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Magnetism in vanadium–molybdenum systems

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Abstract

The magnetism of relaxed and nonrelaxed vanadium–molybdenum (V_n/Mo) systems is investigated for $n = 1$–3 layers in the (001) and (111) orientations. This study is carried out using the the real-space self-consistent tight-binding recursion method in the Hartree–Fock approximation with Hubbard Hamiltonian. The magnetic moment of a V monolayer epitaxially grown on a semi-infinite Mo substrate is found to be larger in the (001) orientation than that in the (111). The magnetisms in bilayer and three layer V systems become comparable in the (001) and the (111) orientations in the nonrelaxed case, but are larger in the (001) for the relaxed systems. The magnetic moments are found to decrease in the relaxed systems for both cases.

1. Introduction

Several investigations [1–3] have indicated the modifications of the electronic structures in transition-metal surfaces, ultrathin films and clusters, which significantly change their magnetic properties compared to the bulk systems. The reduction in the coordination numbers in the 2D systems causes a narrowing of the energy bands, which increases the density of states at the Fermi level and consequently enhances their magnetic properties. Great attention has been directed to theoretical and experimental studies for vanadium (V) due to its great relevance of technological importance, such as hydrogen storage [4] and superconductivity [5]. An isolated vanadium atom possesses a permanent magnetic moment 3 μ_B in the ground state, whereas bulk vanadium does not exhibit magnetism.

The first experimental evidence of magnetism in V clusters was given in 1977 by Akoh and Tasaki [6]. The behaviour of the susceptibility as a function of particle size led them to suggest the existence of magnetic moment localized on surface atoms. Afterwards, many experimental investigations of magnetism in V surfaces took place [7–9]. In 1989 Moodera and Meservery [10] used impedance measurements to study the magnetic properties of V deposited on Ag, Pb, Au and Al substrates, where a ferromagnetic layer formed of about 1.5 monolayers. The inverse photoemission measurements used by Drude and Himpsel [11] showed a magnetic order in V monolayers deposited on Ag(111).

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Many theoretical approaches were devoted to study bulk vanadium, surfaces, thin films and clusters. *Ab initio* methods do provide the highest reliability, but require a great deal of computational effort. Among these methods is the FLAPW used by Fu *et al* [12]; they predicted enhanced 2D magnetism in transition metals. They obtained 1.7 μ_B magnetic moment for monolayers of V adsorbed on Au(001) and 1.98 μ_B for monolayers of V adsorbed on Ag(001). The magnetic moment reduces to 1.15 μ_B when two monolayers are adsorbed on Ag(001). A $c(2 \times 2)$ antiferrmagnetic phase was obtained in adsorbed V overlayers on a Pd(001) surface [13]. Moruzzi and Marcus [14] used the first-principles total-energy band theory with the local-spin-density and spherical-atom approximation to study the onset and the large-volume limit of magnetic behaviour for the 3d transition metals of bcc structures. They found that V undergoes composite first and second order transitions for expanded volumes.

The other approach of the theoretical studies is the real-space self-consistent tight-binding method with unrestricted Hartree–Fock approximation in the Hubbard Hamiltonian. This method requires less time for computation. Although this is an approximate method, it provides good predictions of the magnetic ordering that help experimentalists tailoring artificial magnetic systems. Using this method, Mokrani *et al* [15] confirmed the absence of magnetism in bulk vanadium. They also investigated the thickness dependence of the onset of magnetism in V slabs [16]. Bouarab *et al* [17] have proposed a description for the possible antiferromagnetism (AF) in V slabs. The AF and ferromagnetic (F) configurations for bulk V and epitaxially grown V monolayers on Ag(001) were studied as a function of the exchange parameter J. Some efforts were devoted to study the effect of depositing V on 3d transition metal substrates [18, 19]. Other investigations of the magnetic ordering are held for V surfaces on 4d substrates such as V/Nb systems [20] and on 5d transition metals such as V/Ta [21].

In this work, we discuss the magnetism of V overlayers on molybdenum (Mo) substrate, which is a 4d paramagnetic transition metal. The technological importance of V/Mo systems is due to their uses in fabricating synthetic superconducting materials [5], which motivated us to study the magnetism of such systems. The method of calculation is given in detail elsewhere [17, 20, 21]. This paper is organized as follows: section 2 is devoted to the results and discussion of relaxed and nonrelaxed systems. Section 3 contains the conclusion of this study.

2. The magnetism of V_n/Mo systems

In this section, we investigate the magnetism in V_n overlayers of $n = 1$–3 epitaxially grown on Mo semi-infinite (001) and (111) substrates. The parameters used in this study are the exchange parameters and the lattice constants of the two elements. V and Mo are 3d and 4d transition metals, respectively, which are known to be paramagnetic in their bulk form. The ground states of these two elements have bcc structures with lattice constants 5.71 au and 5.95 au; the numbers of d electrons are taken to be 4 and 5, respectively [22]. Due to the misfit of the lattice constants of the two metals, the interatomic distance in V layers is supposed to increase in the plane of deposition. The surface relaxation is about 6% (inwards) of the interlayer separation. This causes the hopping integrals of the d bands to increase by the fifth power of the interatomic distance [23]. That is, the vertical interatomic distance is reduced in order to recover the bulk volume of V, which leads to a bct V structure. The exchange parameters J_V and J_{Mo} are taken to be 0.5 eV [24]. In contrast, the direct intrasite Coulomb interaction, U, is replaced in the calculations by the site-dependent potential to insure the local charge neutrality condition [25].

2.1. The magnetism of non-relaxed V_n/Mo systems

The magnetism of the non-relaxed V_n overlayers with $n = 1, 2$ and 3 is investigated for (001) and (111) orientations. The (011) is found to be non-magnetic due to the large coordination number, which makes the magnetism less favourable [26]. Figure 1 displays the local density of states of a V overlayer in the (001) orientation and that of the bulk. This figure shows the narrowing of the d band in the 2D V surface as a result of the reduction in the coordination number, which causes the increase in the density of states at the Fermi level. A closer look at the values of the density of states at the Fermi level in the two cases shows that the Stoner criterion, which equals the product of the density of states at the Fermi level $n(\varepsilon_f)$ multiplied by the exchange parameter J_V ($n(\varepsilon_f)J_V > 1$) is satisfied in the (001) case.

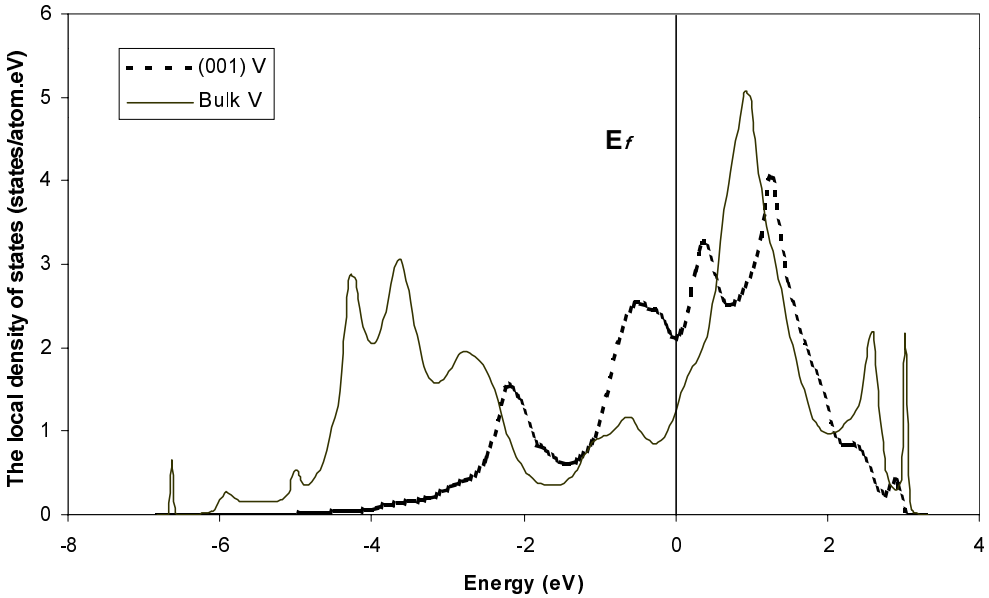

Figure 1. The local density of states (LDOS) of bulk and (001) V monolayer. Full line: bulk V; dotted line: (001) V surface.

Figure 2 displays the local density of states $n(\varepsilon)$ of V monolayers for the three orientations (001), (011) and (111). It exhibits the validity of the Stoner criterion in the (001) and (111) systems, which is not the case in the (011). The magnetic moments of the non-relaxed V_n/Mo systems for $n = 1, 2$ and 3 in the cases of (001) and (111) are given in table 1.

Table 1. Magnetic moment (in Bohr magnetons) for the nonrelaxed V_n/Mo systems for $n = 1, 2$ and 3 overlayers in the (001) and (111) orientations. S: the surface layer; I: the interfacial layer.

	(001)					(111)				
n	I − 1	I	S	S + 1	S + 2	I − 1	I	S	S + 1	S + 2
1	0.22	−0.49	1.8	—	—	0.18	−0.45	1.45	—	—
2	−0.02	0.15	−0.58	2.18	—	−0.21	0.23	−0.72	2.11	—
3	0.03	−0.02	0.10	−0.58	1.96	0.07	−0.18	0.31	−0.84	2.17

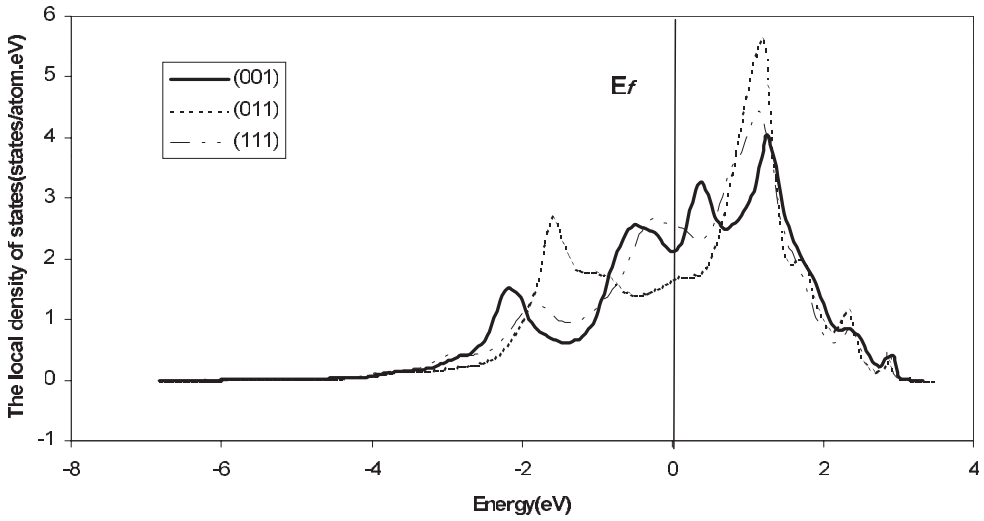

Figure 2. The local density of states (LDOS) of a V monolayer on a Mo substrate in the (001), (011) and (111) orientations. Full line: V(001); dotted line: V(011); dot–dash line: V(111).

The magnetic moment of the V surface layer (S) in the monolayer system is 1.8 μ_B in the (001) system, which is larger than 1.45 μ_B in the (111) case. The increase of the surface magnetism in the (001) orientation as compared to that of the (111) is related to the kind of nearest neighbour of the surface atom. For both cases, (001) and (111), the V surface atom has four Mo first nearest neighbours. However, there are five second nearest neighbours for the (001) case, four of them are V and one is a Mo atom, and three Mo atoms in the (111) case. In spite of the fact that the number of the second nearest neighbours is greater in the (001) system, the magnetism is larger since four of these atoms are the magnetized V atoms. In contrast, all of the second nearest neighbours are Mo atoms in the (111) system which causes hybridization between the 'd' bands of the magnetized V surface atom and unmagnetized Mo atoms, which reduces the magnetic moment. The layers lying below the V surface, the interfacial layer (I) and I−1 Mo layers, acquire induced magnetic moments from the magnetized surface layer. These magetic moments are comparable in the two orientations.

The magnetism is enhanced by adding another V overlayer in both (001) and (111) cases. The magnetic moments of the surface atoms are comparable. In this system all the first nearest neighbours are V atoms in both cases, and four of the second nearest neighbours are V atoms in the (001) system, whereas all of the nearest neighbours are Mo atoms in the (111) system. In the case of the three V layers deposited on Mo substrates, the effect of the coordination number dominates, since all the nearest neighbours are the same in both directions. As a result, the magnetic moment of the V surface layer is larger in the (111) orientation since it has a lower coordination number.

2.2. The magnetism of relaxed V_n/Mo systems

In this section, the relaxation (reduction of the interatomic distance in the direction perpendicular to the surface) is taken into account. Table 2 displays the results of the relaxed V layers in the (001) and (111) orientations. In this case, the magnetic moment of the surface atom in the relaxed systems is decreased in both the (001) and (111) orientations due to the

Table 2. Magnetic moment (in Bohr magnetons) for the relaxed V_n/Mo systems for $n = 1, 2$ and 3 overlayers in the (001) and (111) orientations. S: the surface layer; I: the interfacial layer.

	(001)					(111)				
n	I−1	I	S	S+1	S+2	I−1	I	S	S+1	S+2
1	0.18	−0.39	1.48	—	—	−0.08	−0.21	0.68	—	—
2	−0.03	0.09	−0.36	1.60	—	−0.08	0.07	−0.34	1.25	
3	0.03	−0.05	0.06	0.32	1.25	0.03	−0.07	0.1	−0.35	1.06

reduction of the vertical interatomic distance which causes an increase in the hopping integrals and consequently a decrease in the magnetic moments.

It is obvious that there is an AF coupling between the V and Mo layers, between the successive V layers and also between the successive Mo layers. This is in consistent with the fact that V slabs [17, 27] and V surfaces with expanded lattice constants have an AF interlayer coupling [28]. This is also the case for the Mo semi-infinite surface. One can study its magnetic behavior by increasing the exchange integral J_{Mo}. Figure 3 displays the magnetic moment as a function of the exchange parameter for the surface and the sub-surface layer in a semi-infinite Mo surface. This figure shows the interlayer AF coupling in a Mo semi-infinite surface.

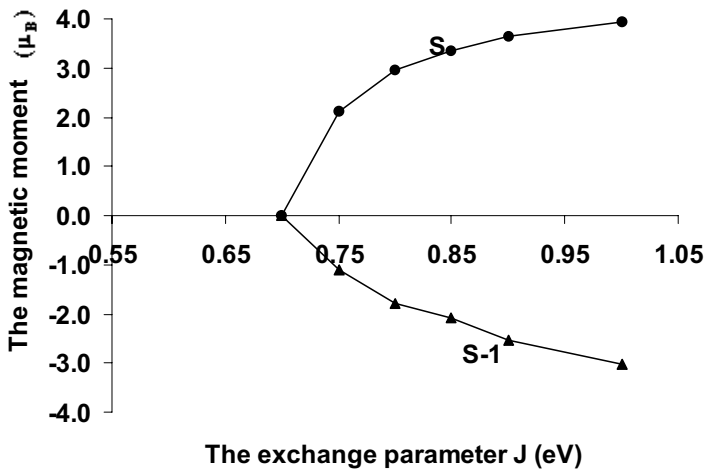

Figure 3. The magnetic moment in (Bohr magnetons) for the surface and sub-surface layers in the semi-infinite Mo surface as a function of the exchange parameter J_{Mo} in eV.

3. Conclusion

In this paper, we investigate the magnetism in V_n/Mo systems for $n = 1$–3 in the relaxed and nonrelaxed case. The main conclusions of these investigations can be summarized as follows:

(a) The magnetic moment in the V monolayer systems is larger in the (001) than that in the (111) orientation due to the kind of nearest neighbour, which are mostly Mo atoms in the (111) case, that causes a reduction of the magnetic moment.
(b) The magnetic moments in the nonrelaxed V bilayer and trilayer systems are comparable in the (001) and (111) cases.

(c) The magnetism in the relaxed systems decreases in both orientations.
(d) The Mo layers lying below the magnetized V layers exhibits induced magnetic moments.
(e) There is an AF coupling between V and Mo layers and also between Mo layers.

References

[1] Muscat J, Beal-Mond M T, Newns D M and Spanjard D 1975 *Phys. Rev.* B **11** 1437
[2] Ying C, Kahn L M and Beal-Mond M T 1976 *Solid State Commun.* **18** 359
[3] Ying C and Kahn L M 1977 *Surf. Sci.* **67** 278
[4] Farrel H H and Strongin M 1973 *Surf. Sci.* **38** 18
[5] Karkut M G, Ariosa D, Triscone J M and Fischer O 1985 *Phys. Rev.* B **32** 4800
[6] Akoh H and Tasaki A 1977 *J. Phys. Soc. Japan* **42** 791
[7] Allen G 1979 *Phys. Rev.* B **19** 4774
[8] Grempel D R and Ying S C 1980 *Phys. Rev. Lett.* **45** 1018
[9] Rau C, Liu C, Schmalzbauer A and Xing G 1986 *Phys. Rev. Lett.* **57** 2311
[10] Moodera J S and Meservery R 1989 *Phys. Rev.* B **40** 8541
[11] Drude W and Himpsel F 1987 *Phys. Rev.* B **35** 4131
[12] Fu C L, Freeman A J and Oguchi T 1985 *Phys. Rev. Lett.* **54** 1018
[13] Blügel S, Weinert M and Dederichs P H 1988 *Phys. Rev. Lett.* **60** 1077
[14] Moruzzi V L and Marcus P M 1988 *Phys. Rev.* B **37** 8003
[15] Mokrani A, Demangeat C and Dreysse H 1990 *Phys. Rev.* B **42** 10 319
[16] Mokrani A, Bouarab S and Demangeat C 1990 *Surf. Sci.* **251/252** 41
[17] Bouarab S, Nait-Laziz H, Demangeat C, Mokrani A and Dreysse H 1992 *Phys. Rev.* B **46** 889
[18] Vega A, Rubio A, Balbas L C, Davila J D, Bouarab S, Demangeat C, Mokrani A and Dreysse H 1991 *J. Appl. Phys.* **69** 4544
[19] M'Passi-Mabiala B, Nait-Laziz H, Bouarab S and Demangeat C 1994 *J. Magn. Magn. Mater.* **129** 200
[20] Khalifeh J 1997 *J. Magn. Magn. Mater.* **168** 25
[21] Khajil T and Khalifeh J 1997 *Surf. Sci.* **389** 310
[22] Papaconstantopoulos D A 1986 *Handbook of the Band Structure of Elemental Solids* (New York: Plenum)
[23] Pettifor D G 1977 *J. Phys. F: Met. Phys.* **7** 613
[24] Christensen N E, Gunnarsson O, Jepsen O and Andersen O K 1988 *J.Physique Coll.* **17** C8 49
[25] Victora R H and Falicov L M 1985 *Phys. Rev.* B **31** 7335
[26] Tomanek D, Muklerjee S and Bennemann K 1983 *Phys. Rev.* B **28** 665
[27] Homouz D M and Khalifeh J M 1996 *J. Magn. Magn. Mater.* **153** 355
[28] Hamad B A and Khalifeh J M 2000 *Surf. Sci.* 000, 000