The Magnetism and Electronic Structures of Rh Monolayer

L. H. Cho, K. S. Yoon, and J. I. Lee
Department of Physics, Inha University, Inchon 402-751, Korea

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Recent Auger electron spectroscopy experiment suggested the possibility of magnetism in Rh overlay on Cu(001). This experimental result was verified by our theoretical study on Rh monolayer on Cu(001). However the calculated total energy difference between para- and ferromagnetic states was found to be very small and it calls for the investigation of another state, i.e., the antiferromagnetic state. The dependence of total energies on the lattice constant was calculated for three magnetic states, i.e., para-, ferro-, and antiferromagnetic ones. It was found that there is no meaningful energy difference between para- and antiferromagnetic states for all the lattice constant. The ferromagnetic state is most stable compared to other states for the lattice constant greater than 6.68 a.u. The energy minima was found at the lattice constant of 6.57 a.u. where it is paramagnetic.

Key words: rhodium, magnetism, electronic structure, monolayer, magnetic moment

1. Introduction

Recently, possible two-dimensional magnetism of 4d transition metal monolayers on nonmagnetic substrates, such as Ag and Au, has attracted extensive attentions \(^1\)–\(^9\). The theoretical calculations of Zhu et al \(^3\) by the pseudopotential method and those of Eriksson et al \(^7\) by the linear muffin-tin orbital method(LMTO) presented that the Rh layers on Au(001) and Ag(001) have large magnetic moments of 1.09 and 0.62 \(\mu_B\), respectively. The more precise calculations of Wu and Freeman \(^8\) by the full-potential linearized augmented plane wave(FLAPW) method confirmed the ferromagnetism for the Rh monolayer(ML) on Ag(001) with a magnetic moment of 0.96 \(\mu_B\)/atom. This value is smaller than that of 1.45 \(\mu_B\) of freestanding Rh monolayer with same square lattice constant of Ag(001) surface.

On the contrary to the theoretical results, the experimental results revealed controversy on the magnetism of Rh/Ag(001) and Rh/Au(001). The experiments of Li et al \(^5\) using the ultraviolet photoemission spectroscopy showed 4s core levels splitting and by this it was suggested that the Rh monolayer on both of Ag(001) and Au(001) are ferromagnetic. The polar Kerr effect \(^4\) and magneto-optic Kerr effect \(^9\) measurements, however, found no evidence for ferromagnetism in Rh/Au(001) and Rh/Ag(001). This is considered due to the surface segregation\(^10\),\(^11\) which was verified by the calculational results showing that an additional Ag overlayer not only diminished the magnetic moment to 0.46 \(\mu_B\)/atom but reduced the magnetization energy to almost zero\(^8\). Recent measurement of inverse photoemission and Auger electron spectroscopy performed by Hayden et al. \(^12\) for Rh thin films on Cu(001) observed that the 4d band widths in both as-deposited submonolayer films and annealed submonolayer films on Cu(001) were much narrower than that in bulk Rh. From this observation, they suggested that more atomic-like character of these states appear to provide the possibility of Rh atoms retaining local magnetic moments and magnetic spin ordering. Our calculated results of the Rh monolayer on Cu(001) by the precise FLAPW method have verified the experimental result\(^13\). The ferromagnetic state had a lower energy than the paramagnetic state and the magnetic moment of overlayer Rh atom was 0.23 \(\mu_B\). The calculated magnetization energy however was very small(3meV/atom) and this small energy difference called for another possible magnetic state, i.e., the antiferromagnetic state.

In this paper, the dependence of magnetic properties of fcc Rh(001) ML on the lattice constant is studied using the FLAPW method. The total energies of fcc Rh(001) ML in paramagnetic(PM), ferromagnetic(FM), and antiferromagnetic(AFM) states with different lattice constants are calculated. The results of calculated magnetic moments with respect to lattice constants are also presented and discussed.

2. Method

In order to investigate the electronic structures by FLAPW method, a single slab model is adopted \(^14\). The total energies of three magnetic states for fcc Rh(001) ML are calculated as a function of lattice constant in the range from 6.54 a.u. to 7.18 a.u.(which corresponds to the lattice constant of bulk Rh).

The Kohn-Sham equations for this single slab are solved selfconsistently using the FLAPW method \(^14\). In this method, no shape approximations are made to the potential or the charge density in solving Poisson's equation. All the matrix elements for a general potential are rigorously taken into account in all parts of space. Lattice harmonics with angular momentum components \(l \leq 8\) are included to describe the charge and potential within the muffin-tin(MT) sphere of which the radius is 2.30 a.u.

The wave functions are expanded by about 150 LAPW basis functions for each of the 21k-points in the \(\frac{1}{8}\) irreducible wedge of the two dimensional Brillouin zone. The explicit forms of the Hedin-Lundqvist\(^15\) and the von Barth-Hedin\(^16\) exchange correlation potential are employed for the paramagnetic and spin-polarized calculations, respectively. The core electrons
are treated fully relativistically whereas the valence electrons are treated semirelativistically \(^{17}\), i.e., ignoring the spin-orbit coupling. Convergence is assumed when the average root-mean-square distances between the input and output total charge and spin densities are less than \(5 \times 10^{-4}\) e/(a.u.) \(^{9}\).

3. Results

In order to investigate the dependence of magnetic properties of fcc(001) Rh monolayer on the lattice constant variation, the total energies with respect to lattice constant are calculated for para-, ferro-, and antiferromagnetic states. The calculated data points, \(\bigcirc, \bigtriangleup\), and + given in Fig. 1 represent the PM, FM, and AFM states, respectively. The total energies for PM and AFM states are equal for all the lattice constant. Thus the possibility of AFM state is excluded in the fcc Rh(001) monolayer. We also find that the total energies for three magnetic states are equal for the lattice constant less than 6.68 a.u. whereas the FM state is more stable than the other states for the lattice constant larger than 6.68 a.u. The total energy minimum was found at the lattice constant of 6.57 a.u. at which it is paramagnetic.

Figure 2 shows the paramagnetic density of states (DOS) for the lattice constant of 7.18 a.u. (lattice constant of bulk Rh) and for the lattice constant of 6.57 a.u. (corresponding to the energy minima), respectively. The band width for 7.18 a.u. is narrower than that for 6.57 a.u. This is easily understood from the fact that the electronic states are more localized for the structures with larger lattice constants. The value of DOS at the Fermi energy for the lattice constant of 7.18 a.u. at which it is FM is almost twice to that for 6.68 a.u. at which it is PM.

The calculated magnetic moments for the ferromagnetic Rh monolayer with respect to the lattice constants are presented in Fig. 3. We find that the magnetic moment increases rapidly with the lattice constant and it is almost saturated to be \(\sim 1.5\mu_B\) at large lattice constant.

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Fig. 1. Calculated total energy of fcc Rh(001) monolayer vs lattice constant. The \(\bigcirc, \bigtriangleup\), and + represent the results for the paramagnetic, ferromagnetic, and antiferromagnetic states, respectively.

Fig. 2. Paramagnetic density of states for the lattice constant of 7.18 a.u.(a) and for 6.57 a.u.(b).

Fig. 3. Magnetic moment of fcc Rh(001) monolayer as a function of lattice constant.
The calculated magnetic moment at the lattice constant of 7.18 a.u. (lattice constant of bulk Rh) is 1.53 \( \mu_B \) which is comparable to those of Zhu et al.\(^3\) and Wu et al.\(^3\). The magnetic moment of Rh monolayer at the bulk Cu lattice constant (6.82 a.u.) is 1.34 \( \mu_B \) which is much larger than that (0.23 \( \mu_B \)) of the Rh monolayer on Cu(001) in which the hybridization between the Rh overlayer and substrate Cu is strong.\(^{13}\)

4. Summary

The magnetic properties of fcc Rh(001) monolayer was studied by the FLAPW method. The possibility of AFM state was excluded for the fcc Rh(001) monolayer by the result that the total energies for PM and AFM states are equal for all the lattice constant. It was FM for the lattice constant greater than 6.68 a.u. and PM for those less than 6.68 a.u.

The magnetic moment increased with the lattice constant and it was saturated to be \( \sim 1.5 \mu_B \) at large lattice constant. The magnetic moment per atom of the fcc Rh(001) ML at the bulk Rh lattice constant was 1.53 \( \mu_B \). The value of magnetic moment at the bulk Cu lattice constant was 1.34 \( \mu_B \) which was much enhanced compared to that of Rh ML on Cu(001).

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References