Magnetism of small V clusters embedded in a Cu fcc matrix: an \textit{ab initio} study

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We present extensive first principles density functional theory (DFT) calculations dedicated to analyze the magnetic and electronic properties of small V$_n$ clusters (n=1, 2, 3, 4, 5, 6) embedded in a Cu fcc matrix. We consider different cluster structures such as: i) a single V impurity, ii) several V$_2$ dimers having different interatomic distance and varying local atomic environment, iii) V$_3$ and iv) V$_4$ clusters for which we assume compact as well as 2- and 1-dimensional atomic configurations and finally, in the case of the v) V$_5$ and vi) V$_6$ structures we consider a square pyramid and a square bipyramid together with linear arrays, respectively. In all cases, the V atoms are embedded as substitutional impurities in the Cu network. In general, and as in the free standing case, we have found that the V clusters tend to form compact atomic arrays within the cooper matrix. Our calculated non spin-polarized density of states at the V sites shows a complex peaked structure around the Fermi level that strongly changes as a function of both the interatomic distance and local atomic environment, a result that anticipates a non trivial magnetic behavior. In fact, our DFT calculations reveal, in each one of our clusters systems, the existence of different magnetic solutions (ferromagnetic, ferrimagnetic, and antiferromagnetic) with very small energy differences among them, a result that could lead to the existence of complex finite-temperature magnetic properties. Finally, we compare our results with recent experimental measurements.

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I. INTRODUCTION

The discovery of magnetism in V metal fine particles\cite{1} with sizes and temperatures ranging from 90 to 300 Å and from 4.2 to 100 K, respectively, served as a starting point for a large number of theoretical and experimental studies of magnetic properties in various types of V low-dimensional systems\cite{2–12}. In particular, bimetallic V-based materials such as bulk alloys\cite{11}, thin films\cite{12}, and deposited clusters\cite{10,13} have attracted considerable attention because of their expected novel optical properties, catalytic activity, and magnetic behavior.

In general the interaction between two components in magnetic bimetallic nanostructures introduces a mutual influence on neighboring atoms and leads to the unique properties already reported for these kinds of materials. Furthermore, it is also clear that their measured average magnetic behavior is not necessarily given by the average properties of their corresponding isolated constituents, and that the observed phenomena are expected to strongly depend on the precise details of the local geometrical and chemical environment.

As is well known, V in the solid state is nonmagnetic; however, it has been clearly established that it could exhibit a magnetic moment under certain conditions like loss of coordination, when its atomic volume is increased, or when it is found in the presence of 3d ferromagnetic materials, due to its large paramagnetic susceptibility. Interestingly, in the last years it has been also demonstrated that V can become magnetic when it is associated with other nonmagnetic elements such as copper\cite{13} or gold\cite{14}. The previous findings are highly relevant since, on the one hand, having two nonmagnetic elements that when combined give raise to magnetic order opens new possibilities to improve the magnetic properties of materials and, on the other hand, from the theoretical point of view it offers a unique opportunity to analyze the role of the structure and dimensionality on the spontaneous appearance of local magnetic moments in metallic nanostructured materials.

Huttel et al\cite{15} have found experimentally the existence of a magnetic moment in V atoms embedded in a Cu matrix. In particular, they have analyzed samples having a Cu$_{96.7}$V$_{3.3}$ composition by means of x-ray absorption spectroscopy and x-ray magnetic circular dichroism experiments. The samples were prepared by a co-evaporation process of both V and Cu over a Cu substrate and the as-prepared Cu-V samples were capped with a few monolayers of Cu in order to avoid oxidation of the surface alloy. Interestingly the authors especulate that, depending on the deposition temperature, different V species seems to be formed (such as isolated V impurities and V particles of different sizes) and that the magnetic properties of the alloy strongly depend on the presence and concentration of these species. They also showed that the V magnetic moment depends on the formation temperature of the samples and found that the alloys prepared at lower temperatures are more magnetic. However, despite all the previous extensive experimental characterization and reported trends, there is still no clear information concerning the precise micro-structural features present in the alloys, neither a clear explanation for the temperature dependence of the average magnetization observed in the samples.
From the point of view of theory, it is important to mention that the possible existence of structural changes, disordered growth, and clustering of the V species in the samples makes more difficult the theoretical analysis of the measured data. However, we believe that the Cu-V alloys synthesized by Huttel and co-workers can be approximately modeled by an infinite Cu matrix with V atoms and clusters embedded in it. In addition, we expect that the influence of the Cu matrix on the V atoms will be mainly due to the hybridization of the V d-electrons with the s-levels of the neighboring Cu atoms and, in this sense, a local analysis in which the behavior of the spin moments at the V sites is studied for different geometrical and chemical environments should be very important and needs to be performed in order to shed some more light in to the possible origin of the measured magnetization data.

In this work, we present a systematic first principles theoretical study of the magnetic properties of model V-dilute fcc Cu-V alloys by using the density functional theory (DFT) approach together with the pseudopotential approximation for the electron-ion interaction. All the calculations are performed with the Plane Wave Self Consistent Field (PWscf) code. We put special emphasis on: i) the electronic and magnetic properties of isolated atoms as well as of small clusters embedded in a fcc Cu matrix, and ii) the possible existence of multiple magnetic solutions in the systems, since if small energy differences are found among them magnetic fluctuations could be present in the samples.

The remainder of the paper is organized as follows. In the next section, the theoretical model used for the calculations is briefly explained. In Sec. III results for the atomic spin magnetic moments, average spin magnetic moments, and differences in total energies (DTEs) for a variety of \( V_N \) clusters embedded in a Cu fcc matrix with \( N \leq 4 \) atoms, and some special cases of \( N = 5 \) (square pyramid) and \( N = 6 \) (square bipyramid), as well as infinite linear chain are presented and discussed. For each system we have studied the nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AF) solutions, i.e., we have used these magnetic configurations as inputs in our calculations. Finally, Sec. IV summarizes the main conclusions.

II. THEORETICAL MODEL

The PWscf code is based on the DFT. The pseudopotentials used here were generated using Vanderbilt code with scalar relativistic calculations and non linear core corrections. The calculations, which were restricted to fixed atomic positions (relaxation was not allowed), were performed with the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) exchange correlation functional. The calculations were performed using a fcc structure with Cu lattice parameter (3.61 Å) and the cell containing 48 (54) atoms (see Fig. 1), ordered as follows: six planes with 8 (9) atoms per plane for the impurity, dimer, trimer and tetramer (pyramide and bipyramide), and the V atoms are located at the ideal positions of the fcc crystal. The Monkhorst-Pack scheme was used to define the \( \vec{k} \) points and the calculations for each cell were performed with a grid of \( 4 \times 4 \times 4 \) mesh in \( \vec{k} \)-space. We have done some tests with a grid of \( 5 \times 5 \times 5 \) and \( 6 \times 6 \times 6 \) mesh, and the values are only 4% less than those presented here. A cutoff energy of 35 \( \text{Ry} \) was used for the plane waves expansion of the pseudowave functions (560 \( \text{Ry} \) for the charge density and potential).

Given that our calculations were restricted to fixed atomic positions, some words about the relaxation effects in this kind of systems seem to be in order. On the one hand, Ramanathan et al., who have studied the magnetism of a V overlayer on Nb(001), have found that the magnetism is drastically reduced when the relaxation effects are considered. On the other hand, Weber et al., who have studied the magnetism of V clusters supported on Cu(001), have analysed the effect of relaxation qualitatively, and they have concluded that relaxation does not yield any significant change in the magnetic moments. Following that, we performed calculations for the V impurity and dimer using a cell with 54 atoms, first without considering relaxation and then considering partial relaxation (only nearest neighbors could reach the equilibrium positions) and we have...
III. RESULTS AND DISCUSSION

A. Geometrical construction

The V clusters geometric arrangements (as well as the lattice structure around them) that we have studied are schematically illustrated in Fig. 2. The V embedded clusters are located as substitutional impurities in the Cu fcc matrix. We present the atomic magnetic moments as $\mu(i) = \mu_{FM}/\mu_{AF}$ in $\mu_B$ for the FM and AF solutions, respectively. We also present the difference in total energies (DTEs) in meV/atom in the special case of the square bipyramide for the NM, FM, and AF solutions, respectively. DTE=DTE$_{NM}$/DTE$_{FM}$/DTE$_{AF}$ refers to the differences in total energies (DTEs) in meV/atom for the nonmagnetic (NM), FM, and AF solutions, respectively. In the special case of the square bipyramide we include two kinds of antiferromagnetic solutions, namely, AF1 and AF2, whose initial magnetic configurations are, respectively, (1 $\uparrow$, 2 $\downarrow$, 3 $\uparrow$, 4 $\downarrow$, 5 $\uparrow$, 6 $\downarrow$) and (1 $\uparrow$, 2 $\downarrow$, 3 $\uparrow$, 4 $\downarrow$, 5 $\uparrow$, 6 $\downarrow$). In this case the DTEs are presented as follows: DTE=DTE$_{NM}$/DTE$_{FM}$/DTE$_{AF1}$/DTE$_{AF2}$. The ground state energies (denoted by 0.00) refer to the minimum energies out of $V_N$ clusters with the same $N$. Obtained that the differences in percentage terms between non-relaxation and partial relaxation calculations are $\Delta E < 4\%$; $\Delta t = 1.0\%$ and $\Delta \mu = 2\%$ for the difference of total energies, difference of distances, and difference of magnetic moments, respectively.

FIG. 2. Illustration of the lattice structure of $V_N$ clusters embedded as substitutional impurities in bulk Cu (fcc structure). The cluster atoms are represented by filled circles and the Cu host atoms by open circles. The numbers label the nonequivalent atomic sites $i$. $\mu(i) = \mu_{FM}/\mu_{AF}$ refers to the magnetic moments (in $\mu_B$) for the ferromagnetic (FM) and antiferromagnetic (AF) solutions, respectively. $\text{DTE} = \text{DTE}_{NM}/\text{DTE}_{FM}/\text{DTE}_{AF}$ refers to the differences in total energies (DTEs) (in meV/Atom) for the nonmagnetic (NM), FM, and AF solutions, respectively. In the special case of the square bipyramide [Fig. 2 (y)] we include two kinds of antiferromagnetic solutions, namely, AF1 and AF2, whose initial magnetic configurations are, respectively, (1 $\uparrow$, 2 $\downarrow$, 3 $\uparrow$, 4 $\downarrow$, 5 $\uparrow$, 6 $\downarrow$) and (1 $\uparrow$, 2 $\downarrow$, 3 $\uparrow$, 4 $\downarrow$, 5 $\uparrow$, 6 $\downarrow$). In this case the DTEs are presented as follows: DTE=DTE$_{NM}$/DTE$_{FM}$/DTE$_{AF1}$/DTE$_{AF2}$. The ground state energies (denoted by 0.00) refer to the minimum energies out of $V_N$ clusters with the same $N$. Obtained that the differences in percentage terms between non-relaxation and partial relaxation calculations are $\Delta E < 4\%$; $\Delta t = 1.0\%$ and $\Delta \mu = 2\%$ for the difference of total energies, difference of distances, and difference of magnetic moments, respectively.
Å is the Cu lattice parameter. Fig. 2 (a) represents the V impurity. The V dimers are also in the first row: (b), (c), (d), (e), and (f). The respective interatomic distances are: \(a/\sqrt{2}, a\sqrt{3}/2, a, a\sqrt{3},\) and \(a\sqrt{2}/2\). The V trimers are in the second row. (g) represents the smallest equilateral triangle whose sides measure \(a/\sqrt{2}\); (h) an isosceles right angle triangle whose hypotenuse and legs measure, respectively, \(a\) and \(a/\sqrt{2}\); (i) a right angle triangle whose hypotenuse measures \(a\sqrt{3}/2\), and whose legs measure \(a/\sqrt{2}\) and \(a\); (j) a linear trimer whose interatomic distances are equal to \(a/\sqrt{2}\); (k) an isosceles right angle triangle whose hypotenuse and legs measure, respectively, \(a\sqrt{3}/2\) and \(a\); (l) a right angle triangle whose hypotenuse measures \(a\sqrt{3}/2\), and whose legs measure \(a\) and \(a\sqrt{2}/2\); and (m) an equilateral triangle whose sides measure \(a\sqrt{2}/2\). The V tetraters are in the third and fourth rows. (n) represents a regular tetrahedron whose interatomic distances are \(a/\sqrt{2}\); (o) a regular rhombus whose sides measure \(a/\sqrt{2}\); (p) a square whose sides measure \(a/\sqrt{2}\); (q) a triangular tetramer with two bonds of length equal to \(a/\sqrt{2}\) and two bonds with length equal to \(a\); (r) a parallelogram whose sides measure \(a\sqrt{3}/2\) and \(a/\sqrt{2}\); (s) a continuous linear tetramer whose interatomic distances are equal to \(a/\sqrt{2}\); (t) a triangular tetramer with two bonds of length equal to \(a/\sqrt{2}\), one bond of length equal to \(a\), and one bond of length equal to \(a\sqrt{3}/2\); (u) a rectangle with sides equal to \(a/\sqrt{2}\) and \(a\); (v) a square with side equal to \(a\); (w) a rectangle with sides equal to \(a\sqrt{2}\) and \(a\); the special cases are (x) a square pyramid whose base measures \(a\sqrt{2} \times a/\sqrt{2}\) and whose sides are all equilateral triangles of edge-length parameter equal to \(a/\sqrt{2}\); (y) a square bipyramid built from two pyramids connected base to base; and finally (z) a continuous linear chain whose interatomic distances are equal to \(a/\sqrt{2}\).

Fig. 2 displays the well-known richness and complexity in the magnetic behaviour characterizing the 3d transition metal low-dimensional systems. There we can see four kinds of magnetic orders: ferromagnetic, ferri magnetic, antiferromagnetic, and nonmagnetic, which depend in a very complicated way on the interatomic distances, the geometrical structures, and the number of atoms in the clusters.

### B. Electronic behavior

Let us first briefly consider the electronic properties derived of our calculations on \(V_N\) clusters embedded in a Cu fcc matrix. Fig. 3 illustrates the \(d\)-component of the nonmagnetic local densities of states (NMLDOS) for all the V dimers and the tetrahedron. The blue, red, violet, black, and green lines represent, respectively, the NMLDOS for the V dimers illustrated in Fig. 2 (b), (c), (d), (e), and (f); while the orange line represents the NMLDOS for the tetrahedron [Fig. 2 (n)]. To study the electronic properties of these systems we use the Stoner criterion. This is given by the following relation:

\[
S = I_SN_{NM}(E_F)
\]

being \(S\) the Stoner factor, \(I_S\) the Stoner parameter and \(N_{NM}(E_F)\) the value of the NMLDOS at the Fermi level. The \(I_S\) for V is equal to 0.3536 eV\(^2\). The Stoner criterion states that the non-magnetic state will be unstable to magnetism if \(S > 1\), while the non-magnetic state will be more favourable if \(S < 1\).

The behaviour of the NMLDOS in Fig. 3 is similar to that reported by Liu, Khana, and Jena\(^{23}\), who studied the magnetism of free small V clusters, in the sense that near the Fermi energy the NMLDOS splits into two peaks with the Fermi energy centered in the valley. This splitting is remarkably pronounced in the case of the tetrahedron. We can see that for all the V dimers the value of the NMLDOS at the Fermi level are high enough (greater than \(1/I_S = 2.8280\)) to get a Stoner factor \(S > 1\); while for the tetrahedron tetramer the NMLDOS at the Fermi level is not (it is much less than \(1/I_S = 2.8280\)). So from the Stoner criterion alone we can predict magnetism for all the V dimer and absence of magnetism for the tetrahedron tetramer. The greatest value of the NMLDOS at Fermi level corresponds to the dimer whose interatomic distance is \(a\sqrt{2} = 5.1\) Å (see 2 (f) and green line in Fig. 3), which, according to the values of the magnetic moments shown in Fig. 2 is that with the greatest magnetic moment out of the V dimers. Additionally, from the NMLDOS we can anticipate a nonlinear behaviour of the magnetic moments of V dimers as a function of the interatomic distances.
C. Magnetic properties

Let us now consider the magnetic behaviour of each cluster as a function of its size. For the V impurity, the magnetic moment is 1.87 $\mu_B$, which is less than that of the V adsorbed atom on Cu(001) surface reported by Weber et al. (3.03 $\mu_B$) and greater than that of the bulk impurity reported by Blügel et al. (1.10 $\mu_B$).

For the V dimers, we can see in Fig. 2(b)-(f) that the magnetic states are energetically ordered in such a way that $E_{NM} > E_{FM} > E_{AF}$ ($E_{NM} > E_{AF} > E_{FM}$) provided that the interatomic distance $d < a$ ($d > a$). So, in the first (second) case the V atoms that form the dimers couple antiferromagnetically (ferromagnetically). In any case, for the V dimers, it is energetically easier to show some kind of magnetic coupling than to become nonmagnetic. Interestingly, the V dimer ground state does not correspond to the V dimer with the minimum interatomic distance, namely $a/\sqrt{2}$, but to that with the third shortest one: $a\sqrt{3}/2$ [see Fig. 2(b) and (c)]. The magnetic moment per V atom for the ground state V dimer is equal to $\pm 1.62 \mu_B$, which is less than adsorbed dimer magnetic moment reported by Weber et al. (2.85 $\mu_B$), but greater than the bulk dimer magnetic moment reported by Blügel et al. (0.00 $\mu_B$). The first three excited states correspond to the V dimer with $d = a/\sqrt{2}$. The DTEs for these states are equal to 0.8, 1.0, and 1.51 meV/atom, respectively, for the antiferromagnetic ($\mu = \pm 1.27 \mu_B$), ferromagnetic ($\mu = 1.00 \mu_B$), and nonmagnetic solutions. So, from the ground state, the most probable transition is that in which the V dimer reduces both its interatomic distance and the magnitude of its magnetic moment, and keeps the same kind of magnetic coupling (antiferromagnetic in this case). Note that it is more probable that from the ground state the V dimer reduces its interatomic distance than it changes its coupling from antiferromagnetic to ferromagnetic, since for the first (second) transition it needs to increase its energy in 0.8 meV/atom (1.6 meV/atom). For the minimum interatomic distance, a transition from antiferromagnetic to ferromagnetic coupling can occur if the V dimer increases its energy in 0.2 meV/atom. This transition implies a reduction of the magnitude of the magnetic moment from 1.27 $\mu_B$ to 1.00 $\mu_B$. In general, the magnitudes of the magnetic moments for the ferromagnetic solutions are less than those for the antiferromagnetic ones (the only exception is that of the V dimer with $d = a\sqrt{2}$ in Fig. 2(f)). Also, in general, the magnitude of the magnetic moments tend to increase (although not monotonously) as the interatomic distance increases. However, in Fig. 1 we can observe that the magnitude of the magnetic moments increase as the DTEs increase in a strictly monotonous way. Note also that although the interatomic distance for the V dimer represented in Fig. 2(e) is greater than that for the V dimer represented in Fig. 2(f) its magnetic moment is smaller (1.85 $\mu_B$ vs. 2 $\mu_B$, and 1.91 $\mu_B$ vs 1.95 $\mu_B$, for the FM and AF solutions, respectively) maybe due to the presence of a Cu atom between the V atoms.

Finally, to compare our calculations with the measurements made by Huttel et al., we note first that for the V dimer the concentration [Cu_{0.64}V_{2.48} (Cu_{0.96}V_{0.04})] coincides approximately with that reported by Huttel et al. (Cu_{0.967}V_{0.033}) who reported a mean magnetic moment in V atoms of approximately 1.00 $\mu_B$, which nicely agrees with the V dimer first state (FM).

In general, the trimers couple ferromagnetically (the only exceptions are the linear chain in Fig. 2(j) and the isosceles triangle in Fig. 2(k)). The order of the magnetic states is not so clearly defined in terms of the geometric characteristics of the clusters as it was in the case of the V dimers. As in the case of the V dimers, for the V trimers, it is energetically easier to show some kind of magnetic coupling than to become nonmagnetic. The V trimer ground state corresponds to the more compact equilateral triangle in the Fig. 2(g), whose interatomic distances are equal to $a/\sqrt{2}$. Practically, this ground state has 2-fold degeneracy since the difference in the DTE for two states of lowest energy is only 0.05 meV/atom. So, we can say that there the ferromagnetic and nonmagnetic states coexist. For the ferromagnetic solution, the magnetic moment per V atom is equal to 0.46 $\mu_B$. If we think of this trimer as a superior stage in the evolution of the dimer in Fig. 2(b) as the number of atoms increase, we note, as expected, a diminishing in the magnetic moment as a consequence of the increment in the coordination number. For the V trimers in Figs. 2(g)-(j), it is easier to change their magnetic coupling than to change their geometric configuration. The opposite occurs for the V trimers in Figs. 2(k)-(m), for example, if the V trimer in Fig. 2(k) is in its ferromagnetic state, it costs less energy to change its geometric configuration to that shown in Fig. 2(l) than to become nonmagnetic while keeping the initial geometric configuration. Finally, we note that for the linear trimer (Fig. 2(i)) the magnetic moments are 1.51 $\mu_B$, −1.08 $\mu_B$ and 1.51 $\mu_B$, these are lower than the moments found by Weber et al. in the adchain of 3 V atoms on Cu(001) fcc.

It is not easy for the V tetramers either to give general rules about their magnetic behaviour in terms of the energies of their states. The ground state corresponds to the triangular pyramid. This state has 3-fold denegeracy, i.e., there coexists the nonmagnetic, ferromagnetic, and antiferromagnetic states. In any case, the magnetic moments per V atom is equal to zero [see Fig. 2(n)]. This does not mean, however, that the V tetramer represents a critical size of V clusters from which the magnetism vanishes since as it will be seen below, V clusters with five and six atoms give nonzero magnetic moments. So, according to our calculations the V magnetic moments fall to zero more slowly than those reported by Blügel et al. In general, we note that for small V clusters embedded in a Cu fcc matrix the most stable structures trend to form compact arrangements: the smallest equilateral trimer and the triangular pyramid. The exception is the V dimer, whose ground state occurs for the dimer with the third shortest interatomic distance. For
the tetramers, the first excited state corresponds to the V rhombus in Fig. 2 (a). This state corresponds to the ferromagnetic solution but in reality the V atoms couple ferromagnetically and has a mean magnetic moment of 0.31 $\mu_B$. The linear chain [Fig. 2 (s)] shows a ferromagnetic order. As expected, its magnetic moments are smaller than those corresponding to the V dimer and the V linear chain trimer.

Beyond $N = 4$, we have considered three other systems, namely, square pyramid ($N = 5$) and square bipyramid ($N = 6$), and continuous linear chain. The ground state for the square pyramid corresponds to the ferromagnetic solution with a mean magnetic moment per V atom equal to 0.70 $\mu_B$. For the square bipyramid we have considered four solutions, namely, nonmagnetic, ferromagnetic, antiferromagnetic one (AF1), and antiferromagnetic two (AF2). The input for AF1 and AF2 are, respectively: (1 $\uparrow$, 2 $\downarrow$, 3 $\uparrow$, 4 $\downarrow$, 5 $\uparrow$, 6 $\uparrow$) and (1 $\uparrow$, 2 $\downarrow$, 3 $\uparrow$, 4 $\downarrow$, 5 $\uparrow$, 6 $\downarrow$) where the numbers label the V atomic sites and the arrows the directions of the input spin magnetic moments. The ground state corresponds to the ferromagnetic solution with a mean magnetic moment per V atom equal to 0.39 $\mu_B$. Practically, the AF1 and AF2 solutions are degenerate. For continuous linear chain, we have studied both ferromagnetic and antiferromagnetic solutions. The ground state is the antiferromagnetic solution with magnetic moments at V sites equal to $\pm 1.16 \mu_B$. If consider the evolution of the linear chain from the dimer to the infinite linear chain keeping the same interatomic distance $a/\sqrt{2}$ [see Fig. 2 (b), (j), (s), and (z)], we note the V atoms always couple antiferromagnetically. Besides, the V atoms located at the extreme sites of the chain trend to the limit of the infinite chain more slowly (1.27, 1.51, 1.39, 1.16 $\mu_B$) than the V atoms located at inner sites of the chain (1.08, 1.17, 1.16 $\mu_B$). We think that for the square pyramid, square bipyramid, and infinite linear chain an increase of the degeneracy can be obtained, because it is possible to find other magnetic states (antiferromagnetic by blocks, for example). For $N > 7$, we also think that it is possible to find magnetic degenerate states with magnetic moments per V atom eventually diminishing to zero (for $N$ large enough).

In the Fig. 4 we illustrate the mean magnetic moments as a function of the DTE, only for the FM state. For V dimers, the mean magnetic moments increase as the DTE increases. We can say that for room temperatures, it will be possible to find higher magnetic moments. For V trimers and tetramers, the behaviour is more complicated, even so we can observe that the mean values show a positive slope.

IV. CONCLUSIONS

We conclude our work as follows: i) we have studied the magnetic behaviour of small V clusters ($N = 1, 2, 3$ and 4 atoms) and some other special geometries for $N = 5$ (square pyramid), and $N = 6$ (square bipyramid), as well as an infinite linear chain embedded in a Cu fcc matrix using an ab initio code; ii) we have reproduced theoretically an experimental result by Huttel for a V concentration of approximately Cu$_{0.96}$V$_{0.04}$; iii) for the ferromagnetic solutions, the magnetic moments per V atom decrease as the cluster size increases; this magnetic behaviour is in agreement with previous theoretical studies; iv) the magnetic moments per V atom have a strong dependence of the geometric structure; v) the mean magnetic moment increases with the difference of total energy; vi) compact structures have lower energy (they have lower mean magnetic moment too), an exception being the V dimer which prefers the third interatomic distance; whereas extended structures have both higher energy and mean magnetic moments; vii) for each one of our considered cluster systems we have found the existence of different magnetic solutions (nonmagnetic, ferromagnetic, and antiferromagnetic) with very small energy differences among them, a result that we believe could lead to the existence of complex finite-temperature magnetic properties.

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