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Magnetic behavior of small vanadium clusters

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The electronic structure of small vanadium clusters is systematically studied as a function of the interaction parameters and cluster size with a bcc-like structure. For each topological arrangement, various possible magnetic states are considered and the transition from nonmagnetic to magnetic order is characterized. The average magnetic moment and the individual magnetic moments are determined self-consistently with the Hubbard tight-binding Hamiltonian. The magnetic behavior of vanadium clusters is very different from that of the bulk. However, some specific trends for cluster magnetism emerge. For the configurations studied, the average magnetic moment stays within a small set of values, whereas the local magnetic moments are very sensitive to the variation of the interparticle distance. A small magnetic moment in clusters is obtained for interatomic distances much smaller than the bulk distance.

I. INTRODUCTION

For a long time, vanadium has attracted the interest of physicists and chemists for its magnetic properties: the isolated atom has a permanent moment of $3\mu_b$; however, it is well known that bulk V is paramagnetic. Moreover, it was shown long ago that an expansion of the bulk lattice parameter will lead to the onset of ferromagnetism.[1,2] Recently, Moruzzi and Marcus[3] carefully studied the onset of antiferromagnetism. According to the Heine-Samson theorem,[4] vanadium, lying in the middle of the $3d$ transition-metal series, should become antiferromagnetic (AF) rather than ferromagnetic (F) when the lattice parameter is increased. The ferromagnetic state should occur only for very large interparticle separation. Vanadium is an ideal case to study how localized electrons on an isolated atom become delocalized with increasing cluster size and finally reach bulk behavior.

In the study of magnetic order, the bond lengths and the direct atomic neighboring are the key quantities. Experimentally, Akoh and Tasaki[5] reported the existence of large localized moments in vanadium particles from 100 to 1000 Å in size. Conflicting results have been reported for very thin V film grown on Ag(001), as well as for the pure V(001) surface.[6–8] These discrepancies could be related to the preparation conditions of the samples and mainly to the crystallographic quality of the films (the presence of steps drastically modifies the magnetic properties[9]).

Theoreticians have the facility to change the parameters used in the calculations. By using the scattered-wave $X\alpha$ technique, Salahub and Messmer found that for the V_{15} cluster a dilation of the bond length leads to a magnetic state.[10] Very recently, by using a self-consistent-field molecular-orbital theory in the density-functional approximation, Liu, Khanna, and Jena[11] found that the magnetic moment at the central atom of a nine-atom bcc-like V cluster vanishes abruptly when the interparticle spacing is reduced by a factor of 10%. For V film a systematical tight-binding study has been realized for the onset of magnetism versus the distance between the V atoms.[12–14] An AF coupling between ferromagnetically (001)-ordered layers was found for the V(001) films. In all cases, the magnetic moment at the surface layer is larger than the nonsurface layers. For the free-standing (001) monolayer, an in-plane antiferromagnetic order has been found by full-potential linear augmented-plane-wave (FLAPW) calculations.[15] Very thin films (two to five layers) are at the verge of onset of magnetism.[14,16] It is important to note that due to the AF coupling between planes the magnetic moment appears gradually as a function of the lattice parameter. In contrast, a ferromagnetic interlayer coupling exhibits first-order transition.[17]

The aim in this paper is to perform a systematical study of small V clusters versus the bond lengths and the cluster size. For a given (bcc-like) structure we compute the local magnetic moments and total energy. Different magnetic arrangements are considered. For each magnetic configuration, the transition from a nonmagnetic to a magnetic state is described. This paper is organized as follows. In Sec. II, we briefly present the theoretical frame. In Sec. III results for V clusters from 9 to 51 atoms are presented. Finally, a discussion is given in Sec. IV.

II. THEORETICAL FRAMEWORK

Sophisticated *ab initio* approaches have been developed in quantum chemistry to study small clusters. Unfortunately, they are limited to rather small sizes.[18] On the other hand, the very precise first-principles band-structure calculations for finite systems are not directly transferable to clusters,[19] due to the lack of translational symmetry, but other methods allow very precise first-principles calculations on small magnetic clusters.[20] The tight-binding scheme provides a unified framework to

study cluster and bulklike structures. The magnetism is described within the Hubbard Hamiltonian in the unrestricted Hartree-Fock approximation. In this way cluster and bulklike crystals have been studied with success.[13,21] Here we shall consider only d electrons, which are expected to contribute dominantly, and spin-independent canonical hopping integrals.[22] The diagonal elements of the Hamiltonian can be written as

$$\varepsilon_\sigma^i = \varepsilon_d^0 + U\Delta n_i - \sigma J \mu_i \ , \tag{1}$$

where ε_d^0 is the d reference level, Δn_i the variation of charge as compared to the bulk paramagnetic value on site i, μ_i the magnetic moment, and U and J the intraatomic Coulomb and the exchange integrals, respectively. U can be estimated from atomic spectroscopic data. U and J will be taken independent of the structure. Let us note that two different definitions of the exchange integral J are used in the literature. The choice made in this work is in agreement with the definition given by Ohnishi, Fu, and Freeman.[16] The other definition leads to a doubly larger value of J, as used by Pastor, Dorantes-Davila, and Bennemann[21] or Dreyssé *et al.*,[13] for instance. With such a Hamiltonian, a charge transfer between different sites is allowed, so that only the global neutrality is required. Full self-consistent treatment of Eq. (1) is performed. The spin-polarized densities of states are computed within the recursion method. For bcc-like clusters, interactions up to next-nearest neighbors are taken. Moreover, the spins are supposed collinear and the average magnetic moment $\bar{\mu}_c$ given by

$$\bar{\mu}_c = \frac{1}{N_c} \sum_{i=1}^{N_c} \mu(i) \tag{2}$$

represents the average magnetization of the cluster c with N_c atoms at $T=0$ K.

The total energy is the sum of the one-electron energy, the double-counting term, and a Born-Meyer term representing the ion-ion repulsion. At a given lattice parameter, by comparing various magnetic states, this repulsive term does not contribute.

In the present study, the exchange integral J plays a major role. The exact determination of the value of J is delicate. A general expression for J can be derived within the local-density-functional approximation.[23] In the linear-muffin-tin-orbital method in the atomic-sphere approximation (LMTO-ASA), a value of 0.30 eV has been found[23] in V bulk. Using a FLAPW method, Ohnishi, Fu, and Freeman deduced a value of 0.46 eV for V films.[16] Previously, a value of 0.35 eV had been obtained by Janak[24] and 0.40 eV by Gunnarsson[25] for the vanadium bulk exchange integral. The higher value obtained by Ohnishi, Fu, and Freeman indicates that J for a very thin film is different than that for the bulk. In the tight-binding approach, no simple relation can be derived between J and the electronic structure. For this reason, J is usually taken as a parameter. The simplest case consists of fitting J in order to recover either the bulk magnetic moment, when it is ferromagnetic (Fe, Co, Ni), or the threshold value, to have onset of ferromagnetism with a known lattice expansion (Pd, for instance). Moreover it has been shown that, in the tight-binding scheme, the use of various sets of hopping integrals for Fe, and thus very different values of J, leads to a very similar magnetic profile of Fe(001) semi-infinite crystals[26] emphasizing the necessity to consider J as a parameter consistently defined rather than having a fixed value given by external ways.

First-principles studies have shown that the variation of J versus the bond length is small and can be approximately fitted by an r^{-d} law ($d \simeq \frac{1}{3}$).[27] Much more important is the variation of the hopping integrals versus the interaction distance: for d orbitals, the r^{-5} law has been shown to be adequate. The curves μ_i vs J can be understood, either by considering J as a varying parameter, or by considering a fixed value of J but changing the mutual distance by an isotropic dilatation.[17] For example, the richness of such curves has been used to determine all possible values of the magnetic moment of structures with equivalent sites (bulk, monolayer, bilayer) versus the d-band filling.[17] The relevant quantity is the dimensionless quantity J/W, where W is the bulk bandwidth ($W=7.48$ eV).

It is well known that the recursion method is another way to diagonalize matrices. For clusters, the size of the space is finite: for a given starting vector of the recursion method, the nondiagonal coefficients of the continued fractions reach exactly the value zero, indicating the exploration of all the space. The upper limit of the dimension of this space is, of course, the number of sites multiplied by the number of different orbitals per site. The necessary number of levels N_L is a function of the starting vector and of the symmetry of the problem. For small clusters ($N_c=9$) complete determination is taken. For larger clusters ($N_c>9$) we check that taking $N_L=35$ is enough to ensure good accuracy. Thus 45 levels have been computed.

III. RESULTS

In these calculations, we study clusters organized into shells: the central atom is the first shell, the second shell is the set of the nearest neighbors of the first-shell atom, the third shell is the set of the nearest neighbors of the second shell which do not belong to the first or second shell. Thus the shells are built by recursion. Properties of such clusters have been studied elsewhere.[28] Starting from a single atom as the first shell, one can notice that the shell of order n is the collection of the neighbors of order $(n-1)$ of the central atom. Such clusters have a high level of symmetry. In this work, we focus on four such V_n clusters: $n=9$, 15, 27, and 51.

There is a higher number of magnetic arrangements for clusters than for an extended structure (i.e., bulk). Due to the geometrical symmetry of the studied clusters, we suppose that in a given shell all the atoms have the same magnetic moment. Finally, the remaining degrees of freedom are the types of interaction between the shells. Here we fixed the types of coupling for very large values of J/W. We denote as ferromagnetic (F) [antiferromagnetic (AF)] coupling between two nearest-neighbor shells when the atoms of these shells have the same (opposite)

polarization. The simplest case is obtained when all interactions are F for *large values* of J/W. This configuration will be denoted F. In the four clusters studied we have found, for each cluster, only one configuration for *large values* of J/W with AF coupling. This configuration will be denoted AF. For V_{27} we found AF coupling between shells 1 and 2 and 2 and 3 and F coupling between shells 3 and 4. This is due to the special geometry of this cluster: the last shell is not the third shell of a bcc bulk crystal.

Once the boundary conditions for large values of J/W (F or AF configuration) are fixed, the calculations are performed for decreasing values of J/W. We found systematically that for values of J/W smaller than a threshold value [J/W (F-AF)], only one magnetic solution is obtained. Let us mention that for AF or F configurations, we have tried without success to obtain, at a given value of J/W, multiple solutions for the electronic occupations and the magnetic moments. More detailed information on the resolution of this problem can be found in Ref. 21. Finally, in order to understand the various magnetic behaviors, we compute systematically the variation of energy relative to the paramagnetic case and the electronic occupation in the different shells versus J/W.

A. V_9 cluster

We report the various magnetic moments of a V_9 cluster versus J/W in Fig. 1. Two magnetic arrangements can be found, according to the coupling between the two shells: F or AF. As expected, for small values of J, only the AF solution exists. The onset of the ferromagnetic arrangement is possible for $J/W \geq 0.066$. On the contrary, an AF solution is found even for very low values of J/W. Let us mention that for the small J/W values the magnetic moment on the central atom is smaller than that on the second-shell atoms. This situation is reversed for higher values of J/W (i.e., $J/W \geq 0.066$) owing to a charge transfer from the external shell to the central atom [Fig. 2(b)]. For the F arrangement, the situation is the opposite: charge transfer occurs from the central atom to the external shell [Fig. 2(a)]. For values of J/W larger than 0.108, the F configuration seems to be somewhat more stable than the AF one.

The average magnetic moment $\bar{\mu}$ displays a surprising behavior. For the AF configuration, apart for very small values of J/W and two zones of strong variation, $\bar{\mu}$ takes only three different values, whereas $\mu(1)$ and $\mu(2)$ change continuously. The region of constant $\bar{\mu}$ is due to the imposed global neutrality in the cluster. For the F configuration, $\bar{\mu}$ displays one supplementary value (4.0 μ_b) due to the ferromagnetic coupling between all sites.

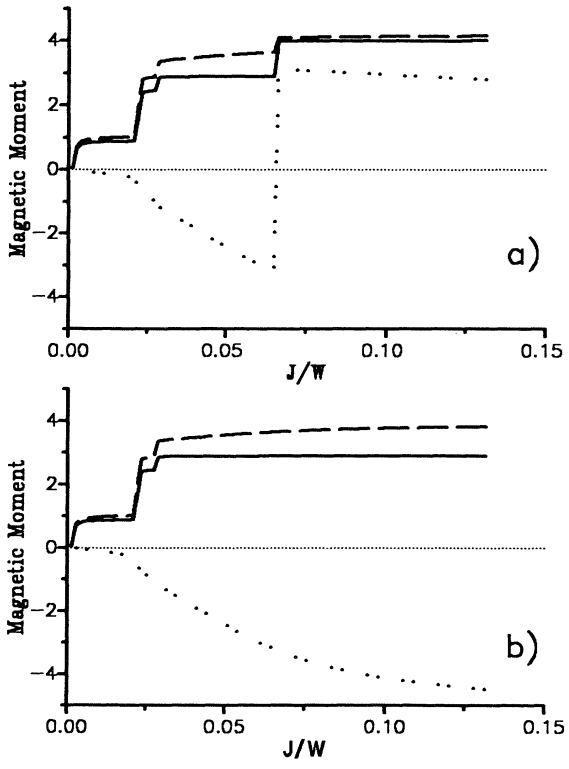

FIG. 1. Magnetic moments $\mu(i)$ of a nine-atom cluster V_9: first-shell atom (dotted line), second-shell atoms (dashed line), and average moment (solid line) vs J/W (J is the exchange integral and W the bandwidth). (a) F configuration is considered. (b) AF configuration is considered.

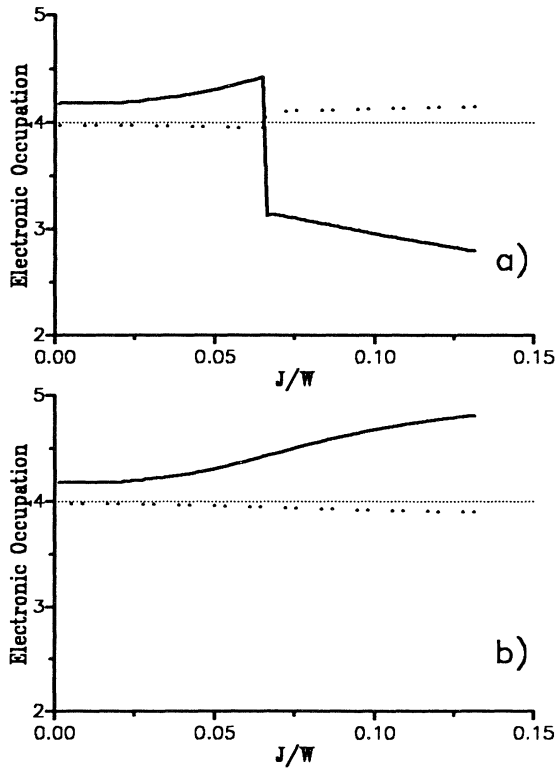

FIG. 2. Electronic occupation of a nine-atom cluster V_9: first-shell atom (solid line), second-shell atoms (dotted line). (a) F configuration is assumed. (b) AF configuration is assumed.

B. V_{15} cluster

More subtle behavior is observed when the size of the clusters increases. Local magnetic moments for V_{15} are reported in Fig. 3. At first, one can see in Figs. 3(a) and 3(b) that for small values of J ($J/W < 0.037$), only F coupling is possible. Contrary to the V_9 cluster, all atoms are ferromagnetically coupled and the magnetic moments are very small. Moreover, they vanish only for a very small value of J/W. For the AF configuration all shells are antiferromagnetically coupled. The magnetic moment on the central atom is always weak, whereas on the other sites it is much stronger. A noticeable charge transfer occurs from the internal shells to the external shell [Fig. 4(b)]. For the F configuration, the charge transfer is less important [Fig. 4(a)]. The magnetic-moment curves corresponding to F and AF configurations are different for J/W greater than 0.053. In the F configuration, for $0.059 < J/W < 0.071$, an original configuration is found: the first shell (central atom) is coupled antiferromagnetically with the second and third shells. Finally, for J/W greater than 0.074, all shells are ferromagnetically coupled. The AF configuration when it exists, is for all values of J/W the most stable configuration.

As already noticed for V_9, the average magnetic moment $\bar{\mu}$ takes only a reduced set of values. For the AF configuration, $\bar{\mu}$ vanishes for J/W greater than 0.062. For the F configuration and for J greater than 0.059, $\bar{\mu}$ shows only two values, whereas the individual magnetic moments, at least for J smaller than 0.070, are not constant.

C. V_{27} cluster

The F and AF configurations lead to similar results for J/W smaller than 0.072 (Fig. 5). For this range of values of J/W, the magnetic moment on the odd shells is small, whereas the magnetic moment on the even shells is more important, especially on the external shell. Roughly speaking, the magnetic order could be described by an AF coupling between the second and the fourth shells with two magnetically quasidead shells. For increasing values of J/W, the second shell is AF coupled to the rest of the shells. For the AF configuration and J/W greater than 0.050 [Fig. 6(b)], the charge transfer is less important than that for V_{15}. For the F configuration and J greater than 0.072 two regimes occur. At first, all sites except the central atom are F coupled. This can be related to an important charge transfer on the central atom [Fig. 6(a)]. Finally for J/W greater than 0.083, completely F order is reached. The AF configuration is the most stable.

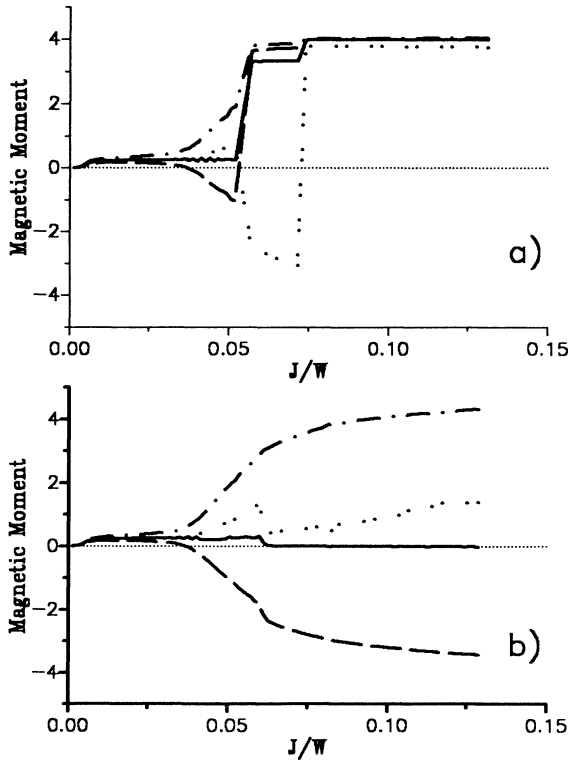

FIG. 3. Magnetic moments $\mu(i)$ of a 15-atom cluster V_{15}: first-shell atom (dotted line), second-shell atoms (dashed line), third-shell atoms (dot-dashed line), and average moment (solid line) vs J/W (J is the exchange integral and W the bandwidth). (a) F configuration is considered. (b) AF configuration is considered.

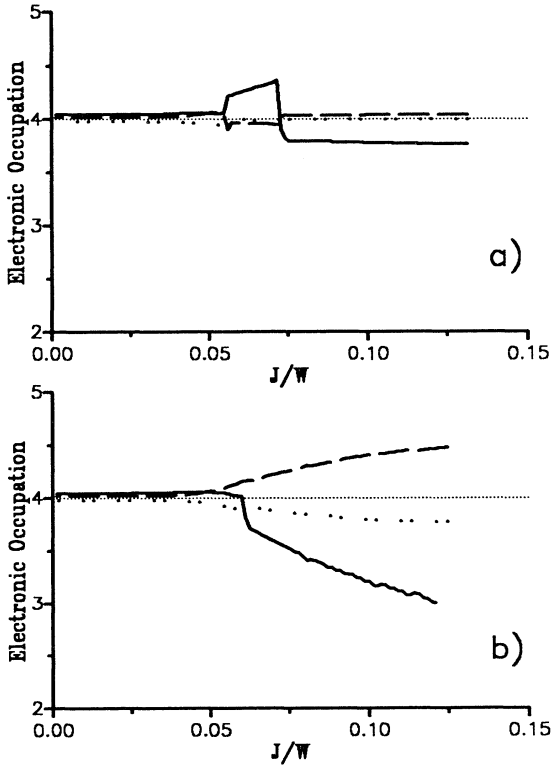

FIG. 4. Electronic occupation of a 15-atom cluster V_{15}: first-shell atom (solid line), second-shell atoms (dotted line), third-shell atoms (dashed line). (a) F configuration is assumed. (b) AF configuration is assumed.

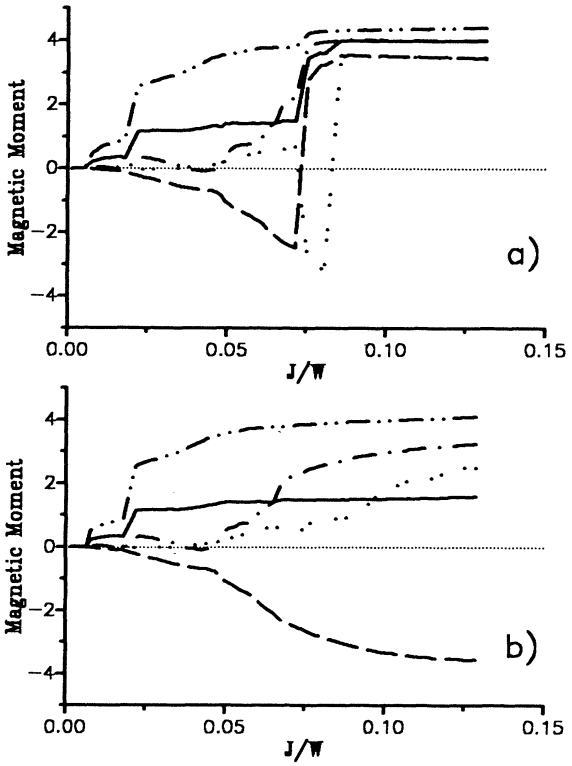

FIG. 5. Magnetic moments $\mu(i)$ of a 27-atom cluster V_{27}: first-shell atom (dotted line), second-shell atoms (dashed line), third-shell atoms (dot-dashed line), fourth-shell atoms (dotted-dot-dashed line), and average moment (solid line) vs J/W (J is the exchange integral and W the bandwidth). (a) F configuration is assumed. (b) AF configuration is considered.

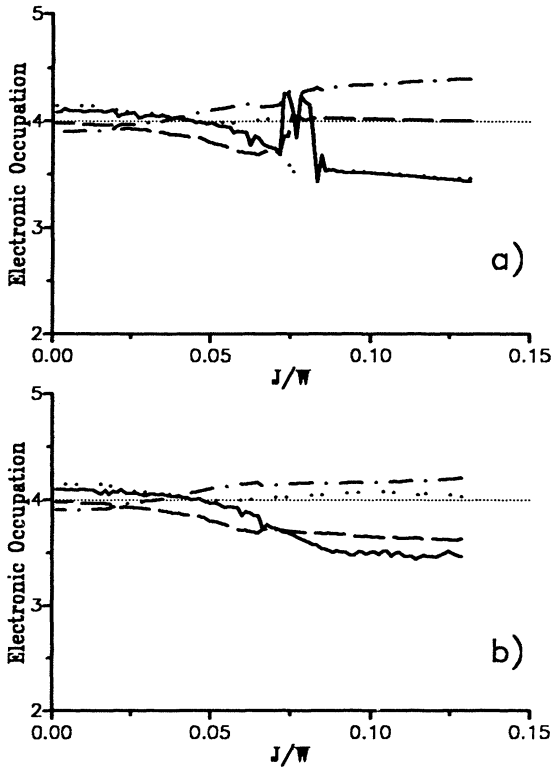

FIG. 6. Electronic occupation of a 27-atom cluster V_{27}: first-shell atom (solid line), second-shell atoms (dotted line), third-shell atoms (dashed line), fourth-shell atoms (dot-dashed line). (a) F configuration is assumed. (b) AF configuration is assumed.

The average magnetic moment $\bar{\mu}$ is not constant and small variations can be observed for both configurations. However, these variations are much less important than the variation of the corresponding individual magnetic moments. Let us notice that for the AF configuration, the saturation value of $\bar{\mu}$ is $1.75\mu_b$, whereas for the F configuration it is equal to $4.0\mu_b$, as for the previous clusters.

D. V_{51} cluster

Only the AF configuration has been studied. The first result is an onset of significant values of the magnetic moment for J/W greater than 0.030 (Fig. 7). This behavior differs strongly from the previously studied clusters. Two other regimes are observed. For large values of J/W (>0.075) an AF coupling between neighboring shells is reached. The charge transfer on the central atom presents strong oscillations due to variations of the local density of states (Fig. 8).

For $0.030 < J/W < 0.075$, the magnetic moments on the first and second shells are very small compared to the more external shells. The shells labeled by 3 and 4 are F coupled whereas the coupling between the fourth and the

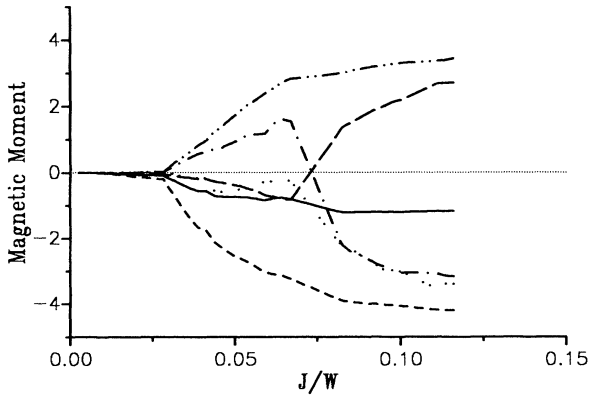

FIG. 7. Magnetic moments $\mu(i)$ of a 51-atom cluster V_{51}: first-shell atom (dotted line), second-shell atoms (long-dashed line), third-shell atoms (dot-dashed line), fourth-shell atoms (dot-dot-dashed line), external-shell atoms (short-dashed line), and average moment (solid line) vs J/W (J is the exchange integral and W the bandwidth). AF configuration is assumed.

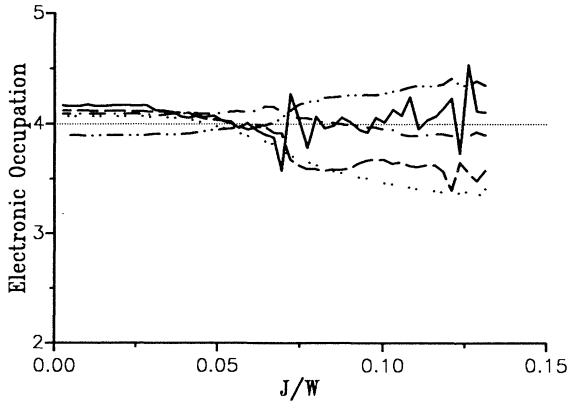

FIG. 8. Electronic occupation of a 51-atom cluster V_{51}: first-shell atom (solid line), second-shell atoms (dotted line), third-shell atoms (dashed line), fourth-shell atoms (dot-dashed line), external-shell atoms (dot-dot-dashed line). AF configuration is assumed.

fifth shells is AF. The average magnetic moment is only constant for values of J/W greater than 0.080 with a saturation value of $1\mu_b$.

IV. DISCUSSION AND CONCLUSION

From these results, some general trends emerge:

(1) The average magnetic moment takes only a reduced set of values and can be considered as constant over large regions of J/W values. The individual magnetic moment displays a very different behavior. Let us recall that the sole condition imposed in these calculations is that the total number of electrons remains constant to an integer multiple of 4 and that at a given geometrical arrangement the local densities of states are self-consistently computed for each value of J/W.

(2) By comparing the F and AF configuration total energies, the AF is generally the more stable. This can be understood by the sharp variation of the magnetic moment observed for the F configuration.

(3) For small values of J/W, F and AF configurations display exactly the same behavior. For V_{15} and V_{27} in the region of the F configuration, before reaching the AF configuration an intermediate phase occurs where all sites except the central atom are ferromagnetically coupled.

(4) Significant magnetic moments are obtained for small values of J/W. Only for V_{51} is the onset of magnetism obtained for a large value of J/W. The influence of the direct neighboring can be emphasized: usually the local magnetic moments on the external shells are larger than for internal atoms. This can be related to a variation of the coordination number. Let us recall that this rule is not always verified (e.g., Pd films[13] and Ni clusters[21]).

In this work, we have assumed that for these clusters, which can be organized into shells, all sites in a given shell bear the same magnetic moment (in magnitude and direction). Also, we neglect, for simplicity, s-p electron contributions which do not seem to contribute much to the size and structural dependency of the magnetic properties of clusters.

By comparing our results with the experimental findings,[5] we obtain reasonable agreement for $J=0.3-0.4$ eV, which is in accordance with previous determinations of J.[16,23–25] In contrast, we found results similar to those of Liu, Khanna, and Jena[11] only for $J=0.22$ eV.

In conclusion, we have studied in detail bcc-like small V clusters. For a given geometrical arrangement usually two different magnetic arrangements have been found. Surprising behaviors of the magnetic moments have been observed. However, some general trends have been given. The average magnetic moment is found to take very few different values: it is constant over a large region of J/W values. For these values of J/W the individual magnetic moments change strongly and noticeable charge transfer occurs. Another important point is the existence of magnetic moment, albeit small, for very small values of J/W. Only for the V_{51} cluster is the onset of magnetism reached for a significant value of J/W.

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