Structural effects on the magnetism of small vanadium clusters

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The size and geometric structure dependence of the magnetic properties of small V_N clusters is studied by using a d-band Hubbard-like Hamiltonian in the unrestricted Hartree-Fock approximation. We determine the average magnetic moment $\bar{\mu}_N$ and local magnetic moments μ_i as a function of the interaction parameters. Different structures are considered and charge transfer effects are discussed. For the considered clusters, usually two different magnetic configurations are obtained. The role of the sp electrons and spd hybridization effects on the magnetic properties is calculated for bcc-like clusters. Results are given for the average magnetic moment, the spin-polarized charge distribution within the clusters, and the sp and d electronic density of states. Small local sp magnetic moments μ_{sp} are obtained, which in most cases are opposite to the d magnetic moment μ_d.

I. INTRODUCTION

The study of free $3d$ transition metal clusters has recently motivated remarkable research activity both theoretically and experimentally.[1] The magnetic properties of these materials are known to derive from the itinerant $3d$ electrons. In particular, vanadium is an ideal case to study how localized electrons delocalize for increasing number of atoms and how this affects its magnetic behavior: the isolated atom has a permanent magnetic moment of $3\mu_b$ and bulk V is paramagnetic. Since vanadium belongs to the middle of the $3d$ transition metal series, it is expected,[2] when the lattice parameter increases, to be in the antiferromagnetic (AF) state. Recent experiments[3] show that the magnetic moment of V_9 cluster is $0.59\mu_B$. This value is qualitatively in agreement with calculations performed by Lee and Callaway.[4] However, as discussed by these authors, a high-spin state might exist for V_N clusters in some range of lattice parameters. This high-spin state was also found for bcc-like V_N clusters by Lui, Khanna, and Jena[5] and in a more systematic study by Dorantes-Dávila and Dreyssé.[6] These systematic studies have revealed a wide variety of magnetic behaviors, as a function of the d-band filling and strength of the interaction parameters. Clearly, previous results[4–7] indicate that in the study of magnetic order, the interaction parameters and local environment are the key quantities.

It is the aim of this paper to complete previous calculations[6] by studying the local environmental effects on the magnetic properties of small V_N clusters. To achieve this, we consider alternative fcc- and icosahedral-like structures. Charge transfer effects are discussed by varying the d-electron occupation number. We use a d-electron tight binding model Hamiltonian since the magnetic properties are expected to be largely dominated by the more localized d electrons. The effects of the sp electrons on the magnetic properties are also studied, by calculating the magnetic properties of V_9 and V_{15} within an spd-electron band Hamiltonian.

II. THEORY

Details of the calculation for the electronic properties of V_N- clusters can be found in Ref. 8. The interaction Hamiltonian H_I in the unrestricted Hartree-Fock approximation is given by

$$H_I = \sum_{i\sigma} \Delta\epsilon_{i\sigma}\, \hat{n}_{i\alpha\sigma} - E_{\rm DC}\,, \tag{1}$$

$$\Delta\epsilon_{i\sigma} = \sum_{\sigma'} U_{\sigma\sigma'}\, \Delta\nu_{i\sigma}\,. \tag{2}$$

Here $\Delta\nu_{i\sigma} = \nu_{i\sigma} - \nu_0$, where $\nu_{i\sigma} = \sum_\alpha \langle \hat{n}_{i\alpha\sigma}\rangle$ is the average electronic occupation at atomic site i in the orbital α with spin σ, and ν_0 refers to the corresponding average occupation in the paramagnetic solution of the bulk. The intra-atomic Coulomb interactions $U_{\sigma\sigma'}$ between d electrons can be written in terms of the exchange Coulomb integral $J = U_{\uparrow\downarrow} - U_{\uparrow\uparrow}$ and average direct Coulomb integral $U = (U_{\uparrow\downarrow} + U_{\uparrow\uparrow})/2$. Finally, $E_{\rm DC} = (1/2)\sum_{i\sigma,j\sigma'} U_{\sigma\sigma'}\, \nu_{i\sigma}\, \nu_{j\sigma'}$ stands for the correction due to double counting.

The number of d electrons ν_i , and the local magnetic moments μ_i at site i, given by

$$\nu_i = \sum_\alpha (\langle \hat{n}_{i\alpha\uparrow}\rangle + \langle \hat{n}_{i\alpha\downarrow}\rangle) \tag{3}$$

and

$$\mu_i = \sum_\alpha (\langle \hat{n}_{i\alpha\uparrow}\rangle - \langle \hat{n}_{i\alpha\downarrow}\rangle), \tag{4}$$

are determined self-consistently by requiring

$$\langle \hat{n}_{i\alpha\sigma} \rangle = \int_{-\infty}^{E_F} \rho_{i\alpha\sigma}(E)\, dE\,. \tag{5}$$

Here, $\rho_{i\alpha\sigma}(E)$ refers to the local density of states (DOS) of spin orbital $\alpha\sigma$ at site i. The energy of the highest occupied state (Fermi energy) E_F is determined from the global charge neutrality condition: $N_d = (1/N)\sum_i \nu_i$, where N_d refers to the number of d electrons per atom. Notice that charge transfer between atoms having different local environments may occur. The LDOS, $\rho_{i\alpha\sigma}(E) = (-1/\pi)\Im m\{G_{i\alpha\sigma,i\alpha\sigma}(E)\}$, is determined by calculating the local Green's functions $G_{i\alpha\sigma,i\alpha\sigma}(E)$ by means of the recursion method.[9] The number of levels M of the continued fraction expansion of $G_{i\alpha\sigma,i\alpha\sigma}(E)$ is chosen large enough so that the results became independent of M.

It is difficult to conclude for an exact value of J computed from *ab initio* calculations.[10] For this reason, J is usually taken as a parameter. Here, in order to study in a systematic way the appearence of magnetism in small V_N clusters, we calculate the local magnetic moments as a function of J. Note that this variation gives the behavior observed by changing the interatomic distance by anisotropic dilatation.[10,11] In such problem, J, or the interatomic distance, is the relevant quantity.

III. RESULTS AND DISCUSSION

In this section we present and discuss results for the size and structural dependence of several magnetic properties V_N clusters. The relevant parameters used for the calculations are (a) number of d electrons per site N_d and (b) bulk bandwidth W. The hopping elements $t_{ij}^{\alpha\beta}$ are obtained from the canonical two center integrals $dd(\sigma,\pi,\delta) = (-6,4,-1)(W/2.5)$.[12] For the geometrical structures we focus on both fcc- and icosahedral-like clusters, bcc clusters have been reported elsewhere.[6,7] The considered structures are obtained by adding to a central atom the sucessive shells of its first, second, etc., neighbors.

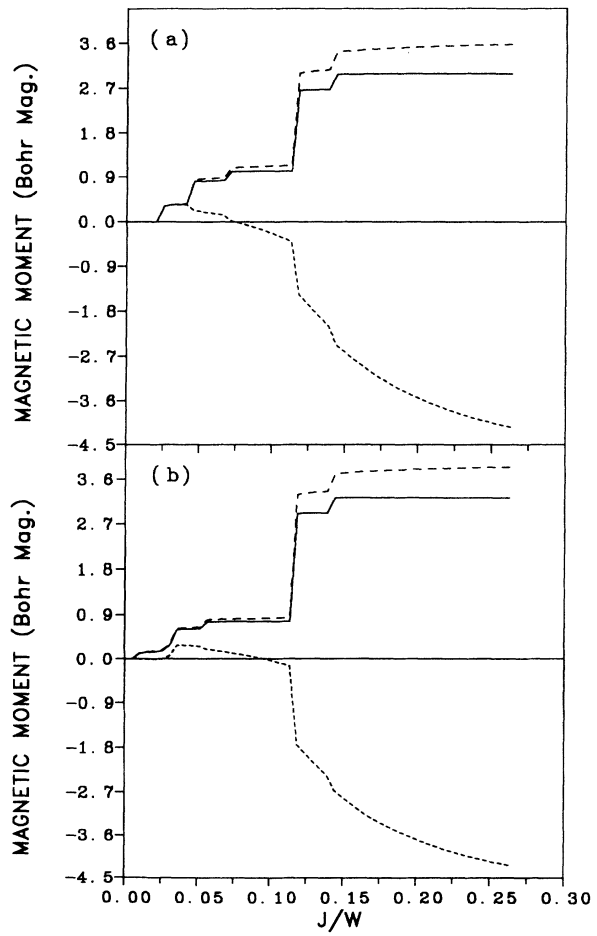

FIG. 1. Local magnetic moments μ_i of fcc-V_{13} in the antiferromagnetic configuration (magnetic moments aligned in the opposite direction): central atom (dotted line), first shell atoms (dashed line), and average magnetic moment (full line) (in units of μ_B) as a function of J/W (J refers to the exchange integral and W to the bandwidth). (a) refers to the calculation for $N_d = 3.75$ and (b) refers to $N_d = 4.0$.

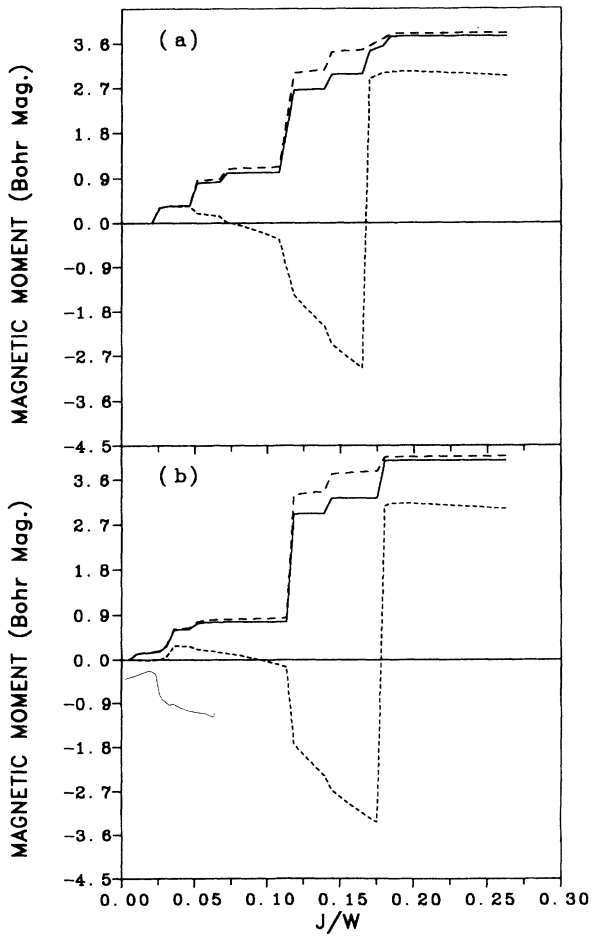

FIG. 2. Local magnetic moments μ_i of fcc-V_{13} in the ferromagnetic configuration (magnetic moments aligned in the same direction): central atom (dotted line), first shell atoms (dashed line), and average magnetic moment (full line) (in units of μ_B) as a function of J/W (J refers to the exchange integral and W to the bandwidth). (a) refers to the calculation for $N_d = 3.75$ and (b) refers to $N_d = 4.0$.

A. V_{13} clusters

Results for fcc-V_{13} and ico-V_{13} clusters are given in Figs. 1–4, respectively. We model the possible *sp-d* charge transfer by considering two different band fillings, (a) refers to $N_d = 3.75$ and (b) to $N_d = 4.0$. Two different magnetic couplings were found: ferromagnetic (F) (magnetic moments between different shells aligned in the same direction), and antiferromagnetic (AF) (magnetic moments between different shells aligned in opposite directions). Note that for fcc clusters (see Figs. 1 and 2), the transition from nonmagnetic to magnetic behavior occurs at a rather small value of J/W. Such large stability of magnetism in small fcc-like clusters can be interpreted as resulting from the increasing importance of Coulomb interactions relative to kinetic energy terms as local coordination number decreases. A similar dependence of μ_i on the values of interaction parameters was also found for bcc-like clusters.

As it can be inferred directly from the results of fcc-V_{13} (Figs. 1 and 2), significant changes between the results obtaind with $N_d = 3.75$ [Figs. 1(a) and 2(a)] and those obtained with $N_d = 4.0$ [Figs. 1(b) and 2(b)], are only seen for small values of J/W. This is expected since for these values of $J/W(\leq 0.075)$, the cluster is at the verge of the onset of magnetism and then the results are sensitive to the details of the LDOS near the Fermi energy. For a value of $J/W > 0.175$, two solutions are found: the central atom has either a F coupling or either an AF coupling with its 12 nearest neighbors. For $J/W < 0.175$, only one solution is found. For this regime two situations occur: $J/W < 0.07$ [Fig. 1(a)] and $J/W < 0.09$ [Fig. 1(b)], all atoms have a F coupling and for $0.07 < J/W < 0.175$ [Fig. 1(a)] $0.09 < J/W < 0.175$ [Fig. 1(b)], the central atom has an AF coupling with the first shell atoms. In such a case the cluster presents frustrations. A given atom on the first shell has two types of nearest neighbors: the central atom with an AF coupling and four atoms on the first shell with a F coupling.

Results for ico-V_{13} clusters are reported on Figs. 3 and

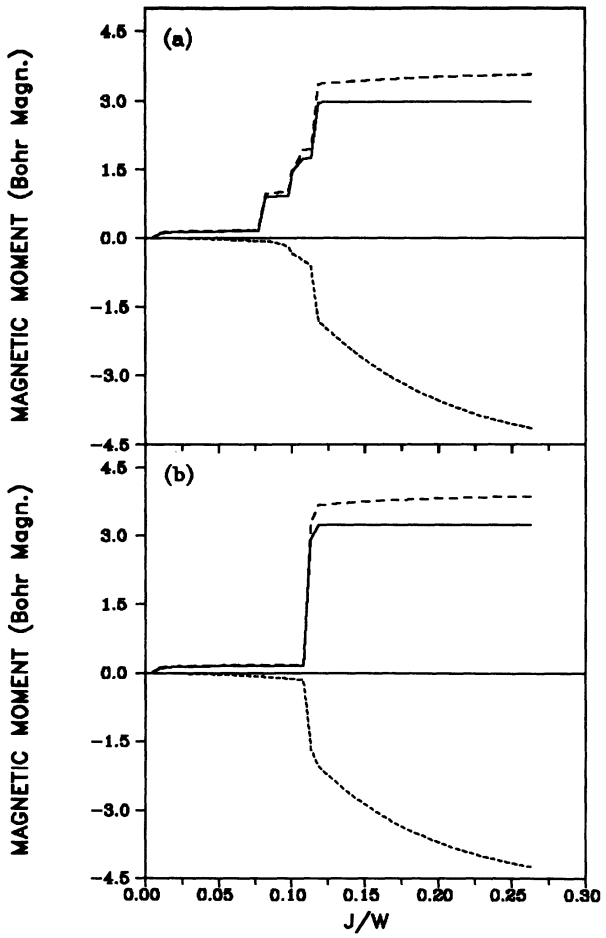

FIG. 3. Local magnetic moments μ_i of ico-V_{13} in the antiferromagnetic configuration (magnetic moments aligned in the opposite direction): central atom (dotted line), first shell atoms (dashed line), and average magnetic moment (full line) (in units of μ_B) as a function of J/W (J refers to the exchange integral and W to the bandwidth). (a) refers to the calculation for $N_d = 3.75$ and (b) refers to $N_d = 4.0$.

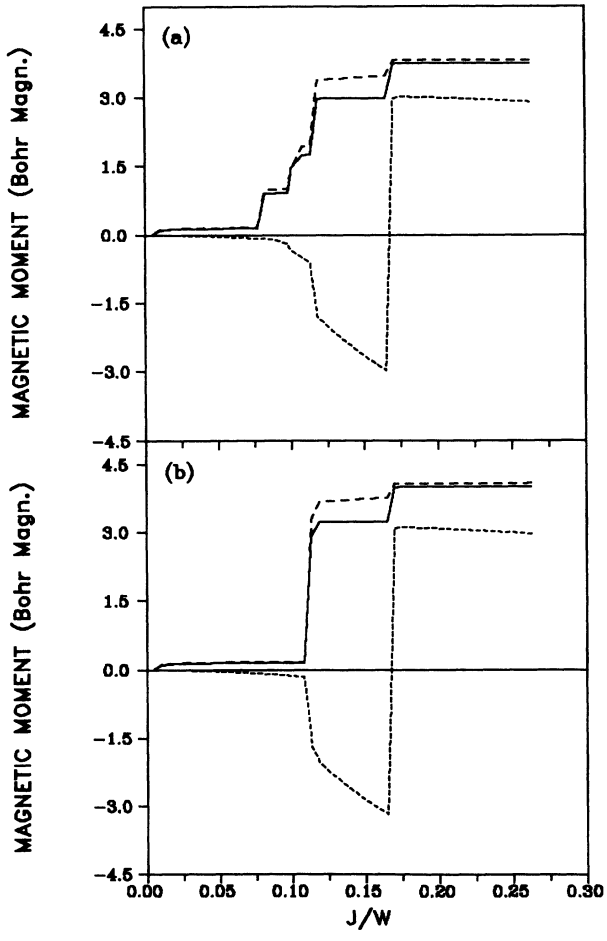

FIG. 4. Local magnetic moments μ_i of ico-V_{13} in the ferromagnetic configuration (magnetic moments aligned in the same direction): central atom (dotted line), first shell atoms (dashed line), and average magnetic moment (full line) (in units of μ_B) as a function of J/W (J refers to the exchange integral and W to the bandwidth). (a) refers to the calculation for $N_d = 3.75$ and (b) refers to $N_d = 4.0$.

4. Two different solutions were found for large values of J/W. Here, in contrast to fcc-V_{13} clusters, the transition from non-magnetic (or very low magnetic regime) to magnetic behavior occurs for large values of J/W. For J/W larger than 0.165, the central atom can be coupled F or AF with the other atoms of the cluster. For $J/W < 0.165$ a unique solution is found where the central atom has an AF coupling with other atoms. The largest magnetic moment is always beared by the atoms on the first shell which are less coordinated. The magnetic moment on the central atom has negligible values for $J/W < 0.10$. Let us notice that for the ico-V_{13}, it has not been possible to find for $J/W < 0.165$ a solution with atoms having all F coupling.

The influence of the d-band filling is more important for ico-V_{13} as compared to fcc-V_{13}. Here, the position of the Fermi energy and the details of the LDOS play a major role. This can be inferred by the results obtained for $0.08 < J/W < 0.165$: for $N_d = 3.75$, several steps in the value of the local magnetic moments are found, whereas for $N_d = 4$ only one step is found.

B. Ico-V_{55} cluster

As compared to V_{13} clusters, the ico-V_{55} cluster presents a much richer magnetic structure. In fact, several magnetic solutions were found. Here we show only those having the lowest energy (Figs. 5 and 6). Let us first discuss the results obtained for the magnetic configuration with the moments of the sucessive shells opposite. These results are shown in Fig. 5 and in analogy with V_{13} clusters we call it AF configuration. The calculated average magnetic moment $\bar{\mu}_{55}$ is very small, even for large values of J/W, and vanishes at $J/W \approx 0.12$. This value is very close to the one obtained with bulk bond length,[10] indicating that a bulklike configuration with bulk bond length tends to suppress magnetism. Notice, however, that the local magnetic moments are still very large, even

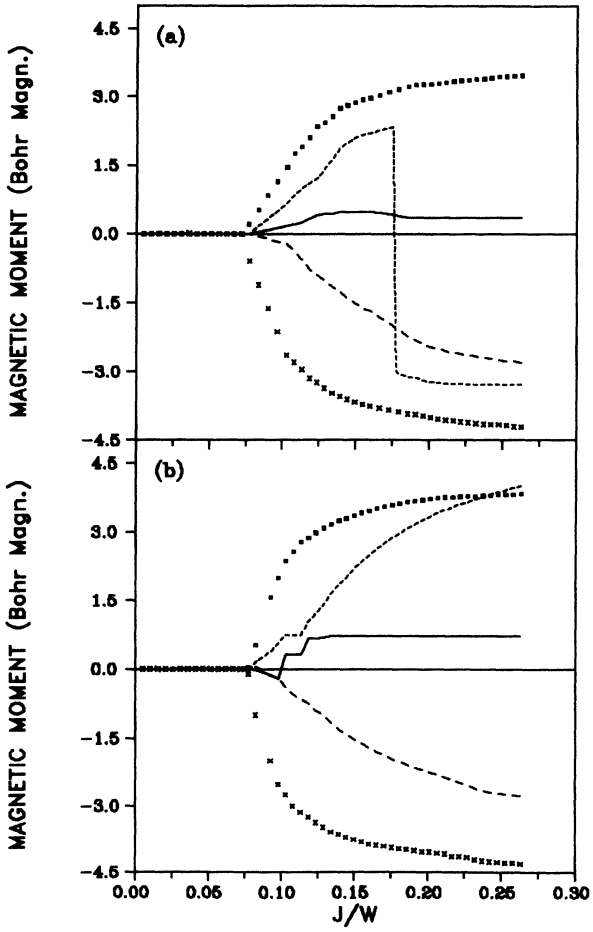

FIG. 5. Local magnetic moments μ_i of ico-V_{55} in the antiferromagnetic configuration (magnetic moments aligned in the opposite direction): central atom (dotted line), first shell atoms (dashed line), second shell atoms (squares), third shell atoms (crosses), and average magnetic moment (full line) (in units of μ_B) as a function of J/W (J refers to the exchange integral and W to the bandwidth). (a) refers to the calculation for $N_d = 3.75$ and (b) refers to $N_d = 4.0$.

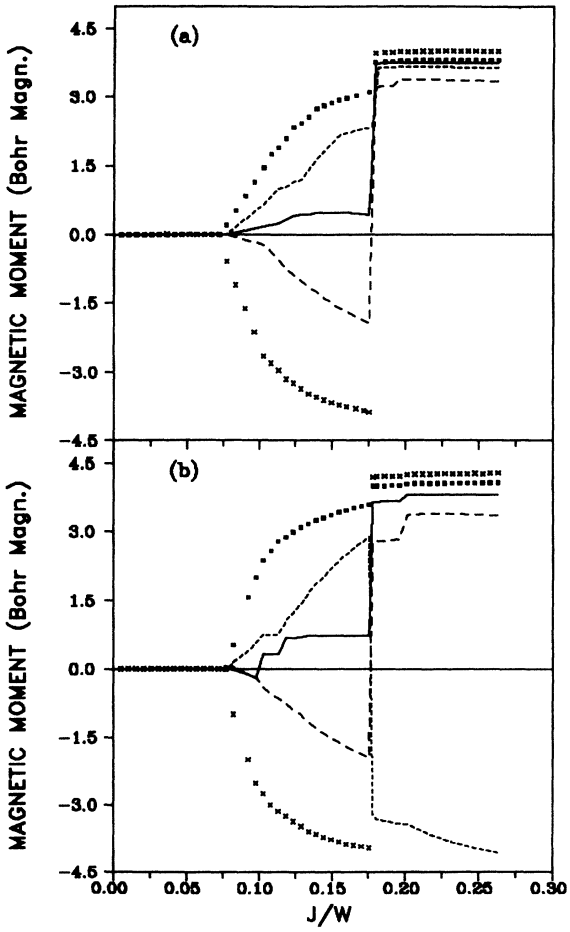

FIG. 6. Local magnetic moments μ_i of ico-V_{55} in the ferromagnetic configuration (magnetic moments aligned in the same direction): central atom (dotted line), first shell atoms (dashed line), second shell atoms (squares), third shell atoms (crosses), and average magnetic moment (full line) (in units of μ_B) as a function of J/W (J refers to the exchange integral and W to the bandwidth). (a) refers to the calculation for $N_d = 3.75$ and (b) refers to $N_d = 4.0$.

for these small values of $\bar{\mu}_{55}$. Moreover, the moments of the first (dashed line) and outermost shell (crosses) are always aligned in the same direction for the whole range of values of J/W.

The second magnetic solution is shown in Fig. 6. Notice that this solution has a magnetic configuration different from that shown in Fig. 5 only for $J/W > 0.175$. For $N_d = 4.0$ [see Fig. 6(b)] we have been unable to obtain a solution where all atoms would have been F coupled. In fact, for large values of J/W, the moment of the central atom is opposite to those of successive shells. This is expected since, in this case, N_d has a value close to the half-band filling. For $J/W > 0.175$ the average magnetic moment is very large, corresponding to an unusual bond length expansion.

C. Role of the *sp* electrons

Here, we discuss the role of the *sp* electrons on the magnetic properties of V_N clusters. Although the magnetic properties of the clusters are expected to be largely dominated by the more localized *d* electrons, *sp-d* hybridizations have an indirect influence on the magnetic properties.[13] In order to study systematically these effects we impose local charge neutrality over the cluster and calculate self-consistently the spin charge distribution as a function of the *d*-electron occupation N_d. Notice that this is a good approximation as suggested by other tight binding calculations.[13,14] In order to improve our calculation in the spin-polarized charge distribution within the cluster one should go further and include overlap interaction effects.[15]

Results are given for the local *d*-magnetic moment μ_d as a function of N_d. The parameters are taken as follows: for the Slater-Koster hopping integrals we use the values reported in Ref. 16, which were obtained from bulk band structure calculations. The ratio between the direct Coulomb integrals $U_{ss} : U_{sd} : U_{dd}$ is derived from atomic Hartree-Fock calculations.[17] The absolute value $U_{dd} = 4.3$ eV is taken to obtain the ionization potential of the atom. We choose for the exchange integral J a value where magnetic solutions can be obtained. We take $J = 0.65$ eV, which is approximately the same obtained in *ab initio* calculations.[10]

Results for bcc-like clusters V_9 and V_{15} are given in Fig. 7. Using the bulk interatomic distance, we obtain a re-

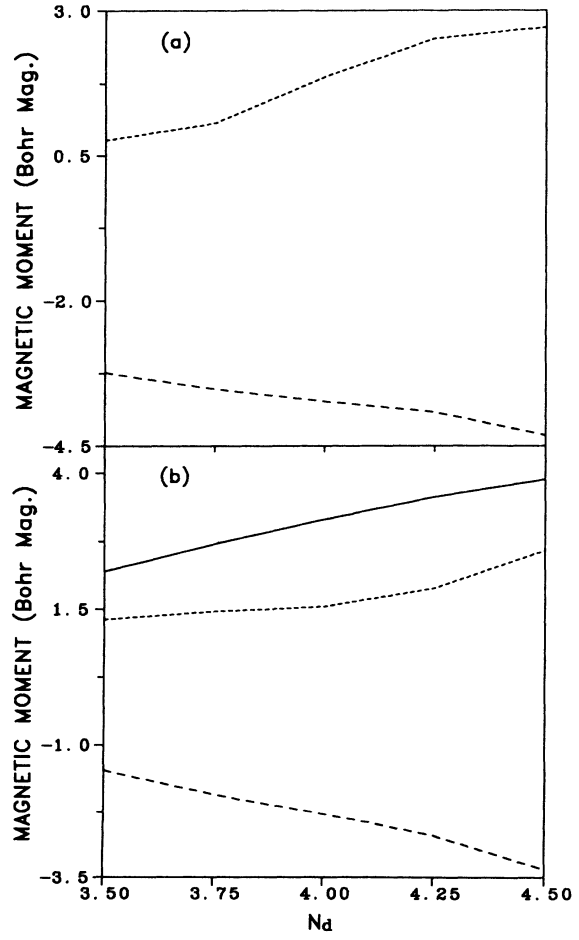

FIG. 7. Local magnetic moment for *d* electrons μ_d as a function of *d* occupation N_d. (a) refers to the calculation for the V_9 cluster and (b) refers to V_{15}.

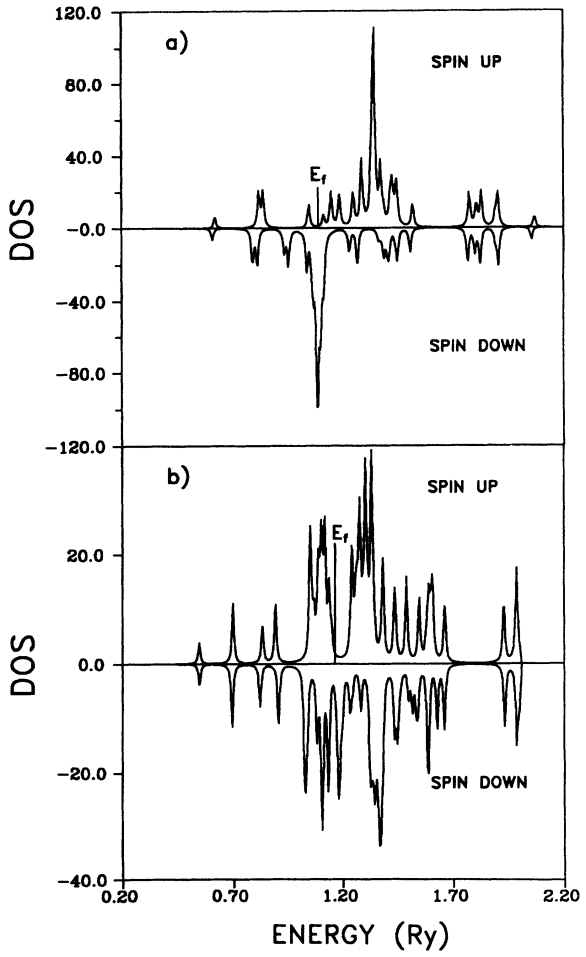

FIG. 8. Average density of states (DOS) for bcc-V_N clusters including *sp* electrons. The electron occupation *s*, *p*, and *d* is taken the same as in bulk V. (a) refers to the DOS for the V_9 cluster and (b) refers to V_{15}.

duction of the average magnetic moment $\bar{\mu}_N$ as compared to previous d-band model calculations.[6] This reduction of $\bar{\mu}_N$ including the sp electrons in the self-consistent calculation is mainly due to the sp hybridization, i.e., the sp-d mixing yields an additional increase of the d-band width and thus reduces the μ_d. Furthermore sp magnetic moments are obtained and in most cases align opposite to the dominant d moments. For the V_9 cluster $\bar{\mu}$ decreases monotonically as a function of N_d. This is due mainly to large changes in the magnetic moment in the central atom which dominates (align opposite) the increase of the magnetic moments in the surface atoms. We also obtain that the sp magnetic moment in the central atom is smaller than that of a surface atom. This can be explained from a reduction of the coordination number in the surface atoms and thus an increase of the magnetic moments. This behavior remains for almost the whole range of N_d values except for very large values (particularly for p electrons) in which $\mu(2) < \mu(1)$.

For the V_{15} cluster the average magnetic moment is very small ($|\bar{\mu}| \approx 0.15\mu_B$) and for $3.5 \leq N_d \leq 4.0$ is approximately constant. We expect the same behavior for larger clusters, indicating that good qualitative results can be inferred from d-model calculations in surfaces using $3.5 \leq N_d \leq 4.0$.

In Fig. 8 results are given for the average spd-electron density of states for bcc-like V_9 [Fig. 8(a)] and V_{15} [Fig. 8(b)], taking bulk s-, p-, and d-electron occupation [i.e., N_d(cluster) = N_d(bulk) and N_{sp}(cluster) = N_{sp}(bulk)]. Notice that the states close to the Fermi energy E_F have dominant d character, while for states well below and above E_F the sp contribution dominates. As was previously found,[4] the shape of the total DOS indicates a resemblance between the general features of the distribution of energy levels of the cluster and those of the bulk.

IV. SUMMARY

The onset of magnetism in V_N clusters has been studied in the framework of a d-electron model Hamiltonian in the unrestricted Hartree-Fock approximation. The local and average magnetic moments were determined as a function of the interaction parameters J/W. For a given geometrical structure and large values of J/W, two different magnetic solutions were found. For these values of J/W, an AF solution where all shells are AF coupled exists. An equivalent F solution is absent for ico-V_{55} with $N_d = 4.0$. For small values of J/W a unique solution remains. Similar behavior has already been obtained for bcc-V_N clusters.[6] Let us recall that we search all possible solutions, and for the case of ico-V_{55} we have shown those having the lowest energy. Moreover, we can conclude that for values of J/W which are not too large and which correspond to values reached for a V-V bond length smaller or in order of the bulk value, only one solution exists.

An estimation for J/W with bulk bond length yields, among the studied clusters, only that the fcc-V_{13} displays a significant value of the local magnetic moments. This value of J/W is at the verge of the onset of magnetism for ico-V_{55}. As for bcc-V_{51}, we found that large compact and symmetrically arranged V clusters with the bulk bond length are near the transition from paramagnetic to magnetic state. This is no longer the case if the atoms are arranged in a two-dimensional-like geometry. Small V_N clusters (20 – 30 atoms) in a bilayerlike arrangement on Ag (001) have been found to present large values of the local magnetic moments. Similar trends are also displayed by varying the number of the d-electron occupation.

The effects of the sp electrons on the magnetic properties of V_N clusters were discussed by calculating the magnetic moments of V_9 by using a parametrized spd-band model Hamiltonian. For interaction parameters close to those of the bulk, we found that the average magnetic moment is very small for V_{15}, in agreement with previous calculations.[4]

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