K, GID Bragg scans were performed at the CDW satellite reflection ($Q(^5/_3 00)$ = 3.513 $Å^{-1}$) and at a reference reflection (Q(200) = 4.215 $Å^{-1}$). At 10.4 keV the critical angle of total external reflection is 0.26°. The reflections were measured at a surface sensitive incidence angle (α_i = 0.16, penetration depth ~ 25 Å) and then at an increased incidence angle for increased bulk sensitivity (α_i = 0.36 °, penetration depth ~ 1500 Å). The temperature dependent evolution of the satellite peak at the surface and in the bulk is shown in figure 1. Both the surface and bulk data contain the characteristic Bragg like and diffuse scattering components. Both components can be separated and fitted to obtain information on the dynamics of the phase transition.

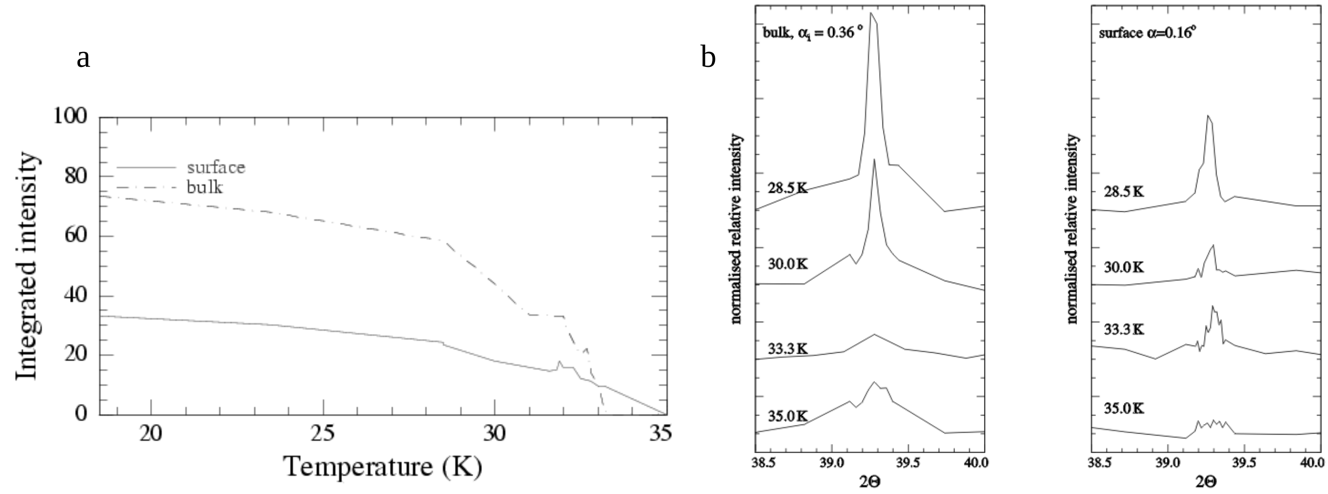

***Figure 1**: a) Temperature dependences of the integrated intensity of the ${}^{5}/_{3}00$ CDW satellite reflection for surface (25 Å penetration depth) and for bulk (1500 Å) collected on ID1 at 10.4 keV. A temperature difference of 2 K in the CDW phase transition temperature is observed on the surface with respect to the bulk. b) Bragg scans through the ${}^{5}/_{3}00$ satellite reflection below and above the CDW phase transition. A Bragg and a diffuse component are observed below the phase transition. The Bragg component decays to zero at the phase transition.*

Figure 1b shows the temperature dependence of the 5/300 satellite normalised intensity for the surface and bulk. For both cases the intensities, which are proportional to the square of the amplitude of the modulation, appear to go continuously to zero as expected at a second order phase transition and previously observed for the bulk [2]. An increased surface transition temperature with respect to the bulk is clearly observed. The bulk transition temperature T_{cb} was found to be 33 ± 0.1 K and the surface transition temperature T_{cs} = 35 ± 0.2 K. This is a significant result, $T_{cs} = T_{cb}+2$ K is a strong indication that this is not an ordinary transition and one must consider the possibility that we observed a 'surface transition' in $NbSe_2$ [9]. The enhanced order on the surface may be due to the change in the coupling constant in the surface region [7, 8]. Plotting intensity vs. the reduced temperature τ on a double logarithmic scale the data follow a power law and the exponents obtained are again consistent with the occurrence of a 'Surface transition'[7]

In conclusion, we have successfully isolated the surface CDW structure, via the 5/300 satellite peak, on single crystal 2H-NbSe2 using grazing incidence X-ray diffraction. The temperature dependence of the surface CDW satellite clearly varies from that in the bulk. We find that at the surface the CDW transition is observed to occur 2 K above that of the bulk. We conclude that we probably observe here the unusual case of a "surface transition":

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