Quantum charge transport in Mo$_6$S$_3$I$_6$ molecular wire circuits

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Charge transport measurements on flexible Mo$_6$S$_3$I$_6$ (MoSI) nanowires with different diameters in highly imperfect 2-terminal circuits reveal systematic power law behaviour of the conductivity $\sigma(T,V)$ as a function of temperature and voltage. On the basis of measurements on a number of circuits we conclude that the behaviour in thin wires can be most convincingly described by tunneling through Tomonaga-Luttinger liquid (TLL) segments of MoSI wire, which is in some cases modified by environmental Coulomb blockade (ECB). The latter are proposed to arise from deformations or imperfections of the MoSI wires, which - in combination with their recognitive terminal sulfur-based connectivity properties - might be useful for creating sub-nanometer scale interconnects as well as non-linear elements for molecular electronics.

I. INTRODUCTION

While the transport properties of one-dimensional systems have been of great interest from the point of view of fundamental physics for some time$,^1$ recently, further interest in the transport properties of nano-scale one-dimensional systems was aroused because of their importance for the development of molecular electronics, where diverse molecular devices (switches, memory elements, sensors) all need to be self-assembled together with electrically conducting molecular-scale wires. To be of practical use, the connectors need to have reliable contacts and also be able to withstand mechanical deformations while retaining their conducting properties. Till now there has been no recognized material which could be used for this purpose, and this has seriously impeded progress in the development of large scale molecular electronics in recent years.

In this paper we investigate the transport properties of Mo$_6$S$_3$I$_6$ molecular wires$,^2$ which have been recently shown to be very promising flexible molecular-scale conductors. Mo$_6$S$_3$I$_6$ wires are air-stable one-dimensional inorganic cluster polymers (see Fig 1), which are unique in that they enable covalent bonding to gold surfaces and organic molecules via sulphur atoms at the ends of each molecular wire$.^3$ Single molecular wires were also recently shown to self-assemble gold particles into critical scale-free networks$.^4$ Such molecular wires may expect their electron transport properties to be governed by quantum properties on the microscopic level. Thus, to make further progress in molecular electronics with MoSI connectors, we must first investigate and understand their molecular scale electronic transport properties. Earlier experimental work has shown metallic signatures, such as a low-frequency Drude response in the optical conductivity$,^5$ but relatively low room temperature conductivities $\sigma \approx 10$ S/m, which decrease with decreasing temperature$.^6$ Recently Venkataraman, Hong and Kim$^7$ described electron transport measurements in multichannel Li$_2$Mo$_6$Se$_6$ nanowires with diameters in the range 7.2 to 12 nm in terms of a Tomonaga-Luttinger liquid (TLL) in contact with Fermi liquid (FL) electrodes. In another related material NbSe$_3$, nanowires ranging between 30 and 300 nm in diameter have been observed to display similar power-law behaviour, albeit over a rather limited range of temperature$.^8$ The extreme one-dimensional nature of the MoSI wires suggests that signatures of TLL behaviour might also be observed in thick multi-strand bundles, and not only in very thin wires. On the other hand, we may expect that the electronic transport properties in MoSI wires might depart from ideal TLL behaviour because of the deformable nature of the S bridges which link together the Mo$_6$ clusters into 1D chains$.^9$

Figure 1: The Structure of Mo$_6$S$_3$I$_6$ wires. The axes are in the frame of the monoclinic space group $P2_1$ with center-to-center distance of $d_0 = 0.958$, and the unit cell length $c = 1.197$ nm. The S atoms linking the Mo clusters form accordion-like deformable bridges and are shown in yellow, while the orange and violet spheres represent I and Mo respectively.

In this paper we present a systematic study of MoSI wires of different diameter from 4 nm to 1000 nm, examining the $T$-dependence, diameter dependence and current-voltage characteristics at different temperatures.
We are particularly interested in the behaviour of realistic circuit configurations, with irregular wire geometries. The intrinsic flexibility of the MoSI wires, arising from their accordion-like structure means that they bend easily to conform to surface contours. We have therefore focused on dielectrophoretically deposited thin wires over contacts in which the wires conform to the surface relief.

Considering the possible transport mechanisms, we confine ourselves to the common ones discussed in literature namely TLL tunneling environmental Coulomb blockade (ECB) and variable range hopping (VRH) in the presence of Coulomb charging effects.

1. The $T$– and $V$– dependence for tunneling into a 1D TL liquid via Fermi-liquid metal contacts is given by:

$$I = I_0 T^{1+\alpha} \sinh \left( \frac{\gamma eV}{2kT} \right) \Gamma \left( 1 + \beta + \frac{\gamma eV}{2\pi kT} \right)^2$$

where $\alpha = (g^{-1} - 1)/4, \beta = (g + g^{-1} - 2)/8$ and the Luttinger parameter $g = v_F/v_p$. $\gamma$ is a fitting parameter that accounts for the voltage drop over the circuit. A collapsed diagram of the underlying transport characteristic is obtained by plotting $I/T^{1+\alpha}$ against $eV/kT$, where $\alpha$ is the slope of zero voltage conductivity against temperature $\sigma = \sigma_0 T^\alpha$. $\beta$ is the exponent for the high voltage limit ($eV \gg kT$) arising from the power law behavior $I \propto V^{\beta+1}$.

2. Unfortunately ECB models cannot be solved analytically for the general case, but the asymptotic behavior is very characteristic. The experimentally obtainable low-temperature behaviour is given by:

$$\sigma_{T \to 0, V \to 0} = \left( \frac{2}{g} + 1 \right) \frac{e^{-2gV/2}}{\gamma(2+2/g)} \frac{1}{\sigma_0} \frac{R_T}{g E_C} \left( \frac{\pi e|V|}{g E_C} \right)^{\frac{1}{3}}$$

where $E_C$ is the charging energy, $g = G_0/G, G$ is the frequency-independent conductance, $G_0 = 2e^2/h$ and $R_T$ is the tunneling resistance. For low voltages and temperatures the current follows a power law behavior $I \propto V^{2/9}$. For high voltages (but low temperatures),

$$I(V) = \frac{1}{R_T} \left[ V - \frac{e}{2C} + \frac{g e^2}{4\pi^2 V^2} \right]$$

which gives a linear $I$– $V$ dependence at high $V$, so the derivative $dI/dV$ is expected to approach an asymptotic constant value of $1/R_T$. It also gives a non-zero intercept for $I = 0$ given by the charging energy $e^2/2C$.

3. For the variable range hopping mode, a plot of $\ln(G)$ (for low voltage) against $T^{-\lambda}$ yields curves which become linear with the correct hopping exponent $\lambda$. The fits to the data typically give a large error in the exponents, so to extract the best value of $\lambda$, fits to the data are tested statistically by calculating Pearson’s correlation coefficients.

Rather than choosing a few measurements which obey one or another type of behaviour, we present here a summary of a number of experiments, to try and understand the different types of behaviour that can arise in nanoscale circuits with MoSI wires.

**II. EXPERIMENTAL DETAILS**

The thin wires were prepared according to the method reported by Nicolosi et al by repeated dispersion and dilution. The dispersion procedure separates the wires into two distinct categories: thin wires, with diameters $4 < D < 10$ nm and thick multichannel bundles with $100 < D < 1000$ nm. In the ultrasonic bath processing procedure, the defective wires break up into shorter segments, leaving less defective long thin wires in solution. The individual strands within the thin wires may thus be expected to have significantly fewer imperfections than within the thick bundles, which may result in different electron transport behaviour in thick and thin wires. This should be evident in the room temperature conductivity ($\sigma_{300K}$) as well as the $T$-dependence and $I$– $V$ systematics.

The wires were dielectrically deposited typically over nickel electrodes prepared by electron beam lithography by placing a drop of solution over the electrodes and applying a $50$Hz AC electric field to the electrodes. The entire circuits were then annealed in vacuum at 700 C for an hour. The circuits after annealing are shown in Figure 2. Typical resistances of the nanowires at room temperature were between 100kOhm, 100MOhm. Care was taken to ensure good thermal contact of the sample with the cryostat cold finger.

**III. EXPERIMENTAL RESULTS AND ANALYSIS**

**Thin wires**

Two thin wire circuits labeled na27 and na23 (shown in Fig. 2) illustrate the most common type of behaviour observed in a number of measured circuits with diameters ranging from $d \sim 4$ to $15$ nm. The room-temperature conductivity $\sigma_{300K}$ for na27 and na23 was $3710$ S/m and $11900$ S/m respectively. Their $I$– $V$ characteristics at temperatures between 18 K and 300K are shown in Figs.3a) and 4a) and exhibit qualitatively different
behaviour. In the case of sample na27, the I-V curves show characteristic inverted S-shaped curves whose curvature is strongly T-dependent. In contrast, circuit na23 shows a clear J-like shape characteristic. (Other circuits we have measured show behaviour in between these two extremes\cite{12}). The T-dependence of the conductance $G = dI/dV$ at $V = 0$ is shown in Figs. 3b) and 4b). The line is a fit to a power law $G = G_0 T^\alpha$ where $\alpha = 2.3$ and 3.5 respectively. The data follow the power law fit reasonably well, but do not give a perfect fit over the entire range of T. Plotting the entire data set $I/T^{\alpha+1}$ against $eV/kT$ according to the TLL prediction, for na27 we see that the data collapse quite well onto a single curve (Fig. 3c), whereas for na23 the data collapse is less satisfactory. (Overall, approximately half our circuits showed the TLL collapse.)

Attempting to fit the ECB model to the data, we would expect the $I/V$ slope to cross over from $\sim 2/g$ at low voltages to $1/R_T$ at high voltages. Correspondingly, the derivative $dI/dV$ should show a systematic $T$-
Figure 5: The derivatives $dI/dV$ obtained from the I-V data plotted in Figs. 3a) and 4a) for circuits a) na23 and b) na27 at different temperatures. The derivative at low $V$ increases in both cases, as $T$ increases from 18K to 300K.

Figure 6: I-V characteristic of sample circuits a) na23 and b) na27 at different temperatures.

**Thick bundles**

A ubiquitous feature of the thick wire bundles ($d = 100 \sim 1000$) is their linear I-V characteristic from 18K to 300K. The room temperature conductivity $\sigma_0$ is typically 3 orders of magnitude smaller than for the thin wires, around 1-10 S/m. This is taken as a clear indication that only a small fraction $f$ of the molecular strands in the bundle contribute to the transport. Confirming earlier preliminary measurements, the $T$-dependence was not very well described by a 1D VRH model. The new systematic data on many circuits now confirms this. The dependence of the conductivity is shown in Figure 7 for a number of bundles of different diameter. Surprisingly, the data for the different bundles all appear to follow power-law behaviour $\sigma = \sigma_0 T^\alpha$ quite well. Moreover, a systematic trend is observed, whereby the larger diameters have a smaller exponent $\alpha$, an indication that the numbers of conducting channels scales with diameter (Figure 8).
The present set of experiments shows a rather wide range of behaviour, suggesting caution in trying to interpret the data by any single model. Discussing the simple VRH model first, our fits give 3D exponents, which is clearly inconsistent with the nature of the system investigated here and is dismissed from further discussion. The calculation of Fogler et al. considered a quasi-1D wire with a finite density of impurities modeled by a series of weakly coupled quantum dots. They predict power law behaviour of the current for both T and V, as \( I \propto V^{\beta+1} \) at high V and \( I \propto T^\alpha V \) at low V with \( \alpha \gg \beta \gg 1 \). The model holds for a large number of parallel statistically independent conduction channels, where power laws are not obscured by the fluctuations of G. This case is fulfilled here for thick wires, with bundle diameters between 100 nm and 1 \( \mu \)m might have \( 10^4 \) to \( 10^6 \) conducting channels. However, the prediction that \( \beta \gg 1 \) is not fulfilled here for either the thin or the thick multichannel bundles, suggesting that this model may not be applicable for describing MoSI circuits.

In circuit na27 the TLL prediction can be confirmed with some degree of confidence by the collapsed plot of \( 1/T^{\alpha+1} \) vs. \( eV/kT \). For tunneling from a Fermi liquid into a perfect TLL without defects, the model prediction is that \( \alpha = \beta \). Imperfections, such as deformations and kinks or stoichiometric defects break up the wire into TLL segments, which introduces TLL-TLL tunneling between these segments \( \beta \) for which the predicted ratio changes to \( \alpha = 2\beta \). The measured value for na27 is \( \alpha/\beta = 1.45 \pm 0.1 \). A similar circuit with a wire diameter of 5 nm (na12, not shown) gives a near-identical collapse as na27 with \( \alpha/\beta = 2.00 \pm 0.1 \).

The exponent \( \alpha \) for a N-channel wire is given by TLL theory\(^{19} \) as:

\[
\alpha = \frac{2}{N}\sqrt{\frac{2N}{g^2}} - 1,
\]

where \( g \) is the electron-electron interaction parameter. The number of conducting channels \( N \) in a nanowire of diameter \( d \) can be written as \( N = 2fD^2/t^2 \), where \( a \) is the lattice constant, and \( f \) is the fraction of molecular wires which actually carry current without interruption. For circuit na27, using \( f = 1, \alpha = 2.3, \) and \( N = 16 \) channels (for \( d = 4 \) nm), we calculate \( g = 0.21 \). This is slightly larger than the value 0.15 obtained by Venkataraman et al for Li\(_2\)Mo\(_2\)Se\(_6\) nanowires. Other wires which we have measured have \( \alpha \) between 2 and 3.5, giving a range of \( 0.09 < g < 0.27 \). Comparing this with \( g \) estimated from materials parameters, we can use the expression from the Coulomb charge screening model\(^{19} \) \( g^2 = v_F R_0 C_0 \), where \( v_F = 7 \times 10^6 \) m/s is the Fermi velocity calculated by DFT calculations, \( R_0 \) is the resistance quantum and the single wire capacitance per unit length is \( C_0 = 2\pi\epsilon\epsilon_0/ln[4t/\delta_0] \). Using \( \epsilon_\tau = 3.9 \) for the Si oxide layer of thickness \( t = 600 \)nm, we obtain \( g = 0.49 \). In this estimate, the DFT value of \( v_F \) is likely to be overestimated, which may account for a large part of the discrepancy between the values obtained directly from the measurements. It has also been noted previously that the static Coulomb screening model overestimates \( g \).

The data in Figure 8 for the thick wires can be fit using the expression (4). A range of values of \( g \) can be obtained from the fits to the present data, \( 0.1 < g < 0.5 \) with corresponding filling factors \( 10^{-5} < f < 10^{-4} \). Values outside this range of \( g \) cannot be made to fit the data. However, since the \( I-V \) characteristics are ubiquitously linear, for the thick wires, this in itself cannot be taken as proof for TLL behaviour.

**Figure 7:** The normalized conductance \( G/G_0 \) of a large number of thick wires, with \( d = 200 \sim 2000 \) nm. In two measurements, a break is observed, which is believed to be strain-induced change in the number of conducting channels.

**Figure 8:** The dependence of the temperature exponent \( \alpha \) of thick wires on bundle diameter \( d \) from the data in Fig. 7.
The low value of $\sigma_0$ in thick wires is assumed to be related to imperfections on the wires. It suggests that the transport along the wires is dominated by tunneling between TLL segments. In fact the resistance of both thick and thin wires is typically of the same order of magnitude, which suggests that in the thick bundles only a very small number of wires are uninterrupted, or that only strands on the outside of the bundle are conducting, with the inner strands being unreachable due to the extremely small perpendicular inter-molecular hopping rates within each wire.

Turning to the case of na23, which shows clear characteristics of ECB behaviour, the intercept of the $I-V$ curve at $I = 0$ gives $V = \frac{e\sigma}{2}\approx 0.15\text{V}$ and consequently $C \approx 5.3 \times 10^{-19}\text{F}$. Comparing this QDOT capacitance with an estimate of $C$ for a single wire over a Si ground plane with a 600 nm SiO$_2$ insulating layer and length $L = 265\text{nm}$ between contacts, we have $C \approx 8 \times 10^{-18}$, for na23. Depending on what we assume for the QDOT shape, its size appears to be some fraction ($\sim 1/10$) of the distance between the electrodes.

Considering the possible origin of the ECB behaviour and the observed departures from the predicted TLL characteristics, we can imagine imperfections and breaks of continuity in the wires of diverse origin. The most obvious and unavoidable effect arises from the deformation of the nanowires adapting to the relief of the contacts (Figure 2). Their inherent flexibility allows for a substantial deformation, which is accompanied by significant changes in electronic structure near the Fermi energy. We can thus envisage that the deformations can lead to breaks in the continuity of individual channels, and as a result the formation of a QDOT in between the breaks. In this case the ECB capacitance would scale with the distance between electrodes. Another effect, which might be important arises from the intrinsic tendency of the wires to form discontinuities in the structure, as shown in the HRTEM image in Figure 5 a). Clear stripes are sometimes observed across the wire bundles, which arise from from stacking faults which appear during the growth process. Indeed such compositional ordering has been recently theoretically predicted. HRTEM diffraction analysis shows that the structure of the wire is identical on both sides of the fault, but clearly continuity is broken at these points. Sections in between the faults may thus act as QDOTs, leading to the ECB behaviour we observe. Considering that the distance between faults may be a few tens of nanometers, the comparison of QDOT capacitance with the static capacitance calculated in the previous paragraph suggests this effect may also be important.

V. CONCLUSION

One of our objectives has been to determine how imperfect, bent and deformed MoSI wires might behave in molecular-scale circuits such as may form upon self-assembly. It is clear from the present experiments that quantum transport dominates their behaviour. The TLL model with its characteristic data collapse of the $I-V$ characteristics at different temperatures appears to hold well for a significant proportion of the thin wire circuits. At the same time clear signatures of the ECB predicted J-shaped $I-V$ curves are also occasionally observed. Discontinuities in the wires either as a result of bending, and/or structural stacking faults within the wire are believed to cause the formation of QDOTs, which lead to the occasional occurrence of ECB behaviour. The diameter of the present MoSI wire bundles is small enough to allow covalent S bonding to individual molecules, so for the construction of molecular scale circuits, where thin and relatively short wires are of interest, they may potentially revolutionize molecular electronics. A point of interest is the possibility of making variable sizes of QDOTs with MoSI wires by stretching them over appropriately sized regular topological features to produce arrays of QDOTs. The other possibility of creating single QDOTs by using the tip of an atomic force microscope, was already recently demonstrated.

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1 J. Voit, Reports on Progress in Physics 58, 977 (1995) and references within.
2 D. Vrbanić et al., Nanotechnology 15, 635 (2004), for a review, see: D. Mihailovic, Rep. Materials Science 54, 309 (2009)
3 I.M. Ploscaru, S. Jenko Kokalj, M. Uplaznik, D. Vengust, D. Turk, A. Mrzel, D. Mihailovic, Nanoletters, 7, 1445 (2007).
4 J. Strle, D. Vengust and D. Mihailovic, Nano Letters 9, 1091 (2009)
5 D. Vengust, F. Pfumer, L. Degiorgi, I. Vilfan, V. Nicolosi, J.N. Coleman, D. Mihailovic, D.D., Physical Review B: Condensed Matter, 76, 075106 (2007)
6 M. Uplaznik, B. Bercic, J. Strle, M.I. Ploscaru, D. Dvorsek, P. Kusar, M. Devetak, D. Vengust, B. Podobnik, D. Mihailovic, Nanotechnology, 17, 5142 (2006), B. Bercic et al Appl. Phys. Lett. 88 173103 (2006)
7 L. Venkataraman, Yeon Suk Hong, P. Kim, Phys. Rev. Lett., 82, 4918 (1999).
8 E. Slot, M.A. Holst, H.S.J. van der Zant, S.V. Zaitsev-Zlotov, Physical Review Letters, 93, 176602 (2004).
9 I. Vilfan, D. Mihailovic, Physical Review B, 74 235411 (2006)
10 Nicolosi et al., Adv Mater 19, 543 (2007)
11 T. Meden et al, Nanotechnology 16, 1578 (2005)
12 M.C. Bockrath, H. David, J. Lu, A. Rinzler, R.E. Smalley,
L. Balents, P/I McEuen, Phys. Rev. Lett., Nature, 397, 596 (1999).
13 H. Grabert, M.H. Devoret, NATO ASI Series B, 294, (1992)
14 V. Nicolosi, D. Vrbanic, A. Mrzel, J. McCauley, S O’Flaherty, C. McGuinness, G. Compagnini, D. Mihailovic, W.J. Blau, J.N. Coleman, The Journal of Physical Chemistry. B, 109 7124 (2005)
15 M.M Fogler, S. Teber, B.I. Shklovskii, Physical Review. B, 35 035413 (2004)
16 K.Matveev and L.Glazman, Phys.Rev.Lett. 70, 990, (1993)
17 M.Uplaznik, PhD Thesis, Univ. of Ljubljana (2009)
18 A.Hassanian et al., Physica E 29, 684 (2005), H.W.Ch.Postma et al, Science 293, 76, (2001)
19 Popov et al. Phys. Rev. Lett. (2007) 99 085503 (2007)
20 T.Yang, S.Berber and D.Tomanek, Phys. Rev. B 77,7 (2008)