Anomalous Conductance Oscillations and Half-Metallicity in Atomic Ag-O Chains

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Using spin density functional theory, we study the electronic and magnetic properties of atomically thin, suspended chains containing silver and oxygen atoms in an alternating sequence. Chains longer than 4 atoms develop a half-metallic ground state implying fully spin-polarized charge carriers. The conductances of the chains exhibit weak even-odd oscillations around an anomalously low value of $0.1 G_0$ ($G_0 = 2e^2/h$) which coincide with the averaged experimental conductance in the long chain limit. The unusual conductance properties are explained in terms of a resonating-chain model, which takes the reflection probability and phase shift of a single bulk-chain interface as the only input. The model also explains the conductance oscillations for other metallic chains.

Atomically thin metallic chains can be formed by pulling a metal contact apart using, e.g., a scanning tunneling microscope or a mechanically controlled break junction [1]. Because of the low coordination number of the involved atoms, these ultimate one-dimensional quantum wires exhibit high mechanical stability and are chemically far more reactive than their bulk counterparts [2–4]. This, combined with their ability to sustain extremely large current densities, makes atomic chains interesting from both a fundamental and a technological point of view.

At sufficiently low temperatures, the conduction electrons in a metal can travel hundreds of nanometers without losing their quantum mechanical phase [1]. Under such conditions, the wave nature of electrons becomes important and manifests itself directly in macroscopic quantities such as the electrical conductivity.

As first predicted by density functional theory (DFT) calculations, the conductances of suspended atomic chains of some elements such as C, Na, and Au oscillate with a period of two as the number of atoms N in the chain is varied [5]. This behavior can be understood from a local charge neutrality condition which implies that the Fermi level must be aligned with the center of a resonance for odd N and lie midway between two resonances for even N, respectively. Deviations from these even-odd oscillations naturally occur for metals with more complex valence configurations such as Al and Pt [6,7]. Common to the oscillations observed for all of the homogeneous metal chains is that the conductance maximum (per contributing channel) is always close to $1 G_0$, while the oscillation amplitude varies significantly from $\sim 0.05 G_0$ in the case of Au [7,8] to $\sim 0.5 G_0$ in the case of Al and C chains [6,9]. We show here that this behavior can be understood in terms of the reflection probability and phase shift at a single bulk-chain interface.

In a recent experiment, Thijssen *et al.* found that the presence of oxygen greatly enhances chain formation when a silver contact is broken at low temperature [10]. It was proposed that the resulting chains, which can exceed 2 nm in length, consist of Ag and O atoms repeated in an alternating fashion [11], consistent with previous DFT calculations for Au-O chains [2,4]. Interestingly, the conductance averaged over many chains and plotted as a function of chain length showed an exponential-like decrease from $1 G_0$ to $0.1 G_0$ after which the conductance stayed constant over almost 1 nm. This is indeed a surprising result: The initial decrease in conductance suggests a chain with a band gap; however, this is not in line with the saturation at a finite conductance for longer chains. On the other hand, a length-independent conductance of $0.1 G_0$ does not comply with the results for metallic chains which exhibit conductance oscillations with a maximum on the order of $1 G_0$. We mention that silver, gold, and nickel contacts with one or two oxygen atoms adsorbed have previously been studied [4,12–15].

In this Letter, we present spin DFT calculations showing that alternating silver-oxygen chains (ASOCs) exhibit small-amplitude ($< 0.07 G_0$) conductance oscillations around a value of $0.1 G_0$ for long chains. The origin of these anomalous conductance oscillations is traced to an additional phase picked up by an electron being reflected at the end of the chain. Furthermore, we find the ASOC to be half-metallic, meaning that only electrons with a given spin direction can pass through the chain, making it a perfect spin valve.

To describe the chains we use the supercell shown in the inset in Fig. 1. It contains the oxygen-terminated ASOC suspended between four-atom Ag pyramids, which are attached to (111) Ag surfaces. Periodic boundary conditions are imposed in all directions. Both the Ag pyramid and the ASOC have been relaxed using the DACAPO plane wave DFT code [16] to obtain the most stable geometry [17].

Assuming phase-coherent transport, the conductance of the chains in the limit of low temperature and bias, is given
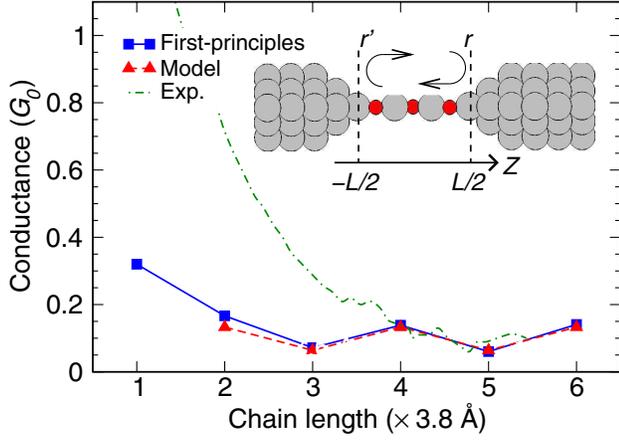
FIG. 1 (color online). Calculated conductance as a function of chain length (blue squares). The length of the chain is given in units of 3.8 Å corresponding to the length of a Ag-O unit. Also shown is the result of the resonating-chain model (red triangles) and a fit to the experimental data of Ref. [10]. The supercell used to model the suspended chains is also shown.

by the Landauer-Büttiker formula $G = G_0 T(\varepsilon_F)$, where $T(\varepsilon)$ is the energy-dependent transmission function. The latter is calculated using the nonequilibrium Green's function method described in Refs. [20,21], where the Kohn-Sham Hamiltonian of the relaxed chains is obtained from the SIESTA code [22].

In Fig. 1, we show the calculated conductance (blue squares) of the relaxed oxygen-terminated ASOCs as a function of the number of oxygen atoms N in the chain. We note in passing that the calculated conductances of silver-terminated chains are significantly lower than the experimental value of $0.1G_0$ [11], but these chains turn out to be less stable than oxygen-terminated chains and will probably break in the Ag-Ag bond when elongated. As indicated in Fig. 1, we have considered relaxed chains with a length up to 23.0 Å, with the Ag-O bond length lying in the range 1.95–2.10 Å. For comparison, the bond length of the infinite linear alternating Ag-O wire is found to be 1.95 Å.

Figure 1 also contains a fit to the experimental data presented in Ref. [10]. The experimental data are obtained by averaging the conductance trace of thousands of chains, and features such as small-amplitude conductance oscillations are not visible. For long chains, however, there is excellent agreement between the measured and calculated (average) conductance. The significantly larger conductances found in the experiments for shorter chains are presumably due to contributions from pure Ag chains which have a conductance around $1G_0$.

The calculated conductance of a single oxygen atom $N = 1$ is $0.3G_0$, which is in good agreement with the calculated results in Ref. [12]. For $N > 1$ the conductance starts to oscillate with a period of two Ag-O units around an average value of $0.1G_0$. For $N = 1$ we find a nonmagnetic

ground state, while for $N > 1$ the ferromagnetic state is energetically favored. For large N the electronic structure of the chain converges toward that of the infinite alternating Ag-O chain which has a ferromagnetic ground state with a magnetic moment of $1\mu_B$ per Ag-O unit. We find the energy gain with respect to the nonmagnetic state to be 0.12 eV per Ag-O unit.

To gain more insight into the nature of the conductance oscillations, we show in Fig. 2(a) how the energy-dependent transmission functions change with N. We first notice that only minority spin states are present at the Fermi level which means that the current will be fully spin-polarized. The peaks in the transmission function coincide with resonances of the chain which are broadened by coupling to the contacts. The resonances have the same character as the Bloch states forming the valence band of the infinite Ag-O chain whose band structure is shown in Fig. 2(b). The spin-polarized valence band is 2 times de-
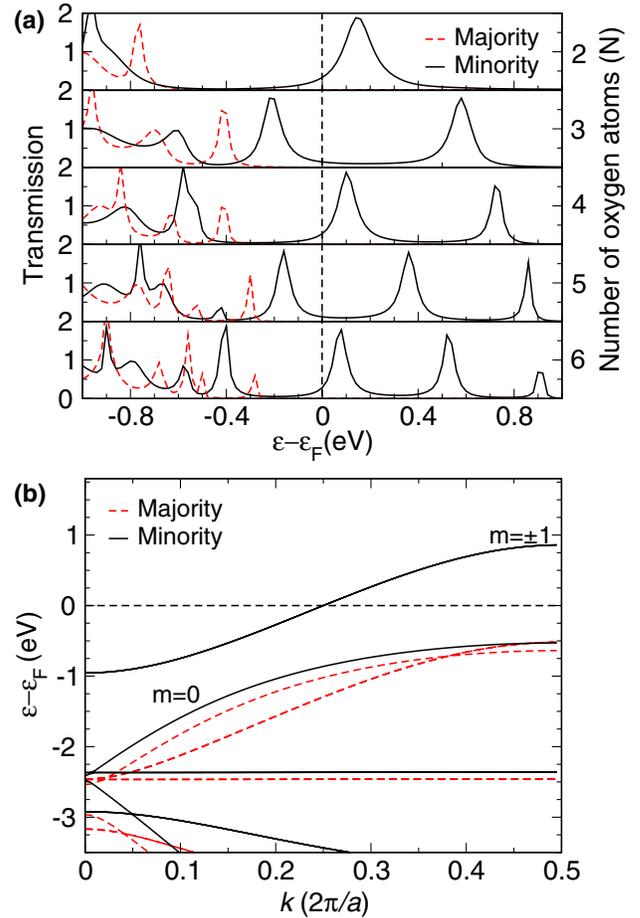
FIG. 2 (color online). (a) Transmission functions for the majority spin (dashed line) and minority spin (solid line) for Ag-O chains containing 2–6 oxygen atoms. (b) Band structure of the infinite Ag-O chain. The band crossing the Fermi level is doubly degenerate, and the Bloch states have $m = \pm 1$ symmetry with respect to rotations around the chain axis.

generate with angular momentum $m = \pm 1$ and Ag(4d)-O(2p) character.

Clearly, the conductance oscillations arise because the Fermi level intersects the nearest resonance closer to its center for even N than odd N. In contrast to the situation for homogeneous chains, however, the transport is never "on resonance" but always takes place via a resonance tail. In particular, this cannot be explained by charge neutrality. Indeed, from Fig. 2(a), it can be seen that the resonances are always almost completely empty or filled, and, since each resonance can accommodate two electrons (due to orbital degeneracy), it seems that all chains accommodate an even number of electrons. But each Ag-O unit contains 5 valence electrons, and local charge neutrality would therefore imply a half-filled resonance for every second Ag-O unit added to the chain. On the other hand, the small-amplitude oscillations around the experimental saturation value of $0.1G_0$ arise exactly because the Fermi level always intersects the tail of a resonance.

In order to rationalize the conductance behavior of the ASOCs, as well as that of other chain systems, we propose the following simple resonating-chain model. An electron approaching the chain from the left lead will have a certain transmission probability T_1 for entering into the chain. Inside the chain, the electron can propagate back and forth between the two (identical) contacts, so that every time the electron impinges on one of the contacts it is reflected with a probability $R_1 = 1 - T_1$, and it furthermore picks up a phase shift, which we denote by ϕ_1. We furthermore assume that the electron in the infinite chain is characterized by a single Fermi Bloch wave vector k. The interference between all of the reflected waves then leads to a total transmission probability T through the chain system of [23]

$$T = \frac{1}{1 + 4\frac{R_1}{(1-R_1)^2}\sin^2(kL + \phi_1)},\qquad(1)$$

where L denotes the distance between the two contacts. This expression is exact for coherent transmission in the limit where the reflections at the two ends can be considered independent. It should be noted that there is a certain arbitrariness in the definition of the distance L between the two contacts. However, different choices for L also give different results for the phase shift ϕ_1 so that Eq. (1) still holds. An additional length ΔL in the definition of the length is exactly balanced by an additional phase of $-k\Delta L$. We take the points of reflections to be at the tip atoms of the contacts.

For a given reflection probability R_1, the total transmission is seen to vary with the chain length between a maximum of 1 and a minimum of $[(1 - R_1)/(1 + R_1)]^2$. However, due to the phase shift and the discrete nature of the length of the chain, the transmission usually oscillates over a more narrow region.

We have determined the parameters R_1 and ϕ_1 for the ASOCs as well as for chains of Al and Au. The parameters are obtained by considering the reflection of an electron in a semi-infinite chain impinging on a contact. We determine the scattering state $|\Psi_s\rangle$ as described in Ref. [24], and the two parameters are then determined by projection onto the incoming (k) and outgoing $(-k)$ states through the relation $\sqrt{R_1}\exp(i\phi_1) = \langle\psi_{-k}|\Psi_s\rangle/\langle\psi_k|\Psi_s\rangle$. The incoming and outgoing states are calculated from the infinite chain.

In Table I, the calculated reflection parameters for the ASOCs and for monoatomic Al and Au chains are shown together with the obtained maximal transmissions and the magnitudes of the oscillations. Since all of the chains have either a single band or only degenerate bands crossing the Fermi level, the Fermi Bloch vectors of the chains become simple fractions of the zone widths resulting in the simple values of kL appearing in Table I. For all three systems, the model reproduces the results of full DFT calculations for varying chain lengths.

The model results for the ASOCs are shown in Fig. 1 to coincide with the full calculations for chains containing two or more oxygen atoms. It should be noted that the low conductance of about $0.1G_0$ comes about not so much because of the reduced reflection probability ($R_1 = 0.64$) which would still allow for a total transmission of 1 if a resonance condition could be met in the chain. Rather, it is the phase shift of $\phi_1 = -0.21\pi \approx -\pi/4$ which leads to destructive interference within the chain. The actual size of this phase shift depends on the electronic structure of both the chain and the contacts and must be obtained from a full calculation. However, we note that a phase shift of $\pi/4$ corresponds to a length of half a unit cell in the chain or, equivalently, an Ag-O distance. We also mention that Eq. (1) reproduces the energy-dependent transmission [Fig. 2(a)] quite well including the resonant structure, thus implicitly resolving the charge neutrality paradox—odd numbers of chain electrons still doubly occupy an integer number of resonances when the effects of the phase shift at the boundaries are included.

The results of the resonating-chain model for the conductances of Al and Au chains are shown in Fig. 3 together with the results of earlier full DFT-transport calculations. The agreement is very good even for rather short chains. In the case of Al, the phase shift is close to π in excellent agreement with the resonant-level model proposed in Ref. [6]. The resonant-level model takes as a starting point the isolated chain (of length N) which is then coupled

TABLE I. Calculated chain-contact reflection parameters for a number of chain systems.

System	R_1	ϕ_1	kL	T_{max}	ΔT_{osc}
Ag-O/Ag	0.64	-0.21π	$N\pi/2$	0.12	0.05
Al/Al(111)	0.32	0.92π	$(N+1)\pi/4$	0.85	0.57
Au/Au(100)	0.004	-0.36π	$(N+1)\pi/2$	0.997	0.010
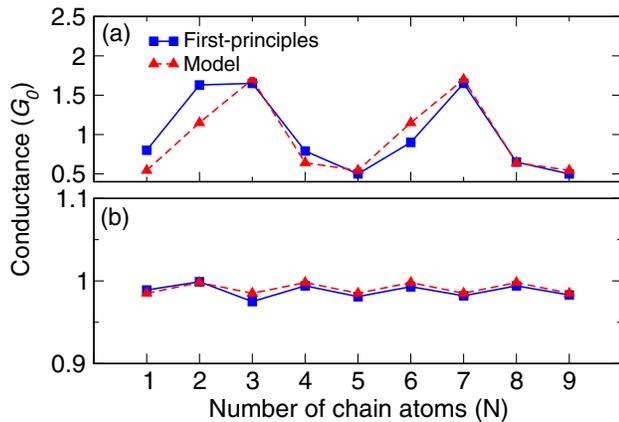
FIG. 3 (color online). (a) Conductance for Al as a function of the number of chain atoms N. The first-principles result (squares) is taken from Ref. [6], while the model result (triangles) is obtained from Eq. (1) with parameters derived using the same procedure as for the Ag-O system. (b) Conductance length dependence for Au with the first-principles result taken from Ref. [8].

weakly to the leads, and this boundary condition corresponds exactly to a phase shift of π. The small deviation of the phase shift from π accounts nicely for the fact that the conductance does not peak at $2G_0$ (the factor of 2 coming from two available channels) but only at $1.7G_0$.

For Au, we find the phase and amplitude of the even-odd conductance oscillations in agreement with the first-principles calculations in Ref. [8]. We note that the phase of the conductance oscillation is not explained by either a charge neutrality argument or a resonant model [6]. However, the phase of the oscillation can be related to our calculated phase shift of -0.36π, while the small oscillation amplitude can be traced to an almost perfectly transparent chain-bulk interface with a reflection coefficient of 0.004.

In summary, we have presented first-principles conductance calculations showing that alternating Ag-O chains suspended between silver bulk contacts are half-metallic and can have an average conductance of $0.1G_0$ as found in a recent experiment [10]. In fact, the conductance oscillates with a small amplitude and a period of two Ag-O units as the chain length is varied. The oscillations can be understood from a resonating-chain model and are fully characterized by only two parameters: the reflection probability R_1 and the reflection phase shift ϕ_1 of a single bulk-chain interface. By extracting these two parameters from the DFT calculation, quantitative agreement between the full calculations and the model is obtained. The half-metallic spin states of the Ag-O chains make them interesting candidates for spin-controlled transport as also suggested

for Ni-O chains, which are, however, found to be insulating for long chains [15]. Suspended between magnetic materials, the Ag-O chains could lead to large magnetoresistance and act as spin valves.

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