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체심 입방구조 Rh(001) 표면의 전자구조와 자성

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최근의 연구에 따르면 체심입방구조(bcc)를 가지는 Rh은 상자성 상태와 약간의 에너지 차를 보이며 강자성체가 된다고 한다. 이 연구에서는 bcc Rh(001) 표면의 전자구조와 자성을 일반기울기 근사 하에서 총퍼텐셜 선형보강 평면파 에너지 띠 계산방법을 이용하여 연구하였다. 표면의 자성상태는 강자성상태를 가졌으며, unrelaxed 된 경우에 표면층의 자기모멘트는 0.48 μ_B로 덩치상태의 0.43 μ_B에 비해 증진되었으나, 표면 바로 밑층의 자기모멘트는 0.23 μ_B으로 상당히 줄어들었다. 총에너지 및 원자힘 계산을 통해 relaxed 된 구조를 구하였는데, 이 때 표면 층은 안쪽으로, 표면 바로 밑층은 바깥 쪽으로 이동하여 원래의 층간격보다 약 7.0 % 줄어들었다. 이러한 층간 간격 변화는 표면 자성을 약화시켜, 표면층과 표면 바로 밑층의 자기모멘트를 0.36 μ_B 및 0.14 μ_B로 줄어들게 하였다.

주제어 : 전자구조, 자성, 체심입방 Rh(001) 표면

The Electronic Structure and Magnetism of bcc Rh(001) Surface

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According to the recent reports the bulk bcc Rh is ferromagnetic with a small difference of energy compared to paramagnetic state. In this study, the electronic structure and magnetism for bcc Rh(001) surface are investigated by means of the all-electron full potential linearized augmented plane wave method within the generalized gradient approximation. It is found that the surface ferromagnetic state is preferable over the paramagnetic one. For unrelaxed system, the magnetic moment of the surface layer, 0.48 μ_B, is slightly increased comparing with the bulk value, 0.41 μ_B while the value of the subsurface layer, 0.23 μ_B, is much smaller than the bulk value. The total energy and atomic force calculations show that the surface layer is relaxed downward and the subsurface layer moves upward to reduce the layer distance between the surface and subsurface layers by 7.0 %. The relaxation effect leads to weakening the surface magnetic properties. Specifically, the value of the magnetic moment of the surface atom is decreased to 0.36 μ_B. Since the spin polarization of the subsurface layer is only 0.14 μ_B, it is concluded that the bcc Rh(001) surface is rather weakly ferromagnetic.

Keywords : electronic structure, magnetism, bcc Rh(001)

I. Introduction

Rhodium, a 4d transition metal (TM) element, does not exhibit ferromagnetic ordering in its naturally occurring bulk structure that is face centered cubic (fcc) structure. There have been continuous experimental and theoretical studies to examine the possibility of ferromagnetism at the surface [1-6]. The pseudopotential *ab initio* density functional calculation for the fcc Rh(001) surface by Morrison *et al.* showed that the surface layer has a considerably large magnetic moment (MM) of 1.797 μ_B [1]. This paper invoked the later experimental and theoretical investigations for the magnetism at the Rh(001) surface. The spin-polarized photoemission experiments by Wu *et al.* [2] showed the fcc Rh(001) surface is ferromagnetic, but the estimated MM of the surface layer is in between 0.1~0.2 μ_B that is much smaller than the value given by Morrison

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et al. The linear magnetic dichroism in 3d core-level photoemission experiments by Goldoni *et al.* [3] indicated the presence of the MM at the Rh(001) surface. Their follow up investigation [4] showed that the fcc Rh(001) surface is weakly ferromagnetic or superparamagnetic. The calculations by Cho and Scheffler [5] were consistent with the measurements by Wu *et al.* [2] in a sense that the Rh surface ferromagnetic state is very close to the critical point with a very small MM. A more recent calculation by Stojic *et al.* [6] showed that the magnetism at the Rh(001) surface is not predicted by the plain local density approximation (LDA) or generalized gradient approximation (GGA), but the surface magnetism is induced if a ultra-soft potential U_{eff} greater than 1.2 eV is included into LDA+U or GGA+U approach.

From the above investigations, it seems that the surface magnetism of Rh is very delicate and therefore there were some discrepancies between the theoretical and experimental data. In this situation, Hüger and Osuch [7] investigated the possibility of magnetism in bulk Rh system with non-close-packed structure. From the electronic structure calculation for the bulk Rh with bcc, fcc, hcp, and dhcp structures, they found that the bcc structured Rh is magnetic at optimum lattice constant of 3.08 Å. They discussed that the inducement and enhancement of magnetism in bcc Rh are related to the four-fold symmetry in non-close packed structure. Their calculation with the local spin density approximation gave the MM on Rh atom equal 0.26 or 0.31 μ_B, depending whether or not the spin-orbit coupling was included, and it was 0.41 μ_B per atom within GGA [4].

In this study, we attempted to investigate the magnetic properties of the (001) surface of bcc Rh with the use of full-potential all-electron first-principles method. For the purpose of comparison we also calculated the bulk properties of bcc Rh.

II. Details of Calculations

In order to determine the optimized lattice constant and the magnetic properties for bulk bcc Rh, we first recalculated the electronic structure for bcc Rh by the full-potential band method. The value of lattice constant for the bcc Rh obtained by the optimization procedure is identical with that reported by Hüger and Osuch [4].

For the study of magnetism on bcc Rh(001) surface, we adopted a single slab model consisted of nine layers of bcc Rh with the initial lattice constant equal to 3.08 Å. Thus the two-dimensional unit cell along the [001] direction is a square with a side of 3.08 Å and the distance between layers is 1.54 Å.

Electronic structure calculations were carried out by using the full-potential linearized augmented plane-wave (FLAPW) method, as embodied in the QMD-FLAPW package [8,9] within the generalized gradient approximation [10], which allows to solve the Kohn-Sham equation [11] for the investigated system in order to obtain its electronic structure. Lattice harmonics with $l \leq 8$ were considered to describe the charge density, the potential and the wavefunctions inside each muffin-tin (MT) sphere within radius of 1.16 Å. A cutoff of 180 Ry was used for star function, and the value of 16 Ry was used for the plane-wave cutoff. Integration inside the Brillouin zone was replaced by summation over 66 irreducible k-points inside the Brillouin zone by the linear tetrahedron method. All core electrons were treated fully relativistically, while valence states were treated scalar relativistically, without spin-orbit coupling [12]. Self-consistency was assumed when the difference between the input and the output charge (spin) densities was less than 2.0×10^{-4} electrons/a.u.^{3}.

In order to study the surface relaxation for bcc Rh(001) slab, we have carried out the total energy and the atomic force calculation [13]. The optimization process was terminated when the atomic force was less than 15 mRy/a.u.

III. Results and Discussion

In the first step of our study we calculated the electronic properties of the optimized bcc Rh bulk structure. In Fig. 1, the obtained electronic densities of states of the paramagnetic and ferromagnetic bcc Rh bulk are presented. When spin polarization in the system was not considered, a large peak in the DOS was found, in accordance with the results obtained by Hüger and Osuch [7]. The presence of a large number of states at the Fermi level (E_F) indicates instability of the system. This instability is corrected when the ferromagnetic ordering is assumed. As it is seen from Fig. 1(b), the number of states at E_F in ferromagnetic bcc bulk Rh is about 3 times smaller than the number of states in the paramagnetic bcc Rh. A separation in energy of the valence d electrons in the majority and minority spin channels is seen, which gives rise to an exchange splitting in this form of Rh bulk. The

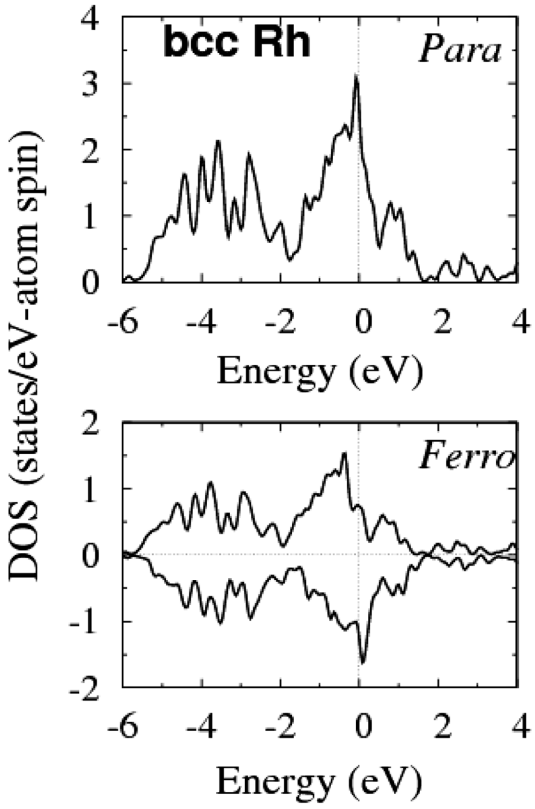

Fig. 1. Calculated total density of states (DOS) of paramagnetic (top panel) and ferromagnetic (bottom panel) bcc Rh. In the ferromagnetic system spin-down states are multiplied by −1. Fermi levels are set to zero.

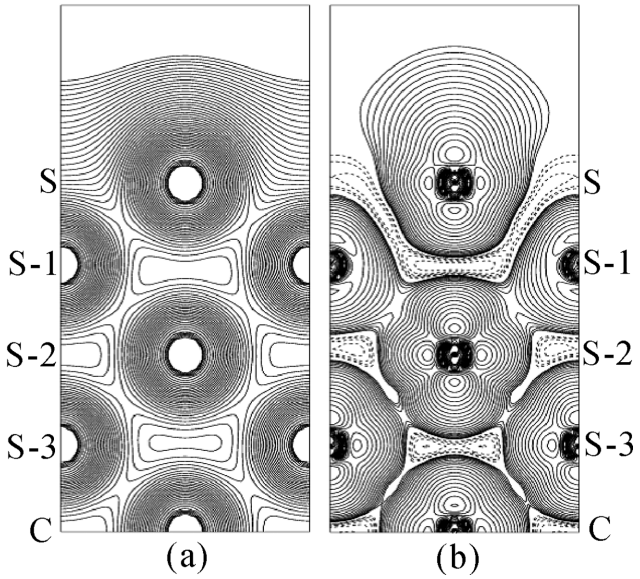

Fig. 2. Charge and spin density contour plots obtained for the fully relaxed bcc Rh(001) surface. The lowest contour starts from 1.0×10^{-4} electrons/(a.u.)^3 and the subsequent lines differ $\sqrt{2}$ times. In the spin contour panel solid lines represent positive polarization, and dashed lines represent negative polarization.

calculated MM on Rh atom in the system is 0.43 μ_B, which is in good agreement with the value obtained by Hüger and Osuch (0.41 μ_B) with the same method of calculations [7].

In the second step, we calculated the electronic structure for the unrelaxed bcc Rh(001) slab, and then we performed the total energy and atomic force calculations to obtain the stable structure. The relaxed surface is energetically more stable than the unrelaxed one by 112 meV. We found that the surface (S) and subsurface (S-1) layers move inward by 0.04 Å and outward by 0.07 Å, respectively. In result we observed a contraction between the S and S-1 layers by about 7.0 %. The second subsurface (S-2) layer also moves outward by 0.03 Å which makes 2.8 % increase of the distance between the S-1

Table I. Calculated *l*-decomposed majority and minority electrons inside each muffin-tin sphere for bcc Rh bulk and bcc Rh(001) surface (unrelaxed and relaxed) together with the magnetic moments (MM) on the atoms.

		unrelaxed				relaxed			
atom	spin	s	p	d	MM (μ_B)	s	p	d	MM (μ_B)
bcc Rh	↑	0.11	0.09	3.44	0.43				
(bulk)	↓	0.11	0.09	3.01					
Rh(S)	↑	0.10	0.05	3.50	0.48	0.11	0.06	3.44	0.36
	↓	0.10	0.05	3.02		0.10	0.06	3.09	
Rh(S-1)	↑	0.11	0.09	3.33	0.23	0.12	0.09	3.29	0.14
	↓	0.11	0.09	3.10		0.12	0.10	3.14	
Rh(S-2)	↑	0.12	0.09	3.44	0.44	0.11	0.09	3.48	0.50
	↓	0.11	0.09	3.00		0.11	0.09	2.98	
Rh(S-3)	↑	0.12	0.09	3.47	0.48	0.11	0.09	3.47	0.51
	↓	0.11	0.09	2.99		0.11	0.09	2.97	
Rh(C)	↑	0.11	0.09	3.44	0.45	0.12	0.09	3.44	0.43
	↓	0.11	0.09	2.99		0.11	0.10	3.01	

and the S-2 layers.

The magnetic properties are changed due to the creation of the surface. In Table I, we present the *l*-decomposed majority and minority electrons inside each MT and the MM of the Rh atoms in the unrelaxed and the relaxed bcc Rh(001) slabs. It is seen that surface effects affect only the surface (S) and the first subsurface (S-1) layers in the system, while the properties of the deeper layers are not much different from the properties of bulk. The calculated MMs of the S and S-1 Rh atoms in the unrelaxed system were 0.48 and 0.23 μ_B and those for the relaxed system were 0.36 and 0.14 μ_B, while the values of the other layers in both systems were similar to bulk one.

The fact that the surface creation does not influence much the electronic and magnetic properties of the deep inner layers can be also confirmed by the charge and spin density contours for the slab system, presented in Fig. 2. The distribution of charge around the atoms in all but the top layer is very uniform. As expected, at the surface the charges are more delocalized and therefore the MM on Rh(S) atom (0.36 μ_B) is smaller than the values associated with the Rh(C), (S-3), and (S-2) atoms. Only the Rh(C) atom's MM is exactly same as the MM of Rh in bcc bulk. The subsurface Rh(S-1) atom has the lowest MM, equal 0.14 μ_B, and the atoms in the second and third subsurface layers have MM equal to 0.50 and 0.51 μ_B, respectively. Those values differ from the values obtained for the unrelaxed surface. Smaller values of MM on the relaxed Rh(S) and Rh(S-1) atoms may be the consequence of the changes in the distances between the nearest neighbors. Although the overall charge density as well as the total occupation of d states is hardly changed due to the relaxation, the data in Table I indicate that the distribution of electrons between the majority and the minority states changes. Comparing the magnetic properties of the unrelaxed and relaxed surfaces we may conclude that ferromagnetism stabilizes the bcc Rh(001) surface, but it experiences structural instability due to the surface effects. This causes surface relaxation that in turn leads to a decrease of the MM of the Rh atoms in the two topmost layers of the surface.

The calculated DOS for the investigated surfaces supports these conclusions. The layer-projected DOS pictures obtained for the unrelaxed and relaxed bcc Rh(001) surfaces are presented in Fig. 3. Since the DOS picture for the inner layers of the systems and the DOS for the center layer are alike, we show here Rh(C), (S-1), and (S) layers only. The most clear

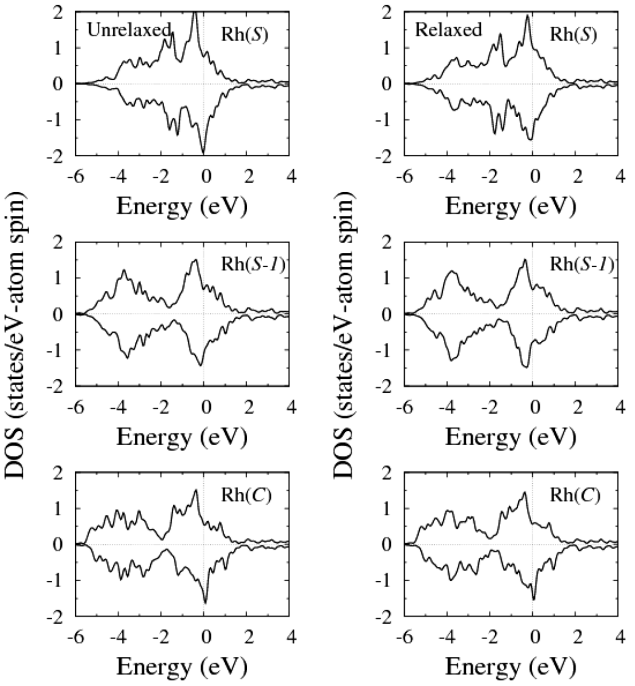

Fig. 3. The layer-projected spin-polarized density of state (DOS) of the bcc Rh(001) surfaces: unrelaxed and relaxed. Spin-down states are multiplied by −1 and the Fermi levels are set to zero.

feature that distinguishes the electronic structure of ferromagnetic bcc Rh(001) surface from that of paramagnetic one is much smaller number of electronic states at E_F. The peak of majority d states is observed at 1 eV below E_F in the unrelaxed surface. There is considerable number of minority d states at E_F. These minority spin states move slightly below E_F, and their number becomes smaller when the relaxation is considered. Also, the majority d states move slightly towards E_F, and this results in a smaller MM on Rh(S) atom. It is noticeable from the DOS pictures obtained for Rh(S-1) layers in the both systems that the subsurface layer is stabilized due to the relaxation. However, its magnetic properties are diluted. The DOS obtained for the Rh(C) layers in the two systems resemble that calculated for the ferromagnetic bcc Rh bulk. The results obtained in our study indicate that the bcc Rh(001) surface may be weakly ferromagnetic, similarly to the fcc Rh(001) surface [3].

IV. Conclusions

We investigated the surface electronic structure and magnetism for bcc Rh(001) surface. We carried on the calculations for the surface in non-magnetic and ferromagnetic

state, and we found the latter to be energetically more stable. The ferromagnetic Rh(001) surface was next fully relaxed. The distance between the surface and subsurface layers was reduced by 7.0 % compared to the unrelaxed system due to the inward and outward relaxations of the surface and subsurface layers, respectively. We found that the relaxation weakens the magnetic properties of the bcc Rh(001) slab. The values of the magnetic moments on Rh atoms are 0.43, 0.51, 0.50, 0.14, and 0.36 μ_B, for the center, S-3, S-2, S-1, and S layers, respectively, which places the bcc Rh(001) surface among weakly ferromagnetic systems.

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