Spin valve effect in single-atom contacts

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Abstract. Magnetic single-atom contacts have been controllably fabricated with a scanning tunnelling microscope. A voltage-dependent spin valve effect with conductance variations of \(\approx 40\%\) is reproducibly observed from contacts comprising a Cr-covered tip and Co and Cr atoms on ferromagnetic nanoscale islands on W(110) with opposite magnetization. The spin-dependent conductances are interpreted from first-principles calculations in terms of the orbital character of the relevant electronic states of the junction.

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1. Introduction

A spin valve exhibits different conductances for electrons with opposite spin directions and is thus a key component of spintronics [1–3]. Giant magnetoresistance (GMR) in layered magnetic materials [4, 5] is a prominent example of a spin valve effect, which is used in current magnetic read heads. Until now, it has not been clear whether very small structures on the scale of single atoms, which electrons can ballistically traverse, may serve as spin valves.

Nanoscale junctions made from ferromagnetic materials show changes in their resistance when the direction of an external magnetic field is reversed [6–13]. This ballistic magnetoresistance (BMR) may be understood from the enhanced scattering of electrons with a given spin at a magnetic domain wall, which is located within the junction [7, 14]. Thus, junctions exhibiting BMR may be considered to be nanoscale spin valves. The size of the BMR effect has sometimes been reported to drastically exceed GMRs in layered systems [6, 7], which could lead to improved performance of detectors based on magnetoresistance. However, the BMR values observed in various experiments scatter widely, and artefacts have been suggested to be the origin of large magnetoresistive effects. For instance, the magnetic fields used to control the magnetization of the electrodes of a junction lead to magnetostriction and may therefore modify the positions of the atoms in the junction [15–18]. Moreover, the methods used to prepare the junctions do not allow atomic-scale control of the junction geometry. According to ab initio transport calculations, however, the conductance will depend on the detailed geometry and the orbital character of the atoms at the junction [19]. Overall, there is a controversial debate about the existence and origin of BMR in nanoscale junctions [16, 20].

Here, we report on the spin valve behaviour of junctions fabricated by contacting single-Co and single-Cr atoms on ferromagnetic double-layer Fe islands on W(110) with spin-polarized Cr tips. The junction geometry and magnetic state were characterized before and after each measurement with scanning tunnelling microscopy (STM). The magnetic moment of Co and Cr atoms is stabilized by the strong exchange interaction with the Fe substrate. As Fe islands with opposite magnetization directions coexist on the W substrate, the spin-dependent transport can be probed without an external magnetic field, thus avoiding magnetostrictive effects. A model of the contact geometry is shown in figure 1(a). Tunnelling data probe the spin-polarized density of electronic states of the sample, similar to earlier work [21–23]. The conductances measured at contact, however, where chemical bonding of the tip and the sample occurs, reflect transport channels of the coupled system, and their spin polarization may a priori be entirely different [19, 24]. Different relative orientations of the magnetic moments of the tip apex and the adsorbed atom (adatom) modify the conductance of Co (Cr) contacts by ≈36% (∼44%) at low voltages. At higher voltages the spin valve effect disappears. Density functional theory (DFT) calculations show that Co and Cr adatoms exhibit, respectively, ferromagnetic and antiferromagnetic coupling to the Fe islands. They further indicate that the spin valve behaviour is due to the orbital character of the states close to the Fermi level.

2. Experiment

Experiments were performed with a home-built STM operated at 7 K and in ultrahigh vacuum with a base pressure of 10⁻⁹ Pa. W(110) surfaces were cleaned by oxidation cycles at 1400 K and brief annealing at 2200 K. Electron beam evaporators were used to prepare Cr-covered tips and Fe bilayer islands on W(110) at room temperature and to deposit single Co atoms onto
Figure 1. Magnetic single-atom junctions. (a) Sketch of a junction fabricated from a Cr-covered W tip (yellow), a Co (blue) or Cr (yellow) adatom and a Fe bilayer island (grey) on W(110) (not included in the sketch). Arrows indicate the magnetic moments of individual atoms and show the ferromagnetic (antiferromagnetic) coupling between the Co (Cr) adatom and the Fe island. (b) Constant-current STM image of two Fe bilayer islands on W(110) with adsorbed Co and Cr atoms (1 nA, 0.7 V). At this sample voltage, Cr adatoms (red) appear higher than Co (yellow). The colour scale ranges from 0 (blue) to 560 pm (red). (c) Map of $dI/dV$ recorded simultaneously with the STM image. Different colours of Fe islands reflect different magnetization directions. The colour scale ranges from 0 (blue) to 4 nS (red).

W(110)-Fe at $\approx$10 K. Single Cr atoms were transferred from the Cr-covered tip by controlled tip–surface contacts [25]. This technique was also used to control the spin polarization of the tip [26]. For spectroscopy of the differential conductance ($dI/dV$), a sinusoidal voltage (10 mV$_{\text{rms}}$, 7.8 kHz) was added to the sample bias and the first harmonic of the current response was recorded with a lock-in amplifier. To verify the reproducibility of the measurements, Cr and Co adatoms were investigated using different microtips, which had been modified by tip–surface contacts.

3. Theoretical method

First-principles calculations based on DFT within the generalized-gradient approximation (GGA) to the exchange-correlation functional [27] were performed using the full-potential linearized augmented plane-wave method (FLAPW) as implemented in the WIEN2K code [28]. The junctions were modelled by a symmetric slab consisting of five atomic layers of W(110) with a Fe double layer on each side, employing a c(4×6) surface unit cell with the theoretical lattice constant of tungsten (0.3181 nm), which is only 0.5% larger than the experimental value (0.3165 nm). A Co (Cr) atom was added on each Fe surface in a hollow-site position. The
Cr tip was modelled by a 14-atom pyramid starting from a (100) surface plane. The muffin-tin radius of W was chosen as 2.5 au and for Fe, Co and Cr it was 2.1 au. The energy cutoff for the plane-wave representation in the interstitial region was $E_{\text{max}}^{\text{WF}} = 12$ Ry and a $(4 \times 4 \times 1)$ Monkhorst–Pack grid was used for the Brillouin-zone integration. Spin–orbit coupling was not included in the calculations. The vertical distance between the tip and its repeated image in the $z$-direction was 0.7 nm to ensure negligible mutual interaction. The sample, namely Co (Cr) on the Fe double layer on W(110), and the Cr tip were first calculated independently and their structure was relaxed via force minimization. The coupled tip–sample system was not further relaxed.

4. Results and discussion

Figure 1(b) shows an STM image of the investigated structure. Single Co and single Cr adatoms protrude from double-layer Fe islands on a W(110) surface. Prior work showed that Fe islands are magnetized along the surface normal [29]. The adatoms may be readily identified by their different apparent heights (Co: $\approx 65$ pm; Cr: $\approx 100$ pm). Figure 1(c) displays a map of $dI/dV$, which was simultaneously recorded with the STM image in figure 1(b). A Cr-covered tip was used and a clear spin contrast was obtained between islands with different magnetization directions. The actual magnetization alignment depends on the spin polarization of the employed tip which is unknown. The spin polarization is defined as $(r_{\text{maj}} - r_{\text{min}})/(r_{\text{maj}} + r_{\text{min}})$, where $r_{\text{maj}}(r_{\text{min}})$ denotes the vacuum local density of states (LDOS) of majority(minority) electrons. For the sake of argument, and since the magnetization of the tip does not change in the experiments, we assume in the following a positive spin polarization consistent with the tip structure employed in the present as well as other recent model calculations [30]. Previous calculations revealed that the vacuum LDOS of an Fe bilayer on W(110) is dominated by minority electrons, i.e. it exhibits a negative spin polarization [31]. As a consequence, an antiparallel alignment of the magnetizations of the tip and island leads to higher conductance. In figure 1(c), islands are accordingly labelled $\uparrow\uparrow$ and $\uparrow\downarrow$.

To probe their spin-dependent transport, Co and Cr adatoms were approached with the STM tip until contact was reached. After each contact measurement, spin-resolved microscopy and spectroscopy were used to verify that the junction had not been modified. Figures 2(a) and (b) display the low-bias conductance versus tip displacement for Co and Cr adatoms adsorbed on Fe islands with parallel and antiparallel magnetizations with respect to the tip. The data cover the tunnelling and contact ranges. A geometrical construction is used to define these ranges and the contact conductance, $G_c$, from the intersection of linear fits to conductance data in the contact and tunnelling ranges (figures 2(a) and (b); dashed lines). $G_c$ clearly depends on the relative electrode magnetizations, demonstrating the spin valve behaviour of such junctions. Co adatoms exhibit a conductance at contact of $G_c^{\uparrow\downarrow} \approx 0.47G_0$ ($G_0 = 2e^2/h$ is the quantum of conductance with $e$ being the electron charge and $h$ the Planck constant) for antiparallel and a higher $G_c^{\uparrow\uparrow} \approx 0.64G_0$ for parallel configuration, which corresponds to a conductance change of $(G_c^{\uparrow\uparrow} - G_c^{\uparrow\downarrow})/G_c^{\uparrow\downarrow} \approx 36\%$. Cr adatoms exhibit an opposite effect. For antiparallel configuration electrode magnetizations, the contact conductance of $G_c^{\uparrow\downarrow} \approx 0.75G_0$ is

In earlier work on noble metals [25, 37, 38], a more rapid transition from tunnelling to contact occurred owing to elastic deformations and was used to define $G_c$. With the stiffer materials used here, this definition cannot be used.

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Figure 2. Conductance and asymmetry versus displacement. The conductance evolution of magnetic single-Co (a) and single-Cr (b) junctions fabricated from Cr-covered W tips and $\uparrow\uparrow$ and $\uparrow\downarrow$ Fe islands on W(110) in the tunnelling and contact regimes. Zero displacement corresponds to the tip–sample distance at $I = 100 \text{nA}$ and $V = 55 \text{mV}$. Negative values indicate the approach of the tip. The apparent heights of adatoms imaged at 55 mV depend on the alignment of the magnetizations of the tip and an island (Co (Cr): 81 pm (100 pm) and 65 pm (111 pm) on $\uparrow\uparrow$ and $\uparrow\downarrow$ islands, respectively). For this reason, the conductance curve of Co for parallel alignment ($\uparrow\uparrow$) were shifted horizontally by +16 pm. Similarly, the Cr data for antiparallel alignment ($\uparrow\downarrow$) was offset by +11 pm. The intersection of exponential fits (dashed lines) in the tunnelling and contact ranges is used to define a contact conductance, $G_c$. (c) Asymmetry ($\Delta G/\Sigma G$) in the tunnelling and contact regimes.

higher by $(G_{\uparrow\uparrow} - G_{\uparrow\downarrow})/G_{\uparrow\uparrow} \approx 44\%$ than that for the parallel case ($G_{\uparrow\uparrow} \approx 0.52G_0$). Additional measurements at 100 mV did not show a spin valve effect (table 1).

It is instructive to consider the evolution of the spin valve effect from tunnelling to contact. To this end, we use the asymmetry $\Delta G/\Sigma G$, where $\Delta G = G_{\uparrow\uparrow} - G_{\uparrow\downarrow}$, $\Sigma G = G_{\uparrow\uparrow} + G_{\uparrow\downarrow}$ and $G_{\uparrow\uparrow}, G_{\uparrow\downarrow}$ are the conductances for parallel and antiparallel electrode magnetizations. Figure 2(c) shows that the asymmetry varies slightly over the entire conductance range. The almost constant asymmetry suggests that essentially the same states dominate the conduction at contact and in the tunnelling range. Small variations in the range of contact formation most likely reflect relaxations of the electrodes and are consistent with first-principles calculations,
Table 1. Contact conductances, $G_c$, in units of $G_0 = 2e^2/h$ for Co and Cr adatoms on ↑↓ and ↑↑ islands. Error margins indicate the scatter of $G_c$ extracted from several data sets.

|     | 50 mV $G_c^{↑↓}$ | 100 mV $G_c^{↑↑}$ |
|-----|------------------|------------------|
| Co  | 0.47 ± 0.05      | 0.64 ± 0.05      |
| Cr  | 0.75 ± 0.05      | 0.52 ± 0.05      |
|     | 0.48 ± 0.05      | 0.46 ± 0.05      |
|     | 0.54 ± 0.05      | 0.53 ± 0.05      |

which show that exchange forces and relaxations depend on the alignment of the magnetic moments [32, 33].

For further analysis of the contact conductances, we performed first-principles calculations based on DFT. Neglecting the tip, the calculations for Co adatoms predict a magnetic moment of 1.90$\mu_B$ ($\mu_B$, Bohr magneton), which ferromagnetically couples to the moment of the Fe film\(^6\). For Cr, a magnetic moment of 3.30$\mu_B$ is found. In this case, antiferromagnetic alignment is more favourable by 1.05 eV. These magnetic couplings are similar to the case of Fe and Cr adatoms on Co islands on Cu(111) [23]. This suggests that the high and low conductance values observed for Co and Cr may be attributed to parallel and antiparallel alignment, respectively, of the moments of the foremost tip atom and the adatom\(^7\).

The calculations performed for short tip–sample separations provide an interpretation of the spin valve effect, which can be understood from the spin-dependent orbital character of the states of the coupled system near $E_F$. Figure 3 shows cross-sectional plots of the spin-resolved local density of states (LDOS) for parallel and antiparallel electrode magnetizations of single-Co and single-Cr junctions depicted in figure 1(a). Majority and minority electrons are defined with respect to the tip. This means that majority(minority) electrons of the adatom are defined as electrons with the same spin direction as the majority(minority) electrons of the tip. For the junction comprised of a Cr tip and a Co adatom with parallel alignment (left panel of figure 3(a)), large overlap occurs in the majority channel between slowly decaying s-states of the Co adatom and sp$_x$d$_{z^2}$-states of the tip. This overlap leads to a conducting channel of sp$_x$d$_{z^2}$-character. The minority channel, on the other hand, is only weakly conducting as the d$_{xy}$Co orbital and the d$_{xy}$tip orbital are more localized. In the antiparallel configuration (right panel of figure 3(a)), two intermediate contributions to the conductance occur. Firstly, slowly decaying sp$_x$d$_{z^2}$-states of the tip exhibit some overlap with the rapidly decaying majority states of the Co adatom. In this energy range, the majority states of Co are mainly of d$_{xy}$ character but

\(^6\) The antiferromagnetic coupling of a Co adatom to the Fe double layer was found to be unstable in the self-consistent cycle and converged to the ferromagnetic configuration.

\(^7\) From our DFT calculations, we are able to determine the energy of the magnetic configuration of the tip and the sample by calculating the distance-dependent magnetic exchange energy $E_{ex}(z) = E_{ap}(z) - E_{p}(z)$, where $E_{ap}(z)$ and $E_{p}(z)$ are the energies for the antiparallel and parallel alignment between the tip and the sample, respectively (figure 1(a)). At a distance of $z = 0.4$ nm, i.e. in the contact regime, we obtain for Co and Cr adatoms 6.8 and −40.8 meV, respectively, i.e. ferromagnetic and antiferromagnetic coupling for Co and Cr adatoms, respectively. These magnetic exchange energies are much smaller than the calculated energy differences between ferromagnetic and antiferromagnetic states of a Cr adatom on Fe islands (1.05 eV) and a Cr tip apex atom (1.6 eV), which indicates that the tip–adatom interaction at contact is too low to significantly tilt the magnetic moments of the tip and adatom.
there are also small contributions from s-states and from the tail of a \(d_z^2\)-state, which are both rotationally symmetric, just like the tip states (figure S1, supporting information, available from stacks.iop.org/NJP/13/085011/mmedia). Secondly, the rather localized minority states of the tip overlap little with the extended s-state of the Co atom\(^8\).\n
\(^8\) The matrix elements of the rotationally symmetric \(s, p_z\) and \(d_z^2\) orbitals with \(d_{xz}\) and \(d_{yz}\) orbitals vanish for purely atomic states owing to symmetry. However, in the energy range corresponding to the applied bias voltage, there is also a small contribution from \(s\)- and \(d_z^2\)-states (figure S1, available from stacks.iop.org/NJP/13/085011/mmedia) that can contribute to the conductance. Thus, for both single-Co and single-Cr junctions, the dominant localized \(d_{xz}\) and \(d_{yz}\) character of the LDOS between \(E_F\) and \(E_F + 50\) meV results in a reduction in the conductance, which, however, is not zero because of the residual overlap of other states.
For junctions with a Cr adatom (figure 3(b)), the situation is reversed due to the opposite spin polarization of the states at the adatom. A highly conducting channel occurs in the antiparallel configuration (right panel of figure 3(b)) between the majority-spin sp$_2$ d$_{z^2}$-tip state and d$_{z^2}$-states of the Cr atom, while a weak contribution to the conductance comes from the minority tip and adatom states with small overlap. With the parallel alignment, corresponding to the left panel of figure 3(b), both majority and minority channels provide an intermediate contribution to the conductance. Calculations for smaller tip–adatom distances revealed that the orbital characters of the states at the adatoms are only weakly affected by the hybridization with the tip, which is consistent with the experimental observation from figure 2(c).

The rotationally symmetric states responsible for the largest contribution to the conductance are localized at the Fermi level (figure S1, supporting information, available from stacks.iop.org/NJP/13/085011/mmedia). At higher energies, the majority-spin s-states of the Co atom fade away, while the d$_{z^2}$-states appear in the minority channel. For the Cr atom, a gradual change from a d$_{z^2}$ to a more localized d$_{yz}$-state is found with increasing energy. These changes of the spin-dependent orbital character of the states can explain the absence of the spin valve effect at increased bias voltages, even though for Co it occurs at larger voltages than in the experiment.

Overall, the DFT results show that high contact conductances ($G_c > G_0/2$) are mainly due to a single majority channel, which is derived from extended orbitals that are rotationally symmetric about the axis of the junction, i.e. s, p, and d$_{z^2}$. The minority states provide only a weakly conducting channel stemming from d-states. This conclusion is consistent with the calculations of the conductance of ferromagnetic Co-based junctions on the basis of the tight-binding method [19, 24] and DFT [34]. On the other hand, in the low conductance configuration ($G_c \approx G_0/2$), minority and majority states contribute similarly to the current.

5. Conclusion

Magnetic contacts comprising Cr-covered tips, Fe nanostructures and Co and Cr adatoms exhibit a spin valve effect at the ultimate size limit, i.e. single atoms. The spin-induced conductance variations of the atomic spin valves presented here are below 100%, which can be reached in ferromagnet/metal multilayers [35]. Other material combinations of tip, adatom and substrate will be explored to optimize these variations. The imaging and spin resolution capabilities of STM are essential for obtaining reproducible data. The experimental and theoretical methods used here may be extended to other systems, including single-molecule contacts, for which intriguing spin effects have been predicted [36].

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