

Observing Spin Polarization of Individual Magnetic Adatoms

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We have used spin-polarized scanning tunneling spectroscopy to observe the spin polarization state of individual Fe and Cr atoms adsorbed onto Co nanoislands. These magnetic adatoms exhibit stationary out-of-plane spin polarization, but have opposite sign of the exchange coupling between electron states of the adatom and the Co island surface state: Fe adatoms exhibit parallel spin polarization to the Co surface state while Cr adatoms exhibit antiparallel spin polarization. First-principles calculations predict ferromagnetic and antiferromagnetic alignment of the spin moment for individual Fe and Cr adatoms on a Co film, respectively, implying negative spin polarization for Fe and Cr adatoms over the energy range of the Co surface state.

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Since the early tunnel-junction measurements of Julliere [1], much work has been aimed at reducing the size of magnetic tunnel junctions. This has led to new possibilities for performing fundamental explorations into the quantum spin behavior of atomic and molecular systems [2] as well as new possibilities for improved performance of magnetic devices [3]. An important goal in this trend is the eventual creation of devices whose functionality can be engineered at the level of individual atomic spins [3]. Measuring the spin polarization state of individual atoms and understanding how atomic spins behave in a condensed matter environment are essential steps toward this goal.

Much progress has already been achieved through atomically resolved spin-polarized scanning tunneling spectroscopy (SPSTS) measurements of magnetic thin films [4,5]. Additionally, spin coupling of conduction electrons to individual magnetic atoms has been observed via the Kondo effect [6], spin flips have been observed via inelastic tunneling through individual magnetic atoms [7,8] and magnetic resonance force microscopy of silicon defects [9], and scanning tunneling spectroscopy has been used to probe magnetic interaction between magnetic atoms [8,10]. However, direct observation of the spin polarization state of isolated adatoms remains challenging, in part because isolated atoms have low magnetic anisotropy energy (MAE) which causes their spin to fluctuate in time due to environmental interactions. Recent measurements of adatom MAE's range from less than 1 to 9 meV/atom, but the techniques used in these measurements are unable to resolve the spin polarization state of an individual magnetic adatom [8,11].

Here we report a measurement of the spin polarization state of individual Fe and Cr adatoms on a metal surface. In order to fix the adatom spin in time, the adatoms were deposited onto ferromagnetic (FM) Co nanoislands, thereby coupling the adatom spin to the island magnetization through the direct exchange interaction. Low temperature (LT) SPSTS [4] was used to probe the local spin-

dependent electronic structure of isolated Fe and Cr adatoms prepared in this way. Clear spin-polarized (SP) contrast is seen between the two possible spin states (up and down) of each magnetic species. Furthermore, Fe and Cr atoms show opposite spin coupling to the underlying cobalt substrate. Over the energy range that includes the cobalt island SP surface state, Fe atoms display parallel spin polarization to the cobalt substrate electrons while Cr atoms display antiparallel spin polarization. First-principles calculations predict FM coupling between an Fe adatom and a Co island, and antiferromagnetic (AFM) coupling between a Cr adatom and a Co island, implying negative spin polarization [minority local density of states (LDOS) is larger than majority LDOS] around 0.3 eV below the Fermi energy for Fe and Cr atoms.

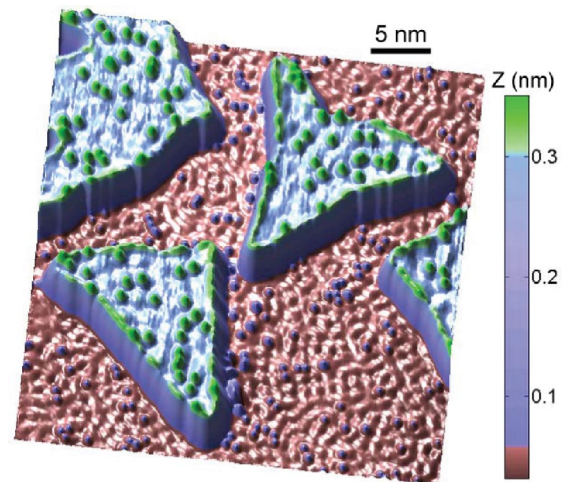


FIG. 1 (color). Topograph of Fe adatoms adsorbed onto triangular Co islands on Cu(111) at $T = 4.8$ K. Fe adatoms are seen as green protrusions on the Co islands and blue protrusions on the bare Cu(111) surface. Scan parameters: $V = -1$ mV, $I = 2$ pA.

Our experiments were conducted using a modified commercial OMICRON LT-STM. All measurements were performed in ultrahigh vacuum (UHV) ($< 10^{-11}$ mb) and at LT (4.8 K). SP tips were created by coating etched tungsten tips with a thin film of Cr to produce an out-of-plane magnetization as described by Pietzsch *et al.* [12]. The Cu(111) single crystal was cleaned in UHV by cycles of Ar ion sputtering and thermal annealing. Magnetic islands were obtained by depositing Co onto Cu(111) at room temperature [12–14]. Fe and Cr atoms were deposited by *e*-beam evaporation while the sample was kept cold (~ 10 K). The differential conductance (dI/dV) signal was measured through lock-in detection of the ac tunneling current modulated by a 477 Hz, 5 mV (rms) signal added to the junction bias (bias voltage here is defined as the sample potential referenced to the tip).

Cobalt islands were chosen as a substrate because their SP electronic structure has been well studied [12,14,15], thus providing a calibrated substrate where different magnetization states (“up” and “down” with respect to the surface plane) are easily accessed. Figure 1 shows a representative topograph of Fe adatoms adsorbed onto triangular Co islands on the Cu(111) surface. Spatial oscillations seen on the Cu(111) surface are due to interference of surface-state electrons scattered from the adatoms and Co islands [16].

The SP electronic structure of individual Fe and Cr adatoms on cobalt nanoislands was characterized using SPSTS (Fig. 2). All dI/dV spectra were obtained from islands oriented spatially in the same crystallographic direction to avoid structure-induced contrast due to fcc versus hcp stacked islands [12,14]. Spin-up and spin-down Co

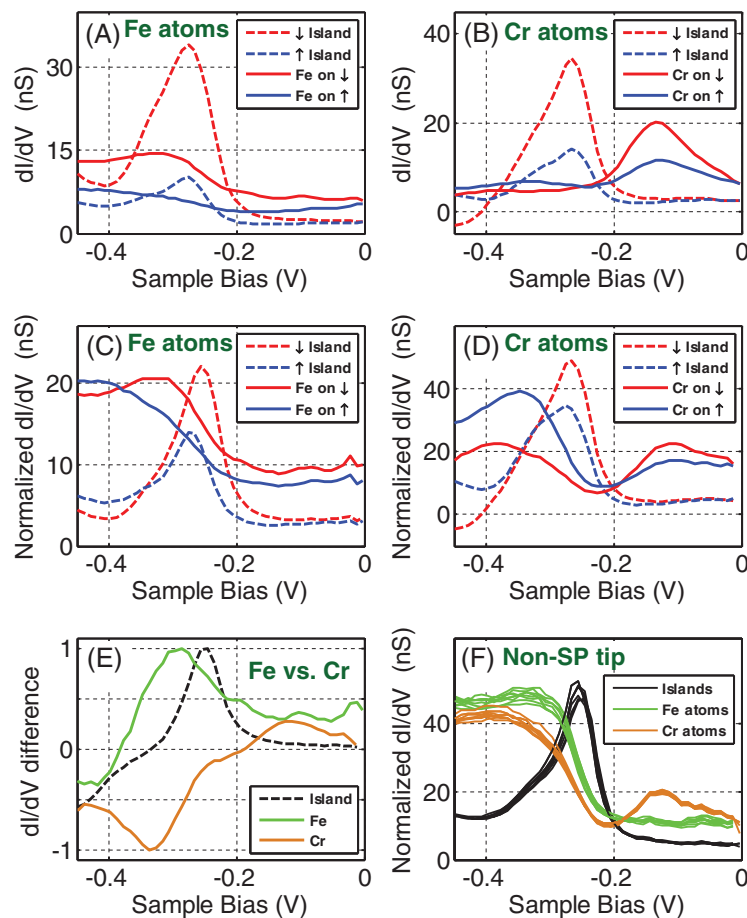


FIG. 2 (color). (a) SP dI/dV spectra of two Co islands with opposite spin orientation (dashed lines), as well as SP dI/dV spectra of Fe adatoms on these two islands (solid lines). Geometry-induced fluctuations are minimized by averaging spectra at 10 different points for each island and averaging spectra of 5 different atoms (on the same island) for each adatom spectrum. (b) SP dI/dV spectra of two Co islands with opposite spin orientation (dashed lines), as well as SP dI/dV spectra of Cr adatoms on these two islands (solid lines). Slight differences in Co island spectra compared to (a) are due to the use of a different SP tip. (c) Normalized Fe dI/dV spectra (see text) from (a). (d) Normalized Cr dI/dV spectra (see text) from (b). (e) Difference between spin-up and spin-down spectra for Co islands (dashed black line), Fe adatoms (green line), and Cr adatoms (orange line) [data taken from (c) and (d), curves are normalized to one at their extrema]. (f) Normalized dI/dV spectra measured with a non-SP tip held over 8 different Co islands (black lines) as well as corresponding Fe adatoms (8 green lines) and Cr adatoms (8 orange lines) on these islands. Initial tunneling parameters for (a) and (c): $V = -25$ meV, $I = 3$ pA, and for (b) and (d): $V = -50$ meV, $I = 2$ pA. Fe and Cr adatom spectra in (a)–(d) and (f) multiplied by a constant factor of 3 for better clarity in plots.

islands were distinguished spectroscopically via contrast arising from a spin-polarized surface state centered 0.28 eV below the Fermi energy, as seen in Fig. 2(a) (dashed lines) [12,14]. This resonance is believed to arise from a SP minority surface state of $d_{3z^2-r^2}$ symmetry [14]. Previous work has shown that the magnetizations of a Co island and a Cr tip are parallel when the dI/dV spectrum shows higher intensity at the island surface-state energy and are antiparallel for lower dI/dV intensity, implying that Co islands and Cr tips both have negative spin polarization in that energy range [12,17]. Therefore, if the tip total spin polarization is oriented down (\downarrow) then the total spin polarization of a Co island displaying a higher magnitude surface-state peak is also (\downarrow), and the total spin polarization of an island displaying a lower magnitude peak is up (\uparrow). Using this convention, SP spectra measured for individual Fe adatoms [Fig. 2(a), solid lines] show strong spin polarization contrast depending on whether they lie on \downarrow or \uparrow Co islands. SP spectra measured for individual Cr adatoms on Co islands [Fig. 2(b), solid lines] also show strong spin polarization contrast depending on the magnetization of the island on which they lie. The magnetic contrast for Cr atoms, however, qualitatively differs from the contrast seen for Fe atoms.

Spectroscopic differences in adatom behavior are best seen here by normalizing the spectra according to the scheme of Ref. [18], which is useful in predicting spin contrast in dI/dV maps from dI/dV point spectroscopy. This scheme normalizes differences in $dI/dV(V)$ that occur due to height-induced differences in $I(V)$ and is given by the following formula:

$$\left(\frac{d\tilde{I}}{dV}\right)_i = \left(\frac{dI}{dV}\right)_i \frac{I_1(V)}{I_i(V)} \quad \text{where } i = 1, 2, \dots, 4. \quad (1)$$

Here i indexes a specific spectrum and $(d\tilde{I}/dV)_i$ is the corresponding normalized spectrum. $I_i(V)$ is measured simultaneously with each corresponding $(dI/dV)_i$ spectrum, and the choice of $I_1(V)$ does not affect the ratio between normalized dI/dV spectra [18]. In the energy range where the Co island spin polarization is most pronounced (-0.35 to -0.20 eV with respect to the Fermi energy) Fe adatoms exhibit spin polarization parallel to the underlying Co island spin polarization [Figs. 2(a) and 2(c)]: Fe atoms on \downarrow islands have a stronger dI/dV signal than Fe atoms on \uparrow islands. Cr atoms, on the other hand, show opposite spin polarization in this energy range compared to the Co island spin polarization [Figs. 2(b) and 2(d)]: Cr atoms on \downarrow islands exhibit a lower dI/dV signal than Cr atoms on \uparrow islands.

The reversed spin-contrast behavior for Fe and Cr adatoms on Co islands is summarized in Fig. 2(e). In the energy range of maximum Co island spin contrast the Fe adatoms are seen to have the same sign of spin contrast as the Co islands while the Cr adatoms display spin contrast with an opposite sign. Over this energy range the Fe adatom spin polarization is thus parallel (FM coupled) to

the Co island spin polarization while the Cr adatom spin polarization is antiparallel (AFM coupled) to the Co island spin polarization. Similar spin contrast was seen for hundreds of Fe and Cr atoms on more than 20 different islands using five different SP tip preparations. SPSTS of Fe and Cr adatoms on the bare Cu(111) substrate showed no spin contrast, and non-SP spectra [Fig. 2(f)] also showed no discernible contrast for Fe and Cr adatoms on different Co islands.

Figure 3(a) shows a color-scaled SP dI/dV map together with topograph contour lines (measured simultaneously) for Fe and Cr atoms codeposited on two Co islands with opposite magnetization. Fe and Cr atoms can be easily distinguished by their topographic signatures (Cr atoms protrude 0.07 nm from the island surface while Fe atoms protrude 0.04 nm). Spin contrast between adatoms sitting on the two islands is seen in line cuts through Fe and Cr atoms shown in Figs. 3(b)–3(e). Fe atoms sitting on the \downarrow island exhibit a larger dI/dV signal than Fe atoms on the \uparrow

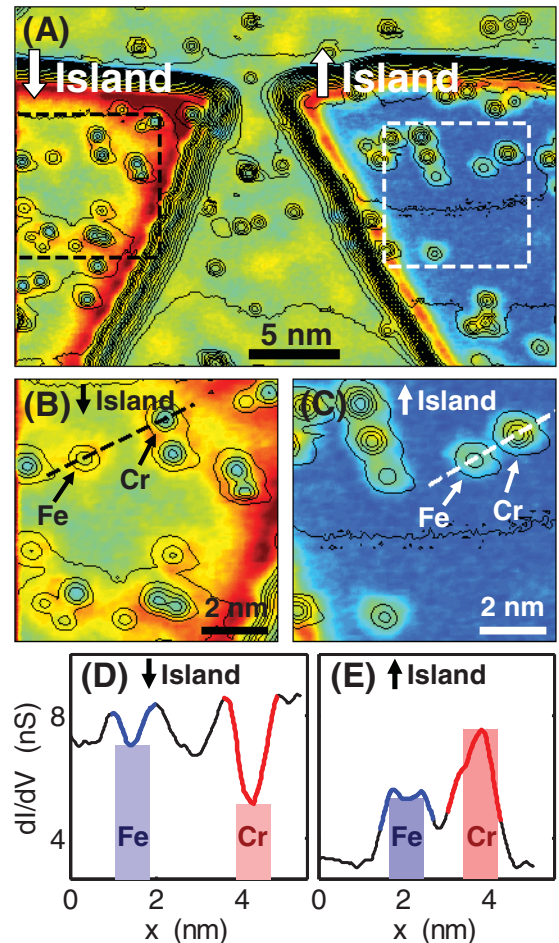


FIG. 3 (color). (a) SP dI/dV map of Fe and Cr adatoms on \downarrow and \uparrow Co islands on Cu(111). Scan parameters: $V = -0.365$ V, $I = 20$ pA, $T = 4.8$ K. (b),(c) Zoom-ins of areas marked by dashed lines on \downarrow and \uparrow islands in (a). (d),(e) Line scans through the centers of Fe and Cr adatoms on \downarrow and \uparrow islands, respectively [(marked by dashed lines in (b) and (c)].

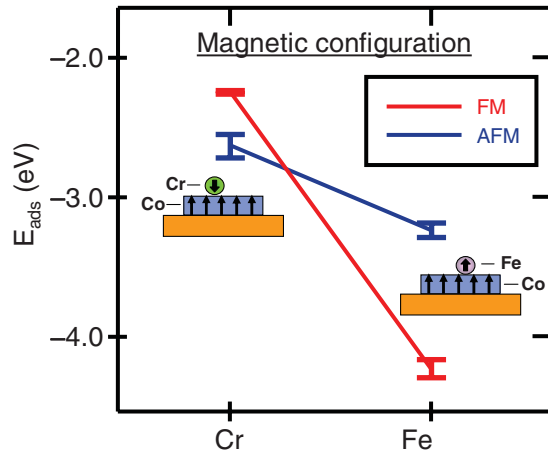


FIG. 4 (color). Calculated binding energies of ferromagnetic and antiferromagnetic configurations for Fe and Cr adatoms on a 2-ML high Co film on Cu(111). Error bars indicate the energy difference between hcp and fcc adatom adsorption sites. Cartoons depict the lowest-energy magnetic coupling configuration for Fe and Cr adatoms on the Co film.

island, while Cr atoms on the \downarrow island show a smaller dI/dV signal than Cr atoms on the \uparrow island. This further confirms the parallel nature of the Fe/Co island spin coupling and the antiparallel nature of the Cr/Co island spin coupling over this energy range. SPSTS thus clearly reveals single adatom spin contrast: each type of adatom yields a distinct spectrum, and over the energy range of the Co island surface-state Fe and Cr adatoms show opposite spin polarization. However, this measurement does not unambiguously determine the direction of the total spin of the adatom because the total spin is an integral over all filled states while the spectra shown here were taken over a finite energy range.

To better understand the magnetic coupling of the adatoms and islands, we performed density-functional theory calculations within the generalized-gradient approximation using the projector-augmented wave method [19]. We calculated adsorption energies of Fe and Cr atoms on a FM 2-ML film of Co on Cu(111), with adatom moment fixed parallel and antiparallel to the magnetization of the Co film. Full relaxation was carried out for the adatom and top three layers, using 3×3 supercells and 2×2 sampling of the Brillouin zone. The resulting energies (Fig. 4) show that Fe adatoms prefer ferromagnetic alignment to the Co film, while Cr adatoms prefer antiferromagnetic alignment. Comparison to our SP measurements implies that Fe and Cr adatoms exhibit negative spin polarization over the energy range of the Co island surface state. Within an effective Heisenberg Hamiltonian, the energy difference between spin-parallel (FM) and antiparallel (AFM) alignments is twice the exchange coupling energy J . We find $J = -0.5$ eV for Fe adatoms and $J = 0.25$ eV for Cr

adatoms, favoring FM and AFM alignment, respectively. These large exchange energies explain how we are able to observe static adatom SP despite our environmental temperature of 4.8 K.

In conclusion, we have used SPSTS to observe the spin polarization state of individual Fe and Cr adatoms adsorbed onto Co nanoislands. Over the energy range of the Co island surface state, Fe adatoms exhibit SP parallel to the Co island while Cr adatoms exhibit antiparallel SP. Calculations predict FM and AFM alignment of the spin moment for Fe and Cr adatoms on a Co film, respectively, implying negative spin polarization for Fe and Cr adatoms over the energy range of the Co surface state.

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