Effect of Atom and Molecule Adhesion on Surface Magnetism of Au Nanoparticle

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Abstract. *ab initio* calculations are carried out on the magnetism of the Au surface where ionic bonded molecules such as HCl and KCl are put on the Au thin layer surface or Au nanoparticle surface. The reason why the ionic molecules are introduced in the model is that the anion contacting with the Au attracts electrons and the charge transfer from the Au atom to anion may be expected to cause the lowering the Fermi level, resulting in the $d$ band crossing the Fermi level. As for the layer structure models, the calculations revealed that the $d$ electron of the Au is still below the Fermi level ($\approx 2$ eV) and that the ferromagnetism should not be the ground state. On the other hand, for the particle model the $d$ band is expected to be crossing the Fermi level. The result of the calculations suggests that the Au surface has a potential to be ferromagnetic (the magnetic moment of $0.1\mu_B$ is expected), but the KCl molecule does not have significant effect on the occurrence of the magnetic moment.

1. Introduction
Surface ferromagnetism induced on normally nonmagnetic nanoparticle surface demonstrated such as for Pd [1] is a curious phenomenon occurred by artificial structure control. In particular we have been interested in the ferromagnetism appeared on the Au nanoparticles of which surfaces are modified with some polymers [2]. Since Au has its $d$ band far below the Fermi level, the spin polarization seems hardly to occur even at the surface. Indeed, we have carried out *ab initio* calculation on the surface magnetism for Au thin layer or nanoparticles [3] and confirmed that the Au surface cannot produce significant magnetic moment. The results were; 1) $d$ band moves toward the Fermi level, but it is still $2$ eV below for the Au thin layer (4–7 monatomic layers), 2) in the case of Au nanoparticles including 79 atoms the $d$ band becomes closer to the Fermi level than in the layer structure and is $1$ eV under the Fermi level.

Yamamoto *et al.* [2] observed the magnetic moment in Au nanoparticle covered by polymers, therefore the adatoms on the Au surface might play an important roll in producing the ferromagnetism. Our previous result indicated that the $d$ state of the surface Au atom in particle model shifted to just below the Fermi level. Hence if electrons in the Au atom are attracted to the adatoms and partially move out to the adatoms, the Fermi level shifts to lower energy direction, and consequently the spin polarization in $d$ band is likely to occur. Then we have put some atoms such as H, C, O and S on the Au surface in the calculation [4]. These atoms are selected because they are included in the polymers. The calculation was done for the Au layer with 4 monatomic layers. It was found that the H, C and S did not make any significant change in the magnetism while when O is placed on the Au the magnetic moment...
appared. The magnitude of the moment was 0.2 $\mu_B$ for Au and 1.0 $\mu_B$ for O, respectively. Only the O atom among all adatoms has a tendency to be anion and to attract electrons in the Au atom. That may cause the spin polarization in the surface Au atoms. However the Au is known to hardly be oxidized, so the Au-O bonding seems to be unlikely to occur. Therefore, in this paper, we will show the results of the calculation on the Au layers and particles on which the molecules are placed. The ionic bonded molecules has electronic polarization and seems to be considered as electric dipoles. The effect of electron attraction due to this polarization is discussed.

2. Models and calculation

Au thin layers and particles are assumed to form fcc structure with bulk lattice constant $(a = 0.40786 \text{ nm})$ and to stand freely in vacuum. The layer models consist 4 monatomic layers of (111) texture as shown in Figs. 1(a) and (b). The reason why (111) texture is selected is that (111) surface of the Au exhibits so called Shockley state spin splitting [5]. Therefore we can expect occurrence of the ferromagnetism resulting from both $d$ band and $sp$ band splitting. The distance between the layers are 2.115 nm, and this value is decided so that the interaction between the layers are neglected. On the top of the Au atom HCl molecule is placed in the manner with H contacting with the Au atom (Fig. 1(a)) and Cl on Au (Fig. 1(b)). The spacings between the H or Cl and Au atoms are decided so that the system energy takes minimum, resulting in 0.164 and 0.400 nm for H and Cl respectively. The particle models include 20 Au atoms are shown in Fig. 2(a) – (c). Particles are periodically arranged in three dimensional space and away from the next particles by 0.861 and 1.410 nm in horizontal and vertical directions, respectively. In this case, the O atom or KCl molecule is placed on the surface Au atom. The spacings between O atom or Cl of KCl molecule and Au atom are 0.270 and 0.400 nm for O and Cl, respectively, and with these spacings the total energy becomes minimum. We put the absorbates only on the surface Au atoms because we are interested to examine the origin of the results obtained by Yamamoto et al. [2].

*Ab initio* calculation is carried out using FLAPW based Wien2k framework [6]. GGA potential [7] is used. Number of k-points is 100. The plane wave cut-off is taken as $7.0/R_{mt}$ where $R_{mt}$ is the smallest of all atomic sphere radii. The modified tetrahedron method is employed as a BZ-integration method. Semi-core electrons which energy is higher than 6.0 eV below the Fermi level are included. Calculation admits the spin polarization in every cases, and this means that the calculations have been started from a spin polarized ferromagnetic starting density. Spin-orbit coupling is introduced in the calculation.

**Figure 1.** Au layer models: (a) H side of HCl is located on the surface Au atom and (b) Cl is on the Au atom.

**Figure 2.** Au particle models: (a) Particle including 20 Au atoms, (b) O adatom on the surface Au and (c) Cl of KCl molecule is on the Au atom.
3. Results and Discussion

3.1. Au thin layers with HCl

Calculations are carried out on the model as shown in Fig. 1 and the results of the magnetic moment are summarized in Table 1. Here the magnetic moments of the bottom layer Au (faced with vacuum), two inner Au layers, and Au in the top layer contacting with adatom and molecule elements are listed. HCl is selected as a molecule because it has straight chemical structure which is advantageous in the calculation and simple ionic bond. HCl is placed in two manners that the H contacts with Au and Cl does.

In the table we can see that the moments are very small such as less than 0.01 $\mu_B$. These small values imply that the ferromagnetism is not likely in these structures. The density of states (DOS) of the model shown in Fig. 1(a) is shown in Fig. 3 also exhibit 2 eV discrepancy between the top of $d$ state and the Fermi level. When we consider this result with our previous calculation [3, 4], the infinite Au layer structure should not be ferromagnetic even if the adatoms or molecules are contacted with surface Au atoms. Similar DOS is obtained for another model.

### Table 1. Magnetic moments in Au, H and Cl in layer models

| Atoms                          | Moments ($\mu_B$) |
|--------------------------------|-------------------|
|                                | H on Au           | Cl on Au         |
| Au in bottom layer             | 0.008             | 0.001            |
| Au in 2nd layer                | -0.004            | -0.003           |
| Au in 3rd layer                | 0.006             | -0.003           |
| Au contacting adatom           | 0.001             | -0.004           |
| H                              | 0.000             | 0.009            |
| Cl                             | -0.005            | 0.013            |

3.2. Au nanoparticles with O or KCl

The results of the calculation on the particle models about the magnetic moment are listed in Table 2. Here the magnetic moment of the Au atoms is indicated for the one at the center of the top layer only. As for the particle models weak magnetic moments appear in the simple particle consisting Au atoms only as shown in the table. The value reaches to 0.129 $\mu_B$ and the rest of Au atoms also exhibits 0.03–0.11 $\mu_B$. The uppermost edge of $d$ state overlaps the Fermi level in DOS as shown in Fig. 4(a), and this may cause the significant band splitting.

### Table 2. Magnetic moments of various atoms in particle models

| Atoms        | Without adatom | O on Au surface | Cl on Au surface |
|--------------|----------------|-----------------|------------------|
| Au at top surface center | 0.129          | 0.223           | 0.003            |
| O on Au      | –              | 1.644           | –                |
| Cl on Au     | –              | –               | -0.001           |
| K            | –              | –               | 0.000            |
When the O atom is placed on the top center Au atom, the magnetic moment of the Au atoms increases up to 0.223 $\mu_B$ while the magnetic moments in the rest of the Au atoms remains the same as 0.002 – 0.006 $\mu_B$. Oxygen itself exhibits large magnetic moment of 1.644 $\mu_B$. On the other hand, even though KCl is put on the Au surface, the significant magnetic moment does not appear in the Au. Charge transfer from Au to molecule does not seem to cause the magnetic moments in the Au. As shown in Fig. 4 (b), $d$ state is extended to the Fermi level in this KCl contacted Au particle, but the spin polarization is not seen in this structure.

From above results, we should consider that the ferromagnetism appeared in the polymer covered Au particles is not attributed to the $d$ band splitting due to the surface structure or adsorbates. Luo et al. [8] pointed out that the $sp$ bands and their Hund’s exchange coupling are responsible for Au nanoparticles. It should be clarified whether this mechanism can work in the Au particles of which diameter reaches up to 5 nm.

![Figure 4.](image_url)

**Figure 4.** Density of states of the Au atom at the top surfaces center of Au nanoparticles: (a) clean nanoparticle and (b) KCl molecule on the particle.

4. **Conclusion**

*ab initio* calculations using Wien2k framework are carried out on the magnetism of the Au surface where ionic bonded molecules such as HCl and KCl are put on the Au thin layer surface or Au nanoparticle surface. As for the layer structure models, the calculations revealed that the $d$ electron of the Au is still far below the Fermi level ($\approx 2$ eV) and that the ferromagnetism should not be the ground state. On the other hand, for the particle model the $d$ band is expected to be crossing the Fermi level. The result of the calculations suggests that the Au surface has a potential to be ferromagnetic (the magnetic moment of 0.1$\mu_B$ is expected), but the KCl molecule does not have any significant effect on the occurrence of the magnetic moment. Only the oxygen does effect on the magnetic moment in the surface Au atom. $sp$ band splitting due to Hund’s exchange coupling pointed out by Luo et al. may play an important role in Au ferromagnetic particles.

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