PRAMANA
— journal of
physics

Vol. 74, No. 4
April 2010
pp. 653–659

Density functional study of ferromagnetism in alkali metal thin films

PRASENJIT SEN
Harish-Chandra Research Institute, Chhatnag Road, Jhunsi, Allahabad 211 019, India
E-mail: prasen@hri.res.in

MS received 18 May 2009; accepted 22 December 2009

Abstract. Electronic and magnetic structures of (1 0 0) films of K and Cs, having thicknesses of one to seven layers, are calculated within the plane-wave projector augmented wave (PAW) formalism of the density functional theory (DFT), using both local spin density approximation (LSDA) and the PW91 generalized gradient approximation (GGA). Only a six-layer Cs film is found to have a ferromagnetic (FM) state which is degenerate with a paramagnetic (PM) state within the accuracy of these calculations. These results are compared with those obtained from calculations on a finite-thickness uniform jellium model (UJM), and it is argued that within LSDA or GGA, alkali metal thin films cannot be claimed to have an FM ground state. Relevance of these results to the experiments on transition metal-doped alkali metal thin films and bulk hosts are also discussed.

Keywords. Alkali metal; thin films; magnetism; density functional theory.

PACS Nos 73.20.+r; 73.20.At

1. Introduction

Bulk and thin films of alkali metals containing 3d transition metal (TM) impurities have been studied experimentally for quite some time now [1–5]. The most intriguing property of these systems is the large magnetic moment they possess. Beckmann and Bergmann [3], through anomalous Hall measurements, showed that a Co impurity on a Cs film has a (total) magnetic moment as large as $9\mu_B$, and that in bulk Cs has a magnetic moment of $8\mu_B$. An Fe impurity has a magnetic moment of $7\mu_B$ on a Cs film as well as inside the bulk Cs. Bergmann and Song [5] predicted large magnetic moments in V-doped alkali metals ranging from 6 to $7\mu_B$ in an Na host to $4\mu_B$ in a Cs host. Nearly two decades ago, Riegel *et al* [1] and Kowallik *et al* [2], through magnetic susceptibility measurements, showed that Fe and Ni impurities in K, Rb and Cs hosts have large magnetic moments. Gambardella *et al* [4] in their X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements found total magnetic moments of $6.63\mu_B$, $5.59\mu_B$ and $3.55\mu_B$ respectively for Fe, Co and Ni impurities on K films.

These startling findings raise the obvious question of the origin of such large magnetic moments. And that is where opinions differ. Riegel and co-workers [1] argued that the TM atoms remained isolated inside an alkali host due to the latter's rather large lattice constant. This isolated nature of the TM atoms help retain their atomic spin and orbital moments, which are, otherwise, quenched in a solid environment due to hybridization and crystal-field effects. The moments are, therefore, essentially those of isolated TM atoms. Gambardella *et al* [4] also subscribed to this view. Comparing their observed XAS spectra with the calculated ones, they showed that the TM atoms were indeed in their atomic configurations. Beckmann and Bergmann [3] and Bergmann and Song [5], on the other hand, argued that the only way to explain the observed moments in the TM–alkali metal systems was to assume that the electrons in the alkali host were polarized in the presence of the TM atoms. This is exactly how an Fe impurity behaves in a Pd host, where it polarizes the Pd electrons leading to a giant moment [6,7].

TM–alkali metal systems have been studied theoretically also. Through LSDA plus local Coulomb energy (U) calculations within the density functional (DFT) theory, Kwon and Min [8] have shown that an Fe impurity behaves differently in a Cs host compared to a Pd host. There is no polarization of the Cs electrons, rather the Fe impurity remains isolated leading to atomic-like large moments. Sahu and Kleinman [9] performed DFT calculations for V impurities in bulk Na, and Co in Na and K. They also rejected the hypothesis that polarization of the host electrons was responsible for the observed moment.

As a counter-argument to these, Bergmann and co-workers cited Okazaki and Teraoka's [10] work in support of their claim. Okazaki and Teraoka used a UJM of finite thickness to study electronic and magnetic properties of thin metal films. Using local spin density approximation (LSDA) for the exchange-correlation functional, they found that depending on the electron density ρ_0 (equivalently $r_s = (3/4\pi\rho_0)^{1/3}$), the UJM could have a ferromagnetic ground state in certain ranges of thickness (D). In a later detailed work [11], they showed that for $r_s = 6$, paramagnetic (PM) and fully polarized ferromagnetic (FPF) solutions existed at every thickness. They also found partially polarized ferromagnetic (PPF) solutions at $11.9 \leq D \leq 18.48$ Bohr and $22.2 \leq D \leq 27.6$ Bohr, and antiferromagnetic (AFM) solutions at $11.5 \leq D \leq 15$ Bohr. The ground state of the system turned out to be FPF at $D \leq 9$ Bohr, PM at $9 \leq D \leq 11.9$ Bohr, PPF at $11.9 \leq D \leq 12.8$ Bohr, FPF at $12.8 \leq D \leq 16.4$ Bohr, PPF at $16.4 \leq D \leq 17.1$ Bohr, PM at $17.1 \leq D \leq 22.1$ Bohr, PPF at $22.1 \leq D \leq 25.6$ Bohr and PM at $25.6 < D$ Bohr. Based on these results, they argued that very thin films of Cs and Rb should be ferromagnetic [10].

In order to throw further light on this debate, it becomes crucial to understand the electronic and magnetic structures of specific alkali metal thin films through atomistic calculations (as opposed to the UJM). One needs to answer the question: are thin films of alkali metals, in particular Cs, really ferromagnetic? In this paper, the central question is: are K and Cs thin films FM within LSDA and GGA of the DFT? The main results are: for most thicknesses, alkali metal thin films do not have an FM state; only a six-layer Cs film has an FM state, which, however, is degenerate with a PM state within the accuracy of present calculations. It is worth remembering that underestimation of band gaps of semiconductors and

insulators is a well-known limitation of L(S)DA and GGA. However, these methods satisfactorily describe the ground states of bulk FM transition metals Fe, Co and Ni. In Fe and Co, the LDA/GGA value of the magnetic moment per atom comes out to be within a few per cent of the experimental values [12]. Since our interest here is in magnetic properties of alkali metal systems, in which the electronic density is distributed more smoothly than in TM systems, LDA and GGA results should be reliable.

2. Method

Calculations were performed within the framework of DFT. VASP [13–16] was used for all the calculations. The wave functions are expressed in a plane-wave basis set with an energy cut-off of 400 eV. The Brillouin zone integrations are performed using the Monkhorst–Pack scheme. Ionic potentials are represented by PAW. Both LSDA and PW91 GGA functionals are used for the exchange-correlation energy. The preconditioned conjugate gradient method as implemented in VASP is used for wave function optimization, and the conjugate gradient is used for ionic relaxation. K(1 0 0) and Cs(1 0 0) thin films are represented by a repeated slab geometry. Each slab contains the desired number of (1 0 0) planes of the alkali metal. In the starting geometry, the atoms in the films were placed at their bulk positions. Values of the bulk lattice constant used were calculated with the particular method (LDA or GGA) in use. For the bcc bulk K, the lattice constants obtained were 5.04 and 5.28 Å using LDA and GGA respectively. For bcc Cs, the corresponding values turned out to be 5.77 Å and 6.13 Å respectively. The experimental lattice constants for K and Cs are 5.23 and 6.05 Å respectively. Thus, the PW91 GGA reproduces the experimental lattice constant within a few per cent. Consecutive slabs were separated by a vacuum space equal to six atomic layers. For one-, two- and three-layer films, a (2×2) surface supercell was used. However, there were practically no forces parallel to the (1 0 0) planes on any of the atoms. Therefore, for thicker films, a (1×1) surface supercell was used to reduce computational cost. Only one of the atoms in the supercell was held fixed, and all other atoms were allowed to relax freely in all three directions without any symmetry constraints till all components of forces were smaller than 10^{-3} eV/Å. A $(6 \times 6 \times 1)$ k-point mesh was used for the (2×2) surface supercell, while for the (1×1) surface supercell, a $(8 \times 8 \times 1)$ k-point mesh was used. Absolute convergence of energy with respect to energy cut-off and the number of k-points were thoroughly tested. Similar methods were used earlier to study thin Al(1 1 0) films by Ciraci and Batra [17].

3. Results

Calculations were done for three-, five- and seven-layer K films, and for Cs films having thicknesses from 1 to 7 atomic layers. I searched for PM and ferromagnetic (FM) solutions for both K and Cs films at each thickness. AFM states are not considered since refs [10] and [11] do not find an AFM ground state at any thickness. In most of the films no FM slutions were found. The only exception was a six-layer

Cs film for which an FM state with a very small moment of $\sim$0.1 μ_B per atom was found in both LSDA and GGA. In order to be convinced that it is, in fact, a ferromagnetic state, the band structures and the electronic densities of states (DOS) are plotted in figure 1 for a six-layer Cs film. As is clearly seen, the minority (down) spin bands are slightly shifted up in energy compared to the majority (up) spin bands. This is reflected in the DOS as well. It should also be noted that a staircase-like DOS expected for a quasi-two-dimensional system of electrons is obtained, as discussed in detail in ref. [17]. It is also important to know where the spin moment resides in the FM Cs film. For this purpose, in figure 2, charge and spin densities averaged over xy planes parallel to the film are plotted as a function of z, the distance perpendicular to the film. The charge density is found to oscillate, being maximum around the atomic planes and small in between two atomic planes, as one would expect. The spin density is found to be roughly two orders of magnitude smaller than the charge density. It is small at the centre, and has peaks roughly half way from the centre of the film to the outermost atomic layers. The difference between a finite-thickness UJM and a real Cs film is noticeable here. In a UJM, because the background positive charge is distributed uniformly, the electron density varies smoothly over the film, and becomes small near the surface. A uniform electron gas is known to have a ferromagnetic instability at smaller densities, that is, at larger values of r_s compared to those in simple metals [18]. Presumably this surface effect leads to an FM state in a finite-thickness UJM. The spin density in such a UJM is also localized near the surfaces [11]. In contrast, the charge density shows more rapid variation in an atomistic film, as seen in figure 2, and has maxima near the surfaces. Away from the film outside the surfaces, the charge density steadily falls to zero, as it should. These differences lead to different consequences in the two situations, and the atomistic thin films do not have magnetic states. Although an FM state is found in a six-layer Cs film, it is degenerate with a PM state. The difference in cohesive energy between the PM and FM states are less than 1 meV/atom in LSDA and equal to 1 meV/atom in GGA. These differences are beyond the limit of accuracy of the present calculations.

According to ref. [11], one requires thinner films for metals with a smaller r_s to find an FM state. As already mentioned, an electron gas has an FM instability at r_s values somewhat larger than those in simple metals. Therefore, it should be easier to obtain an FM state in Cs films, bulk Cs having a larger r_s than bulk K. However, no (unique) FM ground state is found in either K or Cs films. In fact, an FM state is not even found except in a six-layer Cs film. A few points are in order here: (1) In the finite-thickness UJM that Okazaki and Teraoka have considered, thickness is a continuous variable, but for a real metal film, it can only take discrete values determined by the number of atomic layers in the film. Comparing with the LSDA results of ref. [10], Cs films with two layers (thickness of 3.21 Å = 6.07 Bohr) and four layers (thickness 8.93 Å = 16.88 Bohr) are expected to be FPF and PPF respectively. However, both these are found to be PM in the present calculations. A six-layer film (thickness 14.63 Å = 27.66 Bohr) is found to have an FM state, albeit with a small moment, while a finite-thickness UJM is expected to be PM beyond a thickness of 25.6 Bohr. (2) In Okazaki and Teraoka's calculations [10,11] also, the energy difference between a PM and an FM state was rather small ($\sim$meV) (figure 4 of ref. [10]). Their calculations were also based on

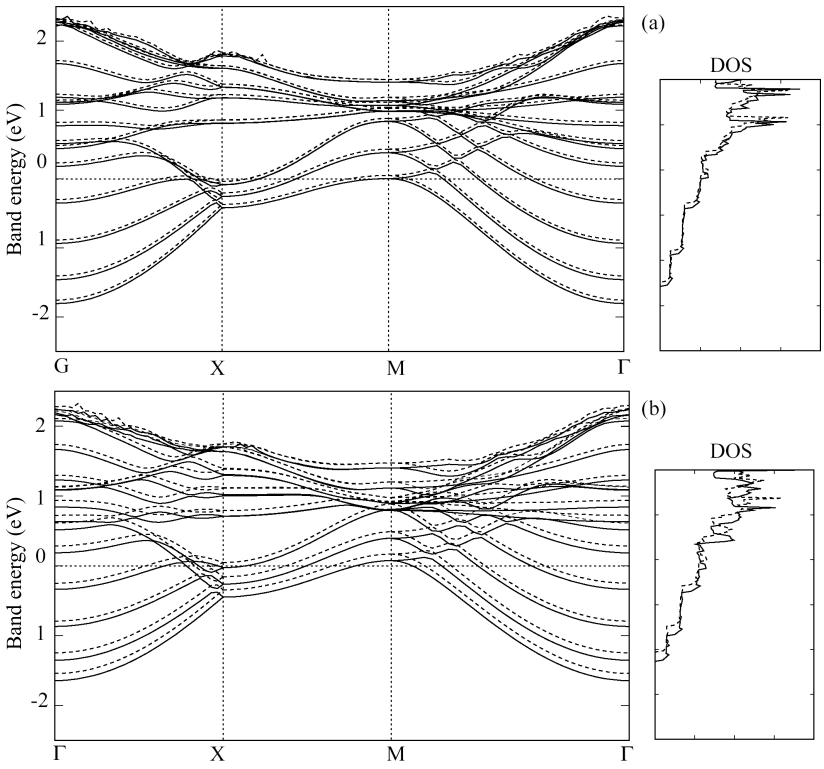

Figure 1. Band structure and electronic DOS for a six-layer Cs film: (**a**) LSDA and (**b**) GGA results. Bands are plotted along lines joining high symmetry points in the surface BZ of the films, and the Fermi energy has been set to zero. Majority (up) and minority (down) spin bands and DOS are shown with solid and dotted lines respectively.

the local density and local spin density approximations of the DFT. Therefore, it would be difficult to argue in favour of an FM ground state on the basis of those calculations. However, admittedly, they found a definite trend at $D = 7$ and 8 with varying r_s. (3) The present calculations bring out important differences between the predictions of UJM and atomistic first-principle calculations as far as electronic and magnetic properties of alkali metal thin films are concerned. It may, therefore, be misleading to base one's arguments on the results of the UJM.

4. Conclusions

In conclusion, through first-principle atomistic calculation using plane-wave PAW formalism, it is showed that neither K nor Cs films can be claimed to have a (unique) FM ground state within the LSDA or GGA of the DFT. Only a six-layer Cs film has an FM ground state, but that is degenerate with a PM state. Present work points out that there are crucial differences in the behaviour of a UJM and a real

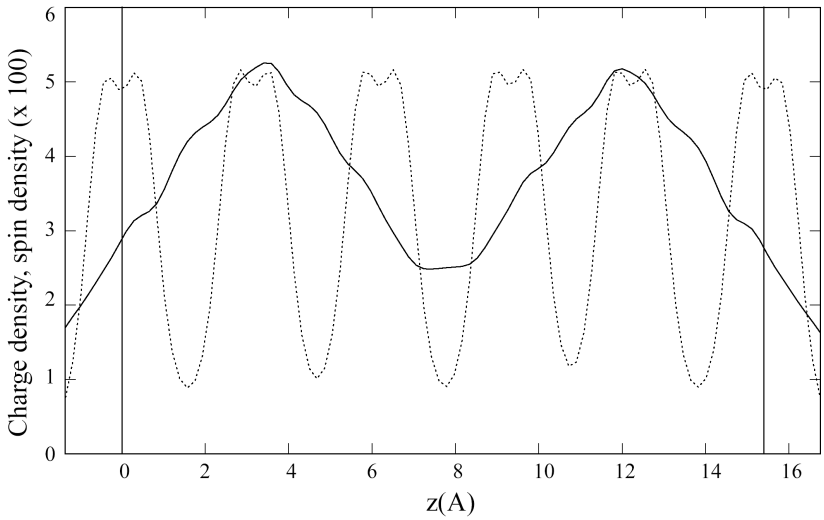

Figure 2. Average areal density (in planes parallel to the surface) of charge (dotted curve) and net spin (solid curve) in a six-layer Cs film as a function of distance perpendicular to the film. Solid vertical lines denote the outermost atomic layers (surfaces) of the film.

atomistic system. More accurate calculations are required to resolve the issue of ferromagnetism in alkali metal thin films from a theoretical point of view. The results presented here, by themselves, do not rule out the possibility of polarization of electrons in an alkali metal film in the presence of TM impurities, but they definitely show that within LSDA and GGA, one cannot claim alkali metal thin films to have an FM ground state.

Acknowledgements

Numerical calculations for this study were carried out at the Cluster Computing Facility in the Harish-Chandra Research Institute (http://cluster.mri.ernet.in).

References

[1] D Riegel, H J Barth, L Büermann, H Haas and Ch Stenzel, *Phys. Rev. Lett.* **57**, 388 (1986)
[2] R Kowallik, H H Bertschat, K Biedermann, H Haas, W Müller, B Spellmeyer and W-D Zeitz, *Phys. Rev. Lett.* **63**, 434 (1989)
[3] H Beckmann and G Bergmann, *Phys. Rev. Lett.* **83**, 2417 (1999)
[4] P Gambardella, S S Dhesi, G Gardonio, C Grazioli, P Ohresser and C Carbone, *Phys. Rev. Lett.* **88**, 047202 (1989)
[5] G Bergmann and F Song, *J. Magn. Mag. Mater.* **272–276**, e863 (2004)
[6] J Crangle and W R Scott, *J. Appl. Phys.* **36**, 921 (1965)

[7] G Bergmann, *Phys. Rev.* **B23**, 3805 (1981)
[8] S K Kwon and B I Min, *Phys. Rev. Lett.* **84**, 3970 (2000)
[9] B R Sahu and L Kleinman, *Phys. Rev.* **B67**, 094424 (2003)
[10] K Okazaki and Y Teraoka, *Surf. Sci.* **433–435**, 672 (1999)
[11] K Okazaki and Y Teraoka, *Phys. Rev.* **B62**, 500 (2000)
[12] M Cěrneý, J Pokluda, M Šob, M Friák and P Šandera, *Phys. Rev.* **B67**, 035116 (2003)
[13] G Kresse and J Hafner, *Phys. Rev.* **B47**, RC558 (1993)
[14] G Kresse, Thesis (Technische Universität, Wien, 1993)
[15] G Kresse and J Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996)
[16] G Kresse and J Furthmüller, *Phys. Rev.* **B54**, 11169 (1996)
[17] S Ciraci and I P Batra, *Phys. Rev.* **B33**, 4294 (1986)
[18] D M Ceperley and B J Alder, *Phys. Rev. Lett.* **45**, 566 (1980)