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# Evidence of surface magnetism in the V/Nb(001) system: A total energy pseudopotential calculation

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**Abstract**

We determine that an overlayer of vanadium (V) on Nb(001) shows ferromagnetic activity, using the pseudopotential method with a local spin density approximation (LSDA), under the density functional theory (DFT). Precisely calculated total energy, with and without relaxation shows the ferromagnetic (FM) state to have lower energy than the paramagnetic one. The non-relaxed V overlayer has appreciable magnetism of 0.76 $\mu_B$. On relaxation, due to the large values of relaxation (−22.5%) obtained there is complete hybridization of the V and Nb d bands and the magnetism is drastically reduced to 0.2 $\mu_B$. Since we know, that the LSDA under estimates the magnetism, a finding of magnetism, however weak, represents the physical reality. This is in qualitative agreement with our previous work and contradicts the results of Kim and Lee.


*Keywords:* Vanadium; DFT; Total energy; Surface magnetism; Relaxation

## 1. Introduction

With more than 20 years of on going research on V surfaces, interfaces and overlayers, we are still not close to resolving the controversial results of various studies. Magnetic behavior of V surfaces has attracted a lot of interest, ever since the finding of Blügel et al. [1], that a free standing V monolayer is ferromagnetic, while that on Ag(001) surface is antiferromagnetic (AF). The problem whether the surface of vanadium is or is not magnetic has been discussed intensely [2–5]. Allan [2] suggested that the V(001) surface could be magnetic even though bulk vanadium is paramagnetic. Yokoyama et al. [3] found 0.2 $\mu_B$ per atom for the V (001) surface using the self consistent charge spin polarized discrete variational $X_\alpha$ method. Rau et al. [4] using electron capture spectroscopy have shown the V(001) surface to be magnetic. Work of Fu et al. [5] indicates that the (100) surface of bulk vanadium may at the most be weakly ordered (magnetic moment of less than 0.1 $\mu_B$). Recently more attention is being devoted to the study of combined systems of V with other transition metals [6–9]. The spin polarization of Fe/V interface was studied by Vega et al. [6]. They found that the spin polarization of the V atoms at the interface is non-zero with AF coupling between the Fe and V interface atoms. Martin et al. [7] investigated the case of V overlayers on Fe(103), and they showed that the V atoms are AF coupled with their nearest neighbors and the value of the V local moments are smaller than those obtained by them for V on Fe(001).

Vanadium–Chromium systems have been studied by Bihlmayer et al. [8]. They found, using the generalized gradient approximation (GGA) the monolayer of V to have a large magnetic moment of 2.1 $\mu_B$. But, that of Cr was drastically reduced to 0.6 $\mu_B$. More recently, Tarawneh et al. [9] investigated the effect of kind and number of co-ordination on the magnetism of Cr/V systems. They found that, regardless of the number of Cr overlayers, the magnetic moment is the highest at the (001) orientation, followed by (111) and the least at the (011) orientation.

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The size and nature of magnetism of V depends, among the many factors, strongly on the substrate used in thin slab calculations. While a lot of studies have been done on V/Fe and V/Cr systems, less attention has been given to V/Nb or V/Ta systems. The interface LDOS for the transition metals V, Nb and Ta obtained by Baquero et al. [10], shows the high probability of the V side of V/Nb and V/Ta interfaces to be magnetic. So far, to the best of our knowledge, the only studies of V/Nb(0 0 1) for a ML of V, have been that of Kim and Lee [11] and Khalifeh [12]. Kim and Lee used a full potential linearized augumented plane wave (FLAPW) method, within the generalized gradient approximation (GGA) and Khalifeh used a tight binding (TB) method with Hubbard-type Hamiltonian. The highly controversial predictions under various environments and different methods of study, is a motivation in itself to study combined V systems. But, what motivated us further is the finding of Kim and Lee [11] of the non-existence of ferromagnetism in V monolayer on Nb(0 0 1) as opposed to our earlier (Khalifeh [12]) prediction of magnetism of the V overlayer on the Nb(0 0 1) surface. Hence, it is fruitful to study this system again, using a precise first principles method, namely the DFT under the local spin density approximation (LSDA). Since we know, that the LSDA under estimates the magnetism, a finding of magnetism, however weak, represents the physical reality.

This paper is organized as follows: Section 2 outlines the computational method, Section 3 gives the discussion of results and conclusions.

## 2. Method of calculations

We used the thin slab supercell technique, based on the density functional theory as implemented in the ABINIT software package [13,14]. Norm-conserving pseudopotentials (NCPP) of Hartwigsen, Goedecker, and Hutter (HGH) [15] were used both for Niobium and Vanadium, to describe the core–valence interaction. For both elements, semi core states were considered with 13 valence electrons. The exchange correlation used was the LSDA functional of Teter Pade [16]. A plane wave basis has been used to expand the Bloch wavefunctions. The importance of the proper choice of pseudopotentials cannot be minimized. The relativistic separable dual space Gaussian HGH pseudopotentials used in our work are of very high quality and have good convergence properties in real and Fourier space. Moreover, they are extended norm-conserving, hard pseudopotentials, as seen from the high values of cutoff energies required. Relativistic effects, which are relevant for heavier elements are included in the pseudopotential calculation. Since the 3d wavefunctions of the 3d elements are strongly localized, there is significant overlap with the 3s,p wavefunctions. This is overcome by the explicit inclusion of semicore electrons into the pseudopotentials.

In order to obtain the theoretical lattice constants for Nb and V, convergence tests with respect to the cut-off energy and $k$-points were performed. Using the converged values, the lattice constants were optimized by using an automatic algorithm for minimizing the total energy (zero of forces). Optimization of the unit cell dimensions along with displacement of the ions is done. The configuration for which the stress almost vanishes is iteratively determined by keeping a force tolerance of $<1 \times 10^{-5}$ Ha/bohr. For structural relaxation we used the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization algorithm modified to take into account the total energy as well as the gradients [17]. Convergence of the self consistent field (SCF) iterations is achieved when the total energy difference between two consecutive iterations is less than $1 \times 10^{-6}$ Ha [18]. A slab of several atomic layers, orientated in the [0 0 1] direction is used to simulate the (0 0 1) surface. For the supercell geometry, we performed convergence tests for the number of atomic and vacuum layers with respect to the bulk density of states (DOS). Consequently, the converged supercell for this system consists of seven atomic layers and seven vacuum layers i.e. 54% vacuum. This much amount of vacuum is required to minimize any Coulomb and exchange interactions between the slabs.

The optimized lattice constant used for the slab is the value obtained for Niobium, namely 6.176 a.u. There are no in-plane components of force and there is no in-plane relaxation because of the two-dimensional (in plane) translational invariance. There are only vertical components of forces. The vertical lattice spacings are allowed to relax simultaneously according to the sign and magnitude of forces. Since all atoms are allowed to relax simultaneously the true minimum is reached. For structural relaxation we used the BFGS minimization algorithm modified to take into account the total energy as well as the gradients [17]. The structure is optimized when the total maximum force is less than 1 mRy/a.u. The convergence criterion for SCF iterations is met by keeping the total difference in forces $<5 \times 10^{-5}$ Ha/Bohr. The tetrahedron method is used to obtain the angular momentum projected LDOS. A uniform grid of 21 $k$-points in the irreducible surface Brillouin zone (ISBZ) and atomic sphere radii of 2.5 and 2.7 a.u. for V and Nb, respectively are used for the integration.

## 3. Results and discussion

### 3.1. Structural results

Both Nb and V have a BCC paramagnetic ground state. The optimized lattice constant of Nb is found to be 6.176 a.u (3.27 Å), which is 0.9% lower than the experimental value of 3.3 Å [19]. We used a cutoff energy of 45 Ha and $6 \times 6 \times 6$ $k$-point grid. The optimized lattice constant of V is found to be 5.589 a.u (2.96 Å) using a kinetic energy cut-off of 55 Ha and a $8 \times 8 \times 8$ grid. Which is 2.3% lower than the experimental value of 3.03 Å [19]. According to our calculations, the mismatch in the lattice constants of these two metals is about 9.5%, whereas the experimental mismatch is about 8.1%. This is a driving force for