Wide band XRD study of 2H-NbSe$_2$ in a CDW-regime

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Abstract. Albeit rather simple structure and ample experimental study of charge density wave (CDW) superconductor 2H-NbSe$_2$ its behaviour in a CDW regime ($T_{CDW} = 32.5$ K, $T_{SN} = 7.2$ K) remains unclear. The relevance of the known mechanisms of CDW formation to this hexagonal modification of the niobium diselenide is not straightforward. Occurrence of the lock-in transition in this compound is still debated despite numerous structural investigations by means of diverse diffraction techniques. Here, we present Debye patterns measured in a detail at temperatures 8-35 K with different sources of X-ray irradiation and energy resolution of about 1eV. New features observed in the temperature range 15-30 K are discussed in terms of fluctuation-mediated phase transition.

1. Introduction
The presence of periodic-lattice-distortion PLD/CDW-state in hexagonal modifications of layered transition-metal dichalcogenides was clearly established by electron diffraction measurements [1] on 2H-TaSe$_2$ and later on 2H-NbSe$_2$. Earlier [2], a transformation of XRD pattern was reported for the latter across $T=40$ K and described by doubling of the in-plane lattice parameter $a$. Using NMR-measurements [3] on the same sample it was attributed to the charge-density modulation. Unambiguous evidence of the CDW-instability in niobium diselenide was presented by observation of incommensurate superlattice satellites in neutron scattering measurements [4]. It was shown that a CDW satellite reflection is incommensurate in 2H-NbSe$_2$ with a wave vector $q_0 = (1 - \delta)a^*/3$, where $a^* = 4\pi/\sqrt{3}a$, moves towards the commensurate position of 2/3 but does not lock in over the temperature range from 32 to 10 K.

Recently, the satellites were observed and studied in a magnetic field [5] by X-ray scattering in high-resolution multi-axis and two-circle diffractometers. For a comparison, a high-resolution muon study has never revealed any static order connected with CDW. The conflict between diffraction data measured with different sources was discussed [6] and explained by observation of static distortions (superlattices) originated from nesting with different wave-vectors [7,8]. In our case, the X-ray study differs by the broad energy window (1eV) for registration of Bragg peaks compared to neutron measurements (0.1 meV) and the synchrotron X-ray source as well.

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2. Experimental details
The powder samples of 2H-NbSe$_2$ with a grain size of 20 mkm were prepared starting with 99.999% Nb and Se by iodine technique. X-ray analysis confirmed their 2H polytype (D$_{6h}^4$). The X-ray scattering was measured in Co-, Cr- and Cu-K$_\alpha$ radiation, HWHM = 25.3 – 72.5 sec within 1eV energy window [9] in the Bragg-Brentano geometry in a continuous-flow cryostat attached to a commercial diffractometer. The slit width was 0.5 mm and the beam intensity made $10^4$ photons/min. X-ray scattering was registered in angular range 20=$10$–$70^\circ$ at T=8–35 K. Data were processed using a Lipson-equations based software and Berstreum-diagram technique (figures 1,2).

![Figure 1. XRD pattern change across T$_{CDW}$](image1)

![Figure 2. The best fitted indexing](image2)

3. Discussion
Figure 1 presents XRD features appeared below T$_{CDW}$. It is hard to index them and figure 2 presents the best though ambiguous fit. The physical origin of the observed phenomenon remains unclear. Nevertheless its analysis within modern approach to phase transitions is apparently fruitful.

3.1. Type of transition observed by XRD patterning

![Figure 3. Temperature dependence of new feature](image3)

![Figure 4. Logarithmic plot of new XRD feature](image4)
The temperature dependence at heating and cooling cycles (figure 3) together with observed evolution of new XRD features with time can be understood if first order nature or fluctuations are taken into account. To clarify this point we analyzed the temperature dependence of new XRD feature when the transition temperature is approached in heating cycle.

3.2. Mechanism of the observed X-ray scattering

Landau [10] considered X-ray scattering near phase transition as comprised of coherent (Bragg) and incoherent (diffuse) parts. The former occurs only below the transition temperatures $T_c$ and vanishes when $T_c$ is approached:

$$ J_{cs} \sim \left(1 - \frac{T}{T_c}\right) $$

Incoherent scattering exists on the either side of $T_c$, gradually increases when $T_c$ is approached from the either side, with a maximum of the order of magnitude

$$ J_{ICS} \sim -\ln\frac{T}{T_c} $$

$$ T<T_c \quad J_{ICS} \sim -\ln\frac{1}{2\frac{T}{T_c} - aq^2} $$

$$ T>T_c \quad J_{ICS} \sim -\ln\frac{1}{\frac{T}{T_c} - aq^2} $$

with $q = \frac{q}{\sqrt{2}}$; $\tilde{q} = \tilde{k}_1 - \tilde{k}_2 + \tilde{K}$ being the incident wave vector; $\tilde{k}_2$ the scattered wave vector; $\tilde{K}$ the reciprocal lattice vector. Moreover, there is the intermediate case of quasi-elastic neutron [11] and light [12] scattering, the so-called Central Peak (CP). In the case of X-ray scattering its quasi-elastic part should obviously be observed with almost the same angular distribution as elastic diffraction patterns. Such scattering is called Quasi-Bragg peaks (QBP). In [13], the common nature of CP and QBP is demonstrated by neutron and X-ray scattering in the structural transition vicinity of perfect KMnF$_3$ crystals as both intensities follow the law:

$$ J_{QBP} \sim |T-T_c|^\gamma $$

with the same, within experimental accuracy, exponent $\gamma_{CP}=1.34\pm0.08$ and $\gamma_{QBP}=1.26\pm0.04$.

The data comparison with theory, equation (1, 3, 5), should consider $1\leq\gamma\leq2$ yielded from modern approach which is based on the Andersons’s soft-mode model (e.g. [14] and references therein).

a) Diffuse scattering (figure 1) is observed on the either side of $T_c=29K$. Its (integral) intensity gradually increases when $T_c$ is approached on the both sides. Therefore, we consider it as incoherent one from the Landau work [10] with equations (3) and (4). The intensity of sharp peaks disagree with equation (1), introduced in [10] for the coherent elastic scattering because in contrast to equation (1) it increases as $T_c$ is approached. Such a behavior matches equation (5) for the Quasi-Bragg scattering. In our case, the exponent $\gamma$ varies then from 1.65 to 1.95 within accuracy of the critical temperature measurement: $\gamma=1.80\pm0.15$ for $T_c=29\pm1K$. In figure 4 the temperature dependence of the sharp new peak is presented in logarithmic plot which falls between the dotted lines corresponding to $\gamma=2$ (upper) and 1(lower) with the measured value $\gamma$ varied from 1.65 to 1.95 ($\gamma=1.80\pm0.15$ for $T_c=29\pm1K$).

3.3. Scattering probability

The XRD patterns measured using high resolution and wide-band techniques differ. In a view of preceding conclusion it is explained by probability of scattering by fluctuations:

$$ P \sim \int d\varepsilon \int dz G_f(z)G_i(\varepsilon-z), $$

(6)
where $G_f(\varepsilon)$ is the energy distribution of fluctuations, represented by the Lorentzian peak of the width $\Delta \varepsilon_f = k T_{n\omega} \approx 20\text{meV}$ and maximum at $\varepsilon = \varepsilon_f$, where $\varepsilon_f$ is the fluctuation frequency, $\Delta \varepsilon_f$ is the fluctuation width, $\Delta \varepsilon \sim 1$. $G_{\varepsilon}(\varepsilon)$ is the energy distribution of radiation (the X-rays or neutrons) of the Lorentzian type as well, and $D_f$ is its range. For X-ray scattering $G_{\varepsilon}(\varepsilon) = G_y(\varepsilon)$, the peak width $\Delta \varepsilon = 1eV \gg \Delta \varepsilon_f$ and is located at $\varepsilon_y \gg \varepsilon_f$. In such a case, for estimation of scattering probability the $G_{\varepsilon}(\varepsilon)$ function in equation (6) can be replaced by the Dirac delta-function $\delta(\varepsilon - \varepsilon_f)$. It yields

$$P_{\chi} \sim \int_{\Delta \varepsilon_{\chi}} d\varepsilon G_{\varepsilon}(\varepsilon - \varepsilon_f)^{-1}$$

as $\varepsilon_f \ll \Delta \varepsilon_{\chi}$. In the case of neutron scattering, the Lorentzian peak $G_{\varepsilon}(\varepsilon) = G_y(\varepsilon)$ is much more narrow than the peak $G_y(\varepsilon) (\Delta \varepsilon_y = 10^{-5} eV \ll \Delta \varepsilon_f; \varepsilon_y = 10^{-7} eV \ll \Delta \varepsilon_f)$ which allows us to estimate scattering probability in equation (6) in assumption that $G_{\varepsilon} \sim \delta(\varepsilon - \varepsilon_y)$. Then, as $\varepsilon_y - \varepsilon_f \gg \Delta \varepsilon_f$

$$P_{\chi} \sim \int_{\Delta \varepsilon_{\chi}} d\varepsilon G_{\varepsilon}(\varepsilon - \varepsilon_y) \ll 1$$

Here, the XRD study differs by a broad energy window (1eV) for registration of Bragg peaks compared to both the neutron measurements (0.1 meV) and the synchrotron X-ray source. It allowed us [15] to range a diverse variety of dynamic instabilities (quantum critical fluctuations) emerged from succession of topological transitions over the FS sheets of $2H$-NbSe$_2$.

Thus, the behavior of new sharp peak together with a diffuse underlying scattering observed in this work qualitatively agrees with concepts of coherent quasi elastic and incoherent X-ray scattering on the critical fluctuations in the phase transition vicinity.

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