PHYSICAL REVIEW B VOLUME 47, NUMBER 8 15 FEBRUARY 1993-II

# Calculated *sp*-electron and *spd*-hybridization effects on the magnetic properties of small Fe$_N$ clusters

A. Vega, J. Dorantes-Dávila,* and L. C. Balbás
*Departamento de Física Teórica, Facultad de Ciencias, Universidad de Valladolid, E-47011 Valladolid, Spain*

G. M. Pastor
*Institut für Theoretische Physik der Universität zu Köln, Zülpicher Strasse 77, W-5000 Köln 41, Germany*
(Received 29 July 1992)

The ground-state magnetic properties and related electronic properties of small Fe$_N$ clusters are calculated by using an *spd*-band model Hamiltonian in the unrestricted Hartree-Fock approximation. Results are given for the average magnetic moment per atom $\overline{\mu}_N$, the spin-polarized charge distribution within the cluster, and the *sp* and *d* electronic density of states. The calculated $\overline{\mu}_N$ ($N \leq 15$) are larger than the bulk value $\mu_b = 2.21\mu_B$. Small local *sp* magnetic moments are obtained, which in most cases are opposite to the dominant *d* magnetic moments ($\mu_{sp} \simeq -0.1\mu_B$, $\mu_d \simeq 2.5$–$2.9\mu_B$). The role of *sp* electrons and *spd* hybridization is discussed particularly, by comparison with previous *d*-band model calculations. The main quantitative effect obtained by including the *sp* electrons in the self-consistent calculations is a reduction of about 10% of the value of $\overline{\mu}_N$.

## I. INTRODUCTION

The magnetic properties and related electronic properties of low-dimensional systems are a subject of considerable current interest.[1] Particularly, the study of free (nonembedded) 3*d* transition-metal clusters has recently motivated remarkable research activity both theoretically and experimentally.[2–10] The magnetization of these materials is known to derive from the itinerant 3*d* electrons. The dominant role of the 3*d* electrons in magnetism has been exploited in recent *d*-band model calculations,[3,4,10] where for simplicity only the 3*d* electrons were considered explicitly in the determination of the electronic structure close to the Fermi energy and magnetic properties derived from it (e.g., magnetization, local magnetic moments, magnetic order). These systematic studies have revealed a wide variety of magnetic behaviors, for example, as a function of cluster size, structure, *d*-band filling, and strength of the interaction parameters.[3,4,10] However, the effects due to *sp* electrons remain unexplored and deserve to be included in more detailed calculations. Even though the cluster spin polarizations are expected to be largely dominated by the more localized *d* electrons, the *sp* electrons should have indirect influence on the magnetic properties, for example, as a result of *spd* hybridization, *spd* charge transfer, and the resulting contributions to the many-body potential, i.e., to the level shifts due to Coulomb interactions. Furthermore, such effects are sensitive to the local environment of the atoms and could therefore yield interesting size and structural dependent contributions. It is the main purpose of this paper to investigate this subject by performing self-consistent calculations of the electronic structure of small Fe$_N$ clusters. We use a parametrized *spd*-band tight-binding model Hamiltonian including intra-atomic and interatomic Coulomb interactions. Similar schemes have already been applied successfully to closely related problems like the magnetism of surfaces, overlayers, and multilayer structures.[1,11,12]

The rest of the paper is organized as follows. In Sec. II the model Hamiltonian used for the calculations is described. Results for Fe$_N$ clusters ($N \leq 15$) are presented and discussed in Sec. III. Finally, Sec. IV summarizes our conclusions.

## II. THEORY

The electronic properties of the clusters are determined by using for the valence *s*, *p*, and *d* electrons a model Hamiltonian including intra-atomic and interatomic Coulomb interactions. In the unrestricted Hartree-Fock approximation it can be written as

$$H = \sum_{i\alpha\sigma} \varepsilon_{i\alpha\sigma}\, \hat{n}_{i\alpha\sigma} + \sum_{\substack{\alpha,\beta,\sigma \\ i\neq j}} t_{ij}^{\alpha\beta}\, \hat{c}_{i\alpha\sigma}^{\dagger}\, \hat{c}_{j\beta\sigma} \ , \qquad (1)$$

where, as usual, $\hat{c}_{i\alpha\sigma}^{\dagger}$, $\hat{c}_{i\alpha\sigma}$, and $\hat{n}_{i\alpha\sigma}$ refer to the creation, annihilation, and number operators of an electron with spin $\sigma$ at the orbital $\alpha$ of atomic site $i$ ($\alpha \equiv s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2}$). The Slater-Koster hopping integrals between neighboring orbitals $t_{ij}^{\alpha\beta}$ are obtained from bulk band-structure calculations.[11] The environment dependent energy levels $\varepsilon_{i\alpha\sigma}$ are given by

$$\varepsilon_{i\alpha\sigma} \;=\; \varepsilon_{i\alpha}^{0} + \sum_{\beta\sigma'} U_{\alpha\beta}^{\sigma\sigma'}\, \Delta\nu_{i\beta\sigma'} + \sum_{j\neq i} \frac{e^2}{R_{ij}}\, \Delta\nu_j + Z_i\, \Omega_\alpha \ . \qquad (2)$$

Here, $\varepsilon_{i\alpha}^{0}$ refers to the orbital energy levels in the paramagnetic solution of the bulk.[11] The second term takes into account the shifts due to intra-atomic Coulomb interactions. $\Delta\nu_{i\beta\sigma} = \nu_{i\beta\sigma} - \nu^0_{i\beta\sigma}$, where $\nu_{i\beta\sigma} = \langle\hat{n}_{i\beta\sigma}\rangle$ is the average electronic occupation of the spin orbital $i\beta\sigma$, and $\nu^0_{i\beta\sigma}$ the corresponding average occupation in the paramagnetic solution of the bulk. The intra-atomic Coulomb integrals $U^{\sigma\sigma'}_{\alpha\beta}$ can be written in terms of the exchange and direct integrals, $J_{\alpha\beta} = U^{\uparrow\downarrow}_{\alpha\beta} - U^{\uparrow\uparrow}_{\alpha\beta}$ and $U_{\alpha\beta} = (U^{\uparrow\downarrow}_{\alpha\beta} + U^{\uparrow\uparrow}_{\alpha\beta})/2$. The third term in Eq. (2) stands for the Coulomb shifts resulting from interatomic charge transfer. $\Delta\nu_j = \nu_j - \nu^0_j$, where $\nu_j = \sum_{\beta\sigma}\langle\hat{n}_{j\beta\sigma}\rangle$ is the total electronic charge at atom $j$, and $\nu^0_j$ the corresponding bulk or atomic value ($\nu^0_j = 8$ for Fe). Note that we have approximated for simplicity the interatomic Coulomb interaction integrals $V_{ij}$ by $V_{ij} = e^2/R_{ij}$, where $R_{ij}$ refers to the interatomic distance. Finally, the last term in Eq. (2) takes into account the energy-level corrections due to nonorthogonality effects[13,14] and the crystal-field potential of the neighboring atoms,[15] which are approximately proportional to the local coordination number $Z_i$. The orbital dependent constant $\Omega_\alpha$ is obtained here from the difference between the bare energy levels (i.e., excluding Coulomb shifts) of the isolated atom and the bulk. Taking into account the distance dependence of $\Omega_\alpha$,[13–15] one can also model effects on the energy levels due to bond length changes associated with the reduction of coordination number.

The number of electrons $\nu_\alpha(i)$ and the local magnetic moments $\mu_\alpha(i)$ at site $i$ and orbital $\alpha$ ($\alpha \equiv s,p,d$), given by

$$\mu_\alpha(i) = \langle\hat{n}_{i\alpha\uparrow}\rangle - \langle\hat{n}_{i\alpha\downarrow}\rangle \tag{3}$$

and

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

are determined self-consistently by requiring

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

The energy of the highest occupied state (Fermi energy) $\varepsilon_F$ is determined from the global charge neutrality condition: $\nu_T = (1/N)\sum_{i\alpha}\nu_\alpha(i)$, where $\nu_T$ refers to the average number of electrons per site ($\nu_T = 8$ for Fe$_N$). Notice that charge transfer between atoms and orbitals having different local environments may occur. The local density of states (DOS) $\rho_{i\alpha\sigma}(\varepsilon) = (-1/\pi)\mathrm{Im}\{G_{i\alpha\sigma,i\alpha\sigma}(\varepsilon)\}$ is determined by calculating the local Green's function $G_{i\alpha\sigma,i\alpha\sigma}(\varepsilon)$ by means of the recursion method.[16] The number of levels $M$ of the continued fraction expansion of $G_{i\alpha\sigma,i\alpha\sigma}$ is chosen large enough so that the results become independent of $M$.

## III. RESULTS AND DISCUSSION

In this section we present and discuss results for several magnetic properties of small Fe$_N$ clusters. The parameters used for the calculations are determined as follows. For the Slater-Koster hopping integrals we use the values reported in Ref. 11, which were obtained from bulk band-structure calculations. The ratio between the direct Coulomb integrals $U_{ss}$:$U_{sd}$:$U_{dd}$ is taken to be 0.32:0.42:1 as derived from atomic Hartree-Fock calculations.[17] The absolute value of $U_{dd} = 5.40$ eV is taken from Ref. 4. The $d$-electron exchange integral $J_{dd} = 0.53$ eV is chosen to yield the proper bulk magnetization $\mu_b = 2.21\mu_B$. Exchange integrals other than $J_{dd}$ are neglected. The parameters $\Omega_\alpha$ ($\alpha = s,p,d$) obtained from the differences between atomic and bulk bare energy levels are $\Omega_s = 0.31$ eV, $\Omega_p = 0.48$ eV, and $\Omega_d = -0.10$ eV. Notice that for *sp* electrons the repulsive overlap effects[13,14] dominate (i.e., $\Omega_\alpha > 0$ for $\alpha = s,p$), while for the more localized $d$ electrons the negative crystal-field-potential shift dominates ($\Omega_d < 0$). A similar negative value for $\Omega_d$ has been already used to explain the size dependence of the ionization energy of Fe$_N$ and Ni$_N$.[15,18] For the cluster structures we consider the geometries illustrated in Fig. 1 with bulk nearest-neighbor distance. These are the same as those considered in Ref. 4 and correspond for $N = 9$ and 15 to portions of the bcc lattice.

The results of our calculations are summarized in Table I. The calculated average number of $d$ electrons $\nu_d$ is not too different from the value $\nu_d = 7$ assumed in Ref. 4 to be independent of cluster size. In particular, for Fe$_2$ the orbital occupations resemble more the $d^7s^1$ atomic configuration than the ground-state $d^6s^2$ atomic configuration. This indicates an important $s$-electron contribution to binding already for very small Fe clusters. Furthermore, the moderate values for interatomic *spd* charge transfer which we obtain by using Eqs. (1) and (2) give further support to the assumption $\Delta\nu_{sp} = \Delta\nu_d = 0$, usually made in tight-binding surface calculations.[11] There is, however, a clear tendency to larger $\nu_d$ for decreasing

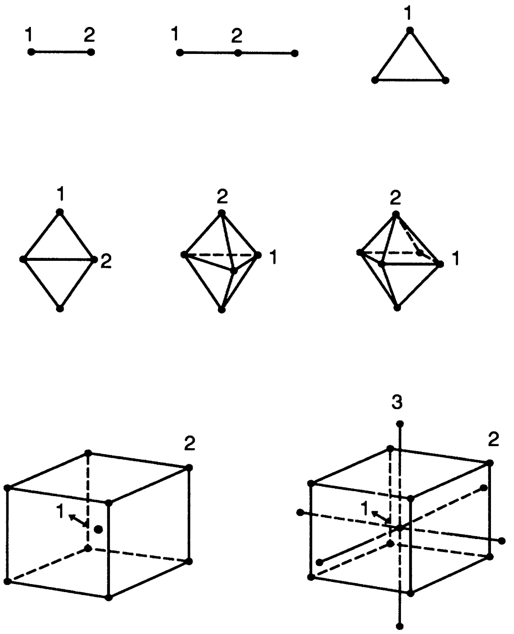

FIG. 1. Illustration of structures assumed for the different clusters. The numbers label the nonequivalent sites.

cluster size [e.g., $\nu_d(\text{bulk}) = 6.8$ and $\nu_d(\text{Fe}_2) = 7.2$]. The same trend holds for the local number of $d$ electrons $\nu_d(i)$, which increases for decreasing local coordination number $Z_i$ (see, for instance, $N = 9$ and 15). This can be qualitatively understood by recalling that the reduction of the effective local bandwidth $W_\alpha(i)$, caused by the reduction of $Z_i$, tends to reduce the band occupation for less than half bandfilling, i.e., for *sp* electrons, and to increase the band occupation for more than half bandfilling, i.e., for $d$ electrons. The level shifts $Z_i\Omega_\alpha$ with $\Omega_d < 0$, $\Omega_s > 0$, and $\Omega_p > 0$, have the opposite tendency and compensate the local bandwidth effect. In fact, setting $\Omega_\alpha = 0$ would result in unphysically large $s \rightarrow d$ charge transfer for small clusters.[19]

The calculated average magnetic moments per atom $\overline{\mu}_N$ ($N \leq 15$) are larger than the bulk magnetization $\mu_b = 2.21\mu_B$. This is qualitatively in agreement with previous calculations[2–4] and experimental evidence.[6] As expected, the spin polarizations are largely dominated by the $d$-electron contributions. Including the *sp* electrons in the self-consistent calculation results in a reduction of $\overline{\mu}_N$ (see results in parenthesis) and also, in almost all cases, in a reduction of the local $d$ magnetic moments $\mu_d(i)$. For very small clusters ($N = 2, 3$) this is mainly due to $s \rightarrow d$ charge transfer, since in these cases the $\mu_d(i)$ are almost saturated as already obtained in Ref. 4 [i.e., $\mu_d(i) \simeq 10 - \nu_d(i)$]. For larger clusters ($N \geq 4$) the $\mu_d(i)$ are no longer saturated. In contrast, neglecting the *sp* electrons in the self-consistent calculation yields saturated $\mu_d(i)$ at the bulk nearest-neighbor distance for $N \leq 13$.[4] This difference is chiefly a consequence of the *spd* hybridization. As shown in Fig. 2 and as a result of the *spd* mixing, a small part of the $d$ DOS is expelled to energies beyond the narrow $d$ "band." This causes an additional increase of the width of $d$-level distribution with increasing cluster size. The kinetic-energy loss involved

TABLE I. Average magnetic moment $\bar{\mu}_N$, local magnetic moments $\mu_\alpha(i)$ (in units of $\mu_B$), and local number of electrons $\nu_\alpha(i)$ of small Fe$_N$ clusters. Here, $\alpha = s, p, d$ refers to the atomic orbitals and $i$ to the different symmetry sites as indicated in Fig. 1. For Fe$_3$, $L(T)$ refers to the linear (triangular) geometry, otherwise the structures shown in Fig. 1 are assumed. The results in parentheses refer to the $d$-band model calculations of Ref. 4.

| | $\bar{\mu}$ | $\alpha$ | $\mu_\alpha(1)$ | $\mu_\alpha(2)$ | $\mu_\alpha(3)$ | $\nu_\alpha(1)$ | $\nu_\alpha(2)$ | $\nu_\alpha(3)$ |
|---|---|---|---|---|---|---|---|---|
| Fe$_2$ | | $s$ | 0.22 | | | 0.63 | | |
| | 3.00 | $p$ | 0.02 | | | 0.17 | | |
| | (3.00) | $d$ | 2.75 | | | 7.20 | | |
| Fe$_3$($L$) | | $s$ | 0.20 | 0.00 | | 0.67 | 0.49 | |
| | 2.85 | $p$ | 0.00 | 0.03 | | 0.14 | 0.46 | |
| | (3.00) | $d$ | 2.76 | 2.61 | | 7.15 | 7.13 | |
| Fe$_3$($T$) | | $s$ | −0.03 | | | 0.57 | | |
| | 2.67 | $p$ | −0.01 | | | 0.24 | | |
| | (3.00) | $d$ | 2.70 | | | 7.19 | | |
| Fe$_4$ | | $s$ | −0.01 | −0.06 | | 0.58 | 0.47 | |
| | 2.50 | $p$ | −0.04 | −0.01 | | 0.31 | 0.21 | |
| | (3.00) | $d$ | 2.49 | 2.63 | | 7.17 | 7.26 | |
| Fe$_5$ | | $s$ | −0.05 | −0.08 | | 0.48 | 0.47 | |
| | 2.40 | $p$ | −0.03 | −0.02 | | 0.31 | 0.25 | |
| | (3.00) | $d$ | 2.43 | 2.57 | | 7.22 | 7.27 | |
| Fe$_6$ | | $s$ | −0.07 | −0.07 | | 0.50 | 0.50 | |
| | 2.34 | $p$ | −0.03 | −0.03 | | 0.31 | 0.31 | |
| | (3.00) | $d$ | 2.44 | 2.44 | | 7.19 | 7.19 | |
| Fe$_9$ | | $s$ | −0.01 | 0.08 | | 0.74 | 0.62 | |
| | 2.89 | $p$ | 0.06 | 0.01 | | 0.95 | 0.20 | |
| | (3.00) | $d$ | 2.34 | 2.86 | | 6.95 | 7.09 | |
| Fe$_{15}$ | | $s$ | −0.02 | −0.02 | −0.07 | 0.54 | 0.54 | 0.57 |
| | 2.53 | $p$ | −0.01 | −0.03 | −0.02 | 0.70 | 0.36 | 0.30 |
| | (2.73) | $d$ | 2.22 | 2.62 | 2.62 | 7.01 | 7.08 | 7.11 |
| Bulk | | $s$ | −0.03 | | | 0.63 | | |
| | 2.21 | $p$ | −0.06 | | | 0.55 | | |
| | (2.21) | $d$ | 2.30 | | | 6.82 | | |

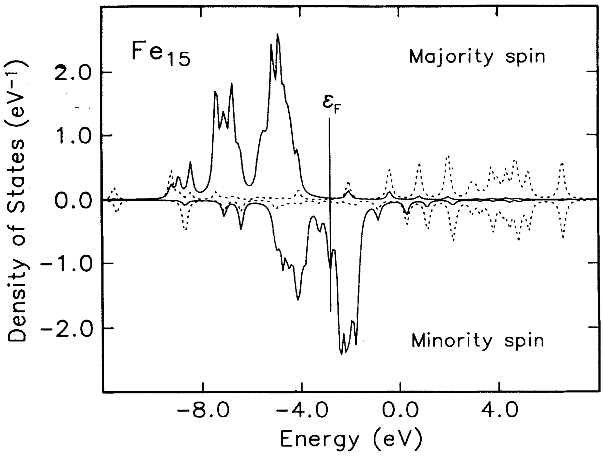

FIG. 2. Average *sp*-electron (dotted curve) and *d*-electron (solid curve) density of states of $Fe_{15}$ with bcc-like structure (see Fig. 1). A Lorentzian was used to broaden the cluster energy levels ($\gamma = 0.003$ eV).

in producing saturated *d* magnetic moments is, therefore, larger when *spd* hybridization effects are included than what one obtains if only the *d*-band broadening due to *dd* hopping is taken into account. Consequently, the tendency towards very large, almost saturated $\mu_d(i)$ is reduced.

The *sp* magnetic moments $\mu_{sp}(i)$ are much smaller than $\mu_d(i)$ (typically $| \mu_{sp}(i) | < 0.1\mu_B$) and usually polarize opposite to $\mu_d(i)$ [i.e., $\mu_{sp}(i) < 0$]. However, a parallel alignment of $\mu_{sp}(i)$ and $\mu_d(i)$ is observed in a few cases ($N = 2, 3, 9$). This situation seems to correlate with specially large values of $\mu_d(i)$ and to be induced by the resulting large local *d* exchange splittings. The negative values of $\mu_{sp}(i)$ also contribute to reduce $\overline{\mu}_N$, though this effect is quantitatively much smaller than the *spd* hybridization effects discussed above. It is interesting to notice that our results for the *s* magnetic moments in $Fe_{15}$, $\mu_s(1) \simeq \mu_s(2) \simeq -0.02\mu_B$ and $\mu_s(3) \simeq -0.07\mu_B$, are qualitatively in agreement with *ab initio* local-spin-density calculations, which yield negative spin densities at the nuclear sites.[2]

In Fig. 2 results are given for the average *sp*- and *d*-electron density of states (DOS) of $Fe_{15}$, from which the characteristic role of *sp* states and *d* states in the cluster electronic structure can be inferred. The main features of the energy-level distribution are in agreement with previous calculations.[2,4] As expected, the states close to the Fermi energy have dominant *d* character, while for states well below and above $\varepsilon_F$ the *sp* contributions dominate. Particularly large *spd* mixing is found close to the edges of the *d* "band." Notice the small but non-negligible *d*-electron contributions to the unoccupied majority-spin states, which result in the already discussed reduction of $\mu_d$ with respect to *d*-band model calculations.[4] This clearly illustrates the influence of *spd*-hybridization effects on the self-consistent DOS and spin-polarized charge distribution.

## IV. SUMMARY AND OUTLOOK

A self-consistent calculation of the magnetic and electronic properties of small $Fe_N$ clusters has been presented. The average magnetizations per atom $\overline{\mu}_N$ are found to be larger than the bulk magnetization, but at the same time about 10% smaller than in previous *d*-band model calculations. This reduction of $\overline{\mu}_N$ obtained by including the valence *sp* electrons in the self-consistent calculation is mainly due to the following two effects.

(i) *sp* → *d* charge transfer. The number of *d* electrons per atom $\nu_d$ increases with decreasing cluster size and local coordination number [e.g., $\nu_d(\text{bulk}) = 6.8$ and $\nu_d(Fe_2) = 7.2$]. This reduces, particularly for very small clusters, the saturation value $\mu_d \simeq 10 - \nu_d$ of the local *d* magnetic moments (see Table I).

(ii) *spd* hybridization. The *spd* mixing causes an additional increase of the width of the *d*-electron DOS with increasing cluster size and thus reduces the tendency to very large $\mu_d(i)$ (see Fig. 2). Furthermore, small *sp* magnetic moments are obtained ($| \mu_{sp} | \simeq 0.1\mu_B$), which in most cases align opposite to the dominant *d* moments.

Useful extensions of the present work would be the study of the role of *sp* electrons on bond length and structure relaxation, which are known to affect strongly the magnetic behavior of these materials,[4,7,10] and the study of *sp*-electron effects on systems having different *d*-band filling (e.g., $Cr_N$, $Ni_N$). Particularly for $Ni_N$, which has a nearly filled *d* band, *spd* charge transfer might yield interesting size and structure dependence of $\overline{\mu}_N$, even if the *d* magnetic moments are saturated, as already observed in Ni-surface calculations.

## ACKNOWLEDGMENTS

This work has been supported by DGICYT (Spain), Junta de Castilla y León, Acciones Integradas Hispano Alemanas, an agreement between the universities of Valladolid and San Luis Potosí, and CONACyT (Grant No. 0932-E9111, Mexico). A.V. acknowledges partial support from Universidad de Valladolid.

---

[*] On leave from Instituto de Física "Manuel Sandoval Vallarta," Universidad de San Luis Potosí, Alvaro Obregón 64, 78000 San Luis Potosí, México.

[1] See, for instance, *Magnetic Properties of Low-Dimensional Systems II*, edited by L.M. Falicov, F. Mejía-Lira, and J.L. Morán-López (Springer, Heildelberg, 1990).

[2] K. Lee, J. Callaway, K. Kwong, R. Tang, and A. Ziegler, Phys. Rev. B **31**, 1796 (1985), and references therein.

[3] G.M. Pastor, J. Dorantes-Dávila, and K.H. Bennemann, Physica B **149**, 22 (1988).

[4] G.M. Pastor, J. Dorantes-Dávila, and K.H. Bennemann, Phys. Rev. B **40**, 7642 (1989).

[5] W.A. de Heer, P. Milani, and A. Chatelain, Phys. Rev. Lett. **65**, 488 (1990).

[6] J.P. Bucher, D.G. Douglass, and L.A. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1991).

[7] B.I. Dunlap, Z. Phys. D **19**, 255 (1991).

[8] P.J. Jensen, S. Mukherjee, and K.H. Bennemann, Z. Phys. D **21**, 349 (1991).

[9] S.N. Khanna and S. Linderoth, Phys. Rev. Lett. **67**, 742 (1991).

[10] J. Dorantes-Dávila, H. Dreyssé, and G.M. Pastor, Phys. Rev. B **46**, 10432 (1992).

[11] R.H. Victora and L.M. Falicov, Phys. Rev. B **31**, 7335 (1985).

[12] A. Vega *et al.*, J. Appl. Phys. **69**, 4544 (1991), and references therein.

[13] W.A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[14] J. Dorantes-Dávila, A. Vega, and G.M. Pastor (unpublished).

[15] G.M. Pastor, J. Dorantes-Dávila, and K.H. Bennemann, Chem. Phys. Lett. **148**, 459 (1988).

[16] R. Haydock, *Solid State Physics* (Academic, London, 1980), Vol. **35**, p. 215.

[17] J.B. Mann (unpublished).

[18] M.B. Knickelbein, S. Yang, and S.J. Riley, J. Chem. Phys. **93**, 94 (1990).

[19] A. Vega, L.C. Balbás, J. Dorantes-Dávila, and G.M. Pastor, *Proceedings of Magnetism, Magnetic Materials and their Applications, La Habana, Cuba, 1991* (IOP, Bristol, 1992), Sec. III, Part 1, p. 219.