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Surface Science 601 (2007) 1218–1230
SURFACE SCIENCE
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# Correlations between magnetic properties and bond formation in Rh–MgO(0 0 1)

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Received 12 July 2006; accepted for publication 12 December 2006
Available online 29 December 2006

## Abstract

We present the results of first principles calculations for the magnetism of Rh adlayers on MgO(0 0 1), at three different adsorption sites and three different coverages, corresponding to 1, 1/2 and 1/8 monolayers. Finite magnetization is found in all cases except that of one Rh monolayer above the oxygen site, which is also the most stable. We examine how the magnetization changes as a function of the Rh–surface distance and relate this to changes in the real-space charge density and in the density of states (DOS) as the Rh adlayer interacts with the surface. We find that increasing either the Rh–Rh interaction strength or the Rh–surface interaction strength leads to reduced magnetization, while increasing the former drives a crossover from localized (atomic) to itinerant magnetism. Neither the magnetic transition itself, nor the localized-to-itinerant magnetism crossover, is found to be directly related to the formation of Rh–surface bonds. From a practical point of view, we predict that magnetism in the Rh–MgO(0 0 1) system is most likely to be found experimentally at reduced coverages and at low temperatures.

*Keywords:* Density functional calculations; Electron density; Excitation spectra calculations; Adhesion; Magnetic phenomena (cyclotron resonance, phase transitions, etc.); Rhodium; Magnesium oxides; Adatoms; Magnetic films

## 1. Introduction

The study of magnetism in transition metals has a very long history. Most of the transition metals have a finite moment for the isolated atom, but magnetism in the three-dimensional (3D) bulk materials is very rare. Indeed, only four of the metals are magnetic and they are all from the first (3d) transition metal elements, with Fe, Co and Ni being ferromagnets and Mn an antiferromagnet. All the other 3d and all of the 4d and 5d transition metal atoms loose their magnetism when they bond together to form the bulk metals. However, in recent years there has been a great deal of interest in the possibility of forcing some of them to remain magnetic by reducing the dimensionality below that of the bulk metal. The interest is both fundamental and important in the context of possible technological applications in spintronics and in magnetic data storage and retrieval. It has largely centred on the search for ferromagnetism in elements from the upper half of the second (4d) and third (5d) transition metal series. In this paper we will focus on one of the more commonly studied examples, Rh.

Rh has been shown to display a rich variety of magnetic behaviour as a function of dimensionality. Starting from *0D systems*: atomic Rh has the electronic configuration $4d^8 5s^1$, leading to a ground state magnetic moment of $3\mu_B$ according to Hund's rules. 0D $Rh_n$ ($n = 9$–34) nano-clusters have been studied experimentally by Cox et al. [1,2], who found moments of 0.4–$0.8\mu_B$ for clusters with $n \leqslant 20$, dropping

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doi:10.1016/j.susc.2006.12.061

to 0.0–0.2$\mu_B$ above this size. Various theoretical studies [3–10] predict a rich variety of magnetic properties, with non-magnetic, ferromagnetic and antiferromagnetic ground states of 0–2$\mu_B$ all appearing for different values of $n$. In addition to this, 0D islands of Rh grown on Ag substrates have also been predicted to be magnetic [11].

Increasing to *1D systems*, Rh chains grown along the $\langle 010\rangle$ and $\langle 110\rangle$ directions on the (001) surface of Ag have been predicted to be magnetic [11,12]. However, experimental growth of such systems has been found to be very hard to control, so they are currently of limited interest technologically.

More interesting is the possibility of keeping Rh magnetic in *2D systems* [13]. The most obvious 2D system is actually the surface of bulk Rh crystals, and spin-dependent photoemission [14] does indeed find a weak magnetization of 0.2$\mu_B$, in agreement with theoretical predictions [15]. More "strictly" 2D systems have also been studied, in the form of Rh thin films and monolayers (MLs) grown on a variety of substrates. Here, most of the systems examined have been Rh adlayers on noble metal substrates. Theoretical predictions have suggested that single Rh MLs will be magnetic on Ag(111) [16,17] and (001) [13,16,18–24], Au(111) [16] and (001) [13,16,23,25], Ni(111) [26] and Cu(001) [16,27–29] but non-magnetic on Ag(110) [16], Au(110) [16], Cu(110) [16] and Cu(111) [16]. In the magnetic cases, the moments are predicted to decrease rapidly with increasing numbers of Rh layers, usually becoming very weak by film thicknesses of just 2 ML [26,30]. Unfortunately, all attempts to experimentally demonstrate the presence of a magnetic moment in such a system have failed [31–33]. The explanation seems to be that layer-by-layer growth is too difficult to obtain on these substrates, due to problems with lattice constant mismatch, interdiffusion and alloying [29,34]. Theoretical work shows that this should indeed destroy the anticipated magnetism [18,24,35].

The obvious alternative is to study MLs grown on non-metallic substrates. So far one such transition metal system has been found to be magnetic: Ru grown on C(0001) [36,37]. Experimental studies of Rh MLs on non-metallic substrates have (to our knowledge) yet to be reported, but theoretical predictions suggest that Rh should remain magnetic on C(0001) [37–39], albeit weakly. One further non-metallic substrate has been considered theoretically: MgO. Experimentally, MgO(001) is used frequently as a substrate for metallic thin film growth (see Refs. [40–48], for example). As for the 3d metals, Li and Freeman [40] have studied magnetism theoretically in the Fe/MgO(001) system. They predicted a very large moment of 3.07$\mu_B$ for Fe, almost the same as that which they found for the free Fe ML (3.10$\mu_B$). Moreover, 2 ML of Fe on MgO(001) has also been predicted to be magnetic, with magnetic moments of 2.85 and 2.96$\mu_B$ for the first and second ML, respectively [40]. Theoretical calculations for various 4d transition metals on MgO(001) have also been reported. Using full-potential linearized augmented-plane-wave (FLAPW) periodic calculations (see Ref. [49] for details) Wu and Freeman [42] found that 1 ML Ru and Rh films on MgO(001) remain magnetic, with moments of 1.95$\mu_B$ and 1.21$\mu_B$, respectively. However, Nokbin et al. [50] recently examined the Rh/MgO system using a plane-wave basis and the projector augmented wave (PAW) method and found finite moments only for adsorption at the metastable Mg and "hollow" sites (see later); at the more stable O site the adsorbed ML was found to be non-magnetic, contradicting the results of Wu and Freeman. (Incidentally, the adhesion energies for the O site, [50] are 2.0, 1.5 and 1.0 eV for 1/8, 1/2 and 1 ML respectively. For the hollow site they are 1.2 and 0.3 eV for 1/2 and 1 ML, respectively, or 0.3 and 0.1 eV for the Mg site.)

In the present paper, we will resolve the discrepancy between these two theoretical predictions. We will examine how magnetism in the Rh/MgO(001) system is switched on and off, and how this depends upon the chemical bonding both within the adsorbed layer (the Rh–Rh interactions) and between the adlayer and the substrate (Rh–surface interactions). In so doing we hope to give a better guide to experimentalists looking for magnetism in 4d transition metal systems, as well as a clearer understanding of the relationship between magnetism and bonding in *metal on metal oxide systems* in general. We will do this by relating the evolution of the magnetic moment to details of the electronic structure as a function of the adlayer–substrate distance and by discussing how this relates to the so-called Stoner criterion. The electronic structure of the Rh/MgO system itself is also interesting in other chemical and technological contexts, most notably in heterogeneous catalysis. The functionality of Rh/MgO catalysts has therefore been studied intensively experimentally; see for example Refs. [51,52].

Magnetic transitions are usually characterized and discussed in terms of the Stoner criterion [53,54]. This states that a system may have a non-zero magnetic moment if the exchange energy gained by becoming magnetic exceeds the kinetic energy penalty: hence if $I \cdot N(\varepsilon_F) > 1$, where $I$ is the Stoner parameter (see below), and $N(\varepsilon_F)$ is the density of states (DOS) at the Fermi level, $\varepsilon_F$. The density of states value $N(\varepsilon_F)$ is inversely proportional to the bandwidth, and hence to the kinetic energy. The exchange energy is quantified by the Stoner parameter, $I$, which becomes large when the spatial confinement of the electrons at $\varepsilon_F$ is large. Magnetism is thus favoured by small bandwidths (large $N(\varepsilon_F)$) and by strong spatial confinement of the electronic wavefunctions (large $I$). The dependence of these on changes in the bonding are easy to track via plots of the DOS and of the charge and spin densities and derivatives of them. In principle, $I$ can be evaluated from the calculated wavefunction, but here we only need a framework for discussion, so we will consider only rough estimates of changes in $I$ as evidenced by changes in charge density and related properties. The more important contributions come from $N(\varepsilon_F)$, however, since $I$ is dominated by the atomic region rather than its surroundings.

The alternative way to view the Stoner criterion is to say that magnetism is favoured when the states near $\varepsilon_F$ (in this