Evidence for 4*d* Ferromagnetism in 2D Systems: Ru Monolayers on C(0001) Substrates

R. Pfandzelter,* G. Steierl, and C. Rau
Department of Physics and Rice Quantum Institute, Rice University, Houston, Texas 77251
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The first observation of 4*d* ferromagnetism in two-dimensional systems is reported. Using Auger electron spectroscopy, we find that the initial growth of Ru on a C(0001) substrate is lateral until a homogeneous monolayer film is formed. The magnetic properties of the films are studied using spin polarized secondary electron spectroscopy. For one monolayer Ru on C(0001), below a surface Curie temperature of approximately 250 K, nonzero in-plane spin polarization is observed and found to saturate in an applied field of a few tenths of an Oe. The results are discussed in the light of theoretical predictions.

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For the vast majority of elements, magnetism is found in isolated atoms, as shown by Hund's rules. In solids, however, the existence of spontaneous, long-range ferromagnetic order is restricted to only a few 3*d*-transition (Fe, Co, and Ni) and 4*f*-rare-earth metals (Gd, Tb, Dy, Ho, Er, and Tm). Electronic structure calculations using state-of-the-art methods now reveal the exciting perspective that more elements might be forced to conserve their atomic magnetism, if properly synthesized at the nanometer scale.

One way to achieve this goal and retain magnetic moments is to grow a metal, which is paramagnetic in its bulk form, epitaxially on an adequate nonmagnetic substrate. Ferromagnetic order in such ultrathin films may be induced by the reduced coordination number and hence reduced interatomic hybridization, band-structure effects due to the restriction to two dimensions, and, compared to the bulk paramagnetic solid, an increased lattice constant imposed by pseudomorphic film growth. An alternate way to preserve magnetic moments is to form small clusters which could be magnetic due to the reduced coordination and high symmetry. This leads to degenerate electronic states, which is an important condition for magnetism.

So far, theoretical work has focused on the study of 4*d*-transition metals. It is found that the elements at the very end of the 4*d* series are likely candidates to exhibit magnetism [1–6]. For small clusters, this prediction recently was confirmed by Cox, Louderbaek, and Bloomfield [7], who found that small Rh clusters consisting of a few tens of atoms show magnetic ordering of the 4*d* electrons; the clusters are superparamagnetic with large magnetic moments. As to thin films, calculations were performed for ultrathin films deposited on the noble metals Ag and Au [1–5], which interact only weakly with the deposited atoms due to the large energy separation of the *d* bands. In addition, the larger lattice constant of Ag and Au would, compared to the bulk lattice constant of these 4*d* metals, increase the lattice constant in the films in the case of a pseudomorphic growth. All authors come to the conclusion that both Ru and Rh monolayers on Ag(001) or Au(001) possess a ferromagnetic ground state.

Subsequent experiments have been done for Rh on Ag(001) as well as Rh and Pd on Au(001), but failed to find any evidence for the existence of spontaneous, long-range ferromagnetic order [8,9], or were inconclusive [10]. There is experimental evidence that an explanation for this discrepancy between theory and experiment can be found in the poor quality of the deposited films: Schmitz *et al.* [11] propose that the equilibrium structure of Rh on Ag(001) is actually that of a sandwich with a Ag monolayer atop. Mulhollan, Fink, and Erskine [9] find evidence for diffusion of Rh into the Ag matrix. Other authors do not rule out islanding [8,9]. These effects are indeed likely to prevent the existence of spontaneous, long-range ferromagnetic order. In addition, it is well known that 4*d* elements respond sensitively to a change in the environment due to the large extent of their valence wave function.

We thus concluded that a different nonmagnetic substrate material should be used and found the graphite C(0001) surface to be a promising candidate for the following reasons: Similar to the noble metals, there is hardly a band overlap with the 4*d*-transition metals due to the small density of states near the Fermi level (the π band has its maximum at 3 eV below the Fermi level E_F), which should prevent effective hybridization with the 4*d* bands. Moreover, the graphite (0001) surface is known to be very flat, possessing only a few steps and nearly no defects. This should effectively suppress interdiffusion and thus considerably increase the time to reach a final equilibrium structure, as suggested from thermodynamic considerations [11,12].

As film material, we selected Ru rather than Rh which is, due to its larger magnetic moment and its larger magnetic energy, thought to be more suitable for experimental verification of 2D 4*d* ferromagnetism [4]. Finally, Ru is hexagonal, with an in-plane nearest neighbor distance which is almost twice that of graphite. This should favor epitaxial or pseudomorphic growth of

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Ru, where the lattice is laterally stretched (5%), compared to that of the bulk phase.

The experiments reported in this Letter address both the growth of one monolayer of Ru on the graphite C(0001) surface and the study of its magnetic properties. To study the growth, we use electron induced Auger electron spectroscopy (AES). For a large series of metal-on-metal systems, it is known that plots of Auger signal amplitudes versus evaporation time or coverage enable one to directly distinguish between different types of (initial) growth modes (lateral growth, islanding, and intermixing) [13]. In the case of lateral growth, the completion of a monolayer is revealed by a breakpoint in the plot, which can be precisely located if small measurement intervals are used. If both adsorbate and substrate signals are measured simultaneously, an effective cross-check of the results is possible, because the two plots provide complementary information.

For magnetometry, we use spin polarized secondary electron emission (SPSEE). In this technique a primary, unpolarized electron beam of energy of a few keV interacts with the sample and induces the emission of secondary electrons. In the case of a ferromagnetic sample, the emitted secondary electrons possess a nonzero, net spin polarization, which is a direct measure of the magnetization of the sample near the surface. From a practical point of view, it is advantageous to detect low-energy electrons (a few eV) because they have the highest intensity and highest spin polarization. The fact that the information depth is more than one atomic layer does not lead to any ambiguities in the present case of a magnetic monolayer on a nonmagnetic substrate.

As substrate, we use highly oriented, pyrolytic graphite (HOPG) ($8 \times 15 \times 1$ mm^3); the c axes of the crystallites are Gaussian distributed, with $\sigma = 0.2$, and the a axes are randomly oriented. The HOPG sample is cleaved in air by peeling off some layers. No further *in situ* treatment is necessary because the extremely low gas adsorption efficiency guarantees a clean surface for ample time. The sample is mounted on a manipulator between the pole caps of an electromagnet and can be cooled to liquid nitrogen temperatures. The temperature is monitored using a (nonmagnetic) copper-constantan thermocouple. Ru (purity 99.95%) is evaporated using electron beam evaporation and evaporation rates of 0.03 ML/min, where ML represents monolayer. The film thickness is monitored by using a quartz microbalance. AES is performed using a single-pass cylindrical mirror analyzer (CMA) with an integrated electron gun (3 keV, 100 nA/mm^2). During AES data collection, the Ru deposition is interrupted by using a shutter.

SPSEE is performed by using a compact, 20 keV Mott polarimeter with a Au target and four channeltrons, positioned at 135° to the incoming beam direction, to measure the left-right spatial asymmetry A of each pair of channeltrons during electron backscattering from the Au target. A is proportional to the spin polarization component P, measured normal to the scattering plane, i.e., $A = SP$, where S is the effective Sherman function ($S \approx 0.1$). In the experiment, we detect the in-plane (parallel to the applied magnetizing field) component of the electron spin polarization (ESP). The spin polarimeter is connected to an *einzellens* system with 90° cylindrical energy analyzer (pass energy 30 eV). Using an extraction voltage of 100 V, we detect low-energy secondary electrons emitted along the surface normal within a solid angle of 1% of 4π. The residual gas pressure during the magnetic measurements was $\approx 3 \times 10^{-10}$ mbar; during evaporation it increased to $\approx 8 \times 10^{-10}$ mbar. The surface cleanliness is checked by using AES.

The growth of Ru on C(0001) was studied by measuring Auger peak-to-peak signals versus deposition time. The most prominent Auger peak of Ru at 273 eV overlaps almost perfectly with the C Auger peak at 272 eV; therefore we used as adsorbate signal the smaller Ru peaks located at 231 and 200 eV, which do not interfere with the graphite Auger profile. Figure 1 shows the 231 eV Ru Auger electron data, where we have converted the x-axis scale from deposition time to coverage, using the quartz reading calibrated by a geometrical factor. We refer the coverage to the atomic density of the (0001) plane in bulk Ru and assume the sticking coefficient to be 1. The data in Fig. 1 are well represented by two straight line segments with a distinct change in slope. This is found for the 200 eV peak as well, although the data points show a little more scattering due to the smaller signal. The linear increase of the Auger signal shows that Ru grows laterally. The completion of the first Ru layer is indicated by a sharp breakpoint, which occurs at a coverage of nearly 1 ML. This value is corroborated by the measured Auger signal ratios between the C 272 eV peak before evaporation and the Ru 231 eV peak after completion of the first layer, using the Palmberg Auger sensitivities [14].

Beyond the breakpoint, the Auger signal still seems to increase linearly, but with a much smaller slope. The

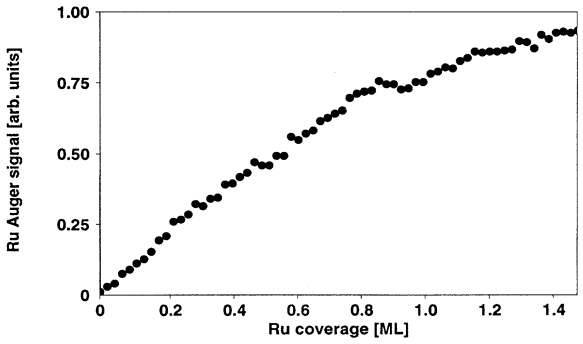

FIG. 1. Auger peak-to-peak height of the Ru 231 eV line versus Ru coverage on C(0001). The coverage is referred to the atomic density of the bulk Ru(0001) plane. Statistical errors are contained within the symbol size.

slope ratio between the second and the first straight line is 0.42. This is smaller than one would expect for a layer-by-layer growth: An inelastic mean free path $\lambda = 0.82$ nm for 231 eV electrons [15] yields for a thickness $d = 0.214$ nm of a Ru layer a ratio of 0.70. This might indicate that, beyond 1 ML, Ru starts to form three-dimensional particles. We are aware, however, that this conclusion is not unambiguous, because it has been shown that Auger peak shape changes at the completion of the first monolayer may affect differentiated signals and cause a reduction in slope (especially the irregularities near the breakpoint in Fig. 1 point to that) [16]. We further note that the breakpoint in Auger signal versus coverage curves might be caused by a premonolayer phase transition, rather than indicating monolayer completion. This, however, seems unlikely in the present case, since the atomic density of the monolayer is nearly that of the (0001) plane in hcp bulk Ru.

In typical growth mode studies using AES, both adsorbate and substrate Auger signals are used. For the present system, however, the almost perfect overlap between the C 272 eV line and the main Ru line at 272 eV poses problems to a straightforward evaluation of the substrate signal. In order to get a measure for the graphite signal, we determined the Ru 273 eV Auger signal by multiplying the Ru 231 eV signal by 2.35 [17] and subtracting the result from the height of the main peak in the measured spectrum. The results are shown in Fig. 2. As expected, the C Auger signal decreases linearly until the first Ru adlayer is completed at around 1 ML. This confirms the findings from the Ru Auger signal curve. We note, however, that the absolute values of the slopes should not be taken too seriously because the composite Auger spectrum cannot be considered a simple sum of the Ru and the C Auger spectra.

In conclusion of this discussion, we find that both the Ru and the C Auger signal versus coverage curves show that Ru grows laterally on graphite until the first monolayer is completed. This is corroborated by UHV scanning tunneling microscopy experiments, showing in the submonolayer coverage range lateral growth of Ru.

Next, we address the question whether Ru monolayer films exhibit long-range ferromagnetic order. Initially we measured the ESP as function of a small external field of up to 2 Oe, which is applied in plane. From the observed magnetization curves (see top inset of Fig. 3), we find that saturation already occurs at a field strength of some tenths of an Oe. Because of the small coercive field and the small remanence, it is experimentally difficult to resolve the transition area of the hysteresis loop. Therefore, it is experimentally more feasible to check for the existence of ferromagnetic order by measuring the saturation value of the ESP than by measuring coercivity and remanence.

In order to eliminate possible instrumental asymmetries, which might be caused by different channeltron efficiencies, by small construction asymmetries, or by a beam trajectory that deviates from the symmetry axes of the Mott detector, we flipped the ESP for each data point by reversing the applied saturation field. For all our data we find that the saturation value P of the ESP is well approximated by $P = [A(\text{up}) - A(\text{down})]/2S$, where $A(\text{up})$

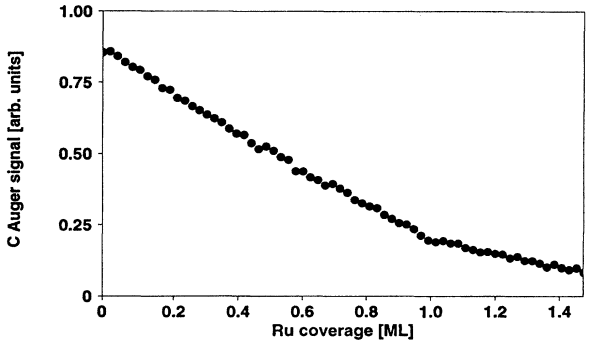

FIG. 2. Auger peak-to-peak height of the C 272 eV line versus Ru coverage on C(0001) (see text for details on the evaluation of the C Auger signal from the composite Ru-C-Auger spectrum). The coverage is referred to the atomic density of the bulk Ru(0001) plane. Statistical errors are contained within the symbol size.

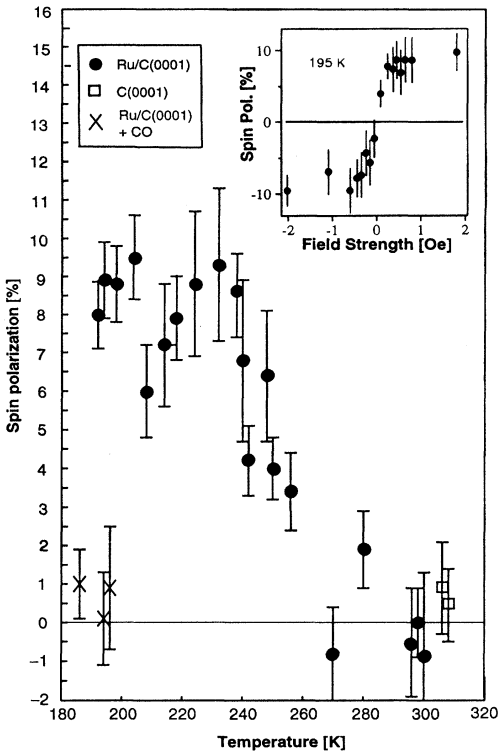

FIG. 3. Electron spin polarization (ESP) as function of temperature for a monolayer-thin Ru film on C(0001) (solid circles), for the clean C(0001) surface (open squares), and for the CO covered Ru monolayer film on C(0001) (crosses). The inset (top of figure) gives the ESP as function of the applied magnetizing field for $T = 195$ K.

and A(down) refer to the values of the normalized countrate difference, measured for opposite saturation magnetization directions by Mott scattering. Further corrections due to the nonvanishing mean value A(mean) = [A(up) + A(down)]/2 were neglectable. For the Sherman function S, we used the value 0.1.

In Fig. 3, we show the results of the SPSEE experiments. Included as an inset in Fig. 3 (top) is a hysteresis curve taken at 195 K which shows the ESP as function of the applied magnetizing field. The solid circles in Fig. 3 represent the observed ESP of a Ru monolayer film and its dependence on the temperature T. We see that at low temperatures an ESP of +(8–9)% is observed, i.e., the films are indeed ferromagnetic. The positive sign of the ESP indicates the presence of a majority ESP, i.e., predominance of electrons with magnetic moment oriented parallel to the small applied magnetizing field. With increasing temperature, the ESP sharply decreases and approaches zero within a narrow temperature range. This behavior of the ESP is found to be completely reversible. Our data thus follow previous experimental findings on the temperature dependence of 2D ferromagnetic, ultrathin films [18]. It is not the intent of the present Letter to evaluate the critical exponent of the 2D phase transition near the surface Curie temperature T_{Cs}. Such a procedure would require more data points near T_{Cs}, which will be reported in a forthcoming study. These results will be of interest to help resolve the current marking issue of the existence of several universality classes of 2D (ultrathin film, monolayer) ferromagnetism. From the data, T_{Cs} is located near 260 K. Note that the five data points average to zero when the error bars are taken into account.

In order to assure that the magnetizing process itself does not influence the measured asymmetry, we performed additional SPSEE measurements on the clean graphite surface using the same magnetizing fields. The clean graphite surface serves as a source of unpolarized electrons, i.e., the ESP is zero. This has actually been observed (Fig. 3, squares).

Further SPSEE measurements were performed on an adsorbate covered Ru monolayer film. At 300 K, we exposed the clean Ru film to 10 L (where 1 L = 10^{-6} Torr s) of CO, which has been found to result in a saturation coverage of CO at the clean Ru(0001) surface. As shown in Fig. 3 (crosses), chemisorption of CO causes a vanishing ESP within the experimental error. A tentative explanation is that the strong bonding of the CO destroys the ferromagnetic order in the Ru film.

In conclusion, we have demonstrated that Ru can be grown laterally on HOPG C(0001) until the first monolayer is completed. We find that the deposited Ru monolayer film is ferromagnetic below a surface Curie temperature $T_{Cs} \approx 250$ K. This is the first observation of spontaneous 2D ferromagnetism of a 4d element and thus the first case where a ferromagnetic film could be synthesized from elements other than those of the 3d or 4f elements. Theoretical models and calculations suggest that Ru, which is paramagnetic in its bulk form, can exhibit ferromagnetic order if properly synthesized as monolayer film on an adequate nonmagnetic substrate. The origin of the existence of ferromagnetic order can be found in the reduced dimensionality, in the reduced coordination number, and in the enhanced lattice constant. In addition, it seems to be favorable that there is nearly no overlayer-substrate band overlap for a Ru monolayer deposited on graphite.

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*Present address: Institut für Physik, Humboldt-Universität, Berlin, Germany.

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