Spin-dependent Smoluchowski effect

O. P. Polyakov,[1,2] M. Corbetta,[1] O. V. Stepanyuk,[1,2] H. Oka,[1] A. M. Saletsky,[2] D. Sander,[1,*]
V. S. Stepanyuk,[1,†] and J. Kirschner[1,3]

[1]*Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle/Saale, Germany*
[2]*Faculty of Physics, Moscow State University, 119899 Moscow, Russia*
[3]*Martin Luther University Halle-Wittenberg, D-06120 Halle, Germany*

(Received 28 August 2012; revised manuscript received 30 October 2012; published 10 December 2012)

Electron charge near atomically sharp corrugations at the surfaces of a solid tends to spill out and smoothen the abrupt variation of the positions of the positively charged atomic nuclei. The reason is that electrons are much less localized than nuclei. This has been discussed already some 70 years ago by Smoluchowski [R. Smoluchowski, Phys. Rev. **60**, 661 (1941)], and the corresponding effect of charge redistribution near surface corrugations bears his name. The Smoluchowski effect focuses on the total electron charge density. It neglects that electrons—in addition to charge—also carry a spin. We discuss spin-dependent electron spill out and demonstrate in a combined theoretical and experimental work that compelling consequences for spin-polarization and spin-dependent transport arise at the edges of magnetic nanostructures due to the spin-dependent Smoluchowski effect. We find a variation of the tunnel magnetoresistance ratio of more than 20% on a length scale of a few atomic diameters.

DOI: 10.1103/PhysRevB.86.235409 PACS number(s): 72.25.Ba, 73.20.At, 75.47.−m, 75.75.Lf

The spreading and smoothing of electron charge density above atomically sharp surface corrugations as described by Smoluchowski[1] is a well established picture in solid state physics, which has significant implications in wide areas of surface science. Examples are the local variation of the workfunction,[1–8] the surface distribution of adsorbates,[9–12] the local variation of the electronic density of states,[13–15] and of forces due to to dipole fields[16] as probed by scanning tunneling microscopy (STM) and spectroscopy (STS).

The hallmark of the Smoluchowski effect is that the spatial corrugation of the atomic cores deviates from that of the electronic charge density, where the latter shows a more smoothed behavior as compared to the former. This has been also revealed by thermal energy He-atom scattering.[17]

Although the above-discussed works have provided an appealing picture of the electronic charge redistribution at surface corrugations, and its influence on physical and chemical properties, our understanding of the effect is still incomplete. The discussion so far focused on the total electronic charge density, and the effect of electron spin has been neglected.

Spin-polarized materials such as ferromagnets show a distinctively different energy dependence of the local density of states (LDOS) for majority and minority electrons. Also the contributions of states with different symmetry to the density of states differs for majority and minority states. Thus, it is *a priori* not clear how majority and minority states contribute to the spin dependence of the Smoluchowski effect. Our work sheds light on the electronic origin of the spin-dependent Smoluchowski effect.

In this work we study spin-dependent electronic and transport properties at the edge of a magnetic nano-island. Our results reveal the spin dependence of the Smoluchowski effect, which leads to an electron spin-dependent charge flow at surface corrugations. Striking spatial variations on the atomic scale of the spin polarization at the edge of a bilayer Co step on Cu(111) are uncovered by theory and experiment. The spin polarization near a step edge changes markedly with energy. We focus on the model system of bilayer Co nano-islands on Cu(111), but our results are of general significance because they demonstrate that the spin-dependent Smoluchowski effect can strongly influence the spin polarization and the tunnel magnetoresistance (TMR) at the edges of magnetic nanostructures on metal surfaces.

The experimental results were obtained by spin-polarized STM and STS at 8 K and in magnetic fields of up to 4 T oriented along the sample normal. The preparation of the sample has been described before.[18] The evaporation of Co on Cu(111) at room temperature leads to the formation of double-layer-high Co islands with base lengths from 1–30 nm (Ref. 19). STS measurements were performed by a lock-in technique (20 mV, 5 kHz) to obtain the differential conductance dI/dV(V) (I: tunnel current, V: sample voltage). The dI/dV(V) signal is related to the local electronic and magnetic properties of sample and tip.[20] To investigate spin-dependent electronic properties, bulk Cr tips were used,[21] and the extraction of the asymmetry of the differential conductance has been discussed.[21,22]

The *ab initio* calculations are performed by means of the Vienna simulation package (VASP)[23] using the Perdew-Wang version of the generalized gradient approximation (GGA-PW91).[24] Ultrasoft pseudopotentials have been exploited in our calculations.[25,26] A criterion of force-on-nuclei convergence to within 0.01 eV/A was used. In the calculations we mimic the edge of a bilayer high Co island on Cu(111) by an infinite stripe of Co atoms, which is four atomic rows wide in the topmost layer and five for the lower layer. The Cu substrate is described by a slab of five layers, with 12 atomic rows in each layer. This structure is sketched in Fig. 1(a). We have also calculated the electronic structure at the edge of Co islands performing calculations for different numbers of atomic rows in the stripe, and we find that the chosen model describes the main aspects reliably. Different orientations of the step edge on the substrate have been investigated. The results for steps with (100) facets and (111) facets are similar, and we discuss results for (111) facets in the following.

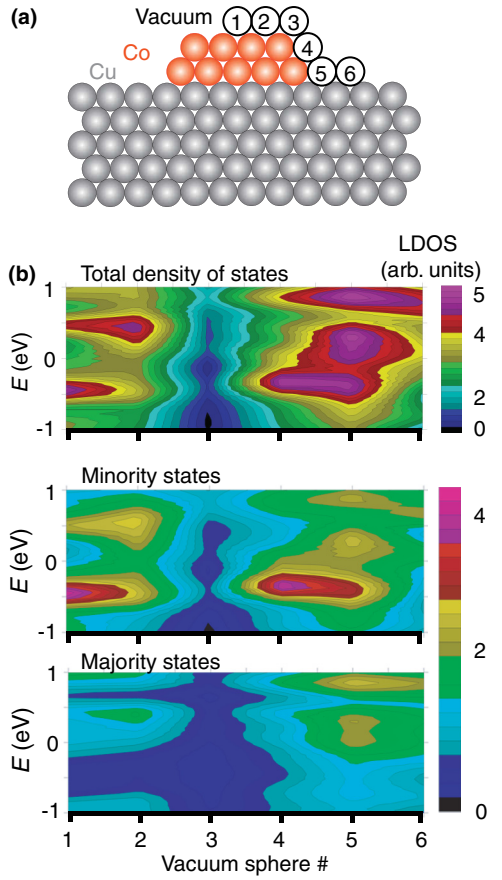

FIG. 1. (Color) (a) Hardsphere model of the system used in the calculations. Note that all atomic positions were allowed to relax. (b) Plots of the energy dependence of the total density of states (top) and of the spin-resolved density of states of minority (center) and majority (bottom) electrons as calculated at the position of the vacuum spheres identified in (a).

The energy and site-resolved plots of the calculated total local density of states and for the minority and majority electrons in the vacuum space above the edge of the Co stripe are presented in Fig. 1(b). The total density of states reveals a nontrivial spatial and energy dependence of the density of states. The total density of states is strongly reduced above the step edge (position 3). Qualitatively we find that the total electron density of states at any given energy is reduced above the Co stripe (position 1) and increased above the Cu surface (position 6). Thus, a positive surface dipole is expected near the step edge, in accordance with Smoluchowski's model. However, the plot also indicates that states of different energy show a different spatial variation. Thus, electron charge spill out and smoothing is an energy-dependent phenomenon.

The plots of the minority and majority states reveal that the LDOS for minority electrons is significantly larger than for majority electrons. The minority LDOS exhibits strong spatial variations across the step, which vary drastically with energy. In both spin channels a deep minimum of the LDOS near the top of the step, which corresponds to the vacuum sphere 3, is revealed. This reflects the spill out of the electronic charge near the top of the step, in accordance with Smoluchowski's proposal. Our treatment advances the Smoluchowski description by identifying that charge redistribution at step edges effects minority and majority electrons differently, as outlined next.

There is a strong local increase in the electron density of the majority electrons at the bottom of the step. This contrasts with the LDOS of the minority electrons, where the LDOS at the bottom is close to that on the top of the step. The behavior of the minority *sp* electrons is strongly affected by the localized minority *d*-rim states recently observed at the edge of Co islands on Cu(111) in spin-polarized STS experiments.[22,27] The rim states have been clearly identified as spin-polarized states having an electronic structure strongly different from that of the island's interior.

The above results give clear evidence of the spin-dependent charge redistribution across a step of a magnetic nanostructure. In other words, one can speak of a spin-dependent Smoluchowski effect at the edges of magnetic nanostructures.

One very interesting and important issue predicted by these results is the possible strong impact of the spin-dependent charge redistribution on the spin polarization of electrons above step edges. In particular, one might expect significant spatial variations of the spin polarization near step edges.

The spin-polarization P is defined as $P(E) = \frac{n_\uparrow(E) - n_\downarrow(E)}{n_\uparrow(E) + n_\downarrow(E)}$, where $n_\uparrow(E)$ and $n_\downarrow(E)$ are the LDOS for the majority and minority electrons, respectively. The calculated spin polarization near the edge of the Co island is presented in Fig. 2.[28]

Figure 2 shows a strong energy and position dependence of the spin polarization across the step edge. For example, at energies close to $E = -0.5$ eV the spin polarization is strongly negative near the upper part of the step, and it decreases towards zero at the bottom of the step. The spin polarization close to the Fermi energy is positive at distances 3–4 Å from the edge, and it is negative directly at the edge. The spin polarization approaches zero at the bottom of the step. For energies close to $E = +0.5$ eV, the spin polarization is large and negative for all sites on the top the step edge, while it changes to small negative values at the bottom of the step.

Spin-polarized STS is the method of choice to determine the spin polarization above nanostructures with high spatial resolution.[29] To check the validity of the calculations we perform measurements of the spin polarization and the TMR ratio above the edge of a bilayer Co island on Cu(111) by

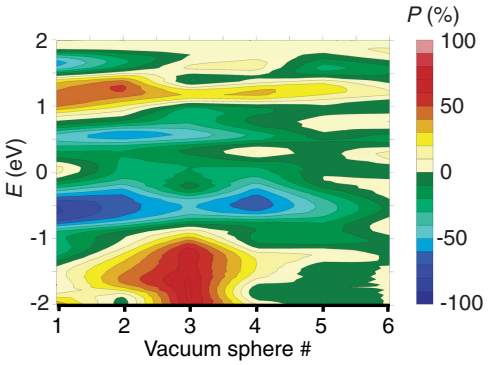

FIG. 2. (Color) Calculation of the energy dependence of the spin-polarization P at the vacuum spheres across the step edge, as defined in Fig. 1(a).

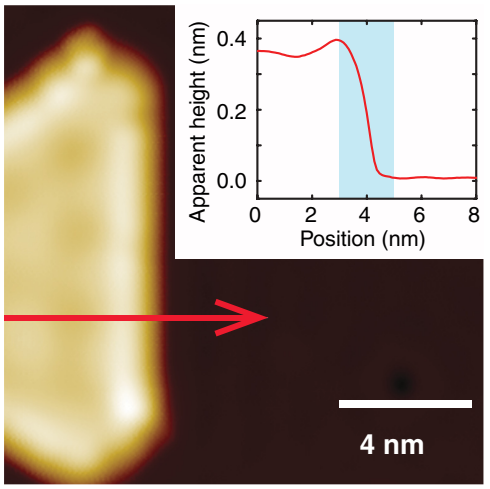

FIG. 3. (Color) Constant current image ($V_{\text{gap}} = 0.1$ V, $I_t = 1$ nA) at the edge of a two-atomic-layer-high Co nano-island on Cu(111). Inset: Line profile along the red line indicated in the figure. The highlighted area indicate the extension of Co island step edge region of the dI/dV asymmetry line profiles in Fig. 4.

spin-polarized STM. Figure 3 shows a constant current map of the step edge and a line scan of the apparent height across the step edge. We measure maps of the differential conductance for states of parallel (P) and anti-parallel (AP) orientation between the tip and sample magnetization. From these maps we extract the asymmetry A of the differential conductance, which is defined as $A = (dI/dV_{AP} - dI/dV_P)/(dI/dV_{AP} + dI/dV_P)$. This asymmetry is proportional to the spin polarization of the sample P_S (Refs. 20,22, and 29). Whereas previous work[27] has focused on the position dependence of the spin polarization *within* a Co island, we reveal its position dependence at the transition to the vacuum above the Cu substrate with subnanometer spatial resolution and investigate its energy dependence.

Three line profiles of the asymmetry of the differential conductance, averaged over six adjacent lines next to the red arrow of Fig. 3, are shown in Figs. 4(a) through (c) for different bias voltages. The data reveal a spatial variation, which is most pronounced near the position 3–3.5 nm, near the upper section of the step edge. The magnitude and sign of the variation of the asymmetry depend on bias voltage.

The comparison between the experimental data of Figs. 4(a) through (c) and the theoretical data of Fig. 2 requires an alignment of the horizontal spatial axis. We choose the position of half-step height as the common point (i.e., the position 4 nm of the experimental line scans corresponds to the lateral position of vacuum sphere 4). Our data reveal that both the experiment and theory observe the same location of the strongest changes of the asymmetry and spin-polarization signal, which is located near the upper section of the step edge (i.e., at position 3–3.5 nm in Fig. 4 and at position 3 in Fig. 2).

The experimental data obtained at a gap voltage of −0.5 V [Fig. 4(a)] show a negative value near the top of the Co island step, and it turns slightly positive before going to zero at the bottom of the step. This resembles favorably the behavior of the spin polarization along the step edge as indicated for

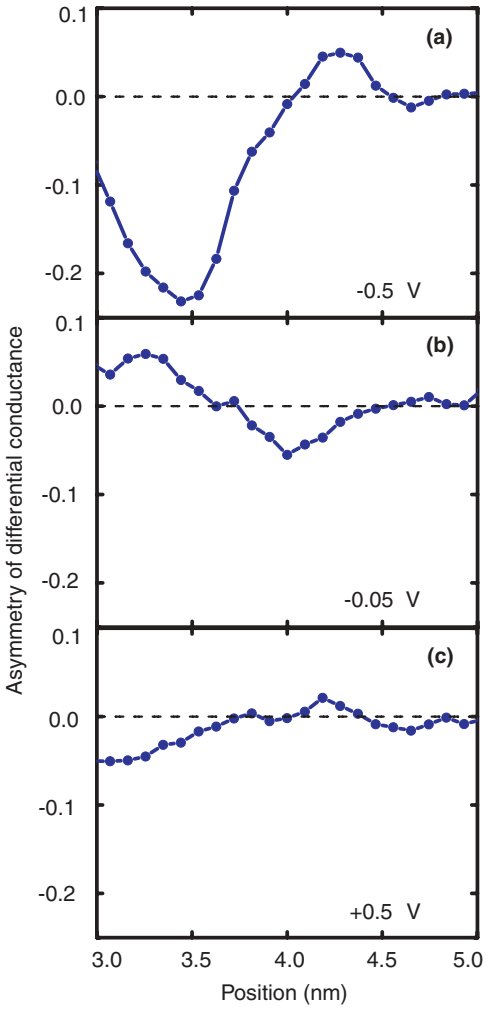

FIG. 4. (Color online) Differential conductance dI/dV asymmetry line profiles measured at different gap voltages applied to the sample of the tunnel junction with reference to the tip. Gap voltage (a) −0.5 V, (b) −0.05 V, and (c) +0.5 V. The line profile is measured along the red arrow in Fig. 3.

a horizontal section through Fig. 2 at −0.5 eV. For −0.05 V [Fig. 4(b)], the dI/dV asymmetry shows small positive values near the upper step edge, and negative values at half height of the step edge (4 nm), changing to zero above the Cu surface. This behavior agrees favorably with the calculation presented in Fig. 2. Also at +0.5 V [Fig. 4(c)] the agreement with the theory is comforting as we measure a negative asymmetry of the differential conductance, indicative of a negative spin polarization over the complete step edge, in agreement with the theory.

A spatial modulation of the spin-polarization impacts also the TMR, as recently described by experiment and theory.[30] In that work, the spatially modulated TMR ratio in the *center* region of a nanostructure has been induced by spin-dependent quantum interference. Here, we expect that the strong spatial variation of the spin polarization at the *edge* of a nanostructure may also strongly modulate the TMR ratio.[31,32] The TMR ratio is related to the spin polarization of tip P_T and sample P_S by $\frac{I_P - I_{AP}}{I_{AP}} = \frac{2\,P_T(E)\,P_S(E)}{1 - P_T(E)\,P_S(E)}$. For small spin polarizations of the

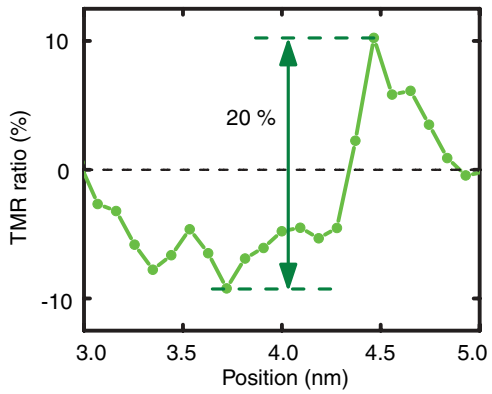

FIG. 5. (Color online) Line scan of the tunnel magnetoresistance ratio (TMR) measured along the red arrow in Fig. 3 at a gap voltage between sample and tip of −0.3 V.

tip and the sample, the TMR ratio is proportional to the spin polarization above the sample.[33]

We extract the TMR ratio along the red line of Fig. 3. Figure 5 shows the TMR ratio at −0.3 V. The plot reveals a drastic variation of the TMR ratio from −10% to +10% within 1 nm along the Co step edge. We ascribe this to the corresponding spatial variation of the spin polarization of the sample, as predicted in the theory and experimentally established above. Thus, our combined calculations and experiments indicate a pronounced spatial variation of the TMR ratio near steps. It is ascribed to the spin-dependent Smoluchowski effect.

In conclusion, our combined theoretical and experimental study establishes the spin dependence of the Smoluchowski effect at the edge of a Co nanostructure. The implications of the spin-dependent Smoluchowski effect are manifold for spin-dependent transport, where tunnel current, differential conductance, and spin polarization are effected. The exploitation of the spin-dependent Smoluchowski effect opens a new way to tune the TMR of nanostructured magnetic tunnel junctions on a scale of a few Angstroms.

The authors thank Safia Ouazi and Yasmine Nahas for discussions, and N. Kurowsky for expert technical support. This work was supported by Deutsche Forschungsgemeinschaft Grant No. SFB 762.

*sander@mpi-halle.de
†stepanyu@mpi-halle.de

[1] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).
[2] K. Besocke and H. Wagner, Phys. Rev. B **8**, 4597 (1973).
[3] K. Besocke, B. Krahl-Urban, and H. Wagner, Surf. Sci. **68**, 39 (1977).
[4] B. Krahl-Urban, E. Niekisch, and H. Wagner, Surf. Sci. **64**, 52 (1977).
[5] K. Wandelt, Surf. Sci. **251-252**, 387 (1991).
[6] H. Ishida and A. Liebsch, Phys. Rev. B **46**, 7153 (1992).
[7] J. F. Jia, K. Inoue, Y. Hasegawa, W. S. Yang, and T. Sakurai, Phys. Rev. B **58**, 1193 (1998).
[8] I. Merrick, J. E. Inglesfield, and G. A. Attard, Phys. Rev. B **71**, 085407 (2005).
[9] M. M. Kamna, S. J. Stranick, and P. S. Weiss, Science **274**, 118 (1996).
[10] M. Vladimirova, M. Stengel, A. De Vita, A. Baldereschi, M. Böhringer, K. Morgenstern, R. Berndt, and W.-D. Schneider, Europhys. Lett. **56**, 254 (2001).
[11] H. Ibach, Surf. Sci. **604**, 377 (2010).
[12] P. Han and P. S. Weiss, Surf. Sci. Rep. **67**, 19 (2012).
[13] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature (London) **363**, 524 (1993).
[14] P. Avouris and I. W. Lyo, Science **264**, 942 (1994).
[15] P. Avouris, I.-W. Lyo, and P. Molinas-Mata, Chem. Phys. Lett. **240**, 423 (1995).
[16] J. Y. Park, G. M. Sacha, M. Enachescu, D. F. Ogletree, R. A. Ribeiro, P. C. Canfield, C. J. Jenks, P. A. Thiel, J. J. Sáenz, and M. Salmeron, Phys. Rev. Lett. **95**, 136802 (2005).
[17] P. Bderossian, B. Poelsema, G. Rosenfeld, L. C. Jooritsma, N. N. Lipkin, and G. Comsa, Surf. Sci. **334**, 1 (1995).
[18] G. Rodary, S. Wedekind, D. Sander, and J. Kirschner, Jpn. J. Appl. Phys. **47**, 9013 (2008).
[19] J. de la Figuera, J. E. Prieto, C. Ocal, and R. Miranda, Phys. Rev. B **47**, 13043 (1993).
[20] D. Wortmann, S. Heinze, P. Kurz, G. Bihlmayer, and S. Blügel, Phys. Rev. Lett. **86**, 4132 (2001).
[21] M. Corbetta, S. Ouazi, J. Borme, Y. Nahas, F. Donati, H. Oka, S. Wedekind, D. Sander, and J. Kirschner, Jpn. J. Appl. Phys. **51**, 030208 (2012).
[22] H. Oka, P. A. Ignatiev, S. Wedekind, G. Rodary, L. Niebergall, V. S. Stepanyuk, D. Sander, and J. Kirschner, Science **327**, 843 (2010).
[23] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[24] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[25] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[26] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
[27] O. Pietzsch, S. Okatov, A. Kubetzka, M. Bode, S. Heinze, A. Lichtenstein, and R. Wiesendanger, Phys. Rev. Lett. **96**, 237203 (2006).
[28] The position of occupied minority Co *d* states calculated by VASP or by the Korringa-Kohn-Rostoker method is about 0.1 eV higher than the experimental results (Refs. 30 and 34). Therefore, we shift the Fermi level on the map of the SP to the higher energy by 0.1 eV.
[29] M. Bode, Rep. Prog. Phys. **66**, 523 (2003).
[30] H. Oka, K. Tao, S. Wedekind, G. Rodary, V. S. Stepanyuk, D. Sander, and J. Kirschner, Phys. Rev. Lett. **107**, 187201 (2011).
[31] M. Julliere, Physics Letters A **54**, 225 (1975).
[32] E. Y. Tsymbal, O. N. Mryasov, and P. R. LeClair, J. Phys.: Condens. Matter **15**, R109 (2003).
[33] P. A. Ignatiev, O. O. Brovko, and V. S. Stepanyuk, Phys. Rev. B **86**, 045409 (2012).
[34] M. V. Rastei, B. Heinrich, L. Limot, P. A. Ignatiev, V. S. Stepanyuk, P. Bruno, and J. P. Bucher, Phys. Rev. Lett. **99**, 246102 (2007).