Size effects on the magnetism of vanadium clusters

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The magnetism of free vanadium clusters (V_N, $2 \leq N \leq 169$) with a bcc-like structure is studied using a *d* electron tight binding Hamiltonian. The spin polarized density of states is calculated self-consistently in the unrestricted Hartree-Fock approximation. We have found that the free V clusters shown different magnetic behavior depending on their size. Results for the local magnetic moments, μ_i, average magnetic moment, $\bar{\mu}$, and the magnetic order at $T = 0$ are obtained as a function of N. For the V_N clusters $\bar{\mu}$ varies as a function of N due to the interplay between the changes in coordination number and local environment; for $N \leq 4$ the ground state is ferromagnetic whereas for $N \geq 9$ the ground state is mainly antiferromagnetic in agreement with *ab initio* and tight binding calculations, respectively. In the case of large size clusters the local magnetic moments of most of the internal atomic shells vanish to avoid local frustrations leading the system in this way to very small magnetic moment as the cluster size increases.

Keywords: Local magnetic moments; magnetic order; compiting magnetic interactions.

Se estudia el magnetismo de cúmulos libres de vanadio (V_N, $2 \leq N \leq 169$) con estructura bcc usando un hamiltoniano de amarre fuerte considerando sólo electrones tipo d. La densidad de estados de espín se calcula de forma auto-consistente dentro de la aproximación no-restringida de Hartree-Fock. Encontramos que los cúmulos libres de vanadio presentan comportamientos magnéticos muy diferentes dependiendo del tamaño. Resultados para el momento local, μ_i, la magnetización promedio, $\bar{\mu}$, y el orden magnético a $T = 0$, se obtienen como función del tamaño N. En los cúmulos de vanadio $\bar{\mu}$ varía como función del tamaño debido a la interrelación entre la coordinación y el entorno local; para $N \leq 4$ el estado base es ferromagnético, mientras que para $N \geq 9$ el estado base es primordialmente antiferromagnético, en concordancia con cálculos *ab initio* y de amarre fuerte, respectivamente. En el caso de cúmulos grandes los momentos magnéticos locales de las capas internas se desvanecen para evitar la frustración, conduciendo de esta manera a valores muy pequeños del momento magnético en los cúmulos al aumentar su tamaño.

Descriptores: Momentos magnéticos locales; orden magnético; competencia entre interacciones magnéticas.

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1. Introduction

The capability of experimentalists to synthesize materials with reduced size (clusters and nanostructures) and dimension (one dimensional chains and multilayers), has given rise to a renewed interest in the study of magnetism in the material science and engineering [1]. It is well established that the magnetic moment per atom is enhanced when the system size and/or dimensionality is decreased, this is because both of these factors reduce the coordination number therefore reduces the bandwidth [2]. Consequently, the density of states near the Fermi energy is enhanced originating an increasing in the magnetic moment. Experiments [1, 3] on clusters, nanostructures and ultra-thin films back up this qualitative description.

The fact that the reduced size and dimension can produce magnetism in materials that are non-magnetic in bulk has lead to numerous investigations, both experimental and theoretical [4–7]. For example, it was theoretically predicted [4] and later experimentally verified [5] that alkali metal clusters as well as Rh clusters [6] could be magnetic.

One of the most controversial results on the magnetism in non-magnetic bulk materials are for the vanadium clusters. For example, a number of theoretical calculations with varying degrees of approximation have predicted V monolayers to be magnetic [8]. However, there are conflicting experimental results. While spin-polarized photoemission measurements provided no evidence [9] for ferromagnetism of V on Ag(001), magnetism of ultra-thin V layers sandwiched in Ag layers has been observed using a SQUID magnetometer [10].

The study of magnetism of free V clusters also suffers from the same controversy; an early experiment [11] confirmed that small particles of vanadium in the size range 100–1000 atoms are magnetic. However, an experiment performed by Douglass *et al.* [12] found no evidence of magnetism in free V clusters containing as few as 9 atoms. This disagreement between the two experimental results is maybe related with the different experimental techniques used in the preparation of the samples. The disagreement among theoretical results is less severe. A number of groups have studied the magnetism of V clusters. These clusters were confined to the bulk bcc geometry and bulk interatomic spacing. All calculations predict that small V clusters are magnetic although the magnitudes of the magnetic moments differ depending on the approximations used [2, 13].

The aim of this paper is to perform a study of the magnetism of small V_N in a more extended range that the previous results reported in the literature, for example Dorantes and Dreyssé [13] ($2 \leq N \leq 169$) in terms of the cluster size with bulk interatomic spacing. For a given (bcc-like) structure we compute the local magnetic moments, the average magnetic moment and the magnetic order into the clusters, the paper is organized as follow. In Sec. 2 we present the model. In Sec. 3 the results and discussion for clusters from $N = 2$ to 169 are presented. Conclusions are presented in Sec. 4.

2. Model

The magnetism of V clusters in this work is described within the Hubbard Hamiltonian in the unrestricted Hartree-Fock approximation. The magnetic properties of clusters for other transition metals have been studied successfully in this way [7, 14, 15]. Here we consider only *d* electrons, which are expected to be the main contribution in the magnetism. Details of the calculation for the electronic properties of V_N clusters can be found in Ref. 6. The interaction Hamiltonian H_I in the unrestricted Hartree-Fock approximation is given by

$$H_I = \frac{1}{2}\sum_{i\alpha\sigma} U_{i\alpha\sigma,j\beta\sigma'}\hat{n}_{i\alpha\sigma}\hat{n}_{j\beta\sigma'}, \tag{1}$$

due to the potential between the ions is strongly screened, we take the columbic interaction on one site depending only of the spin (the reader can find a more extended discussion on the nature of this approximation in Refs. 7, 13, 16 and papers cited therein), $U_{i\alpha\sigma,j\beta\sigma'} = U_{\sigma\sigma'}$, with this the interaction Hamiltonian is given by

$$H_I = \sum_{i\alpha\sigma} \Delta\varepsilon_{i\alpha\sigma}\hat{n}_{i\alpha\sigma} - E_{DC}, \tag{2}$$

where

$$\Delta\varepsilon_{i\alpha\sigma} = \sum_{\beta\sigma'} U_{\sigma\sigma'}\nu_{i\beta\sigma'}$$

and

$$E_{DC} = \sum_{i\alpha\sigma} \Delta\varepsilon_{i\alpha\sigma}\nu_{i\beta\sigma'}$$

here $\Delta\nu_{i\alpha\sigma} = \nu_{i\alpha\sigma} - \nu_0$, where $\nu_{i\sigma} = \sum_\alpha \langle\hat{n}_{i\alpha\sigma}\rangle$ is the average electronic occupation in the 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, and the E_{DC} is the term for the double counting correction ($E_{DC} = (1/2)\sum_{i\sigma,j\sigma'} U_{\sigma\sigma'}\nu_{i\sigma}\nu_{j\sigma'}$). 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 $U = (U_{\uparrow\downarrow} + U_{\uparrow\uparrow})/2$.

The diagonal elements of the Hamiltonian can be written as follow:

$$\varepsilon^i_\sigma = \varepsilon^0_d + U\Delta\nu_i - \frac{1}{2}\sigma J\mu_i, \tag{3}$$

where ε^0_d is the *d* reference level, $\Delta\nu_i$ the variation of charge as compared to the bulk paramagnetic value on site *i*, μ_i the magnetic moment, and U and J the intra-atomic Coulomb and the exchange integral, respectively. The number of *d* electrons ν_i, and the local magnetic moments μ_i at site i, are given by

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

$$\mu_i = \sum_\alpha (\langle\hat{n}_{i\alpha\uparrow}\rangle - \langle\hat{n}_{i\alpha\downarrow}\rangle), \tag{5}$$

both of them are determined self-consistenly by requiring

$$\langle\hat{n}_{i\alpha\sigma}\rangle = \int_{-\infty}^{\varepsilon_F} \rho_{i\alpha\sigma}(\varepsilon)d\varepsilon, \tag{6}$$

here, $\rho_{i\alpha\sigma}(\varepsilon)$ refers to the local density of states (LDOS) of spin orbital $\alpha\sigma$ at site i. The energy of the highest occupied state (Fermi energy) ε_F is determined from the global charge neutrality condition: $n_d = (1/N)\sum_i \nu_i$, where n_d is the number of d electrons per atom fixed at 3 as in the bulk case. The LDOS, is determined by using the recursion method. The parameters J and U are determined as follows; the exchange integral J is taken from *ab initio* calculations in the local-density-functional approximation [17], this value has been employed in other tight binding calculations [18] and its value is $J = 0.72$ eV, for the Coulomb integral we used $U = 4.3$ eV, this value is taken to obtain the ionization potential of the atom. The interatomic separation in the studied clusters are bulk-like, and the widht band $W_d = 7.48eV$. The structures of the V_N clusters studied are shown in Fig. 1 for $N \leq 59$.

3. Results and discussion

In Table I we show the results for the average magnetic moment, $\bar{\mu}$, and the local magnetic moments, $\mu(i)$, for the small and intermedial size structures ($2 \leq N \leq 59$) considered in this work. For smaller clusters $N \leq 4$, we consider some of the probable structures and for intermedial and large clusters bcc structures (bcc-fragments) are assumed. These are obtained by adding to a central atom (first shell) the successive atoms of the first, second, ..., series of neighbor atoms, called second shell, third shell, ..., respectively. In Table II, we present the coordination of each atomic site and the number of atoms in every shells for intermedial size clusters ($9 \leq N \leq 59$). Our electronic calculation is a self-consistent one, we consider two initial magnetic configurations, antiferromagnetic (AF) and ferromagnetic (F), and

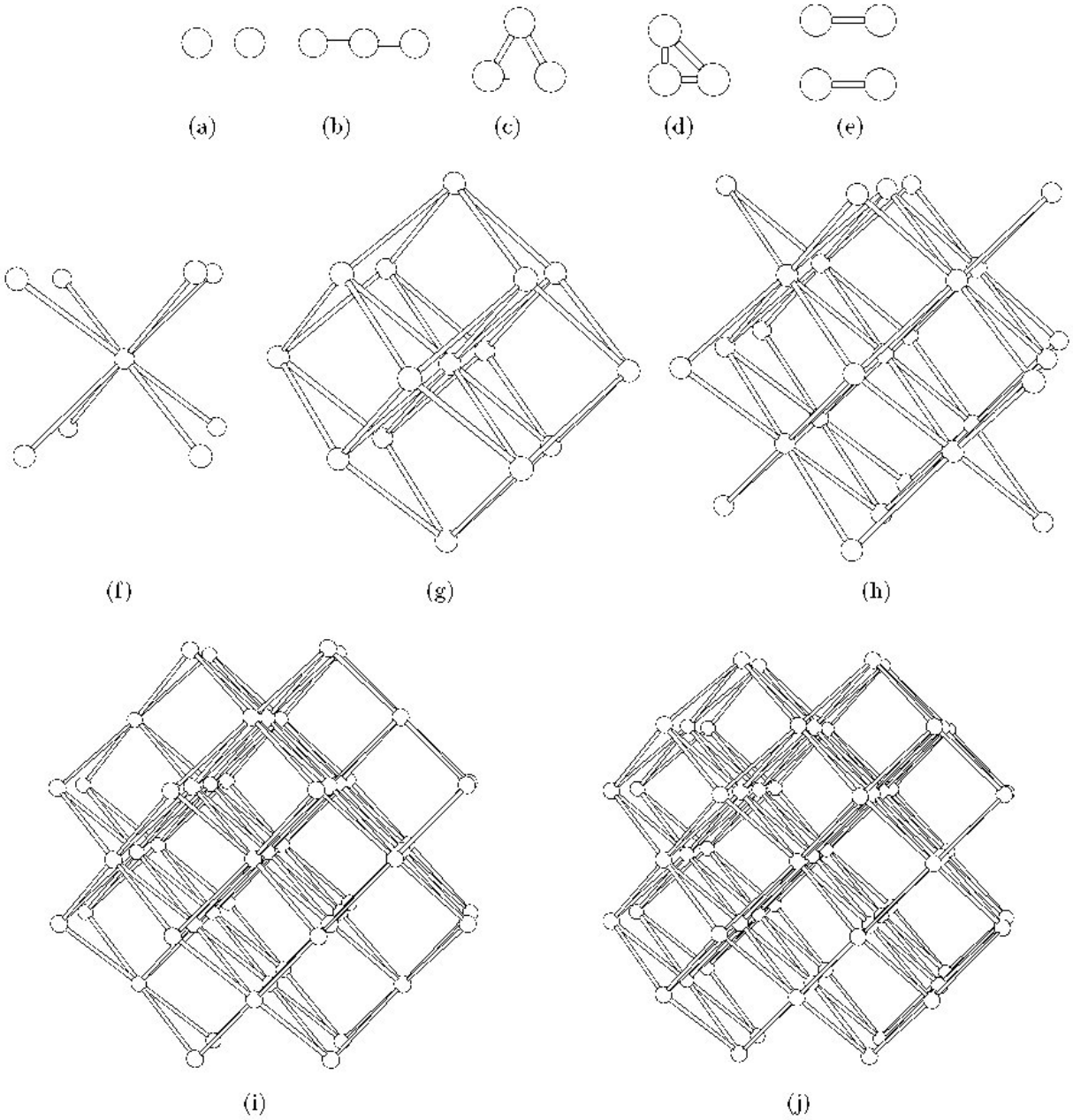

FIGURE 1. Geometrical structures of the different clusters studied here, a) $N = 2$, b) $N = 3$ linear, c) $N = 3$ equilateral triangle, d) $N = 3$ rectangular triangle, e) $N = 4$; bcc cluster for f) $N = 9$, g) $N = 15$, h) $N = 27$, i) $N = 51$, and j) $N = 59$.

the method of calculation search for the most stable magnetic configuration, AF or F. An AF configuration is one where the nearest neighbors (NN) magnetic moments are antiparallel while in the F configuration the magnetic moments point in the same direction; we report only the most stable configuration in every case. Our results are symmetrical with respect to the change in the direction of the local magnetic moments $\mu(i)$.

In Table I, we notice that for small clusters the most stable magnetic configurations are F, except for V_{3L} where the stable configuration is AF. When the cluster size is increased, V_N, $N \geq 9$, the local environment and the coordination number of each atom are changing and play a major role in the magnetism of V cluster, for example, for V_9 the magnetic coupling is AF and the local magnetic moments are comparable with the magnetic moments of V_{3L}, whereas for V_{15} the AF coupling is partially broken, see Table III (where the magnetic type interactions for $N = 15$, 27 and 51 are presented). For V_{15} the atomic shell 2 cannot couple AF with its NN atomic shells 1 and 3 at the same time, therefore $\mu(2)$ is smaller than $\mu(1)$ and $\mu(3)$ (to reduce the energy of the system), this situation is known as magnetic frustration; the same phenomena is also present in V_{27}, as illustrated in Table III, the AF coupling is only between $\mu(2)$ and $\mu(3)$, and F

TABLE I. Average magnetic moment and local magnetic moments, in units of μ_B for small and intermedium cluster sizes here studied.

V_N	$\bar{\mu}$	$\mu(1)$	$\mu(2)$	$\mu(3)$	$\mu(4)$	$\mu(5)$	$\mu(6)$
V_2	2.99	2.99	2.99				
V_{3L}	-1.06	1.42	-2.30				
V_{3E}	2.95	2.95					
V_{3R}	2.98	2.95	2.99				
V_4	2.46	2.46					
V_9	1.88	-1.48	2.30				
V_{15}	0.73	-0.63	0.51	1.25			
V_{27}	-0.83	-0.28	-0.12	0.80	-2.18		
V_{51}	0.51	-0.31	-0.29	-0.02	0.46	0.97	
V_{59}	-0.22	0.15	0.05	-0.01	0.25	-0.33	-1.08

TABLE II. Coordination numbers between the different shells and the number of atoms per shell for the bcc clusters $N \geq 9$.

No. of atoms per shell	Total No. of atoms in cluster	shell $i \setminus j$	1	2	3	4	5	6
1	1	1	0	8	0	0	0	0
8	9	2	1	0	3	3	0	1
6	15	3	0	4	0	0	4	0
12	27	4	0	2	0	0	4	0
24	51	5	0	0	1	2	0	1
8	59	6	0	1	0	0	3	0

TABLE III. Magnetic type of coupling between the different shells for $N = 15, 27$, and 51 bcc clusters, respectively. The bold numbers indicate the surface shell atoms.

$N = 15$				$N = 27$					$N = 51$					
shell				shell					shell					
$i \setminus j$	1	**2**	**3**	$i \setminus j$	1	**2**	**3**	**4**	$i \setminus j$	1	**2**	3	**4**	**5**
1	0	AF		1		F			1	0	F	0	0	0
2	AF	0	F	**2**	F		AF	F	**2**	F	0	F	AF	0
3	0	F	0	**3**		AF		F	3	0	F	0	0	AF
				4		F	F		**4**	0	AF	0	0	F
									5	0	0	AF	F	0

between $\mu(2)$ with its NN $\mu(1)$ and $\mu(4)$. In the case of V_{51} we can see that the magnetic frustration is also present in the external atomic shells 2, 4 and 5 (see Table III), where frustration is present between $\mu(4)$ with $\mu(2)$ and $\mu(5)$, not all of them can be coupling AF at the same time. The frustration can be seen also between the internal shell 3 and the external shells 2 and 5, however to reduce the energy related with the frustration the internal shell decreases the value of its local magnetic moment $\mu(3)$. For V_{59} the frustration is mainly at the surface shells, since the internal local moments practically vanished although we can see still some amount of frustration in the internal shells. These results are in good agreement with other calculations in the tight binding scheme, Dorantes and Dreyysé [13].

Finally, in Fig. 2 we present the results for the average magnetic moment of all the cluster with bcc structure as a function of the size N, the fast decreasing for $N \leq 27$ in the magnetic moments is due to the AF coupling, the large maxima for $N = 51$ and 89 are due to the large surface contribution of the magnetic moment and the F coupling of the surface atoms whereas for the large size clusters the relative low values are due to the fact that in the internal shells the local magnetic moments vanish to avoid local frustration. In the case of the clusters $N \geq 65$ we find that the surface

TABLE IV. Average magnetic moments, for the core, surface and the total, for the large size clusters, $65 \leq N \leq 169$. Core atoms are those with the same bulk coordination whereas the surface one are those with lower coordination than the bulk.

N	$\mu_{\rm core}$	$\mu_{\rm surf.}$	$\bar{\mu}$
65	0.056	0.204	0.170
89	−0.083	0.757	0.502
113	−0.003	−0.01	−0.008
137	0.156	−0.21	−0.076
169	0.047	0.057	0.053

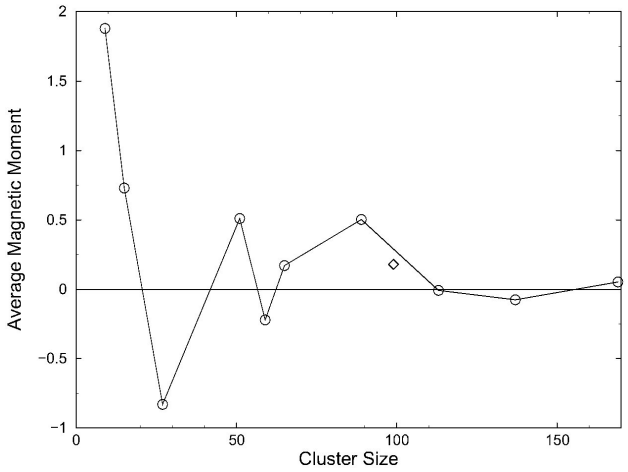

FIGURE 2. Average magnetic moment for clusters with bcc structures as a function of the size N. Theoretical calculations on ○ and the maximal possible value estimated from experimental results ◇.

contribution of the magnetic moment is much larger than the core contribution. In Table IV, we present the results of the average magnetic moments for the core and surface for large size clusters $65 \leq N \leq 169$, we notice that the core atoms have practically zero magnetic moment and that the magnetic moments of the cluster come from the surface contribution, although the average magnetic moment at the surface is relatively low for some cluster sizes, the local magnetic contributions are finite, and the AF couplings are the ones that originate the low average surface values. In Fig. 2, we have also included the maximal possible value estimated from Douglas *et al.* [12] based on the experimental results for a V_{99}, which fairly agree with our theoretical calculations, our results for large size clusters also agree with experiments performed by Akoh and Tasaki in the sense that magnetic moment in the cluster comes mainly from surface atoms [11].

4. Conclusions

We have studied the magnetism of bcc V_N atomic clusters by using a tight binding Hamiltonian in the unrestricted Hartree-Fock approximation. The average magnetic moment $\bar{\mu}_N$, local magnetic moments $\mu(i)$ and the magnetic order were calculated at $T = 0$. Our conclusions can be summarized as follows:

i) For small V_N ($N \leq 4$) clusters, the magnetic order in the cluster is F, these results are in agreement with *ab-initio* calculations. The exception is V_{3L}, where we found an AF coupling.

ii) For V_9 the AF order is well established and the local magnetic moments have large values on a qualitative agreement with Liu's *ab initio* calculations [2].

iii) For $N \geq 15$ frustrated bonds are present, the AF coupling between NN atomic sites is broken, these frustrations are the responsible of the small value of the magnetic moments, we have found that when N is increased the number of frustrated interactions is increased too.

iv) In general for large size clusters ($N \geq 27$) the local magnetic moment of the intermedial shells decrease to avoid the magnetic frustration and in this way decreasing the magnetic energy associated with the frustrated bonds.

v) The magnetic moments of the large size clusters come mainly from the surface contribution.

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1. H. Brune, H. Röder, H. Boragno, and K. Kern, *Phys. Rev. Lett.* **73** (1994) 1955.

2. F. Liu, S.N. Khanna, and P. Jena, *Phys. Rev. B* **43** (1991) 8179.

3. S.E. Apsel, J.W. Emmert, J. Deng, and L.A. Bloomfield, *Phys. Rev. Lett.* **76** (1996) 1414; I.M. Billas, A. Chatelain, and W.A. de Heer, *Science* **265** (1994) 1682; J. Shi, S. Gider, K. Babcock, and D.D. Awschalom, *Science* **271** (1996) 1682.

4. B.V. Reddy, S.N. Khanna, and B.I. Dunlap, *Phys. Rev. Lett.* **70** (1993) 3323.

5. Y. Nozue, T. Kodaira, and T. Goto, *Phys. Rev. Lett.* **68** (1992) 3789.

6. A.J. Cox, J.G. Louderback, and L.A. Bloomfield, *Phys. Rev. Lett.* **71** (1993) 923.

7. P. Villaseñor-Gonzáles, J. Dorantes-Dávila, H. Dreyysé, and G.M. Pastor, *Phys. Rev. B* **55** (1997) 15084; R. Guirado-López,

D. Spanjaard, and M.C. Desjonqueres, *Phys. Rev. B* **57** (1998) 6305.

8. C.L. Fu, A.J. Freeman, and T. Oguchi, *Phys. Rev. Lett.* **54** (1985) 2700; J.G. Gay and R. Richter, *Phys. Rev. Lett.* **56** (1985) 2728; A. Mokrani, H. Dreyysé, S. Bouarab, and C. Demangeat, *J. Magn. Magn. Matter.* **113** (1992) 201.
9. M. Stampoani, A. Vaterlaus, D. Pescia, M. Aeschlimann, F. Meier, W. Dürr, and D. Blügel, *Phys. Rev. B* **37** (1988) 10380.
10. K. Shinataku, T. Mizutani, N. Hosoito, and T. Shinjo, *J. Phys. Soc. Japan* **60** (1991) 1078.
11. H. Akoh and A. Tasaki, *J. Appl. Phys.* **49** (1978)1410.
12. D.C. Douglass, J.P. Boucher, and L.A. Bloomfield, *Phys. Rev. B* **45** (1992) 6341.
13. K. Lee and J. Callaway, *Phys. Rev. B* **49** 15358, (1993); *ibid* **49** (1994) 13906; J. Dorantes-Dávila and H. Dreyysé, *ibid* **47** (1993) 3857; P. Alvarado, J. Dorantes-Dávila, and H. Dreyssé, *ibid* **50** (1994) 1039.
14. J.A. Franco, A. Vega, and F. Aguilera-Granja, *Phys. Rev. B* **60** (1999) 434; R. Guirado-López, F. Aguilera-Granja, and J.M. Montejano-Carrizales, *ibid* **65** (2002) 045420.
15. J. Guevara, A.M. Llois, F. Aguilera-Granja, and J.M. Montejano-Carrizales, *Solid State Commun.* **111** (1999) 335.
16. G.M. Pastor, J. Dorantes-Dávila, and K.H. Bennemann, *Phys. Rev. B* **40** (1989) 7642.
17. N.E. Christensen, O. Gunnarsson, O. Jepsen, and O.K. Andersen, *J. Phys.* (Paris) **49** (1988) C8-17.
18. P. Alvarado, J. Dorantes-Dávila, and G.M. Pastor, *Phys. Rev. B* **58** (1998) 12216.