Luttinger-liquid-like behavior in bulk crystals of the quasi-one-dimensional conductor NbSe$_3$

S.V. Zaitsev-Zotova, M.S.H. Go$^b$, E. Slot$^b$, H.S.J. van der Zant$^b$

$^a$Institute of Radioengineering and Electronics of Russian Academy of Sciences, Mokhovaya 11, 103907 Moscow, Russia and
$^b$DIMES and Department of Applied Sciences, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands

CDW/Normal metal/CDW junctions and nanoconstrictions in crystals of the quasi-one-dimensional conductor NbSe$_3$ are manufactured using a focused-ion-beam. It is found that the low-temperature conduction of these structures changes dramatically and loses the features of the charge-density-wave transition. Instead, a dielectric phase is developed. Up to 6-order power-law variations of the conduction as a function of both temperature and electric field can be observed for this new phase. The transition from quasi-one-dimensional behavior to one-dimensional behavior is associated with destruction of the three-dimensional order of the charge-density waves by fluctuations. It results in a recovery of the Luttinger-liquid properties of metallic chains, like it takes place in sliding Luttinger liquid phase.

I. INTRODUCTION

Transport properties of electron systems strongly depend on dimensionality. In one dimension the Coulomb interaction between carriers modifies the ground state and dramatically changes the transport properties. In a one-dimensional (1D) metal, instead of a Fermi liquid of electrons, a so-called Luttinger liquid (LL) is developed. Elementary excitations in a LL are collective charge and spin boson modes, rather than fermion quasi-particles as in 3D metals. The ground state of a LL is characterized by a power-law suppression of the tunneling density of states. Impurities in a LL act as tunneling barriers. Therefore, the conduction $G$ of impure LLs is a power-law function of temperature, $G \propto T^\alpha$, and voltage, $G \propto V^{\beta-1}$ ($I \propto V^\beta$ in current-voltage curves). These dependencies are considered as a fingerprint of 1D behavior.

The experimental study of 1D effects in long nanowires remains a challenge. The main efforts are focused on developing a technology to fabricate metal or semiconductor quantum wires with transverse sizes on the order of 10 nm or less and attaching them to an external circuit. At the present, both problems were successfully solved for a number of physical systems including single-wall carbon nanotubes, Mo$_6$O$_6$ molecular wires, Si whiskers, InSb nanowires in asbestos matrices, Bi nanowires in various matrices (see e.g.\cite{7} and references therein), etc. Experimental observation of the power-law-supporting LL theories has been reported for single-wall carbon nanotubes\cite{8,9}, Mo$_6$O$_6$ nanowires\cite{9} and InSb nanowires\cite{9}. In all cases the nanowire diameters do not exceed 10 nm.

There is a wide class of materials suitable for experimental search and study of 1D effects: quasi-one-dimensional (quasi-1D) conductors with a charge-density wave (CDW) ground state. Such materials consist of metallic chains connected in a crystal through the relatively weak Van der Waals interaction. At temperatures below the Peierls transition temperature, $T_p$, the Peierls instability leads to the development of the CDW, which is a 3D-ordered periodic modulation of the electron density accompanied by a periodic distortion of the crystalline lattice.

An example of these materials is NbSe$_3$. It has a monoclinic unit cell with lattice parameters $a = 10.01$ Å, $b = 3.48$ Å, $c = 15.63$ Å, and $\beta = 109.5^\circ$\cite{10}. The conducting chains are along the $b$ direction. NbSe$_3$ exhibits two Peierls transitions leading to the partial delocalization of the electron spectrum, at $T_{p1} = 145$ K and $T_{p2} = 59$ K. The remaining non-condensed electrons provide metallic conduction down to the lowest temperatures.

In some sense, the CDW state results from an instability of LLs with respect to 3D coupling at low enough temperatures. It is also widely accepted that in quasi-1D conductors LL exists at temperatures above $T_p$ (see e.g.\cite{11}). As $T_p$ decreases with the sample cross-section area\cite{12}, one could expect the area of existence of LL to grow towards the low-temperature region for sufficiently thin crystals.

Transitions from quasi-1D to 1D behavior with reduction of the transverse sample sizes has recently been observed in the quasi-1D conductors NbSe$_3$ and TaS$_3$\cite{13}. Here we present the results of our observation of even more dramatic changes in the conduction of quasi-1D conductors found in two novel (for quasi-1D conductors) types of structures: CDW/normal-metal/CDW (C/N/C) junctions and nanoconstrictions. Surprisingly, 1D behavior has been observed in samples with transverse sizes in the $\mu$m-range scale.
FIG. 1: a) FIB fabricated nanoconstriction in NbSe$_3$ crystal. b) FIB fabrication of a C/N/C junction. Inset: a gap of 1 $\mu$m width is etched into a crystal. Left: the gap is filled with platinum.

II. TECHNOLOGY

Structures were prepared at the Delft Institute for Microfabrication and Submicron technology (DIMES). We used a standard Fei Inc. 200xP focus-ion-beam (FIB) system with a gallium ion source. This FIB system was used for imaging, etching and platinum deposition in situ. In all cases the FIB was used at 30 kV. When imaging, the lowest beam currents were used ($I = 1 - 4$ pA) to minimize possible damage of incoming gallium ions.

For the fabrication of the CDW devices, a long, narrow and flat quasi-1D crystal is placed on top of a sapphire substrate with preliminary deposited gold contacts. For nanoconstriction fabrication, the FIB is used to remove part of a crystal between two gold terminals (Fig. 1(a)).

C/N/C junctions were fabricated in two steps. In the first step the FIB is used to make a gap in the crystal (right part of Fig. 1(b)). In the second step the gap is filled in situ with platinum by FIB deposition (left part of Fig. 1(b)). In some cases additional platinum voltage terminals were attached to the crystal using FIB platinum deposition.

III. RESULTS

A. Nanoconstrictions

Damage during etching may have important consequences for the interpretation of the data. However, up to now we have not found any indication for serious damage to our samples due to FIB milling. For example, Shapiro step measurements on samples etched with the FIB still show complete mode-locking indicating their good quality. In addition, for NbSe$_3$ the resistance ratios, $RRR = R(300 \text{ K})/R(4.2 \text{ K})$, of etched sample parts are the same as the ones of unetched parts.

Reduction of the transverse sample sizes reveals interesting finite-size effect (Fig. 2). First of all, when the resistance per unit length, $\rho = R(300 \text{ K})/L$, of thin cleaved (none-etched) crystals of NbSe$_3$ exceeds 0.1 k$\Omega$/µm, the resistance ratio, RRR, starts to decrease. When $\rho$ approaches to 1 k$\Omega$/µm, the low-temperature metallic conduction ($dR/dT < 0$) converts into nonmetallic behavior ($dR/dT < 0$). Further reduction of the transverse sample sizes done by the FIB leads to further changes in the entire $R(T)$ dependence: disappearance of both Peierls transitions and appearance of a nonmetallic behavior which can be approximated by the power law, $R \propto T^{-\alpha}$, with $\alpha = 1 - 3$. Finally, the $R(T)$ curves of the thinnest crystals have nothing in common with the initial $R(T)$ of thick samples.

The inset in Fig. 2 shows a typical low-temperature I-V curve of a nanoconstriction. It is nonlinear and the nonlinear part can be approximated by the power
Transport measurements of C/N/C junctions have been done in a two-terminal configuration. Before a junction is fabricated into a crystal, the \( R(T) \) is measured and demonstrates the expected behavior for NbSe\(_3\). After fabrication of a metallic junction, the \( R(T) \) measurement exhibits a steep rise in resistance below 160 K, as illustrated in Fig. 3. At low temperatures the resistance increases dramatically and at \( T \sim 10\) K it has increased over 6 orders of magnitude when compared to the room temperature resistance. Below 100 K, the logarithm of conductance is a linear function of the logarithm of temperature (Fig. 3), i.e. \( G(T) \propto T^\alpha \). Among 10 studied C/N/C junctions, three exponents lies in the region \( 2.9 \leq \alpha \leq 3.4 \), and seven belong to the interval \( 5.5 \leq \alpha < 6.5 \).

Fig. 4 shows a typical temperature set of current-voltage characteristics (I-V curves) of a C/N/C junction. At temperatures above 100 K the I-V curves are linear. Upon cooling, the I-V curves become more and more nonlinear. Finally, at the lowest temperature studied, \( T = 10\) K, nonlinear growth of the conduction, \( G = I/V \), by four orders of magnitude is observed.

Four-terminal samples have been fabricated to investigate to what extent the interface between NbSe\(_3\) and platinum is important for the observation of behavior described above. For this purpose two platinum probes are deposited on top of the crystal surface by FIB deposition 40 \( \mu \)m apart of each other. At this stage temperature variations of the sample resistance have been measured to verify its character before junction fabrication. Then a junction is fabricated on some distance \( L \) outside this 40 \( \mu \)m region. The platinum probes are used as voltage probes in a four-terminal setup. It has been found that for \( L \geq 20 \) \( \mu \)m the junction fabrication does not affect the sample properties, whereas for \( L = 5 \) and 10 \( \mu \)m a rapid increase in resistance is observed when going down in temperature. These measurements rule out the possibility that the resistance growth is solely an interface phenomena. It was also found that both etching alone and deposition of platinum on the top of the crystal alone do not dramatically change the CDW properties of crystals as measured by electric transport. Thus, the resistance increase outside the junction region only occurs when the crystal has been etched through and platinum has subsequently been deposited.

**IV. DISCUSSION**

Our results show that quasi-one dimensional conductors with a CDW can demonstrate the temperature and electric-field dependent conduction expected for 1D systems. The electric properties of nanoconstrictions in NbSe\(_3\) reproduce quantitatively the results obtained for long thin crystals of NbSe\(_3\) \([3]\). The electric properties of C/N/C junctions reveal qualitatively the same type of behavior, but for much bigger transverse sizes of samples: 1D behavior is observed even in samples with a width of the order of 10 \( \mu \)m.

A quasi-1D conductor can be considered as a set of metallic chains with LL coupled by an interchain hopping \( t_\perp \). At \( T < t_\perp \) the LLs are unstable towards 3D coupling \([1]\), and the 3D ordered CDW may be formed. Reduction of the transverse sizes of quasi-1D conductors decreases the stiffness of the CDW. This results in growth of dynamic CDW fluctuations. In NbSe\(_3\) a growth of fluctuations is noticeable in thin samples with submicrometer transverse sizes \([4]\). At a critical transverse...
where \( \Gamma \) is the gamma-function, and \( C = 5 \times 10^{-20}, \gamma = 0.108, \alpha = 6, \beta = 4 \).

size, when the amplitude of fluctuation of a CDW phase difference between neighboring chains reaches a value of the order of \( \pi \), the stiffness of the shear deformation modes vanishes. This leads to destruction of the 3D order of the CDW, and the system starts to behave as a set of LLs, like it is expected in a sliding LL phase at sufficiently small \( t_{\perp} \). An additional contribution may come from static CDW disorder. Growth of static CDW fluctuations may result from an increase of the surface contribution, as well as from introduction of defects and impurities. In this case one can also expect frustration of the formation of a 3D-ordered CDW and recovery of LL properties. It has been argued that the power laws expected for LLs, survive for the sliding LL phase formed in 2D and 3D ordered chains of coupled LLs, at least in some range of \( t_{\perp} \).

If the scenario described above is correct, one could expect that the measured temperature dependencies of the linear resistance, as well as I-V curves, can be fitted by LL-like equations. According to Ref. [17], for a single-channel LL the temperature set of I-V curves collapses into a master curve described by:

\[
\frac{I}{T^{\alpha+1}} = C \text{sinh} \left( \gamma \frac{eV}{kT} \right) \left| \Gamma \left( 1 + \frac{\beta}{2} + i \gamma \frac{eV}{k\beta T} \right) \right|^2, \tag{1}
\]

where \( \Gamma \) is the gamma-function, and \( C \) and \( \gamma \) are the fitting parameters. One could expect that a similar equation, but with modified \( \alpha \) and \( \beta \), describes stacks of LLs. Fig. 4 shows the best fit of the data of Fig. 3 by Eq. 1 with \( C = 5 \times 10^{-20}, \gamma = 0.108, \alpha = 6, \beta = 4 \). Apparently, Eq. 1 describes the data well over the entire studied temperature and voltage range.

The conduction of a set of coupled LLs is provided by both tunneling along LLs through impurity barriers and tunneling between the chains with LLs. The conduction exponents are \( 1/g - 1 \) for impurity barriers, and \((g + 1/g - 2)/2 \) for interchain tunneling [13]. Both conduction channels are connected in parallel. The relative contribution of each conduction channel depends also on the strength of impurities, temperature and the electric field. As the resistance along the chains grows faster upon cooling than the resistance across the chains, interchain tunneling dominates at low temperatures.

It is interesting to compare the observed exponents with the predictions of LL theories. The biggest observed exponent is \( \approx 6 \). In the case of intrachain tunneling we get \( 1/g = 7 \). Taking \( 1/g = \sqrt{1 + U/2E_F} \) [12], where \( U \) denotes the potential energy of electron-electron interaction and \( E_F \) is the Fermi energy, one gets \( U \approx 100E_F \). As \( E_F \approx 1 \text{ eV in NbSe}_3 \) [10], the respective \( U \approx 10^2 \text{ eV} \) is too big (In the case of interchain tunneling, the discrepancy is even more dramatic). Similar discrepancies are observed if we use a more accurate way of estimating \( g \) [13]. In accordance with Ref. [15], to get \( \alpha \approx 6 \), we need \( k_Fd \approx 0.1 \), where \( d \) is the effective wire diameter, and \( k_F \) is the Fermi wave vector. As \( k_F = Q_{CDW}/2 = 0.45 \text{ Å} \), where \( Q_{CDW} \) is the CDW wave vector, the diameter \( d \approx 0.2 \text{ Å} \). Such an effective wire diameter is too small. Also for this estimation, an even more serious disagreement arises if we assume interchain tunneling as the dominant mechanism of conduction.

The observed disagreement with predictions of LL theory for a single chain may be caused by a renormalization of exponents by interchain interactions [15-16]. We would like to note that the CDW-like component of the electron density [19] — which is expected to be large in our quasi-1D crystals — can increase dielectrization. Additional dielectricization (especially for C/N/C junctions) may come from Friedel oscillations around impurity sites [20, 21]. Further study is necessary to clarify the origin of the observed behavior.

V. CONCLUSION

Our results show that quasi-1D conductors with a CDW ground state can demonstrate the temperature and electric-field dependent conduction expected for 1D systems. For FIB-etched thin crystals we reproduced results obtained earlier on thin un-etched crystals [13]. For C/N/C structures, the LL features are more pronounced: we observed power laws up to 6 orders of magnitude in conduction. The observed behavior corresponds to the destruction of 3D CDW ordering by fluctuations and the recovery of the Luttinger liquid features of metallic chains.

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