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Molybdenum Selenide Molecular Wires as One-Dimensional Conductors

Latha Venkataraman¹ and Charles M. Lieber^{2,*}

¹*Department of Physics, Harvard University, Cambridge, Massachusetts 02138*

²*Department of Chemistry and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138*

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Scanning tunneling microscopy (STM) has been used to characterize the structure and electronic properties of molybdenum selenide (Mo_6Se_6) molecular wires. STM images resolve the 0.45 nm unit cell repeat in isolated molecular wires and bundles of wires. Tunneling spectroscopy measurements exhibit sharp peaks in the local density of states that are consistent with the Van Hove singularities expected for a one-dimensional (1D) system. These data have been compared with previous band structure calculations. Preliminary measurements at 5 K show no evidence of a gap opening at low temperatures. The implications of these results to metal-insulator transitions in 1D systems are discussed.

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Quantum wires, such as nanowires and nanotubes, are attracting considerable attention for exploring physics in one-dimensional (1D) systems and as building blocks for nanoscale electronic devices [1,2]. Scanning tunneling microscopy (STM) studies of single-walled carbon nanotubes (SWNTs) have shown that the metallic or semiconducting properties of SWNTs can be related to their diameter and helicity and have observed [3,4] and quantitatively explained [5] Van Hove singularities (VHS) in the density of states arising from the 1D SWNT band structure. In addition, transport studies of SWNTs have demonstrated the existence of extended electronic states [6,7] and have recently provided intriguing evidence for Luttinger liquid behavior [8]. Despite these advances, the structural and corresponding electronic diversity of SWNTs have complicated the interpretation of transport studies. For example, it is necessary to make *ad hoc* arguments about the number or metallic SWNTs within the ropes of tubes typically probed in transport experiments.

It should be possible to obtain additional understanding of the behavior of 1D materials, if one could probe samples in which each quantum wire was identical. A strategy for achieving this ideal involves the disassembly of quasi-1D crystals into molecular wires. Because these wires correspond to the chains that pack together to form a crystal, they will be structurally and electronically identical. Herein, we report the first STM studies on molecular wires prepared in this way by the dissolution of crystals of the quasi-1D material $\text{Li}_2\text{Mo}_6\text{Se}_6$. The structure of $\text{Li}_2\text{Mo}_6\text{Se}_6$ consists of hexagonal close packed chains of Mo_6Se_6 clusters separated by Li, with the Mo_6Se_6 chains made of staggered stacks of triangular Mo_3Se_3 units [Fig. 1(a)] [9,10]. $\text{Li}_2\text{Mo}_6\text{Se}_6$ dissolves in polar organic solvents yielding subnanometer wide molecular wires and larger bundles containing multiple wires [11]. Our STM images show clearly isolated molecular wires and bundles of wires and resolve the 0.45 nm Mo_6Se_6 unit. Tunneling spectroscopy measurements

made on the atomically resolved wires exhibit sharp peaks in the normalized conductance that are consistent with the Van Hove singularities expected for this 1D system. Comparison of the normalized conductance data to previous band structure calculations [12,13] shows agreement with the overall features but also differences. Last, low-temperature STM measurements suggest that these molecular wires do not undergo a Peierls transition and remain metallic to at least 5 K.

Crystalline $\text{Li}_2\text{Mo}_6\text{Se}_6$ was prepared as described previously [9,10]. The structure and composition were

FIG. 1. (a) Structural model of a Mo_6Se_6 (MoSe) molecular wire based on the $\text{Li}_2\text{Mo}_6\text{Se}_6$ crystal structure [9,10]. (b) Tapping mode atomic force microscopy (AFM) image of a MoSe wire deposited on a cleaved mica surface from methanol solution. The white scale bar corresponds to 1 μm . Inset: Section across the sample at the position of the white line. The width of the section is much larger than the height due to the convolution of the AFM tip.

confirmed by x-ray diffraction and energy dispersive x-ray fluorescence, respectively. LiMo_3Se_3 crystals were dissolved in anhydrous dimethylsulfoxide, acetonitrile, and methanol in a nitrogen filled glove box ($[\text{O}_2] \sim [\text{H}_2\text{O}] < 1$ ppm) to produce 10^{-4} – 10^{-6} M solutions [14]. Samples for STM studies were prepared by depositing a drop of dilute solution on Au(111)/mica [4] or highly oriented pyrolytic graphite (HOPG) substrates within the glove box. Samples were transferred to the load-lock chamber of the ultrahigh vacuum STMs in a “suitcase” without exposure to air. The room temperature and low temperature STM data were acquired with commercial (Omicron) and homebuilt systems, respectively, using electrochemically etched tungsten tips. Details of imaging, spectroscopy, and data analysis have been described previously [4,5,15].

A typical AFM image of a molybdenum selenide (MoSe) molecular wire deposited from solution is shown in Fig. 1(b). The wirelike structure in this image has a diameter of 1 nm and a length exceeding $5\ \mu\text{m}$. Based on the 0.85 nm diameter of a single wire [Fig. 1(a)], we conclude that this structure corresponds to one or at most several molecular wires. Despite the small diameter of MoSe molecular wires, we find that they maintain a well-defined linear structure over considerable (micron) lengths like SWNTs. Our AFM studies also show that larger diameter MoSe molecular wire bundles (up to and exceeding 15 nm) can be produced by increasing the solution concentration used for deposition. These latter results are consistent with previous TEM studies [11].

STM has been used to obtain atomically resolved images and spectroscopy data on isolated MoSe molecular wires and bundles of wires (Fig. 2). A typical STM image of an isolated single MoSe chain [Fig. 2(a)] exhibits a 0.45 ± 0.01 nm lattice repeat that is in good agreement with the 0.448 nm *c*-axis constant for the bulk material [9]. The measured 0.53 ± 0.07 nm width of this single chain is smaller than the diameter calculated from the crystal structure but is consistent with the fact that the Mo core of the wire is expected to make a dominant contribution to images for moderate bias voltages [12,13]. It is interesting to note that the conduction electrons in individual MoSe molecular wires are confined to a significantly smaller diameter than SWNTs, and this could lead to stronger electron-electron interactions within chains. Atomically resolved images have also been obtained on bundles of wires [Fig. 2(b)], and these data show a unit repeat, 0.45 ± 0.01 nm, consistent with our single wire measurements and the bulk crystal. In general, the wires are quite stable in these experiments; however, wires can be cut by moving the tip close to the surface while scanning perpendicular to the long axis or by applying bias pulses. Although not the focus of this paper, it was possible to make wire fragments as small as several unit cells [Figs. 2(c) and 2(d)] that we believe offer a number of exciting prospects, such as

FIG. 2. STM height images, obtained in constant current mode, of MoSe chains deposited from methanol or acetonitrile solutions of $\text{Li}_2\text{Mo}_6\text{Se}_6$ on an Au(111) substrate at 298 K. (a) A single chain imaged at a sample bias of 0.8 V and a tunneling current of 50 pA (scale bar is 1 nm), and (b) a MoSe wire bundle imaged at a sample bias of 0.75 V and a tunneling current of 50 pA (scale bar is 5 nm). (c) and (d) Images of MoSe wire fragments containing 5 (0.8 V, 50 pA) and 3 (0.5 V, 150 pA) unit cells, respectively; the scale bars are 1 nm.

exploring the evolution from an isolated cluster to a periodic 1D system.

Central to the focus of this paper is our ability to obtain reproducible tunneling spectroscopy data on atomically resolved MoSe molecular wires (Fig. 3) [15]. Typical current vs voltage, I - V , and normalized conductance, $(V/I)dI/dV$, results obtained on a wire deposited on a Au(111) substrate show clear steplike features and sharp peaks, respectively [Fig. 3(a)]. These peaks are suggestive of the VHS in the density of states expected for a 1D system, since the normalized conductance provides a good measure of the local density of electronic states (LDOS) [3–5]. Examination of $(V/I)dI/dV$ shows a region of low LDOS around the Fermi level (E_F) sharp band edges at ca. +1.2 and –0.2 eV. Data recorded on the Au(111) substrate before and after measurements on the wire were featureless and thus show that this sharp structure is intrinsic to the MoSe molecular wires. Tunneling spectroscopy data recorded on MoSe wires deposited on HOPG [Fig. 3(b)] show the same overall features in the normalized conductance, although the peaks are typically broadened compared to data obtained from Au(111). This broadening may reflect variations in the wire-substrate coupling. We believe that the similarity in the positions of the band edges obtained

FIG. 3. I - V data (inset) and normalized conductance of MoSe wires deposited on (a) Au(111) and (b) HOPG. The features in (b) are not as sharp as in (a) but the positions of the peaks are the same. The data in (a) and (b) were recorded at 298 K. The approach of $(V/I)dI/dV$ to 0 at voltage limits in (b) is an artifact of the data treatment. (c) Density of states (DOS) calculated from the band structure of [13,16] showing a 1.8 eV separation between the first VHS arising from bonding and antibonding d bands.

from measurements on the two distinct substrates provides further support that these LDOS features are an intrinsic property of the MoSe molecular wires. The observation of sharp peaks in the LDOS of bundles indicates that there is weak interwire coupling [17]. Last, we find the same overall structure in the LDOS obtained on single wires and large bundles, although it was not possible to sample as large voltage ranges on single chains due to the voltage-induced cutting described above.

In general, singularities in the DOS are a signature of the electronic structure of 1D materials. The peaks in our spectroscopy data [Figs. 3(a) and 3(b)] are suggestive of this expectation. To provide a more quantitative support, we have compared the measured LDOS for MoSe molecular wires to the DOS calculated from published band structures [12,13,16] [Fig. 3(c)]. In both the measured and calculated DOS, there is a region of low DOS around E_F and sharp DOS peaks—singularities—

in the occupied and unoccupied states. The region of low DOS corresponds to a single wide Mo d_{xz} band (with the z axis oriented along the chain), which spans the first VHS between the bonding and antibonding Mo d bands. Our data show a measured separation, ca. 1.4 eV, that is significantly closer to the calculation in [13], 1.7 eV, than that in [12], 0.8 eV.

We have also compared the position of E_F relative to the band edges and find a reproducible shift compared to calculations. The observed shift could correspond to either charge transfer to the substrate, partial wire oxidation, or inaccuracies in the band calculations. Because the position of E_F in our data is independent of substrate, the latter two possibilities may be more likely. In this regard, it is interesting that our integration of the calculated DOS up to the experimental E_F corresponds to a loss of one electron per MoSe unit. This analysis suggests that the solvated $\text{Li}^+/\text{Mo}_3\text{Se}_3^-$ chains may undergo oxidation and be better described as neutral Mo_3Se_3 units in our experiments. Future studies will be required to better understand this point, although we note that both forms (i.e., Mo_3Se_3^- and Mo_3Se_3) are expected to be 1D metals.

Last, we have carried out preliminary studies of MoSe molecular wires at low temperatures to investigate the possibility of Peierls metal/insulator (M/I) transition, which is often observed in quasi-1D crystals [18]. First, atomically resolved images of single wires and small bundles recorded at 77 and 5 K show no differences in the lattice constant and periodicity, which would reflect a charge density wave state. Second, low [Fig. 4(a)] and high [Fig. 4(b)] resolution spectroscopy data exhibit no evidence of an energy gap at 5 K. These data show that neither individual MoSe molecular wires nor small MoSe wire bundles undergo a M/I transition above 5 K. We believe that the absence of a M/I transition is not surprising, since fluctuations should suppress the Peierls transition temperature in single wires or in bundles with weak interwire coupling below that expected from mean field theory [19]. We are currently carrying out transport measurements on the MoSe molecular wires to investigate further this interesting issue.

In summary, we have shown that disassembly of $\text{Li}_2\text{Mo}_6\text{Se}_6$ crystals provides a source of molecular wires that can be used to probe the physics of metallic 1D systems. STM measurements have shown that single MoSe molecular wires, which are significantly smaller in diameter than SWNTs, bundles of MoSe wires, and very small single wire fragments can be imaged with atomic resolution. Tunneling spectroscopy studies of the wires show sharp peaks in the LDOS that are characteristic of the singularities expected for 1D materials. The measured peaks in the LDOS also have been shown to compare to overall features of two independent calculations, although additional work will be required to resolve differences. Last, low-temperature STM measurements have shown that the structure and LDOS of MoSe molecular wires

FIG. 4. (a) Low resolution and (b) high resolution I - V and normalized conductance data recorded on a MoSe wire at 5 K; the substrate was Au(111). The high-resolution data was recorded after advancing the tip closer to the wire to improve the signal to noise in the current. The variation in $(V/I)dI/dV$ in (b) corresponds to noise.

do not depend on temperature down to 5 K, suggesting that fluctuations intrinsic to nearly ideal 1D conductors suppress the Peierls M/I transition. We believe that these MoSe molecular wires represent a unique and exciting system for future study and hope that this work will stimulate further experimental and theoretical investigations.

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*Electronic address: cml@cmliris.harvard.edu

- [1] C. Dekker, *Phys. Today* **52**, No. 5, 22 (1999).
- [2] C.M. Lieber, *Solid State Commun.* **107**, 607 (1998); J. Hu, T.W. Odom, and C.M. Lieber, *Acc. Chem. Res.* **32**, 435 (1999).
- [3] J.W.G. Wildoer, L.C. Venema, A.G. Rinzler, R.E. Smalley, and C. Dekker, *Nature (London)* **391**, 59 (1998).
- [4] T.W. Odom, J.L. Huang, P. Kim, and C.M. Lieber, *Nature (London)* **391**, 62 (1998).
- [5] P. Kim, T.W. Odom, J.L. Huang, and C.M. Lieber, *Phys. Rev. Lett.* **82**, 1225 (1999).
- [6] S.J. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerligs, and C. Dekker, *Nature (London)* **386**, 474 (1997).
- [7] M. Bockrath, D.H. Cobden, P.L. McEuen, N.G. Chopra, A. Zettl, A. Thess, and R.E. Smalley, *Science* **275**, 1922 (1997).
- [8] M. Bockrath, D.H. Cobden, J. Lu, A.G. Rinzler, R.E. Smalley, L. Balents, and P.L. McEuen, *Nature (London)* **397**, 598 (1999).
- [9] M. Potel, R. Chevrel, M. Sergent, J.C. Armici, M. Decroux, and O. Fischer, *J. Solid State Chem.* **35**, 286 (1980); J.M. Tarascon, G.W. Hull, and F.J. DiSalvo, *Mater. Res. Bull.* **19**, 915 (1984).
- [10] W. Hönlé, H.G. von Schnering, A. Lopka, and K. Yvon, *J. Less-Common Met.* **71**, 135 (1980).
- [11] J.M. Tarascon, F.J. DiSalvo, C.H. Chen, P.J. Carrol, M. Walsh, and L. Rupp, *J. Solid State Chem.* **58**, 290 (1985); J.H. Golden, F.J. DiSalvo, and J.M.J. Fréchet, *Chem. Mater.* **7**, 232 (1995); J.H. Golden, F.J. DiSalvo, J.M.J. Fréchet, J. Silcox, M. Thomas, and J. Elman, *Science* **273**, 782 (1996).
- [12] T. Hughbanks and R. Hoffman, *J. Am. Chem. Soc.* **105**, 1150 (1983).
- [13] P.J. Kelly and O.K. Andersen, in *Superconductivity in d- and f-Band Metals*, edited by H. Sohl and M.B. Maple (Academic Press, New York, 1982), p. 137.
- [14] TEM and STM studies showed that MoSe wires from dimethylsulfoxide solutions were contaminated with solvent, and thus the data presented were from either acetonitrile or methanol solutions of $\text{Li}_2\text{Mo}_6\text{Se}_6$. Single molecular chains were routinely observed for samples deposited from dilute (10^{-6} M) solutions, while thicker bundles of wires were produced from more concentrated solutions. Atomically resolved STM images were independent of tunneling current, 50–200 pA, and bias voltage, [300] to [800] mV.
- [15] Each plotted I - V curve is an average of 5–9 curves taken at a specific position on the wire with each curve containing 1024 points. dI/dV was obtained by numerically differentiating the averaged I - V data. The I - V data were sometimes smoothed prior to differentiation, although we were always careful to check that smoothing did not introduce (or remove) features. The normalized conductance was obtained by dividing the derivative by I/V . This method of normalization is valid in metallic systems like MoSe. Close to $V = 0$ we divided dI/dV by a polynomial fit to I/V to avoid the singularity at $V = 0$. Similar results were obtained at many different locations on the wires.
- [16] The DOS were calculated from the published energy band diagrams [12,13] by summing the energy levels at every energy, E . The summation was carried out numerically for 1000 k points between the Γ and $k = 2\pi/c$ points.
- [17] Because bundles are formed by the aggregation of wires in solution, it is likely that they pack more loosely than the crystal, for example, due to solvent inclusion.
- [18] G. Gruner, *Rev. Mod. Phys.* **60**, 1129 (1988).
- [19] In the limit of a pure 1D wire, fluctuations will suppress the transition to 0 K. Coupling of the MoSe wires to the substrate may influence the details of the M/I transition; however, we expect qualitatively that this coupling will reduce fluctuations (raising the transition temperature) and not suppress the transition.