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# Magnetic character of $V_2$ dimers on Cu(001)

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Theoretical electronic-structure calculations of a $V_2$ dimer adsorbed on a Cu(001) surface have been carried out to determine the ground-state geometry and magnetic moment at the V sites. For the unrelaxed surface, the V sites have a large magnetic moment as predicted by previous studies. The surface Cu atoms, however, undergo significant relaxations and the V-V distance at the surface is close to that of an isolated $V_2$ molecule. These relaxations quench the magnetic moments at the V sites showing that V dimers on a Cu(001) are actually nonmagnetic. [S0163-1829(97)52412-X]

Although isolated atoms of most elements in the Periodic Table have finite magnetic moments, there are only a few ferromagnetic solids. Even in these cases, the magnetic moments in solids are less than in free atoms. The progression of magnetism as one collects atoms to form extended structures leading to solids has therefore attracted considerable attention. Theoretical studies indicate that the local moment at a given site is primarily governed by the local coordination[1] and that the moment increases as the coordination is reduced. Indeed, small clusters of Fe, Co, and Ni have been found to have higher moments per atom compared to solids.[2,3] It has also been found that small clusters of nonmagnetic solids like Rh can be magnetic.[4,5] Ordered surface alloys of Cu and Mn [6] and the ultrathin monolayers of Ru and Rh on Ag(001)[7] have also been proposed to be magnetic. The appearence of magnetism is due to geometry and reduced coordination of surface sites. In the case of surface films, the magnetism is found to be sensitive to structural imperfections.[7]

One way of using clusters for practical applications is to deposit them on surfaces. Previous studies indicate that the clusters often undergo significant change in shape upon deposition.[8] Size selected deposited clusters therefore provide a new class of systems whose geometries are different from free clusters or bulk and therefore can be expected to provide a new class of magnetic behaviors. It is with this in mind that there has been a surge in studies involving magnetic behavior of atoms/clusters on surfaces. For example, Lang *et al.*[9] have studied the local moments of $3d$, $4d$, and $5d$ atoms on the Cu and Ag(001) using the Korringa-Kohn-Rostocker method and a Green's-function approach. They find that most atoms of nonmagnetic solids have significant moments. Using the same approach, Stepanyuk *et al.*[10] have recently studied $3d$, $4d$, and $5d$ clusters on (001) surfaces of Cu, Ag, Pd, and Pt and have shown that dimers of many nonmagnetic solids will be magnetic. In particular a $V_2$ dimer on a Cu(001) surface has been predicted to have a magnetic moment of about $3\mu_B$ per atom that would make it more magnetic than bulk Fe. A similar high moment for V clusters on Ag(001) has been predicted by Nati-Laziz[11] using tight-binding methods. Despite these predictions, no experiments have been able to detect any moments in V clusters deposited on surfaces. One feature of all of these calculations is that surface relaxations were ignored and that adsorbates were placed at positions corresponding to the substrate lattice.

The purpose of the present paper is to show that a complete accounting of all *local* interactions can resolve the apparent disagreement between theory and experiment. By including all local interactions that are present and accounting for the adsorbate induced relaxations, we have shown that such relaxations play a key role in controlling magnetism of clusters on surfaces. We demonstrate this point for the case of a $V_2$ dimer on a Cu(001) surface. It is shown that the surface atoms undergo significant relaxations upon the adsorption of clusters. This is in line with numerous previous studies of clusters on surfaces that show similar effects. We also show that V atoms of the deposited molecule do not occupy the empty lattice sites of the Cu substrate but that the V-V distances are close to that in a free $V_2$ molecule. This finding is consistent with the fact that V and Cu are immiscible in the liquid phase[12] indicating that the V-V or Cu-Cu interactions are collectively stronger than the V-Cu interactions. It is shown that both of these effects conspire to completely quench the V moments. The adsorbed $V_2$ molecule is therefore nonmagnetic, which is in accord with the experiments. The studies indicate that the relaxation effects cannot be ignored when looking for magnetic properties of clusters on surfaces.

The theoretical calculations were carried out by modeling the Cu(100) surface by a cluster of 28 atoms (Fig. 1). The size of this model was selected so that when a $V_2$ is adsorbed, the V atoms have their first and second nearest-neighbor Cu atoms within the cluster. To investigate effects due to cluster size, calculations were also carried out using a smaller cluster containing only near neighbors of the adsorbed species. The electronic structure was studied using a linear combination of atomic-orbitals molecular-orbital

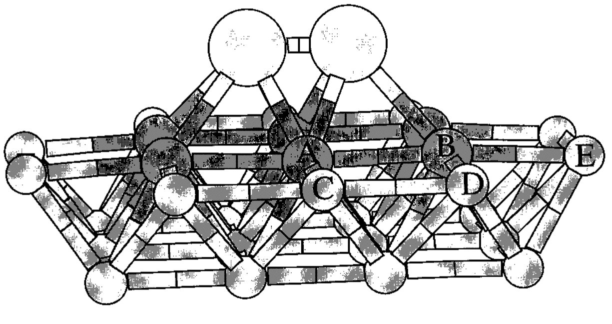

FIG. 1. The ground-state geometry of the $V_2Cu_{28}$ cluster. The V-V separation is slightly larger than observed in the gas phase. The net spin of the $V_2$ molecule is reduced from a triplet to a singlet upon adsorption.

TABLE I. The equilibrium nearest-neighbor separations for the $V_2Cu_{28}$ surface-adsorbate model.

| Bond | Distance | Bond | Distance |
|---|---|---|---|
| $Cu_A$-$Cu_A$ | 5.02 | $Cu_C$-$Cu_D$ | 4.57 |
| $Cu_A$-$Cu_B$ | 4.60 | $Cu_E$-$Cu_E$ | 4.57 |
| $Cu_B$-$Cu_B$ | 4.60 | $Cu_A$-V | 4.60 |
| $Cu_A$-$Cu_C$ | 4.34 | $Cu_B$-V | 5.03 |
| $Cu_B$-$Cu_D$ | 4.56 | V-V | 3.34 |
| $Cu_B$-$Cu_E$ | 4.55 | | |

approach.[13] The exchange-correlation effects were included within the local-density-approximation (LDA) to the density-functional formalism. In brief, the cluster molecular orbitals are expanded in a linear combination of atomic orbitals $\phi(\mathbf{r}-\mathbf{R_j})$ centered at the atomic sites $R_j$, i.e.,

$$\psi_i=\Sigma_j C_{ij}\phi_j(\mathbf{r}-\mathbf{R_j}), \tag{1}$$

$$(-\tfrac{1}{2}\nabla^2+V_{ion}+V_H+V_{xc}^{\alpha})|\psi_n^{\alpha}\rangle=\epsilon_n^{\alpha}|\psi_n^{\alpha}\rangle. \tag{2}$$

The $C_{ij}'s$ are the variational coefficients obtained by solving the one-electron Kohn-Sham[14] equations self-consistently. In Eq. (2), the first term is the kinetic energy operator, $V_{ion}$ represents the ionic potential, $V_H$ is the Hartree potential, and $V_{xc}$ is the exchange-correlation potential depending on spin $\alpha$, and $\psi_n^{\alpha}$ is the $n$th molecular orbital for that spin.

There are several similar approaches for solving the Kohn-Sham equations[14] that primarily differ in the form of the basis functions, the method for solving Poisson's equation, and the numerical methods for calculating matrix elements, total energies and forces. In this paper we have elected to use two different approaches that are based on the linear combination of atomic orbitals. The calculations on the smaller clusters and the initial calculations on the larger clusters have been performed within the discrete variational method (DVM).[15] In this program the radial part of the atomic basis functions are represented numerically and the secular equation is constructed by calculating the various matrix elements numerically on a mesh of points. Calculations within the DVM code have been based on the von Barth–Hedin form[16] of the exchange-correlation functional and we have used frozen cores to further reduce the computational effort. Use of the very fast DVM method has allowed for an efficient search of the interesting regions of parameter space.

To address any questions that may arise from the use of the frozen core, the particular form of the exchange-correlation functional, or the numerical details, we have repeated some of the calculations with the cluster codes of Pederson and Jackson[17,18] that we refer to as NRLMOL. In this all-electron method, the atomic basis functions are represented in terms of contracted Gaussians, Poisson's equation is solved analytically, and the integrals associated with construction of the secular equation are performed numerically with a numerically precise variational integration mesh.[17] The exchange-correlation functional used for these studies is the Perdew-Zunger[19] parametrization of the Ceperley-Alder[20] exchange-correlation results. With respect to basis sets we have used a total of 17 even-tempered Gaussians to construct a $(6s,4p,3d)$ contracted Gaussian-basis set. This leads to 36 basis functions per atom. The Gaussian decay parameters range between 0.05–252 300 for Cu and 0.05–158 700 for V, respectively. Before discussing the quantitative results, which unless otherwise stated correspond to the NRLMOL values, we note that we have found no *qualitative* differences between the DVM and NRLMOL results. We first consider our results on the free systems.

Within LDA the free $V_2$ dimer is found to be a triplet with a bond length of 3.30 au and a cohesive energy of 4.39 eV. The bond length agrees well with the experimental value of 3.34 au and, as expected, the LDA cohesive energy is larger than the experimental value (1.85 eV). However, it appears that the measured binding energy is a lower bound to the actual value.[21] For comparison, previous local density calculations[21] have obtained a bond length of 3.31 au and a binding energy of 3.8 eV. As mentioned above, the Cu(001) surface has been modeled by a 28-atom cluster shown in Fig. 1. The geometry of the free cluster was optimized by varying the interlayer and interatomic distances within the layers to minimize the energy. It was found that the Cu-Cu interlayer distance was less than in the bulk, which is consistent with the observed surface relaxation in the bulk. We find that the ground state of the 28-atom surface model is a spin singlet.

In order to study the $V_2$ adsorbed on the Cu(001) surface, one can bring the $V_2$ molecule towards the surface in various configurations. Previous studies[22] of various adatoms on (100) surfaces show that the adatoms line up along the (110) directions on the surface. In this configuration (see Fig. 1) the adatoms can effectively bond between themselves and the substrate atoms. Keeping this in mind, the $V_2$ molecule was allowed to come towards the (100) surface as shown in Fig. 1. To find the ground-state configuration, several nuclear degrees of freedom were optimized. The vanadium atoms and the Cu $A$ and $B$ atoms were fully relaxed with the constraint of $C_{2v}$ symmetry. In addition the atoms marked $C$, $D$, and $E$ were allowed to move horizontally and vertically. However, deviations of atoms $C$–$E$ from their isolated $Cu_{28}$ sites were minimal.

In Fig. 1, we show the ground-state configuration. The nearest-neighbor distances associated with the surface and adsorbate atoms are presented in Table I. The minimum energy configuration corresponds to the $V_2$ dimer 3.64 a.u. above the plane with a V-V bond length of 3.34 a.u. One notices that atoms $A$ and $B$ relax upward by 0.17 and 0.25

a.u., respectively. The V-V distance of 3.34 a.u. is slightly stretched with respect to the isolated molecule. This is significantly shorter than the 4.48-a.u. V-V separation if the V atoms were constrained to reside above Cu lattice sites as done in previous calculations.

The ground state was found to have no net spin with a HOMO (highest occupied molecular orbital)/LUMO (lowest unoccupied molecular orbital) gap of 0.27 eV. Since the possibility of either antiferromagnetic or ferromagnetic ordering was allowed for in our calculations it was necessary to perform a Mulliken population analysis to guarantee that the equilibrium geometry was indeed a singlet. The local moment at the V sites was found to be zero. We have also calculated the spin up and down charge in spheres of increasing radii around the V sites. The net spin was always zero confirming that the V atoms on Cu (001) have no net magnetic moment.

As mentioned above, the previous calculations had obtained a moment of $3.0\mu_B$ per atom for the V sites on Cu(001). These calculations neglected two important effects. Firstly, the V atoms were placed at the lattice sites corresponding to the host lattice thereby ignoring the fact that V-V interactions will alter their spacing on the surface. Secondly, the studies ignored the relaxations of the host lattice. To show that these can have qualitative effects, we carried out a calculation of an isolated V atom on the Cu(001) surface by modeling the surface by a cluster of 28 atoms. The V atom had a moment of $3.0\mu_B$ per atom similar to that obtained in the previous studies.[10] It therefore seems that the quenching of magnetic moments in a molecule is largely due to contraction of the V-V distance from 4.48 a.u. corresponding to positioning of V atoms at the lattice sites to the relaxed value of 3.34 a.u. on Cu(001). This decrease is understandable noting that the moment per atom in a free $V_2$ molecule (with interparticle spacing of 3.34 a.u.) is only $1.0\mu_B$ per atom compared to $5.0\mu_B$ in an isolated V atom. This shows that the V atoms in $V_2$ will be more magnetic if the V-V bond is stretched. To further confirm that this is indeed the source of discrepancy, we carried out a calculation of a $V_2$ on Cu(001) by forcing V atoms to occupy lattice sites, and neglecting surface relaxations. The V sites were *highly* magnetic.

In Fig. 2 we show the $s$, $p$, and $d$ local density of states at the V sites, the total V density of states, and the total density of states of the cluster. The one-electron levels have been broadened by 0.03 eV for the purpose of presentation. The gap between the HOMO and the LUMO was about 0.27 eV. From the projected density of states it is clear that the LUMO level is predominantly associated with the Cu conduction band, and the lowest molecular orbital that is localized in the vicinity of the V atoms lies 0.35 eV above the HOMO. The V states are fairly narrow and the majority of the occupied $d$-states are approximately 1 eV below the Fermi energy. We have verified that increasing the V-V distance from 3.34 to 3.81 a.u decreases the HOMO/LUMO level from 0.27 eV to 0.07 eV. A further increase of the V-V distance or neglect of relaxation, such as the calculation discussed above, would lead to a peak at the Fermi energy and the formation of a magnetic moment. A Mulliken population analysis shows that there is a charge transfer from V to Cu sites. Charge transfer from the V to the Cu is further supported by the fact that the HOMO level of a $V_2$ molecule lies at −4.19 eV, which is slightly higher than the LUMO level of the $Cu_{28}$ surface at −4.24 eV. Our calculations on stretched $V_2$ molecules show that the isolated molecules increase their magnetism with increasing separations and that HOMO levels of these systems are further increased to the range −2.97 to −3.16 eV depending on configuration. The large difference between the majority-spin stretched $V_2$ HOMO levels and the unpolarized $Cu_{28}$ LUMO levels further explains why the resulting electronic charge transfer leads to a partial quenching of the V moments for the nonequilibrium geometries and a complete quenching of the V moments for the equilibrium $V_2$ molecule. Since long-range Coulomb multipolar interactions (partially neglected in any finite model) are invariant to the sign of charge transfer, the possibility of additional magnetism due to *negatively* charged $V_2$ molecules need not be considered. Further, since our calculated moment $(3.2\mu_B)$ for an isolated V atom on a Cu surface is in accord with the results of Ref. 10 and since this moment is reduced with respect to the LDA value for an isolated atom, the indication is that the primary charge transfer effects within our model are the same as in Ref. 10.

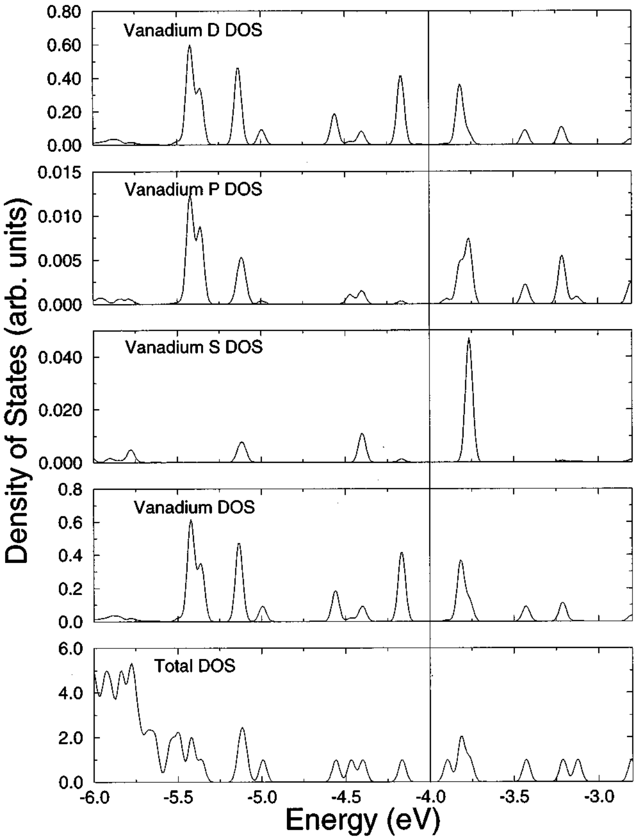

FIG. 2. The density of states associated with the surface and adsorbates atoms for the $V_2Cu_{28}$ cluster. The lower panel shows the total density of states. The second panel shows the local vanadium density of states. Panels 3–5 show the vanadium $s$, $p$, and $d$ density of states, respectively. Note that arbitrary units are used but that the scales are different from one panel to the next. The vertical line separates the occupied and unoccupied states.

We also studied the effect of cluster size on our results. Using the DVM code we carried out calculations on a smaller $Cu_8V_2$ cluster. In this case the cluster includes only the nearest neighbors of the V sites. Again the V and Cu atoms were relaxed to minimize the energy. The moment at the V sites was again zero. This shows that a change in size is not likely to affect our main result in which V atoms on Cu(001) are nonmagnetic.

To conclude, we have studied small to intermediate sized models for a low concentration of V atoms on Cu surfaces. These models include all short-range interactions between the adsorbate and the surfaces. We show that consideration of atomic relaxations is critical for determining the magnetic properties of clusters deposited on such surfaces. For small concentrations, the deposited adatoms do not necessarily occupy the vacant sites of the underlying lattice and the intracluster interactions are important. The surface atoms also undergo significant relaxations and in the case of vanadium on Cu(001) the resulting dimerization quenches moments on the V sites. While these calculations show that low concentrations of V atoms on Cu surfaces would not exhibit magnetism, it is not clear whether this conclusion would hold true for higher densities of V atoms (e.g., a monolayer) on Cu. In this case the underlying Cu atoms may not be able to relax in the same way, which might allow for V-V bond breaking.

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