“Extraordinary” Surface Phase Transition at (100) Surface of NbSe$_3$

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We have investigated both $q_1$ and $q_2$ charge-density wave transitions occurring in NbSe$_3$ by means of low temperature scanning tunneling microscopy under ultra-high vacuum on in-situ cleaved (100) surface. High-resolution topographical images with molecular resolution were obtained in the temperature range between 5K and 140K. We studied the temperature dependency of the order parameters of both transitions using Fourier transform of the STM images. Our results show that at the free (100) NbSe$_3$ surface, the low temperature $q_2$ CDW transition occurs above 70K, i.e. more than 10K above the bulk transition temperature reported by x-ray diffraction experiment or by tunneling junction measurements involving an unfree NbSe$_3$ surface. We propose that as $q_2$ phonon modes in NbSe$_3$ possess a component transverse to the surface, they might be softer in the top layer than in the bulk, leading to an extraordinary phase transition for the $q_2$ CDW at surface. Additionally, at variance with previously reported STM measurements, our images show a bias voltage polarity dependency that could be interpreted in a lower density of states on Se atoms of chain II for the occupied states than for the empty states.

1. Introduction

NbSe$_3$ was the first inorganic low dimensional conductor discovered to exhibit non linear conductivity and it has become one of the most widely studied charge-density wave (CDW) system [1]. Quasi-one dimensional (1D) NbSe$_3$ has a linear chain structure consisting in metallic chains running along the b axis, built of triangular prisms of selenium (Se) atoms having a niobium (Nb) atom at their center. Depending on the length of the Se-Se bonds of the triangular basis, three types of chains can be distinguished, conventionally referred as chains I, II and III (see figure 1). NbSe$_3$ undergoes two successive Peierls transitions at $T_1$=144K and $T_2$=59K involving two different CDW vectors $q_1 = q_1 b^*$ (high-temperature CDW) and $q_2 = 0.5a^* + q_2 b^* + 0.5c^*$ (low-temperature CDW) with $q_1$=0.241 and $q_2$=0.259 (at low temperature) referring to the $P2_1/m$ monoclinic unit cell. Lattice parameters at room temperature are $a=10.009$ Å, $b=3.48$ Å, $c=15.629$ Å and $\beta=109.47^\circ$. NMR [2,3] and high-resolution x-ray diffraction [4] show that $q_1$ CDW mainly affects the Nb atoms of chain III while $q_2$ CDW mainly affects the Nb atoms of chain I. Early scanning tunneling microscopy (STM) experiments on the (b,c) plane of NbSe$_3$ were carried out in liquid media and three chains could be identified [5,6]. Results obtained at 77K didn’t give clear evidence for the presence of the $q_1$ CDW in constant current STM images. Authors argued that, due to poor signal to noise ratio, the $q_1$ modulation could only be detected on some STM scans along the b direction on one of the three chains which was therefore identified as chain III [5]. Those 77K results were inconsistent with the results obtained at 4K concerning the correct identification of chains I, II and III. Results obtained at 4K in liquid helium suggested that all three chains carry a strong CDW modulation. Both $q_1$ and $q_2$ CDWs could be
observed by STM with wave vectors components in agreement with bulk results [6]. A controversy arose because x-ray results showed that the largest displacive modulations occur on Nb(III) and Nb(I) while smaller displacive modulations affect the Se atoms of chains I, II and III directly bonded to Nb(III) and Nb(I) [7]. This discrepancy between x-ray and STM results, concerning the strong $\mathbf{q}_1$ CDW modulation measured by STM on chain II, was partially solved by tight-binding calculations for a slab [8]. Due to the exponential decrease of the atomic-orbital amplitudes with distances, it was shown that STM should probe only the local density of states (LDOS) associated with the surface Se atoms [8,9]. According to those calculations, chain II should also be involved in the $\mathbf{q}_1$ CDW formation but STM should measure a smaller CDW amplitude on chains II than on chains I and III. Recently we reported STM results at 5K under ultra-high vacuum (UHV) conditions leading to conclusions concerning the $\mathbf{q}_1$ CDW on chain II different from those obtained by early STM measurements [10]. Our results were in agreement with the above picture described by Ren et al. [8].

With the advent of scanning tunneling microscopy (STM) and high-resolution angle resolved photoemission (ARPES) under UHV conditions, there is increasing interest in looking for order in correlated electron systems by studying the electronic structure of the surface layer. A persistent question about such studies is then, “Does the surface electronic structure behaves similarly as the bulk one?” When a bulk system undergoes a phase transition to broken symmetry state, such as the CDW state, the surface of the system must reflect the broken symmetry as well, usually with a weaker order at surface. But there are known cases of surface phase transitions in which an “extraordinary transition” occurs, i.e. a phase transition in which the surface orders at a higher temperature than the bulk [11]. In this paper we report the first experimental evidence for an “extraordinary transition” occurring for the $\mathbf{q}_1$ CDW at (100) surface of NbSe$_3$.

![Cross section of NbSe$_3$ unit cell perpendicular to the chain axis. Filled Nb and Se atoms lie in the plane of the figure. Remaining empty Nb and Se atoms lie out of plane by b/2. At the (b,c) plane surface are lying chains I, II and III, exposing Se atoms at the surface after cleavage. The height variation of the surface Se atoms is of 1.5Å (Drawing from E. Machado).](image)

2. Experimental Set-up. Identification of $\mathbf{q}_1$ and $\mathbf{q}_2$ CDW transitions and identification of chains I, II and III.

The present work was performed in an Omicron low-temperature UHV STM system with two separation chambers on in-situ cleaved (100) surfaces of fiber-like NbSe$_3$ single crystals. Well characterized samples with typical dimensions of $0.02 \times 10 \times 0.05$ mm$^3$ were selected. The samples were cleaved at room temperature, then optically flat (100) surface was carefully inspected before loading the sample into the STM head and finally slowly cooling down the system. Performing STM measurement on cleaved NbSe$_3$ surface is tricky and delicate because the sample width is only of tens of microns and because there always remain floating NbSe$_3$ fibers over the sample surface after cleavage, creating easy possibilities for STM tip contamination. Both mechanically sharpened Pt/Ir tips and electrochemically etched W tips were used for the experiments leading to similar results.
We have studied the $q_1$ and $q_2$ CDW modulations from 5K to about 140K in cooling and in warming the system. Our study allows a clear identification of the three chains existing inside a single unit cell (u.c) at all temperatures. We found that at variance with former STM results there is a bias voltage polarity dependency of the STM images in usual tunneling conditions. In particular, when imaging the empty states of the sample, three chains could always be identified having their mutual distances and carrying CDW modulations in agreement with a straightforward interpretation in terms of chains I, II and III (see Fig. 2). On the contrary, when imaging the occupied states of NbSe$_3$, the chain II was found to exhibit lower LDOS resulting in STM images showing mostly two chains: I and III (see Fig. 2).

![Fig. 2: Three constant current STM images of NbSe$_3$ (b,c) plane taken at T=78K on the same 7*7nm$^2$ area, showing bias voltage polarity dependency of the STM image. 78K is below the $q_1$ CDW bulk transition temperature ($T_1$=144K) but above the $q_2$ CDW bulk transition temperature ($T_2$=59K). For positive bias voltage $V_{bias}$ applied to the sample the empty states are seen, whereas for negative $V_{bias}$ the occupied states of the sample are probed. All three images are taken with tunneling current $I_t$=100pA.](image)

**a)** $V_{bias}$=+200mV. Three chains can be identified, one of them carrying a strong $q_1$ CDW modulation and therefore identified as chain III. CDW modulation forms bright maxima along the chains, and the superlattice cell is indicated by a white rectangle. The two remaining chains are consistently identified as chains I and II (see text). Transverse corrugation is of 0.2 Å and $q_1$ CDW corrugation is of 0.1 Å.

**b)** Change from $V_{bias}$=+200mV in the bottom half of the image to $V_{bias}$=-200mV in the upper half. There is a change of contrast on chain II from the empty to the occupied states STM image and only chains I and III are clearly seen for $V_{bias}$=-200mV. Interestingly maxima of CDW hole and electron states present a $\pi$ phase shift (indicated by continuous lines), as expected for a quasi-1D system.

**c)** $V_{bias}$=-200mV. Only chains I and III are clearly visible. Transverse corrugation is of 0.4 Å and $q_1$ CDW corrugation is of 0.1 Å.

At 78K, high-resolution topographical constant current STM images with atomic resolution show that chain III carries most of the $q_1$ CDW. Two dimensional (2D) Fourier transform (FT) of the STM images shows both the surface lattice spots and the $q_1$ CDW superlattice spots. The $q_1$ value at the surface is 0.24$b^*$ in good agreement with 0.241$b^*$ reported by x-ray diffraction experiments (see fig. 3). Figure 3 shows a typical STM image of the empty states for a bias voltage of 100mV applied to the sample, close to the gap edge value reported by other spectroscopic techniques. Three chains are
clearly visible, one of them strongly carrying the $q_1$ CDW modulation. According to previous considerations, this chain is therefore identified as the chain III of NbSe$_3$. The fact that this interpretation is correct is confirmed by further experimental observations. First, at variance with early STM experiments in liquid medias, there is consistency between all our measurements in the whole range of probed temperatures (5K – 140K). Second, one expects from crystallographic datas, as the right surface Se atom of chain III in figure 1 is the highest atom at (100) NbSe$_3$ surface, that for larger applied voltages (well above the $q_1$ CDW gap value) the chain III should be the highest in the STM images for both polarities, because previous band structure calculations showed that the Se sites have comparable DOS at $E_f$ [8]. As it is seen in figure 2, this is indeed the case. Third, crystallographic datas show that the mutual distances between neighboring chains are not identical. It is the largest between chains I and III and the smallest between chains II and III. The interpretation proposed in figures 2 and 3 agrees obviously with this requirement. Fourth at lower temperatures, according to x-ray reports, the occurrence of the $q_2$ CDW should predominantly affect the chain identified as chain I of NbSe$_3$ and should less strongly affect chain II.

![Figure 3](image)

**FIG. 3:** a) Constant current STM image of the (b,c) plane of in-situ cleaved NbSe$_3$ taken at $T=78K$. 78K is below the $q_1$ CDW bulk transition temperature (144K) but above the $q_2$ CDW bulk transition temperature (59K). The bias voltage applied to the sample is $V_{bias}=+100mV$ and the tunneling current $I_{t}=1nA$. Three different chains are visible and mutual distances between them are consistent with i) the identification of the 3 different chains of NbSe$_3$ as proposed in fig. 3 a) and ii) with low temperature measurements (see text). Surface lattice and $q_1$ CDW superlattice cells are indicated by green (light) and purple (dark) unit vectors. b) 2D Fourier transform of the STM image showing lattice Bragg spots, corresponding to $b^*$ and $c^*$ vectors indicated by green (light) arrows, and $q_1$ CDW superlattice spots indicated by purple (dark) vectors. STM measurement gives $q_1=0.24b^*$ in good agreement with bulk reported values. Weaker superlattice spots associated to the $q_2$ CDW are also visible about 20K above bulk transition temperature (see text).

As it is shown in high-resolution STM image on figure 4 a) at 5K, this is indeed the case: $q_2$ CDW predominantly affects chains I and less strongly chain II, in agreement with our previous results [10]. Figure 4 b) shows the 2D FT of fig. 4 a). Both $q_1$ and $q_2$ CDW superlattice spots together with lattice Bragg spots are clearly visible. From this 2D FT, we can precisely extract both CDW vectors $q_1=0.24b^*$ and $q_2=0.26b^* + 0.5c^*$ in good agreement with bulk reported values. It can be seen that STM measurement allows a precise extraction of the small difference, that exists for both CDWs vectors, from the commensurate 0.25$b^*$ value.
FIG. 4: a) Constant current STM image of the (b,c) plane of in-situ cleaved NbSe₃ taken at 5K, well below both CDW transition temperatures. The bias voltage applied to the sample is V_{bias}=+200mV and the tunneling current is I_t=150pA. Three chains are visible and the proposed identification of chain I, II, III is consistent with 78K measurement shown on Fig. 2 and Fig. 3. Surface lattice and q₂ CDW superlattice cells are indicated by green (light) and blue (black) arrows. b) 2D Fourier transform (2D FT) of the STM image shows lattice Bragg spots, corresponding to b* and c* vectors indicated by green (light) arrows, and q₁ and q₂ CDW superlattice spots indicated respectively by purple (dark) and blue (black) arrows. STM measurement gives q₁ = 0.24b* and q₂ = 0.26b* + 0.5c* in good agreement with bulk reported values. Surprisingly q₂ CDW extends also on chain III making difficult the direct visualization of the q₁ CDW superlattice (see text). However 2D FT shows clearly its existence.

Surprisingly below q₂ surface transition temperature (see part 3) the q₁ CDW superlattice is no more directly visible in the STM image on the chains III (see figure 4), whereas above the q₂ surface transition temperature it is directly visible (see figure 3). Moreover when carefully examine the STM image along chains III, one can find a long range new modulation which has opposite phase on neighboring type III chains. However 2D FT of the STM image clearly shows that the q₁ CDW superlattice exists at 5K with the same wave vector as at 78K. Fourier analysis shows that this phenomenon happens because q₂ CDW is not only confined on chains I but also extends on chains II and III. It leads to a beating between q₁ and q₂ periodicities on chain III that is mainly responsible for this appearance of chain III below the q₂ surface transition temperature [12].

3. Extraordinary surface phase transition for q₂ CDW
Strikingly at 78K, i.e. almost 20K above T₂, we can easily find the presence of superlattice spots of the q₂ CDW that have more or less diffuse shape depending on the probed location at the sample surface, but have a much lower intensity than the q₁ ones. At 63K, i.e. 4K above T₂, the q₂ superlattice is already developped leading to well defined spots in the FT of the STM image, having already higher intensity than the q₁ ones. This indicates that q₂ CDW ordering occurs at higher temperature at the surface than in the bulk. Figure 5 illustrates this situation by showing 60*60nm² to 80*80nm² STM images taken at 5K, 63K and 78K all measured with V_{bias}=-300mV and I_t=100pA. One sees clearly that while at 78K the STM image shows an almost perfect q₁ CDW superlattice (see the inset in Fig.
at 63K the beating phenomenon occurring on chain III with the formation of the $q_2$ CDW is already present and blurs the direct visualization of the $q_1$ CDW superlattice.

FIG. 5: Three typical constant current STM images of in-situ cleaved (100) surface of NbSe$_3$ taken at various temperatures a) $T=78K$, b) $T=63K$, c) $T=5K$ with the same tunneling conditions: $V_{bias}=-300mV$ and $I_t=100pA$, but at different locations on the surface. Scanned areas range from 60*60nm$^2$ to 80*80nm$^2$. In each image, an inset shows a smaller portion of the image at larger scale for clarity. Under each STM image, its 2D Fourier transform (2D FT) shows the lattice Bragg spots (indicated by c*, perpendicular to the chains) and the $q_1$ and $q_2$ superlattice spots. At 78K the $q_1$ CDW superlattice is clearly seen whereas $q_2$ superlattice spots are diffuse. At 63K, i.e. 4K above the bulk transition temperature, $q_2$ CDW superlattice spots are already well defined, having a higher intensity than the $q_1$ ones. At 5K the ratio of the $q_2$ intensity to the $q_1$ one’s is slightly higher than at 63K.

This led us to study precisely the temperature dependency of the $q_2$ CDW amplitude to find the transition temperature at surface. We have chosen as order parameter of the transition the sum of the amplitude of the two first-order $q_2$ spots present in the Fourier transform of the STM images. To avoid problems related to changes in tip conditions and changes in piezoelectric constants when varying the temperature, we normalized the above defined order parameter by the amplitude of the $q_1$ first-order superlattice spot. For each temperature, we extracted the normalized order parameter from 2D FT of 30*30nm$^2$ STM images taken at various locations on the surface for identical tunneling conditions, $V_{bias}=-300mV$ and $I_t=100pA$. The result is plotted on figure 6 together with former x-ray [13] and recent CDW-CDW tunneling experiments [14]. One can see that there is a sharp transition observed by STM at a temperature slightly higher than 70K, whereas other reported results either for bulk or for an unfree surface led to a transition temperature of about 60K. Hence there is evidence for an “extraordinary” phase transition occurring at (100) NbSe$_3$ surface for the $q_2$ CDW, leading to CDW ordering at higher temperature by about 10-15K.
FIG. 6: In this graph red filled squares shows the temperature dependency of the amplitude of the low
temperature $q_2$ CDW at in-situ cleaved (100) surface of NbSe$_3$ probed by STM. For each temperature,
this amplitude was extracted from the Fourier transform of 30*30nm$^2$ STM images taken at various
locations for identical tunneling conditions: $V_{bias}=$-0.3V, $I_t=100pA$ (see text). Empty blue squares show
the temperature dependency of the low temperature $q_2$ CDW superlattice spots obtained from $x$-ray
diffraction experiment [13]. Filled green dots show the temperature dependency of the gap in NbSe$_3$
CDW-CDW tunneling junction [14]. STM experiment shows that the free surface undergoes the phase
transition at about 10-15K above the bulk transition temperature, leading to an extraordinary phase
transition.

By the same method, we also studied the $q_1$ CDW phase transition as a function of temperature. In
this case, we had more uncertainty concerning the precise measure of the absolute temperature of the
sample, but the transition temperature at surface seems to be about 140K in agreement with bulk
results reported by other experimental techniques.

4. Discussion
Recently Brown et al. [15] tried to explain the charge ordering occurring at the surface in Ca$_{2-x}$
$\text{Na}_x\text{CuO}_2\text{Cl}_2$ (NaCCOC) by STM [16], whereas it is not present in the bulk. They emphasized the role
of the phonon modes associated with the motion of atoms transverse to the layers, because they tend to
be softer at the surface than in the bulk. In particular, they have shown that if the coupling of the
electronic density to such modes is sufficient, an extraordinary surface phase transition occurs. We
believe that this situation is likely to happen in NbSe$_3$. Indeed we already know that NbSe$_3$ undergoes
a bulk CDW transition involving phonon modes having for both transitions their wave vector lying in
the $(b,c)$ with a $2k_f$ component along the chain direction. But $x$-ray diffraction experiment showed that
above the $q_2$ bulk transition, when the fluctuations of $q_2$ CDW become two dimensional (2D), they are
transverse in the $(a,b)$ plane [17] and not in the $(b,c)$ plane. This result is also consistent with former
$x$-ray refinements of the superlattice modulation at 4K, showing that $q_2$ CDW involves lattice
displacements larger in the $a$ direction than in the $c$ direction [4]. So both $x$-ray results support the idea
that the elastic constants of those transverse phonon modes should be smaller for the top NbSe$_3$ layer
than for internal layers, because they don’t have upper neighboring atoms anymore. This would
therefore result in softer phonons and larger electron-phonon coupling in the top layer, leading to a
CDW ordering at higher critical temperature. This appears as a plausible mechanism when trying to
figure out what might be the differences between a free surface and the bulk. One could objects that
other tunneling junction techniques, as they are also sensitive to the density of states at the surface,
should also observe an ordering at a higher critical temperature. But in those cases the surface is
unfree, because there are always upper layers either of insulator [18] or of NbSe$_3$ itself [14], upon the
probed NbSe$_3$ layer(s).
Conclusion
With high-resolution LT-UHV-STM images on in-situ cleaved (100) NbSe$_3$ surface, we showed the first consistent study of both $q_1$ and $q_2$ CDW transitions together with the identification of the three different chains I, II and III in the temperature range 5K-140K. A precise study of the temperature dependency of the $q_2$ CDW amplitude shows that this $q_2$ CDW undergoes a sharp “extraordinary” transition at the surface, leading to a critical temperature higher than the bulk one by about 10-15K. We suggest that a possible mechanism to explain this extraordinary phase transition might be the existence of transverse phonon modes at the top layer of NbSe$_3$ being then softer than bulk ones. As developed in [15] this would lead to larger electron-phonon coupling in the top layer, leading to a CDW ordering at higher critical temperature at surface. Additionally, at variance with previous STM measurements, our images shows a bias voltage polarity dependency leading to lower density of states on Se atoms of chain II for the occupied states than for the empty states in the energy range of hundreds meV.

Acknowledgments
We thank P. Monceau for many instructive discussions. We also thank E. Machado, P. Machado, E. Canadell, N. Kirova, S. Brazovskii, S. Van Smaalen, A. Ayari, and J-C. Girard for helpful discussions. The technical assistance of C. David is greatly acknowledged. The high-quality NbSe$_3$ samples used in this study were synthesized by H. Berger and F. Lévy.

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