(a)

(b)

Pt(111) surface, (a) side view (b) top view

Electric field induced modification of magnetism in platinum tripod on pt (111) surface

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I. ABSTRACT

Pt(111) hexagonal surface with tripod geometry constructed from four Pt atoms is investigated by first principle calculation. Interestingly, appreciable spin magnetic moment of $0.11\mu_B$ per Pt tripod atom and $0.9\mu_B$ per unit cell is observed without application of external electric field (EF). Further, the magnetic moment per Pt atom and/or unit cell can be tuned using EF of $\pm 0.5\text{V}/\text{\AA}$. Negative EF enhances the spin magnetic moment of tripod Pt atom and unit cell up to $0.137\mu_B$ and $1.29\mu_B$ respectively. Positive EF reduces the spin magnetic moment of tripod Pt atom and unit cell down to $0.087\mu_B$ and $0.45\mu_B$ respectively.

Keywords- hexagonal surface, magnetic moment, electric field, tuning of magnetism.

II. INTRODUCTION

Two dimensional surface systems have attracted lot of attention from both fundamental and application point of view due to phenomenon of induced magnetism [1]. The slab model geometries are well known for exhibiting entirely different properties in comparison to the bulk counterpart. A novel magnetism can be observed by including atomic clusters (Pt) on the thin film substrate [2]. Further, magnetization can be altered by external forces such as magnetic field and/or electric field (EF) [3]. A new branch of research, i.e. all electrical spintronics, has received much attention as it provides spin manipulation and control of magnetization by application of EF [4]. Control of magnetization using EF is considered very effective in ultra-low power consumption utility.

The numerous reports reveal EF controlled magnetism as a rich physical phenomenon [4, 5, 6]. Manipulation of magnetization has received a lot of attention in the research area related to thin film metals including Pt [7], ferromagnetic semiconductors [8], insulators [9] multiferroics [10, 11], multilayers etc. [12] under the influence of external EF. The face

center cubic (FCC) transition material like palladium holds significant attention towards intense research because they show ferromagnetic instability in moderate EF [13]. Sun et. al. [13] observed that the ferromagnetism can be induced and modulated on an otherwise paramagnetic Pd metal thin-film surface through application of an external EF. Platinum is another face center cubic (FCC) transition material which has not been much explored to identify its near ferromagnetic behavior.

In principle, EF is screened by conduction electrons over the screening length when the metal thin film is exposed to EF. The EF does not penetrate to the bulk metal and EF induced electric charges get confined to a certain depth. This phenomenon has enormous applications in spintronics industries and storage devices. This kind of physical phenomenon generally occurs in metallic thin films [14, 15]. Among the various calculation techniques, the first calculation on charge density screening near metal surface using EF has been done by Lang and Kohn [16]. There are many experimental studies which revealed modification of magnetization under the application of EF [17,18,19,20]. The state-of-the-art of controlling magnetic properties of metal surfaces by non magnetic means is reviewed thoroughly by Brovko et. al. [21].

Pt metal is considered as nearly magnetic but not quite like other ferromagnetic metals [22]. It generally acts as an exchange enhanced paramagnetic material and, thus, it is indeed an opportunity to investigate magnetism at nanoscale applying stimuli like external EF. It has good physical properties like high magnetic susceptibility, and it also shows proximity effect [23]. Previously, emergence of magnetism has been observed in platinum nanostructures like nanowires [24], metals and alloys [25], platinum atomic chains [26]. Structural properties and magnetic properties of small platinum clusters have been investigated by X. Liu et al. [27]. Richard Korytár et al. observed a typical trend of spin locking and spin polarization in the case of platinum pristine tip [28]. The bulk platinum 5d band is too wide to provoke spin polarization and there is no evidence of magnetism in Pt monolayer surface on Ag/Au (001) either [29]. However, an experimental study by Shimizu et al. [22] reveals that the platinum thin film can be used in devices and the magnetic properties can be altered under the external EF. Recently, the study of nanostructures and nanomaterials placed on nonmagnetic metal surfaces is in progress due to the intriguing feature of induced magnetism [21].

In this present work, in order to get better insight about the magnetic properties of platinum, the paramagnetic thin film of Pt (111) with tripod type geometry, made up of platinum atoms, has been considered for a theoretical study. The geometry of the present system is shown in

Figure.1. The effect of application of electric field on magnetism of this system has also been studied.

Fig.1 Structure of hexagonal Pt (111) surface [three layers] with tripod type geometry made up from four atoms of platinum (a) side view (b) top view.

III. COMPUTATIONAL METHOD

Platinum (111) hexagonal surface with tripod geometry constructed from four platinum atoms is considered for spin polarized DFT calculation. The lattice parameters, $a=11.04592\text{\AA}$ and $c/a=2.44949$, are used in our simulation for the aforementioned geometry. The ab-initio calculation is performed within the framework of density function theory using projector augmented wave technique, [30,31] as implemented in the VASP code [32, 33]. The exchange correlation effects are treated using Perdew–Burke–Ernzerh (PBE) [34] approximation during optimization. The charge density cut off energy of 230.3eV is taken into account, and energies tolerance of 10^{-7}eV are taken in kohn-sham equation during the self consistent iteration. The size of vacuum $\sim 17\text{\AA}$ is applied in Z direction in order to eliminate contact between two successive slabs. The (8 8 1) K-point mesh in the Brillouin zone is used for convergence of charge density. The electric field is applied in perpendicular direction to the slab geometry considering dipole at the centre of the slab. The dipole correction [35] is taken into account to study the tailoring behavior of magnetization. EF is applied on the system in the range from $-0.5\text{V/\AA}$ to $0.5\text{V/\AA}$ and the effect of applied EF is scrutinized.

IV. RESULT AND DISCUSSIONS

A. Effect of electric field on spin magnetism: tripod atoms

The paramagnetic transition metal Pt with modified surface geometry is a promising model which shows appreciable magnetism and the applied external EF plays pivotal role to alter the spin magnetic moment per Pt atom.

Table-1 shows the calculated spin magnetic moments of platinum tripod atoms on Pt (111) surface at different applied EF. The major contribution of magnetism in this system is due to platinum tripod atoms. The hexagonal three layers of thin film have negligible spin magnetic moment of $\sim 0.01\mu_B$. On the application of EF ($-0.5\text{V}/\text{\AA}$) in negative direction, the spin moment is enhanced up to $0.137\mu_B$ per platinum atom in tripod geometry, whereas spin magnetic moment is reduced down to $0.087\mu_B$ when EF is applied in positive direction. Moreover, it has been also observed that the spin magnetic moment per platinum atoms, vertically nearer to the slab geometry (i.e. atoms 2, 3, 4), have larger spin magnetic moment than the platinum atom 1 [36]. In the absence of EF, the spin magnetic moments for all four atoms are observed due to reduced coordination sites of platinum. After the application of an external EF in both directions, variation in spin magnetic moments per platinum atom has been noticed.

Table 1

The significant magnetic moment (μ_B) of Pt four atoms with electric field ($\text{V}/\text{\AA}$) in tripod atoms

Pt atoms	E=-0.5	E=-0.4	E=-0.3	E=-0.2	E=-0.1	E=0	E=0.1	E=0.2	E=0.3	E=0.4	E=0.5
1	0.122	0.119	0.117	0.113	0.110	0.108	0.103	0.104	0.098	0.093	0.087
2	0.137	0.133	0.129	0.124	0.118	0.113	0.109	0.108	0.101	0.095	0.087
3	0.136	0.132	0.128	0.123	0.118	0.116	0.109	0.108	0.10	0.094	0.087
4	0.137	0.133	0.129	0.124	0.118	0.116	0.109	0.108	0.101	0.095	0.087

B. Effect of electric field on density of states of tripod atoms and of unit cell

It has been revealed that there is an interesting connection between external EF and density of state for the platinum hexagonal surface with tripod geometry. As shown in table-1, the

spin magnetic moment of platinum atoms varies under the application of EF which can be explained by change in electronic structure of the system. Densities of states (DOS) (majority states and minority states) at zero EF and at a particular EF are plotted in figure-2. The Fermi level is represented by dotted line at zero of energy axis. The d orbital of platinum tripod atoms has major contribution in exhibiting spin magnetism per unit cell. The majority spins and minority spins at Fermi level are altered by EF in different manner.

Fig.2 (a)-(d) shows the contribution of platinum atoms 1-4 in spin magnetism respectively. It has been observed that the difference of spin up DOS and spin down DOS of all the four atoms, at Fermi level, for an external negative EF of $0.5\text{V}/\text{\AA}$, is greater than that of positive EF of $0.5\text{V}/\text{\AA}$. Therefore negative EF enhances the magnetic moment per atom where as the response to the positive EF is opposite (Table-1). The fig.2 (e) depicts the total DOS of unit cell for different applied EF. The total DOS is also shifted due to applied EF [14] and it is clearly observed that majority spin total DOS in case of $E=-0.5\text{V}/\text{\AA}$ is greater than that of other EF whereas minority spins total DOS for all the applied EF is nearly same. As a result, the difference of both spins favors high magnetism in the case of negative EF. Thus, the change in total DOS of proposed system is directly associated to the applied EF.

Moreover, application of electric field leads to change in electrostatic potential at the surface due to screening effect which may be responsible for shifting of DOS towards higher and/or lower energy at Fermi level. Due to altering and/or shifting of DOS at Fermi level, the spin magnetic moments of tripod atoms as well as unit cell can be tuned with respect to applied EF [36]. In calculated system, shifting and/or altering of DOS at Fermi level is enough to control the magnetic moment per platinum atom in both cases (i.e tripod atoms and whole unit cell).

Fig.2. External effect of an applied electric field on the system- DFT calculated density of states of tripod atoms. (a), (b), (c), (d) are plotted d orbital DOS for tripod atoms (1,2,3,4) respectively. Upper panel shows spin up DOS and lower panel shows spin down. (e) DFT calculated total DOS of unit cell.

C. Screening of an applied electric field and the corresponding effect on spin magnetism

The figure 3 shows an effect of applied EF on the ground state charge density in case of two dimensional modified thin film surface. The calculated difference of charge densities has been plotted i.e. (a) the difference of charge densities for applied EF of $-0.5 \text{ V/\AA}$ and $0 \text{ V/\AA}$ and (b) the difference of charge densities for applied EF of $0.5 \text{ V/\AA}$ and $0 \text{ V/\AA}$. The difference of charge densities (with and without EF) across the cross sectional plane is shown to

understand the screening effect due to applied EF. (i.e. conduction electrons in metal always strive to screen the applied EF). Partially, some of the charges may get induced in to the slab geometry. The typical screening of an applied field has been observed by C-G.Duan et al. [37]. An applied EF, $E=0.5\text{V}/\text{\AA}$, in both positive and negative directions, results in changing concentration of charges and as a result it is possible to tune the magnetization of the present system [36]. In metallic system, the external EF causes the charge distribution in order to screen the electric field inside the conductor. The screening length depends upon the conductivity of particular metal. Thus, enrichment/depletion of electron density, on the application of EF, can be observed. The change in electron density is directly proportional to the magnetic properties of the system.

Fig.3. Charge density difference in the applied electric field compared to one in ground state ($E=0$). An applied EF is normal to the surface. Electron charge density difference is plotted- (a) $(-0.5 \text{ and } 0)\text{V}/\text{\AA}$ (b) $(0.5 \text{ and } 0)\text{V}/\text{\AA}$. The reading scale indicates the range from $[-0.0005 \text{ to } 0.0005(\text{e}/\text{\AA}^3)]$

D. Electric field effect on bandstructures: majority spins and minority spins

It is really worth exploring the effect of application of EF on the electronic band structure. The band structures can be manipulated using external EF [38]. The electronic configuration of the Pt tripod on Pt (111) system is calculated using non self-consistent approach. In order to do so, already converged collinear self consistent charge density is kept fixed and Kohn-Sham eigenvalues for all k points in reciprocal space are calculated. The investigated band structures with EF and without EF are shown in fig.4. Fig.4 (a) and (b) illustrate band structures of majority spins and minority spins respectively. All the energy bands are evaluated using high symmetry hexagonal brillouine zone KPOINTS K- Γ -M. The dispersion curves for majority spins as well as minority spins are shifted upon the exposure of an electric field [39] up to $0.5 \text{ V}/\text{\AA}$. The Fermi energy is changed with applied EF and energy bands also

get shifted. At positive EF (i.e $+0.5\text{V}/\text{\AA}$), all the bands for majority spin are shifted upward. Negative field (i.e $-0.5\text{V}/\text{\AA}$) induces shifting of bands towards lower energy. Similar trend like shifting of bands has been observed in the dispersion curves of minority spin carriers in the case of application of external EF. It is well known that injected electrons are responsible to change the population of majority spin bands and minority spin bands [40] and as a result change in spin magnetism has been observed.

(a)

(b)

Fig.4 DFT calculated band structure of Pt tripod on Pt (111) thin film. (a) band structures of majority spins (b) band structure of minority spins. Blue, red, black indicate EF of $E=0.5 \text{ V/\AA}$, $E=0 \text{ V/\AA}$ and $E= -0.5 \text{ V/\AA}$ respectively. The Fermi level is set to 0 eV . Field implemented dispersion curves either in negative direction or positive direction looks similar due to symmetry.

E. Effect of electric field on spin magnetism of unit cell

To the best of our knowledge, the significant variation of spin magnetic moment per unit cell as a function of applied EF, is a novel observation. Fig. 5 demonstrates the variation of calculated magnetic moment per unit cell with applied EF. The investigation has revealed sufficiently large magnetic moment of $0.9062 \mu_B$ per unit cell at zero EF. The application of EF of $0.5 \text{ V/\AA}$ (i) in positive direction enhances the spin magnetic moment up to $1.2928 \mu_B$ per unit cell ($\sim 43\%$ higher than zero EF) and (ii) in negative direction reduces of magnetic moment down to $0.4215 \mu_B$ per unit cell ($\sim 55\%$ lower than zero EF). The magnetic properties per unit cell can be varied in a controlled way with the application of EF. Typically, linear trend of change in magnetic moment with EF has been observed [14, 37]. The magnitude of change in magnetic moment per unit cell is not comparable to others thin film ferromagnets [41] but significant for platinum thin film with modified geometry.

Fig.5. Effect of applied electric field on magnetic moment of unit cell in range of EF from $-0.5 \text{ V/\AA}$ to $0.5 \text{ V/\AA}$. A linear trend (blue line) is shown in both directions.

V. Conclusions

In summary, ground state magnetic properties of Pt tripod atoms on Pt(111) surface system have been studied using self-consistent calculation based on spin density functional theory. The proposed system exhibits considerable magnetism and the influence of an external EF on magnetism is systematically analysed. It is revealed that an applied EF becomes primary cause of altering the spin magnetic moment per platinum atom upon changing the direction of applied EF. The electric field of $0.5\text{V}/\text{\AA}$ is reasonable for tuning the magnetic properties. The change of DOS and the shifting of DOS, of platinum tripod and unit cell (platinum surface including tripod), favor the behavior of spin magnetism under the influence of external EF. Moreover, the screening of an applied EF and shifting of energy band structures with applied EF also support the phenomenon of tuning spin magnetism. The magnetic moment per platinum atom is enhanced using negative field and reduced by positive EF. It can be concluded that manipulation of spin magnetic moment of platinum atom as well as unit cell of the proposed system can be achieved by application of external EF.

Acknowledgment

This work was supported by AFOSR and NSF (Grant No. DMR-1310542). The University of Nebraska Holland Computing Center has provided computations resources.

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Figure captions:

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