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Evidence of spin-dependent quantum transport effects in CuO nanowires

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Abstract

We have observed strongly spin-dependent quantum transport in nanowires created by bringing macroscopic Cu wires into and out of contact under an applied magnetic field when exposed to air. A 70% increase in the strength of the first spin split conduction mode obtained from conductance histograms is observed for a field of 2 mT at room temperature, implying the existence of a robust spin polarization. Density functional full potential linearized augmented plane wave (FLAPW) calculations reveal that a CuO chain when stretched becomes spin polarized and has half-metallic character. We therefore attribute the surprisingly strong magnetic effect on the conductance to the formation of spin polarized CuO chains within the nanowire by spontaneous atmospheric oxidation.

Nanostructured magnetic materials are currently being very intensively investigated due to their unusual transport properties and promise for possible spintronic device applications [1]. They provide the opportunity to control the spin switching characteristics and the resulting magnetotransport behaviour. For example, ferromagnetic regions within nanowires (fabricated on stepped surfaces [2, 3], grown in pinholes [4] or formed by stretching metal contacts [5]) may be magnetically aligned in a small magnetic field, which hence makes the ballistic [4]or domain wall [6] magnetoresistance extremely large and easy to control. To date, the achievement of 100% polarization in ferromagnetic materials as required for polarizing electrical contacts in spintronics has proved elusive. However, as we shall show, a spin polarization can arise in nanostructured materials that are non-magnetic in the bulk. Here we present the experimental observation and theoretical explanation of spin-dependent quantum transport in nanowires transiently formed from macroscopic Cu wires in air. Strikingly, we detected a large magnetic signal, which we attribute to the robust spin polarized electronic structure we find through density functional calculations, potentially promising a 100% spin injection rate.

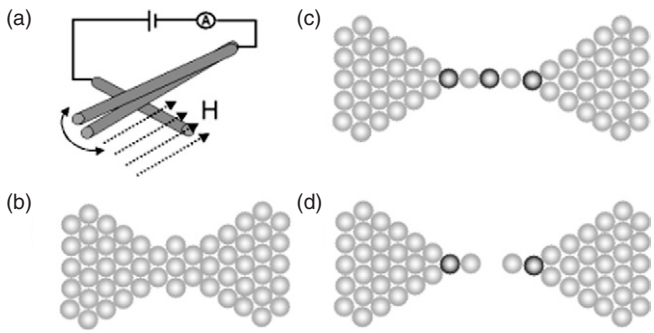

Figure 1. An outline of the experimental system used. (a) A schematic diagram of the equipment; the nanowire is made where the wires come into contact. The magnetic field is applied in the direction of the dashed arrows. (b)–(d) An illustration of how the nanowires are created. When the macroscopic wires are in contact, atoms bind to both wires (b); as the wires separate the metal forms a neck which stretches out until it is atomic sized (c), then it snaps (d). The quantum conduction is seen in region (c) close to (d) where the wires snap.

A nanowire can be considered to be an atomic sized constriction between two electron reservoirs. If such a nanowire is small enough, the electrical conduction (G) can be quantized according to the Landauer equation [7–9]

$$G = G_0 \sum n\sigma T_{n\sigma} \tag{1}$$

where $G_0 = e^2/h$ is the conductance quantum (e is the electronic charge, h is Planck's constant), $T_{n\sigma}$ is a transmission coefficient for the nth channel and electron spin σ (which can take one of two values either $\uparrow$ or $\downarrow$). In theory, for ballistic transport $T_{n\sigma}$ can either be 1 or 0 corresponding to an open or closed channel; however, in real systems values in between can be obtained. For non-magnetic materials (e.g. Au [10]) one would expect the two spin channels to be degenerate, and G is thereby quantized with a unit of $2e^2/h$. By contrast, if the system is magnetic the unit of quantization for G is reduced to e^2/h, as has been illustrated in many magnetic systems (e.g. Ni [11], Fe [12]). Quantum transport in atomic sized nanowires of various metals formed by mechanical means have been widely studied by several groups; a good review can be found in [13].

In this experiment, the nanowires were formed by tapping macroscopic Cu wires together in air at room temperature. The experimental set-up is shown in figure 1(a). The Cu wires were 250 μm in diameter and of 99.99+% purity. The nanowires were created by a necking process, as shown schematically in figures 1(b)–(d). At the start of the process (figure 1(b)) the two macroscopic wires are in contact and the atoms on the surface bond to atoms on the other wire. As the wires move apart this contact is stretched into a filament; as the filament is further stretched it gets thinner and as it approaches the nanoscale conduction channels close (figure 1(c)). At the very end of the process only a few conduction channels remain and quantized conduction is observed until the wire breaks (figure 1(d)). Since the electrical resistance of the wider filaments will be considerably less than those of the narrower filaments, the wider filaments will carry the majority of the current. Therefore, when we observe quantized conduction we can be confident that very few nanowires remain.

A bias of 20 mV was applied across the two macroscopic wires so the current flowing in the system was about 1 μA per open conduction channel. The current was amplified by a transimpedance amplifier and together with the bias was captured by a Tektronix TDS430A digital oscilloscope. Since nanowires were not formed every time the wires came together, the data sets had to be filtered to separate out the 5–10% of the data sets which demonstrated

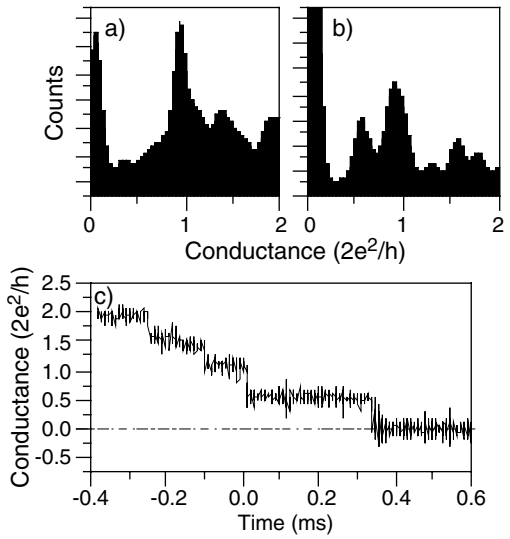

Figure 2. Conductance histograms taken (a) without and (b) with a field of 5 mT applied. Panel (c) shows a conductance versus time curve that clearly demonstrates e^2/h quantization. About 50 contacts were used to make each of (a) and (b).

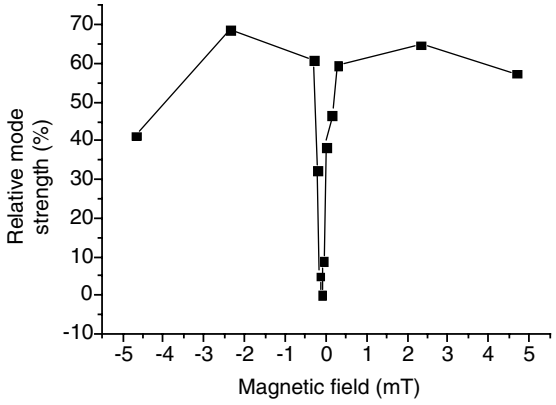

Figure 3. Magnetic field dependence of RMS of the $G = e^2/h$ mode.

quantum conduction. The criterion used was the presence of a staircase like conductance versus time curve—no assumption was made on the size of the steps. A magnetic field was applied perpendicular to the nanowires via a pair of Helmholtz coils that were capable of producing ± 5 mT.

The experimental results presented in figure 2 clearly demonstrate the presence of quantized conductance in the nanowires. Figure 2(a) shows a conductance histogram taken with no applied field and shows a clear $2e^2/h$ quantization. However, figure 2(b) was taken with a field of 5 mT applied; the e^2/h mode becomes stronger with the application of the magnetic field. Figure 2(c) shows a conductance versus time curve that clearly exhibits the e^2/h mode. The additional non-integer features seen for higher conductances (above $2e^2/h$) are not readily explained but similar effects have been seen in other adsorbate covered nanowires [14]. Figure 3

shows the magnetic field dependence of the relative mode strength (RMS) of the $G = e^2/h$ mode, which is defined as

$$\text{RMS} = [N(e^2/h, H) - N(e^2/h, 0)]/N(e^2/h, 0). \tag{2}$$

Here $N(e^2/h, H)$ corresponds to the height of the e^2/h peak at a magnetic field H obtained from a histogram normalized to the number of curves that made up the histogram. This quantity also provides a measure of the relative stability of the contacts which give rise to this conductance value. We find a well-defined variation of mode strength with field and, in particular, a 70% *magnetic effect on the conductance* for $H = 2$ mT. While we are aware of other experiments in the literature which report non-integer conductance features induced by non-magnetic adsorbates [15], these effects are distinct from our case given the field-dependent behaviour we observe. It should be emphasized that the well-defined behaviour we observe corresponds to a large number of measurements on many nanocontacts and so demonstrates that the effect is highly repeatable. As we now show, these results suggest that, remarkably, nanowires become magnetic when stretched in air during the experiment.

To explain this surprising phenomenon, we carried out density functional calculations for several Cu systems, using the full potential linearized augmented plane wave (FLAPW) method [16]. No shape approximation in the charge, potential and wavefunction expansions is assumed. The core electrons are treated fully relativistically and the spin–orbit coupling term is invoked second-variationally for the valence states. The generalized gradient approximation (GGA) [17] was adopted to describe the exchange–correlation interaction. Spherical harmonics with $l_{\max} = 8$ was used to expand charge, potential and wavefunctions in the muffin tin region. Energy cutoffs of 225 and 25 Ryd were used for the plane wave expansions in the interstitial region for charge, potential and bases, respectively.

We first explored the possibility of a ferromagnetic state occurring in pure Cu 1D monatomic wires, using supercell geometry with a 2D square lattice of 15 au in the lateral plane. Cu atoms align vertically along the z-axis with a varying interatomic distance. It was found that the unsupported 1D pure Cu nanowires have no magnetic moment within a wide range of Cu–Cu distances (4.4–6.0 au). Therefore, the conclusion was drawn that Cu cannot become magnetic by just reducing the number of neighbours. Since our experiment is done in air active elements such as oxygen are expected to be present in the nanowire. It is well known that the spontaneous formation of oxides on Cu surfaces [18] requires only microseconds whereas the present experiment lasts for 100–1000 μs, and so CuO will cover the nanowire surface. Alternatively, since CuO is already present on the surface of the wires it is possibly that the CuO chains are formed directly. We note that CuO is an antiferromagnet with a Néel temperature of 230 K. Total energy calculations indicate that an alternating CuO monatomic chain is lower in energy by 3.25 eV/molecule than the case simply with O_2 molecules inserted in the middle of the Cu chain, implying that the CuO monatomic chain is extremely stable and its formation is highly feasible.

Calculations for CuO diatomic wires were done in the same supercell fashion, except that now we have two or four (for the antiferromagnetic configuration) atoms in the unit cell. From the equilibrium distance, $d_{\text{Cu–O}} = 3.23$ au, the CuO monatomic wire was elongated along the z-axis to simulate the stretch in the experiment. The total energies are presented in figure 4. They can be well fitted by a cubic polynomial (dotted line), from which we further obtain the one-dimensional stress (solid line) by taking the first derivative of the total energy curve with respect to the interatomic distance. The stress increases almost linearly up to a distance of 3.8 au (elastic range), and reaches its maximum at around 4.1 au, where we expect that the wire breaks down.

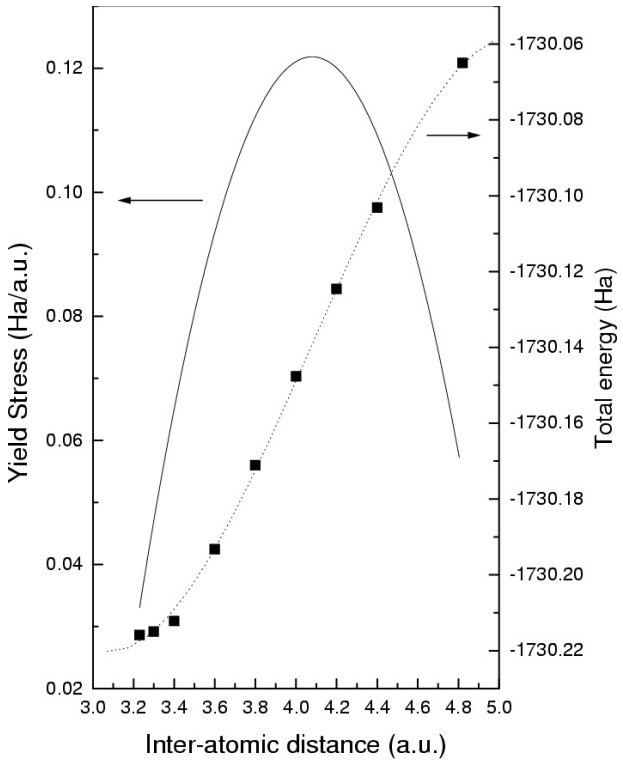

Figure 4. The calculated total energy and one-dimensional stress (the first derivative of the total energy curve with respect to the interatomic distance) for a CuO monatomic wire.

Dramatically, it was found that both Cu and O atoms have large magnetic moments, except at the equilibrium distance in figure 5. These results nicely explain the data in figure 2 as follows. When the contact is stretched, a CuO chain is formed with an elongated Cu–O distance. The wire is magnetic as shown in figure 5 and thus we detected magnetic quantum transport. Although the magnetic moments for Cu and O are very sensitive to the interatomic distance, their sum appears to be very stable when $d_{\mathrm{Cu-O}}$ varies in the range of 3.3–4.8 au. This finding is of key importance in explaining why spin polarized effects are observed in practice since the nanowires which form in the experiment are likely to experience a range of strain values. One may see that magnetic moment jumps from zero to a finite value when the interatomic distance changes very slightly. Calculations in a small range indicate that, as presented in the inset of figure 5, the magnetic moments of both Cu and O atoms increase eventually with strain from low to high spin states.

It is instructive to further investigate the origin of the Cu magnetization through the density of states (DOS) of CuO diatomic nanowire for three different cases in figure 6. Strong Cu–O hybridization can be found in all three separations. With the equilibrium distance of 3.23 au, the Cu and O bands are wide and their two spin channels are degenerate. Stunningly, the elongated CuO wires simultaneously display *both* the formation of a magnetic state *and* a half-metallic phase, a feature that is highly desired for spintronics applications [19]. From this we infer that the magnetic transport effects we observe result from the formation of CuO: specifically the observation of a spin split conductance channel is a consequence of the fact

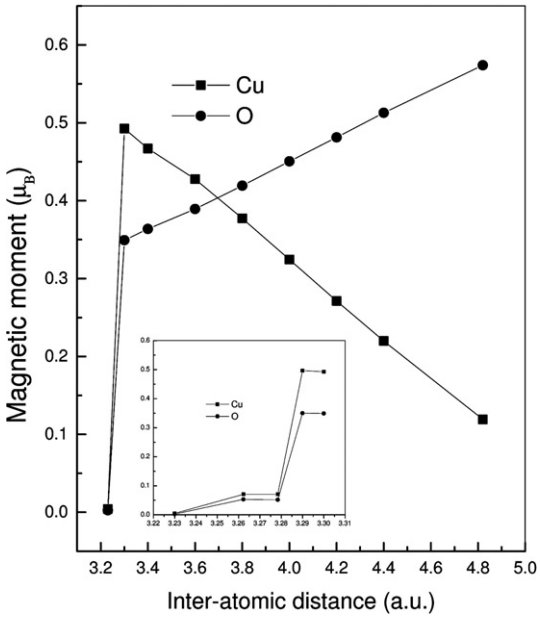

Figure 5. The calculated magnetic moment of Cu and O in the CuO diatomic wire as a function of interatomic distance. The inset shows the detailed variation of the moments near the equilibrium separation.

that a spin polarization forms for a wide range of interatomic distances within the strained CuO chains. By contrast, no magnetic signal was found in Cu wires when a similar experiment was undertaken in a vacuum [20], supporting our view that oxidation determines the magnetic transport properties.

Finally, we also investigated the possibility of the formation of an antiferromagnetic ground state in the CuO nanowire. This state, however, does not appear even as a metastable phase since different initial magnetic configurations all converge to the ferromagnetic ground state. Experimentally, the magnetic field dependence of the relative strength of the $G = e^2/h$ mode also indicates the stability of the ferromagnetic state in the wire. The calculated magnetic anisotropy energy for the ferromagnetic CuO wire (e.g. $d_{\mathrm{Cu-O}} = 3.8$ au) is 1.20 meV per CuO unit, but the easy axis aligns perpendicularly to the wire axis. The direction of magnetization thus may fluctuate in the xy-plane without any energy barrier. Nevertheless, the magnetic quantized transport will show up, as long as the characteristic time of spin fluctuation is longer than that of the ballistic electron transport since the spins of all the atoms are strongly coupled in the short wire. Figure 3 indicates that a small magnetic field, e.g. 2 mT, is sufficient to suppress thermal fluctuations.

To summarize, we have both observed and explained a significant magnetic effect on the conductance in nanowires formed from macroscopic Cu wires. The magnetic signal is attributed to the presence of O, which introduces both magnetization and half-metallic features to the CuO diatomic wire when the wire is elongated along the chain axis. The fact that we see the signature of spin polarized effects in our experiments indicates that both the reduced dimensionality and the strain are crucial in giving rise to a spin polarization supported by the calculations. This may offer a new approach in developing spintronic devices, differing from the current research effort devoted to developing bulk materials, which have 100% spin polarization. We conjecture that this effect could be seen in other non-magnetic metals when

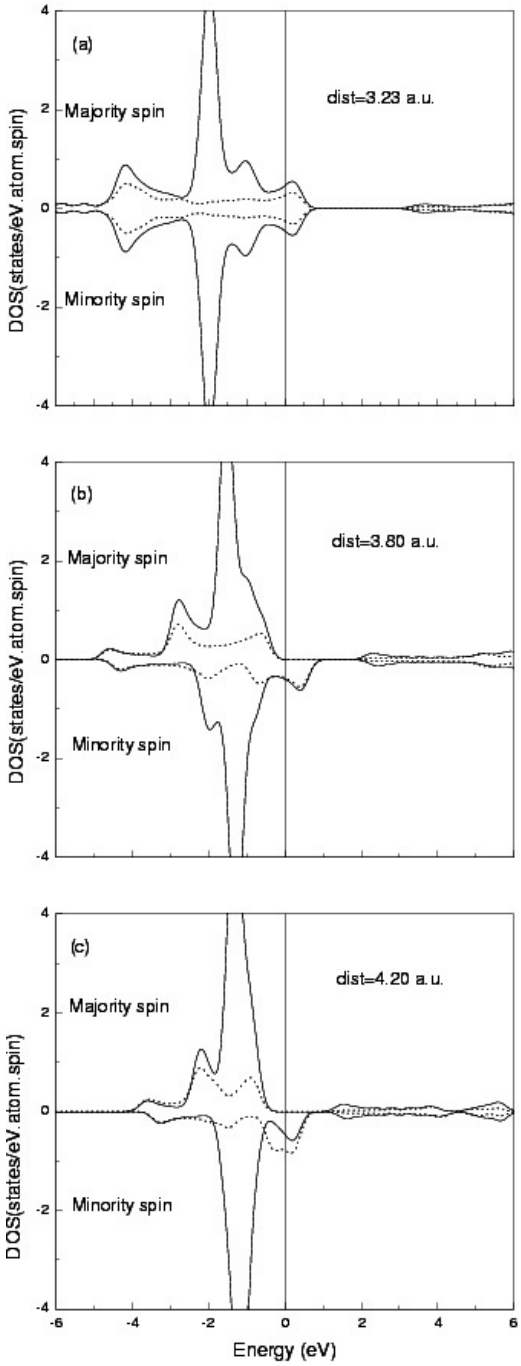

Figure 6. The calculated DOS for the CuO wire. Solid and dotted lines are for DOS of Cu and O atoms, respectively.

formed into nanowires under the correct conditions. For device applications one may need to further explore the properties of these wires embedded in insulating materials.

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