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Magnetic ordering of V_n/Mo(001) systems: Ab-initio calculations

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Abstract

A density-functional theory (DFT) study is performed using a full-potential linearized-augmented-plane-waves (FP-LAPW) method to investigate the magnetic structure of vanadium–molybdenum systems (V_n/Mo(001), $n = 1, 2$). The topmost V layers relax inward in both systems with a larger contraction in V_2/Mo(001) system. A p(1 × 1) in-plane ferromagnetic ordering with appreciable magnetic moments is obtained on V overlayers, which is found to be the ground state in both systems. The layers below the surface exhibit induced magnetism with antiferromagnetic interlayer coupling.

Keywords: Surface magnetism; DFT; FP-LAPW; V; Mo

1. Introduction

Since the experimental evidence of magnetism on V clusters in 1977 [1], several experimental studies have been carried out to investigate V surface magnetism. However, the attempts to observe ordering in V systems have led to controversy. While Rau et al. [2] have detected ferromagnetism at the surface of V(001) single crystal using electron capture spectroscopy, no evidence of magnetic ordering has been obtained neither by MOKE [3] nor SPPES [4] studies. This controversy appears also in theoretical predictions. While Grempel and Ying [5] have predicted an antiferromagnetic V(100) surface, Yokoyama et al. [6] have obtained a ferromagnetic state of magnetic moment 0.2 μ_B per atom. On the other hand, Ohnishi et al. have predicted a paramagnetic state for V(001) surface using the FP-LAPW method [7]. Khalifeh and I have shown that V(001) surface is nonmagnetic, using a self-consistent tight-binding method within Hartree–Fock approximation. However, we reported an onset of magnetism, with 0.86 μ_B magnetic moment, when the lattice constant is increased by 1% larger than the equilibrium value [8]. However, Bryk et al., have obtained appreciable magnetic moments using plane waves method and norm-conserving pseudopotentials with generalized-gradient-approximation [9]. They obtained 1.705 μ_B magnetization for a nonrelaxed V(001) surface and 1.45 μ_B for the relaxed V(001) surface of relaxations $\Delta_{12} = -6.25\%$ and $\Delta_{23} = 0.0\%$. Bihlmayer et al., on the other hand, have obtained 1.5 μ_B magnetic moment at V(001) when using inappropriate k-point sampling, however, by using a proper choice of the k-set using 7-layer slab they obtained 0.04 μ_B, but with 15 layer relaxed slab, the magnetism has disappeared completely [10]. Furthermore, Robles et al. [11] have shown that the inclusion of some semicore states in the valence configuration of the pseudopotential leads to a drastic diminution in the magnetic moment. They have shown, using GGA calculations within the linear combination of atomic orbitals (LCAO) and the norm-conserving pseudopotentials, that the conventional valence $4s^2 3d^3$ pseudopotential, including nonlinear core corrections (NLCC), leads to a high polarization on V(001) surface modeled by 7, 9 and 15 layers (with and without relaxation). However, by treating the semicore $3p^6$ state explicitly as valence electrons, the surface has become nonmagnetic for the relaxed 15-layer slab.

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Using tight-binding (TB) semi-empirical calculations appreciable magnetic moments have been predicted for V overlayers on different transition-metal substrates [8,12–14]. Among these investigated systems is the vanadium–molybdenum (V–Mo) system. This system shows its significance in technological applications such as fabricating synthetic superconducting materials [15]. Furthermore, V–Mo superlattices have been widely used as hydrogen hosts. Owing to the difference of the hydrogen solution enthalpies of Mo and V, hydrogen is found to occupy vanadium layers rather than Mo [16–22] . Another interesting feature about this system is that the lattice constant of Mo is larger than V, the fact that gives rise to the appearance of magnetism on V layers. Experimentally, the magnetic structure of V–Mo multilayer system has been investigated by Koreniviski et al., who obtained a small magnetic moment of 0.1 μ_B on V layers [23]. However, a much larger moment was obtained for V overlayer on Mo(0 0 1) substrate [14], since the hybridization between V and Mo d-bands is less than the case of V–Mo superlattice. All the above-mentioned interesting properties of such a system are behind adopting the present study to provide a thorough understanding of its structural, magnetic and electrical properties.

This paper is organized as follows: Section 2 is devoted to the method of calculation, Section 3 contains the results and discussions and Section 4 contains a summary for the main points of this work.

2. Method of calculation

The calculations are performed using WIEN2k package. The total energies are computed using DFT calculations that are based on the full-potential linearized-augmented-plane-wave (FP-LAPW) [24,25] method. The basis set is described by Augmented plane waves plus local orbitals (APW + lo) method [26]. In FP-LAPW method the space is divided into two regions, non-overlapping muffin tins surrounding the atoms and an interstitial region. Therefore, the wavefunctions inside the muffin tins is described by the linear combination of (hydrogen like) atomic functions. As for the interstitial region the wavefunction is described by a sum of plane waves. The exchange–correlation functional is described using generalized-gradient-approximation (GGA) [27], which is more reliable for magnetic structure calculations than the local spin density approximation (LSDA) [28]. Thus, GGA description for the exchange–correlation functional give better results in magnetism as compared to experiment [29–34].

The core states were treated fully relativistically, while the semicore and valence states were treated by the scalar relativistic approximation (the spin–orbit interaction is ignored for the semicore and valence electrons).

In this work, thorough tests were performed for the computational parameters used in bulk and surface Mo structures to obtain reliable quantitative calculations. The detailed procedure is described in the subsections below.

2.1. Bulk calculations

For bulk V and Mo structure, convergence tests were performed for the number of k-points in the irreducible Brillouin zone and the cutoff energy for the plane waves in the interstitial region between the muffin tins. The convergence of the total energy for these values is within 1.5 and 1 meV for the number of k-points and the cutoff energy, respectively. Therefore, the cutoff energy of the plane waves in the interstitial region between the muffin tins was taken as 16 Ry for the wavefunction and 169 Ry for the potential. The k-point sampling was performed using a $(12 \times 12 \times 12)$ Monkhorst–Pack grid in the irreducible part of the Brillouin zone. The other parameters used in the calculations are : the muffin tin radius, $R_{MT} = 2.0$ bohr, the core energy cutoff of -6.0 Ry. The wavefunction expansion inside the muffin tins were taken up to $l_{max} = 10$ and the potential expansion up to $l_{max} = 4$. These parameters were chosen to set the self-consistent calculations where the convergence was taken with respect to the total charge of the system with a tolerance of 0.0001 electron charges.

Using the above-mentioned computational setup, the bulk lattice constants were obtained by structural optimization with 17 lattice constants above and below the experimental values of V (5.73 bohr [35]) and Mo (5.945 bohr) [36], by steps of ± 0.05 bohr. This was followed by fitting the obtained total energies with Murnaghan equation of state [37]. Thus, the optimum lattice constants obtained for V and Mo are $a_V = 5.661$ bohr and $a_{Mo} = 5.985$ bohr, respectively. Tables 1 and 2 summarize the optimized lattice constant and the bulk moduli of the present work as compared to the experimental values and previous calculations. The calculated lattice constant and bulk modulus of V are found to be 1.2% smaller and 4.8% larger than the experimental value [35], respectively. However, the lattice constant of Mo is 0.72% larger than its experimental value and the bulk modulus is larger by 8% [36]. The present calculations are also in a fair agreement with previous calculations [10,38–42].

2.2. Surface calculations

In this study, the calculations are performed for (1×1) and (2×2) surfaces. These surfaces are modeled by the

Table 1
The bulk modulus and lattice constant of V of the present calculations are compared with the previous calculations: (a) Ref. [10], (b) Ref. [38], (c) Ref. [39], and experimental results: (d) Ref. [35]

	Lattice constant (bohr)	Bulk modulus (Mbar)
Pseudopotential method (a)	5.99	2.57
Pseudopotential method (b)	5.93	2.82
FLAPW method (c)	5.917	2.91
Experiment (d)	5.942	2.73
Present work (FLAPW)	5.985	2.52