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Magnetic anisotropies of iron on the Pt(111) surface

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Abstract. We have studied magnetic anisotropies of Fe atoms on the platinum(111) surface, employing a fully relativistic pseudopotential and planewave method with the local spin density approximation. We investigated three surface structures of different coverage for Fe monolayer: the full coverage, the half coverage and the quarter coverage. The effect of surface relaxation has been included. It was found that the magnetic easy axis of system is within the surface plane for all systems investigated. In the system of Fe-chain on Pt(111), having an anisotropic local structure, the magnetic anisotropy energy is much enhanced after surface relaxation. This absolute value is larger, compared with the value of bulk alloy and the magnetic easy axis is directed to the alignment of Fe atoms.

1. Introduction

The stable high-density magnetic recording media whose magnetic moment is rigid against thermal fluctuations is required. Magnetic anisotropy is the important property for stability of the media. FePt and CoPt alloys are considered as good candidate of materials for developing a new media in the next generation due to their large perpendicular magnetic anisotropy energy (MAE) [1, 2, 3, 4].

Gambardella and his co-workers fabricated a Co nano-wire on Pt surface by using a self-assembly epitaxial technique and characterized magnetic properties of the system [5]. Successively, his group also investigate magnetic property of Co nanoparticles containing several Co atoms on Pt surface both experimentally and theoretically [6]. The similar system, thin Fe layer on the Pt surfaces, has been studied experimentally by several groups [7, 8, 9]. The result of Repetto *et al.* indicated that the direction of magnetic easy axis was changed depending on the coverage of iron layers. Thus the magnetic anisotropy is sensitive to the local structure in the system consisting of magnetic atoms and transition metal substrate. The bottom-up approaches which have been performed theoretically would be important to understand magnetic anisotropy deeply [6, 10, 11]. For example, Gambardella *et al.* predicted a larger magnetic anisotropy energy of single cobalt atoms deposited onto Pt(111) surface. The work on the surface magnetism for Fe monolayer on W(110) have used an optimized atomic structure to calculate magnetic anisotropy [12].

Figure 1. The schematic view of the surfaces; Fe-full-layer(left), Fe-chain(middle), Fe-quarter-layer(right). Fe and Pt atoms are specified by dark and light gray balls, respectively. The indications of Pt(I) and Pt(II) in the middle and right panels specify two types of Pt atoms in the top layer of Pt substrate.

In the present work, by means of a fully relativistic pseudopotential approach, we have studied magnetic anisotropies and presented MAE of the assumed Fe monolayers on Pt(111) surface. These systems were found to have in-plane magnetic anisotropy. Although the preliminary results have been partially published elsewhere [13], in this work we found a larger MAE as a consequence of geometry optimizations and added results of a new surface having a low coverage.

2. System and Method

The system considered is a repeated slab model with Fe atoms on Pt(111) surface. The surface structures of Fe and Pt atoms have never been determined yet. To estimate MAEs, however, we investigated the prototypes of three coverages for Fe monolayer: the full coverage, the half coverage and the quarter coverage. In this work, we assumed that the Fe atoms occupied the fcc-hollow sites on Pt(111) surface in all cases. For the half coverage, Fe atoms were assumed to form chains along x -direction. The surface normal was taken as z -direction. In case of the quarter coverage, the Fe atom does not touch to the other Fe atoms. The schematic view from the surface normal are shown in Fig. 1. In case of half and quarter coverages, there are two types of Pt atoms in the top layer. They are presented by Pt(I) and Pt(II) in Fig. 1. In the Fe-chain system, the Fe atom has three Pt neighbors; one Pt(I) and two Pt(II) atoms, while in the Fe-quarter-layer system Fe has three Pt(I) neighbors and Pt(II) has no touch on Fe atom.

The distance between Fe and Pt was set to the length of the nearest Fe-Pt bond in the FePt alloy (5.11 a.u.) as the initial geometry for the systems of full and half coverages. For the Fe-Pt length in the quarter coverage, we used the optimized counterpart in the system of half coverage. We used the Pt substrate having a (111) surface and four atomic monolayers, which is extracted from the Pt crystal structure. The vacuum layer of about 14 a.u. thick was assumed.

We employed the local spin density approximation [14] in the Kohn-Sham theory

Table 1. The coordinates of surface Pt atoms (in a.u.) with respect to the Fe atom. The case of ideal means that Fe atoms are located at the fcc-hollow sites extracted from Pt crystal structure and no surface relaxation is introduced. The third columns specify the number of nearest neighbors of Fe atom around the Pt atom. The fourth columns indicate the distance between Fe and Pt atom (in a.u.).

		number	Fe-Pt(1)	x	y	z
Fe-full-layer (ideal)	Pt	3	5.23	0.00	3.02	-4.27
Fe-full-layer	Pt	3	4.89	0.00	3.02	-3.85
Fe-chain	Pt(I)	1	4.56	0.00	2.94	-3.50
	Pt(II)	2	4.69	2.62	-1.69	-3.51
Fe-quarter-layer	Pt(I)	1	4.49	0.00	3.11	-3.25
	Pt(II)	0	6.90	5.23	3.02	-3.34

Table 2. The magnetic anisotropy energies (in meV/Fe atom) for Fe-full-layer, Fe-chain(Fe-half-layer) and Fe-quarter-layer on Pt(111) surface. The values in parentheses specify the data before introducing atomic relaxations.

	$E_x - E_z$		$E_y - E_z$	
Fe-full-layer (ideal)	-0.66		-0.61	
Fe-full-layer	-0.47	(-0.72)	-0.41	(-0.60)
Fe-chain	-4.13	(-2.31)	-1.88	(-0.79)
Fe-quarter-layer	-0.77	(-0.89)	-0.98	(-0.99)

[15]. We used the pseudopotential planewave method [16, 17] with the fully relativistic version [18, 19] in which the wavefunction has the two-component spinor form [20]. This method self-consistently contains the spin-orbit coupling (SOC), which is the main origin of magnetic anisotropy. The energy cutoffs of 30 and 300 Ry were taken for wavefunctions and densities, respectively [17]. With this approach, we have relaxed only the atomic positions of Fe and Pt atoms in the first and second layers. The MAE is estimated from $E_x - E_z$ and $E_y - E_z$, where E_α is the total energy when the system is magnetized in α -direction.

We have obtained the MAE in FePt alloy as a reasonable value previously [19], in which we used a dense mesh for $\mathbf{k}$ -point sampling. In the present work we used the 12×12 mesh for the system of Fe-quarter-layer and the 24×24 mesh for all the other cases [21]. The MAEs would be fairly converged with respect to $\mathbf{k}$ -points [13]. The spin and orbital magnetizations on atoms are estimated in the sphere with the radius of 2.5 a.u for Fe and Pt atoms.

3. Results and Discussions

The Fe-full-layer of ideal has the distance of 4.27 a.u. ($= d_0$) between layers. The second layer (top layer of Pt) imposes an attractive force on the first (iron) layer and a

Table 3. The spin and orbital magnetic moments (in μ_B) for Fe and Pt atoms in surface layers. The labels of x, y, z indicate the magnetization direction of the systems. The third columns indicate spin magnetic moments for the systems magnetized along z -direction. The spin magnetic moment of x - and y -polarizations are not shown due to a small difference (less than $0.002 \mu_B$) from the value of z -polarization.

		spin		orbital	
		z	x	y	z
Fe-full-layer (ideal)	Fe	2.943	0.082	0.082	0.087
	Pt	0.193	0.034	0.034	0.040
Fe-full-layer	Fe	2.883	0.074	0.074	0.082
	Pt	0.245	0.035	0.035	0.048
Fe-chain	Fe	3.045	0.107	0.091	0.098
	Pt(I)	0.266	0.058	0.046	0.037
	Pt(II)	0.262	0.057	0.044	0.047
Fe-quarter-layer	Fe	3.161	0.100	0.100	0.097
	Pt(I)	0.251	0.057	0.042	0.032
	Pt(II)	0.089	0.026	0.025	0.009

repulsive one on the third layer. The distances between the second and third layers are 4.39, 4.43, and 4.39 a.u. for the systems of Fe-full-layer, Fe-chain and the Fe-quarter-layer, respectively. The two latter values are averaged ones due to slight bucklings. These distances are larger by a few % of d_0 [22]. The coordinates of surface Pt atoms with respect to the Fe atom are presented in Table 1. As shown in Table 1, the distance between the first and second layers(= d_{12}) is 3.85 a.u. for the system of Fe-full-layer, decreased by 20 % from the value of d_0 . As the coverage of Fe atoms decreases to the Fe-chain and the Fe-quarter-layer, the values of d_{12} are clearly decreased. In the system of Fe-quarter-layer, the Pt(I) is pushed up to the Fe atom and the Pt(II) sinks down in the substrate, due to a strong attractive interaction between the Fe and Pt atoms and a slight repulsive one between Pt layers. The distortion of Pt atoms within the plane make relaxation of the attractive forces between neighboring Fe and Pt atoms. In the system of Fe-chain, the geometry of Fe atoms is more anisotropic within xy -plane than the other systems.

Table 2 presents MAEs for systems investigated. For the Fe-full-layer and the Fe-chain, the MAEs of similar systems have been reported in the previous work, in which the Pt atoms in the top layer of substrate was not relaxed. The values of MAE have a similar order of the value of bulk alloy (2.61 meV/Fe atom) which was estimated in the same method [19]. In Table 2, all the values is smaller than the bulk value except the MAE of $E_x - E_z$ in the system of Fe-chain. The ideal case for Fe-full-layer provides a different value of about 40-50 %, compared with the values from the optimized structure. The effect of geometry optimizations appears in MAE within factors of about twice. For the full and quarter monolayers, optimizations reduce the modulus of MAE, while for the chain enhances. The revers of sign is not observed in our calculation after optimizations.

The magnetic easy axis is directed to x -direction for the full and half coverages and to y -direction for the quarter coverage. As in the previous work [13], it was found that the magnetic easy axis is within the surface plane for all cases calculated. In the case of full and quarter coverages, the MAEs obtained both from $E_x - E_z$ and $E_y - E_z$ are almost the same. This is due to the small anisotropy of geometries within the surface plane. In the Fe-chain case, the magnetic easy axis is directed to the alignment of Fe atoms. The absolute of the MAE for $E_x - E_z$ is the largest in the present work, which seems to be related with an anisotropic geometry of surface.

In the experiment, the Fe-chain at the step on the Pt(997) surface showed that the easy axis was normal to the chain direction and was canted from the surface plane by 10 degree, having an out-of-plane component of magnetic anisotropy [9]. This experimental direction is different from that of our result. This could be ascribed to the existence of edge Pt atoms at the step in the experiment. As we will refer in the later paragraphs, our result of Fe-chain on Pt(111) would imply that the detail of the local structure changes the magnetic anisotropy sensitively. The out-of-plane component of experiment was qualitatively reproduced in the previous calculations which have taken into account the step in their models without surface relaxation [10, 11]. However, the magnetic anisotropy for Fe-chain at the step has been slightly controversial. The inclusion of surface relaxation at the step might solve the controversy.

The in-plane magnetization anisotropy may correspond to the recent experiment for the molecular beam epitaxy-grown superlattices with (111) orientation [23]. Repetto *et al.* in their experiment showed the direction of easy axis was out-of-plane below three monolayer coverage for the systems of Fe layers on Pt(111) surface [9], which seems to be contrary to our results. This difference may be attributed to an intrinsic difference of the local atomic structures between our models and their structures of experiment. In the latter they observed the weak tendency of Fe incorporation into Pt top layer and the three dimensional islands which have Fe second and third layers even at the coverages lower than one monolayer, while our models could be too simple to include an essential local network of atoms at the surfaces.

The spin and orbital magnetic moments are presented for Fe and Pt atoms in surface layers in Table 3. The plus sign in orbital moments means that the moment is parallel to the spin moment. The magnetic moments on Fe atoms gradually increases almost overall as the coordination number of Fe atom decrease. The values presented are comparable to the values in the results in the bulk alloy [19]. The relationship between the MAE and the orbital moment anisotropy was previously derived from the second perturbational formula [24]. This relation requires a large orbital moment and a strong SOC to obtain a large MAE. However, it is difficult to see a property of magnetic anisotropy by observing a table of orbital magnetic moments, like Table 3.

Assuming a large exchange splitting, the MAE of $E_x - E_z$ may be well understood by the second perturbational formula [25];

$$E_x - E_z = (\xi)^2 \sum_{o,u} \frac{|\langle o|\ell_z|u\rangle|^2 - |\langle o|\ell_x|u\rangle|^2}{\epsilon_u - \epsilon_o}, \quad (1)$$

where o and u specify occupied and unoccupied minority spin states and the ℓ_x and ℓ_z are angular momentum operators. The formula of $E_y - E_z$ is obtained by replacing x with y in eq.(1). The parameter of ξ is an average of SOC coefficient. The large ξ value for Pt is one of reasons for large MAE of CoPt and FePt alloys. The pair of occupied and unoccupied states around the Fermi level is important. In Fe-Pt systems, the Fermi level exist in minority spin states of Fe-3d, which sensitively depends on the hybridizations among Fe-3d orbitals and with Pt-5d orbitals. These hybridizations largely affect the above matrix elements of ℓ_x and ℓ_z through changes of the orbitals on Fe atoms.

The partial density of states contributed from the individual atom is estimated by the formula;

$$D_{LM}^I(\varepsilon) = \sum_i d_{LM,i}^I \delta(\varepsilon_i - \varepsilon) \quad (2)$$

$$d_{LM,i}^I = \int_0^{r_c} |R_{LM,i}^I(r_I)|^2 r_I^2 dr_I + \sum_{nm} \langle \Phi_i | \beta_m^I \rangle q_{nm}^I \langle \beta_n^I | \Phi_i \rangle \delta_{L,L_n} \delta_{L,L_m} \delta_{M,M_n} \delta_{M,M_m} \quad (3)$$

$$R_{LM,i}^I(r_I) = \int Y_{LM}^*(\hat{r}_I) \Phi_i(\mathbf{r}) d\hat{r}_I \quad (4)$$

$$\Phi_i(\mathbf{r}) = \sum_{LM} Y_{LM}(\hat{r}_I) R_{LM,i}^I(r_I) \quad (5)$$

where i and LM specify the complex index of band and $\mathbf{k}$ and the angular quantum numbers, respectively. Φ_i is a pseudo wavefunction and Y_{LM} is a cubic harmonic function. The q_{nm}^I and β_n^I are staffs of pseudopotential formalism [17].

Figure 2 shows densities of states projected to the components of $d_{3z^2-r^2}$, d_{xz} , d_{yz} , d_{xy} and $d_{x^2-y^2}$ for the Fe atom of systems. When we pay attention to the systems of Fe-full-layer and the Fe-chain, the components of d_{yz} , d_{xy} , and $d_{x^2-y^2}$ shows large differences due to differences of surface geometry, namely because in the system of Fe-chain there is no Fe atom at the nearest fcc-hollow site in y -direction.

At first, we note that on the minority spin state, the density of states of d_{yz} component for the minority spin around the Fermi level in the Fe-chain system is decreased from the counterpart for Fe-full-layer.

Based on the analysis of matrix elements (for example $\langle d_{yz} | \ell_z | d_{xz} \rangle = 1$, $\langle d_{yz} | \ell_x | d_{3z^2-r^2} \rangle = \sqrt{3}$, ... etc. [25]), the eq.(1) implies that decreases of the SOC between d_{yz} and d_{xz} give a negative contribution to the MAE of $E_x - E_z$. Along this consideration, decreases of the SOC between d_{yz} and $d_{3z^2-r^2}$ and between d_{yz} and $d_{x^2-y^2}$ give a positive to $E_x - E_z$. It is supposed that the increase of in-plane magnetic anisotropy in Fe-chain is mainly attributed to the decrease of SOC interactions between d_{xz} and d_{yz} states. By geometry optimizations for the Fe-chain the Fe-Pt(I) bond length is shortened and, thus, the increase of hybridization between Fe $3d_{yz}$ and Pt(I) $5d_{yz}$ in the minority spin state lower the density of minority spin states around the Fermi level. This may be a main reason for the large enhancement of in-plane anisotropy in the Fe-chain (see Table 2).

The SOC between d_{xy} and d_{xz} (d_{yz}) give a negative contribution to the MAE of

Figure 2. Partial densities of states projected to the components of d_{xy} , d_{xz} , $d_{3z^2-r^2}$, d_{yz} , $d_{x^2-y^2}$ in Fe atom for the Fe-full-layer(top), Fe-chain(middle) and Fe-quarter-layer(down) on Pt(111) surface.

$E_x - E_z$ ($E_y - E_z$), implying that the anisotropy within the in-plane would be explained for the Fe-chain system. This consideration is consistent with the similar values between $E_x - E_z$ and $E_y - E_z$ in the systems of Fe-full-layer and Fe-quarter-layer. Although the electronic structures would seem to benefit a relatively large quantity of $|\langle o | \ell_x | u \rangle|^2$ for the systems of Fe and Pt(111) surface, which implying an in-plane easy axis, the estimation of MAE requires a realistic calculation.

For the system of the Fe-quarter-layer, minority spin states are considerably pushed up to above the Fermi level and the densities of states for all d components at vicinity of the Fermi level is much decreased, resulting to a decrease of MAE. The decreases at the Fermi level are originated from disappearing of the hybridization between the neighboring Fe atoms. If we assume a rigid band picture, the large magnetic anisotropy energy, which was predicted for the single Co atom on Pt(111) surface [6], may be supported by a large peak in the minority spin state above the Fermi level.

4. Summary

We have studied three surface structures of different coverage for Fe atomic monolayer on Pt(111) surface, with using the local spin density approximation. We have estimated the MAEs and investigated effects of surface relaxation. The results show that the MAEs are sensitive to the atomic local geometry of surface through the hybridizations

among Fe 3d and Pt 5d orbitals. Unlike the perpendicular magnetic anisotropy of bulk alloy, the magnetic easy axes were found to be the in-plane directions to the nearest neighbors within the Fe layer. The system of Fe-chain, having an anisotropic local atomic structure, shows the largest MAE in the present work and the magnetic easy axis which is directed to the alignment of Fe atoms. The system of Fe-quarter-layer, in which the disappearance of neighboring Fe atoms lowers the density of state at the Fermi level, has a smaller MAE in a given surface area. To make a direct comparison with the experiment of Fe thin layers on Pt(111), we may use a more complex surface in which the local structure provide out-of-plane magnetic anisotropies.

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References

- [1] Ravindran P, Kjekshus A, Fjellvag H, James P, Nordström L, Johansson B, and Eriksson O 2001 *Phys. Rev. B* **67** 144409
- [2] Staunton J B, Ostanin S, Razee S S A, Gyroffly B L, Szunyogh L, Ginatempo B, and Bruno E 2004 *Phys. Rev. Lett.* **93** 257204
- [3] Staunton J B, Szunyogh L, Buruzs A, Gyroffly B L, Ostanin S, and Udvardi L 2006 *Phys. Rev. B* **74** 144411
- [4] Burkert T, Eriksson O, Simak S I, Ruban A V, Sanyal B, Nordström L and Wills J M 2005 *Phys. Rev. B* **71** 134411
- [5] Gambardella P, Dallmeyer A, Maiti K, Malagoli M C, Eberhardt W, Kern K, Carbone C 2002 *Nature* **416** 301
- [6] Gambardella P, Rusponi S, Veronese M, Dhessi S S, Grazioli C, Dallmeyer A, Cabria I, Zeller R, Dederichs P H, Kern K, Carbone C, Brune H 2003 *Science* **300** 1130
- [7] Cheng R, Guslineko K Y, Fradin F Y, Pearson J E, Ding H F, Li D and Bader S D 2005 *Phys. Rev. B* **72** 014409
- [8] Cheng R, Pearson J, Li D, and Fradin F Y 2006 *J. Appl. Phys.* **100** 073911
- [9] Repetto D, Lee T Y, Rusponi S, Honolda J, Kuhnke K, Sessi V, Brune H, Gambardella P, Carbone C, Enders A, and Kern K 2006 *Phys. Rev. B* **74** 054408
- [10] Shick A B, Máca F, Oppeneer P M 2005 *J. Magn. Magn. Mater.* **290-291** 257
- [11] Komelj M, Steiauf D, and Föhnle M 2006 *Phys. Rev. B* **73** 134428
- [12] Andersen T, and Hübner W 2006 *Phys. Rev. B* **74** 184415
- [13] Tsujikawa M, Hosokawa A and Oda T 2006 *J. Magn. Magn. Mater.*, in press
- [14] Perdew J P and Zunger A 1981 *Phys. Rev. B* **23** 5048
- [15] Hohenberg P, and Kohn W 1964 *Phys. Rev.* **136** B864; Kohn W, and Sham L J 1965 *ibid* **140** A1133
- [16] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892

- [17] Laasonen K, Pasquarello A, Car R, Lee C, and Vanderbilt D 1993 *Phys. Rev. B* **47** 10142
- [18] Dal Corso A and Mosca Conte A 2005 *Phys. Rev. B* **71** 115106
- [19] Oda T and Hosokawa A 2005 *Phys. Rev. B* **72** 224428
- [20] Oda T, Pasquarello A, and Car R 1998 *Phys. Rev. Lett.* **80** 3622
- [21] Monkhost H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [22] Baud S, Ramseyer C, Bihlmayer G, Blügel S, Barreteau C, Desjonquères C, Spanjaard D, Bernstein N 2004 *Phys. Rev. B* **70** 235423
- [23] Yamamoto S, Kato T, Iwata S, and Tsunashima S 2004 *Appl. Phys.* **95** 7285
- [24] Bruno P 1989 *Phys. Rev. B* **39** 865
- [25] Wang D S, Wu R, Freeman A J 1993 *Phys. Rev. B* **47** 14932