Calculation of electronic and magnetic properties of metallic superlattices

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We calculate charge-transfer profiles and layer magnetizations for Cu/Ni-like superlattices in the tight-binding approximation. The effects of local and nonlocal electron-electron interactions and magnetic band splitting are included only in the diagonal elements of the Hamiltonian. We discuss the importance of considering the electrostatic interactions among layers through a Madelung-type term.

I. INTRODUCTION

Artificially made metallic multilayers have offered in the last years an interesting field of research.[1] Much work has been done experimentally in order to study physical phenomena which seem to be characteristic of these materials and, as a consequence, a large number of metallic multilayer systems are being synthetized nowadays. Among the phenomena studied, the supermodulus effect,[2] that is, anomalous values of the elastic constants of these systems, either larger or smaller than the values corresponding to the constituents of the superlattice, and the magnetic properties of the metallic interfaces[3] have attracted our attention.

In order to explain the appearance of the supermodulus effect Grimsditch *et al.*[4] suggested that it may be due to the charge transfers within these layers. On the other hand, early LMTO calculations for Cu/Ni superlattices by Jarlborg and Freeman[5] give very small charge transfers that change sign depending on the number of layers. This has led us to calculate, within a simple tight-binding model, the charge transfer profiles. We have limited ourselves, for the moment, to superlattices whose constituents have the same crystalline structure. Actually, we have focused on Ni/Cu-like systems with interfaces perpendicular to the fcc [111] direction, this direction being the technologically more interesting one. As these materials can be constructed with a variable number of layers, the calculations were made as a function of the number of layers and also of overall concentration. Magnetism in the Ni-like type of atoms was also considered, with the aim of studying the effect of interfaces in the magnetization of the samples.

In actual superlattices of two metals that are very close in the Periodic Table, the interfaces are not abrupt, as there is a tendency toward mixing,[6] but as a first approximation we consider that the interfaces are perfect and make use of periodicity in order to calculate local densities of states.

Previous calculations of the electronic structure of systems made of transition metals in amorphous, bilayer, or superlattice structures have been performed by different methods. In the tight-binding calculations by Falicov, Tersoff, and Victora they postulate local charge neutrality,[7] and LMTO or LAPW calculations have been performed only for a few specific systems.[8,9] We have chosen the tight-binding formalism because it has the advantage that it is possible to increase the complexity of the model by introducing one by one different contributions to the Hamiltonian. In this way it is possible to evaluate the relative contribution of each of these effects on the properties we are studying. In the present work the effects of local and nonlocal e^--e^- interactions and magnetic band splitting were studied by including them only in the diagonal elements of the Hamiltonian. To calculate charge transfers and magnetizations we used the Hartree-Fock approximation and evaluated the long-range electrostatic contributions by an explicit Madelung term. In this first approach to the problem we have also replaced d orbitals by five degenerate s bands. As our aim is to introduce the d-orbital symmetry in future work, this will enable us to separate effects coming from the superlattice symmetry from those stemming from orbital symmetry.

II. DESCRIPTION OF THE MODEL

We consider a tight-binding (TB) Hamiltonian with nearest-neighbor interactions for a superlattice growing in the fcc structure along the [111] direction.

The superlattice consists of N_A layers of A-type atoms and N_B of B-type atoms, periodically repeated, A and B being transition metals. The TB Hamiltonian in the Hartree-Fock approximation, written in a local orbital basis set, has the general form

$$H=\sum_{i,m,\sigma}\varepsilon_{i\sigma}^{m}c_{i\sigma}^{m\dagger}c_{i\sigma}^{m}+\sum_{\substack{i,j,m,m',\sigma\\(i\neq j)}}t_{ij}^{mm'}c_{i\sigma}^{m\dagger}c_{j\sigma}^{m'}, \tag{1}$$

where $c_{i\sigma}^{m\dagger}$ ($c_{i\sigma}^{m}$) is the creation (annihilation) operator of

an electron state on lattice site i, m denotes the band, and σ the spin and $t_{ij}^{mm'}$ are the nearest-neighbor hopping elements of the Hamiltonian. The $\varepsilon_{i\sigma}^{m}$ are the single-site Hartree-Fock energies. The different contributions to the Hamiltonian, such as the e^{-}-e^{-} interaction and the magnetic effects are introduced by us through different approximations of the diagonal terms of the Hamiltonian, that is, as different ways of evaluating the $\varepsilon_{i\sigma}^{m}$. The $\varepsilon_{i\sigma}^{m}$ are to be related to their values in the pure metal atoms, ε_{i}^{0m}, through

$$\varepsilon_{i\sigma}^{m}=\varepsilon_{i}^{0m}+U_{imm}n_{im-\sigma}+\sum_{\substack{\sigma',\\ m'\ (\neq m)}}U_{imm'}n_{im'\sigma'}-\sum_{m'\ (\neq m)}J_{imm'}n_{im'\sigma}+\Delta\varepsilon_{i}^{m(M)}. \tag{2}$$

In this expression $n_{im\sigma}=<c_{i\sigma}^{m\dagger}c_{i\sigma}^{m}>$, $U_{imm'}$ are the intrasite Coulomb integrals in the solid, and $J_{imm'}$ the corresponding exchange ones. $\Delta\varepsilon_{i}^{m(M)}$ is the "Madelung term," which is important due to the symmetry of the superlattices and will be considered in detail in Sec. IV.

In this first stage of research we take into account only the d orbitals and consider that these orbitals have spherical symmetry, that is, the d orbitals are replaced by five degenerate s bands. Hence, we omit the m indexes in the rest of the paper. The values of the t_{ij}'s are chosen so that t_{AA} and t_{BB} give the bandwidths of A and B bulks and t_{AB} is the arithmetic mean of the preceding ones.

We finally have for the diagonal elements of the Hamiltonian,

$$\varepsilon_{i\sigma}=\varepsilon_{i}'+\frac{1}{10}(9U_i-4J_i)\Delta\eta_i-\sigma\frac{m_i}{10}(U_i+4J_i)+\Delta\varepsilon_{i}^{(M)}. \tag{3}$$

In Eq. (3) $\varepsilon_{i}'=\varepsilon_{i}^{0}+\frac{1}{10}(9U_i-4J_i)\eta_{i}^{0}$ and $\Delta\eta_i=\eta_i-\eta_{i}^{0}$ being η_i and η_{i}^{0} the d-orbital occupations on the ith site of the superlattice and pure material, respectively. Therefore, $\eta_i=5(n_{i+}+n_{i-})$, and $m_i=5(n_{i+}-n_{i-})$ is the magnetization of the ith atom in units of μ_B, + or − for σ indicating, respectively, majority or minority spins.

To carry out the calculations we assume J_i=0 as it is, in general, much smaller than U_i.[10] On the other hand, the same U_i is used for A and B atoms (magnetic and nonmagnetic), as the values of intrasite Coulomb integrals do not change much along each transition series and we are considering A and B belonging both to the first series. We therefore use only a single parameter U to account for charge transfers and magnetic effects.

The Hamiltonian is solved self-consistently, in an iterative way. As the periodicity of the superlattice is taken into account we work in reciprocal space. Due to the periodicity in the z direction and to the fact that all atoms are identical in each plane we denote, from now on, with index i the atom number within a cell ($i=1,N$ with $N=N_A+N_B$). We start, then, diagonalizing the Hamiltonian matrix $H(k)$ for the two values of σ, beginning with $\Delta\eta_i=0$ and $m_i=m_0, m_0$ being the bulk magnetization of the pure magnetic material. A recent paper[11] shows that fairly good results are obtained for the magnetic properties on surfaces using a constant split between majority and minority bands, obtained from molecular calculations. Following this idea we have held m_0 fixed in the iterative process. We calculate the electronic occupations, $n_{i\sigma}$, per site and spin, through

$$n_{i\sigma}=\int_{-\infty}^{E_F}n_{i\sigma}(E)dE, \tag{4}$$

with $n_{i\sigma}(E)$ being the local density of states per site on plane i with spin σ,

$$n_{i\sigma}(E)=\frac{1}{\Omega_k}\int_{\Omega_k}d^3\mathbf{k}\sum_{j=1}^{N}|\,C_{i\sigma}^{j}(\mathbf{k})\,|^2\,\delta(E-\varepsilon_{j\sigma}(\mathbf{k})). \tag{5}$$

In this expression $C_{i\sigma}^{j}(\mathbf{k})$ and $\varepsilon_{j\sigma}(\mathbf{k})$ are the eigenvectors and eigenvalues, respectively, and Ω_k is the cell volume in reciprocal space. The points in reciprocal space are selected at random, so that it has not been necessary to obtain the shape of the first Brillouin zone. The Fermi level is determined by the conservation of the total number of electrons:

$$\int_{-\infty}^{E_F}n(E)dE=Q,\qquad Q=N_A\eta_{A}^{0}+N_B\eta_{B}^{0}, \tag{6}$$

with $n(E)$ the total density of states. Once the values of $n_{i\sigma}$ and so the charge transfers are obtained, the diagonal elements of the Hamiltonian are recalculated, and the process repeated until self-consistency is achieved. The magnetizations per layer atom, m_i, are finally obtained from the self-consistent values of n_{i+} and n_{i-}.

III. DIFFERENT APPROXIMATIONS FOR THE SELF-ENERGIES

A. Nonmagnetic problem

We consider first the nonmagnetic problem, that is, m_0=0. Three different ways of performing the charge self-consistency have been tried,

(a) Average self-consistency. In this case the iterative process is carried out by taking for ε_{i}^{A} (and similarly for ε_{i}^{B}),

$$\varepsilon_{i}^{A}=\varepsilon_{i}'^{A}+\tfrac{9}{10}U\,\Delta\overline{\eta}^{A}, \tag{7}$$

where $-e\Delta\overline{\eta}^{A}$ is the average charge transfer in the N_A layers. In this case the site energies of all atom layers of type A are the same.

(b) Self-consistency layer by layer. In this approximation the site energies are

$$\varepsilon_i=\varepsilon_{i}'+(\tfrac{9}{10})U\,\Delta\eta_i. \tag{8}$$

A different charge transfer is used as input for each layer in the iterative process.

(c) Layer by layer self-consistency plus Madelung contribution. Using approximations (a) and (b), which give reasonable results for the charge transfers in alloys, the total charge transfers from the A-type to B-type layers (or vice versa) increases as $N = N_A + N_B$ becomes larger. The large electrostatic interactions due to the special symmetry of a superlattice must be taken into account. To do this we introduce an additional term in the diagonal elements of the Hamiltonian, which consists of a sum in real space of electrostatic potentials over all lattice sites:

$$\Delta\varepsilon_i^{(M)} = \sum_{l\ (\neq i)} V_{il}. \tag{9}$$

The V_{il} contain the interatomic electron-electron and electron-ion contributions between atoms sitting on site $\mathbf{R}_i$ and $\mathbf{R}_l$.

B. The magnetic problem

In order to take into account magnetism we use Eq. (3), with $m_i = m_0$, for the site energies of the magnetic element in the superlattice and solve the Hamiltonian layer by layer self-consistently, including the Madelung contribution.

For the site energies of the magnetic layers, we have then,

$$\begin{aligned}\varepsilon_{i+} &= \varepsilon_i' + \frac{9}{10}U\,\Delta\eta_i - \frac{\Delta}{2} + \Delta\varepsilon_i^{(M)},\\ \varepsilon_{i-} &= \varepsilon_i' + \frac{9}{10}U\,\Delta\eta_i + \frac{\Delta}{2} + \Delta\varepsilon_i^{(M)},\end{aligned} \tag{10}$$

where $\Delta = Um_0/5$ and m_0 is the bulk magnetization of the magnetic material. As already discussed, only one parameter, U, is used to account for charge transfer and magnetization. We selected the value of U in such a way as to obtain the experimental magnetization of the bulk magnetic material.

IV. THE MADELUNG SUM

The sum in Eq. (9) of the electrostatic potentials over real space presents problems of convergence that are usual in systems showing planar geometry.[12] Therefore, it is worthwhile to describe with some detail how the difficulties were solved in this particular case.

Taking into account that for $|\mathbf{R}_i - \mathbf{R}_l|$ much larger than the lattice parameter $V_{il} \approx (1/|\mathbf{R}_i - \mathbf{R}_l|)\Delta\eta_l$ and that for small values of the interatomic distance correlation effects appear, we interpolate with

$$V_{il} = \gamma_{il}\,\Delta\eta_l \text{ with } \gamma_{il} = \frac{U}{(1 + (U\,|\mathbf{R}_i - \mathbf{R}_l|)^{\tau})^{1/\tau}}. \tag{11}$$

The exponent $\tau = 2$ is usual in molecular calculations[13] and $\tau = 1$ has been used by Giner *et al.*[14] for calculations in alloys.

In order to evaluate the sum we assume that the superlattice consists of N_π circular planes of radius R perpendicular to the z direction. In the limit N_π and R going to infinity the solutions of the problem should verify that (i) all atoms belonging to the same plane have the same charge transfer; (ii) all cells are equivalent; and (iii) inside a cell, site i is equivalent to site $N_A - i + 1 (i = 1, 2, \ldots, N_A)$ and site $N_A + j$ is equivalent to $N - j + 1 (j = 1, 2, \ldots, N_B)$.

Then, due to periodicity in the xy plane we can rewrite

$$\Delta\varepsilon_i^{(M)} = \sum_r \Gamma_{ir}\,\Delta\eta_r \text{ with } \Gamma_{ir} = \sum_{l \in \text{plane } r} \gamma_{il}. \tag{12}$$

Γ_{ir} is a sum over the sites of plane r. Due to the fact that the charge transfers should be equal in all cells, we can reduce the sum further by introducing a matrix $\tilde{G}$, such that

$$\Delta\varepsilon_i^{(M)} = \sum_{j=1}^{N} \tilde{G}_{ij}\Delta\eta_j \text{ with } \tilde{G}_{ij} = \sum_{p=-N_z}^{N_z} \Gamma_{i,p\times N+j}. \tag{13}$$

$\tilde{G}_{ij}$ contains the contribution to the electrostatic energy per electron and site due to all equivalent planes with charge $-e\,\Delta\eta_j$. $2N_z + 1$ is the number of cells considered in the z direction.

It is easy to see that $\tilde{G}_{ij}$ depends only on $|i - j|$, so that we can use only $g(l) = \tilde{G}_{1l}$ with $l = |i - j| + 1$ and due to the symmetry inside the cell, we should have

$$g(l) = g(N - l + 2). \tag{14}$$

To study the convergence of the $\Delta\varepsilon_i^{(M)}$ we notice that the physics of the problem does not change if we subtract a constant from all the $g(l)$'s. By choosing this constant to be the minimum of all the $g(l)$'s we avoid divergences and can compare increasing ranges of the sum. We may summarize the results obtained in the following way, if $N_z \leq N_x$ ($2N_z + 1$ and $2N_x + 1$ being the number of cells considered along the z and x directions, respectively), the $g(l)$'s converge to different values if the relation N_x/N_z is varied and Eq. (14) does not hold. For $N_z \gg N_x$, $g(l)$ converges to the same value independently of the relation N_x/N_z and Eq. (14) is verified. The results obtained depend, therefore, on the way in which the limits are taken.

To clarify this point we attempted a different kind of calculation for a finite slab, without considering periodicity along z. To simplify the problem further we used a rigid-band model, with rectangular densities of states. This led to a linear system of $N_\pi \cdot N_\pi$ equations. The results obtained were (i) there exists a border effect, which cancels charge transfers in the $N_B/2$ and $N_A/2$ border layers of the slab; (ii) a few cells inside the borders the charge transfers, $\Delta\eta_i$, already have the same values as those of the central cell of the slab and fulfill the symmetry properties which led to Eq. (14); and (iii) these values for $\Delta\eta_i$ in the central cell are independent of N_x and N_z, provided that N_x and N_z are sufficiently large.

We compared the values obtained for the cell in the pe-

riodic system in the limit $N_z \gg N_x$, with those obtained for the slab and saw that the values corresponding to the central cells of the slab coincide with those of the periodic problem in this limit.

We understand that these are intrinsic properties of the $1/r$ dependence of the Coulomb interaction and of the planar structure of the superlattice and do not depend on the rigid-band model used to solve the problem. Therefore, all subsequent calculations for the periodic problem were made with $N_z \gg N_x$ and using symmetry to evaluate the Madelung sum [Eq. (13)].

V. RESULTS

We applied the models described to a superlattice of Ni-type atoms (A) and Cu-type ones (B). The bulk occupations of the d bands were taken as $\eta^0_{\mathrm{Ni}} = 8.6$ and $\eta^0_{\mathrm{Cu}} = 9.6$, considering that the s-band occupation of the first transition series is approximately 1.4 in all the cases.[15] We get the off-diagonal Hamiltonian elements from the bandwidths of Moruzzi,[16] $t_{\mathrm{NiNi}} = 0.307$ eV and $t_{\mathrm{CuCu}} = 0.230$ eV and also $\varepsilon'_{\mathrm{Cu}} - \varepsilon'_{\mathrm{Ni}} = -1.1$ eV. For U we set 1.7 eV, in order to obtain $m_0^{\mathrm{Ni}} = 0.59$ in units of μ_B. For the lattice parameter we took $a = 3.52$ Å.

A. Nonmagnetic results

In Table I we show the results obtained using the different ways of achieving self-consistency for the particular case $N_{\mathrm{Ni}} = N_{\mathrm{Cu}} = 4$. $i = 1$ indicates the interface layer and increasing i indicates inner layers. We see that models (a) and (b) give similar results for the charge transfers and for the averages, but local self-consistency leads to a decrease in the charge fluctuations in Ni with respect to the results obtained doing self-consistency in the average. When introducing the Madelung contribution with $\tau = 2$ we obtain an average charge transfer similar to the one obtained in (a) and (b) and large fluctuations on Ni. The profiles obtained using model (c) with $\tau = 1$ follow the same trends as those obtained in Ref. 9 for Nb/Zr multilayers making LAPW calculations and on the other hand the values of the charge transfers obtained in this way are of the same order of magnitude as those calculated by Giner *et al.*[14] for transition metal alloys and by Jarlborg and Freeman for Cu/Ni superlattices.[5] The average charge transfers within model (c) with $\tau=1$ are much less than within the other models and essentially concentrating on the interface layers. When using $\tau=2$, even if for an increasing number of layers the average charge transfer diminishes, the transfers at the interfaces are unphysically large. In molecular calculations the parameter U is usually taken to be much larger than in a solid, of the order of 10 eV, and then, in that case, $\tau=2$ is adequate.

The important aspect, which is not evident when analyzing results for a superlayer with $N = 8$, is that the charge transfers obtained within models (a) and (b) do not go to zero as N is increased, leading to unphysically large total charge transfers. This does not happen in model (c).

From now on and taking into account the previous considerations, all results shown have been obtained using model (c) with $\tau=1$.

In Table II we show the results obtained for superlattices having increasing numbers of Ni and Cu layers. It is seen that the average charge transfer diminishes as N increases, the total charge transfer among the two materials remaining almost the same. As N increases the charge transfer concentrates more and more at the interface layers.

In Table III we study the effect of composition. We see that the total charge transfers are larger when the number of Ni layers is greater than the number of Cu layers and that the transfers concentrate mainly at the interfaces as before.

B. Magnetic problem

In Table IV we show the values obtained for the magnetization in superlattices having the same number of Cu and Ni layers. It is seen that within this model the magnetization increases at the Ni interfaces with respect to Ni bulk and decreases in the internal layers. The average magnetization per Ni atom is larger than in the bulk and is nearly the same in all cases studied.

In Table V we show the results for $N_{\mathrm{Ni}}=3$ and differ-

TABLE I. Self-consistent charge transfer results for a Cu/Ni superlattice with $N_{\mathrm{Ni}} = N_{\mathrm{Cu}} = 4$ using different approximations for the self-energies, (a) average self-consistency, (b) layer by layer self-consistency, (c) layer by layer self-consistency plus Madelung contribution. i indicates layer number and increases with increasing distance from the interface, $\Delta\eta_i = \eta_i - \eta_0$, - $\overline{\Delta\eta}$ average charge transfer per atom type in units of e.

		a		b		c ($\tau = 2$)		c ($\tau = 1$)	
	i	$\Delta\eta_i$	$\overline{\Delta\eta}$	$\Delta\eta_i$	$\overline{\Delta\eta}$	$\Delta\eta_i$	$\overline{\Delta\eta}$	$\Delta\eta_i$	$\overline{\Delta\eta}$
Cu	1	0.2	0.29	0.24	0.31	0.22	0.28	0.19	0.11
	2	0.37		0.37		0.34		0.03	
Ni	1	−0.12	−0.29	−0.29	−0.31	−1.42	−0.28	−0.35	−0.11
	2	−0.45		−0.32		0.86		0.13	

TABLE II. Charge transfers for Cu/Ni superlattices as a function of modulation wavelength using approximation (c), $\tau = 1$, $\Delta\eta$ = absolute value of the total charge transfer from one constituent type to the other in units of e.

		$N_{Cu}=N_{Ni}=3$		$N_{Cu}=N_{Ni}=4$		$N_{Cu}=N_{Ni}=5$	
	i	$\Delta\eta_i$	$\overline{\Delta\eta}$	$\Delta\eta_i$	$\overline{\Delta\eta}$	$\Delta\eta_i$	$\overline{\Delta\eta}$
Cu	1	0.15	0.16	0.19	0.11	0.21	0.09
	2	0.17		0.03		0.06	
	3					−0.09	
Ni	1	−0.31	−0.16	−0.35	−0.11	−0.33	−0.09
	2	0.14		0.13		0.06	
	3					0.09	
		$\Delta\eta = 0.48$		$\Delta\eta = 0.44$		$\Delta\eta = 0.45$	

TABLE III. Same as Table II but as a function of composition.

		$N_{Cu}=2$, $N_{Ni}=6$		$N_{Cu}=3$, $N_{Ni}=5$		$N_{Cu}=N_{Ni}=4$	
	i	$\Delta\eta_i$	$\overline{\Delta\eta}$	$\Delta\eta_i$	$\overline{\Delta\eta}$	$\Delta\eta_i$	$\overline{\Delta\eta}$
Cu	1	0.26	0.26	0.19	0.19	0.19	0.11
	2			0.16		0.03	
	3						
Ni	1	−0.32	−0.09	−0.39	−0.11	−0.35	−0.11
	2	0.00		0.06		0.13	
	3	0.06		0.12			
		$\Delta\eta = 0.52$		$\Delta\eta = 0.53$		$\Delta\eta = 0.44$	

		$N_{Cu}=5$, $N_{Ni}=3$		$N_{Cu}=6$, $N_{Ni}=2$	
	i	$\Delta\eta_i$	$\overline{\Delta\eta}$	$\Delta\eta_i$	$\overline{\Delta\eta}$
Cu	1	0.21	0.08	0.21	0.08
	2	0.07		0.1	
	3	−0.13		−0.08	
Ni	1	−0.26	−0.14	−0.24	−0.24
	2	0.09			
	3				
		$\Delta\eta = 0.43$		$\Delta\eta = 0.48$	

TABLE IV. Layer magnetizations as a function of modulation wavelength for Cu/Ni superlattices. m_i indicates magnetization of the ith layer in units of μ_B. $\overline{m}_{Ni}$ is the average magnetization per Ni atom.

		$N_{Cu}=N_{Ni}=3$		$N_{Cu}=N_{Ni}=4$		$N_{Cu}=N_{Ni}=5$	
	i	$\Delta\eta_i$	m_i	$\Delta\eta_i$	m_i	$\Delta\eta_i$	m_i
Cu	1	0.16	0.05	0.19	0.06	0.21	0.05
	2	0.17	−0.02	0.04	−0.07	0.06	−0.05
	3					−0.10	−0.10
Ni	1	−0.34	0.86	−0.36	0.98	−0.33	0.98
	2	0.19	0.49	0.13	0.51	0.06	0.55
	3					0.09	0.48
		$\overline{m}_{Ni} = 0.76$		$\overline{m}_{Ni} = 074$		$\overline{m}_{Ni} = 0.69$	

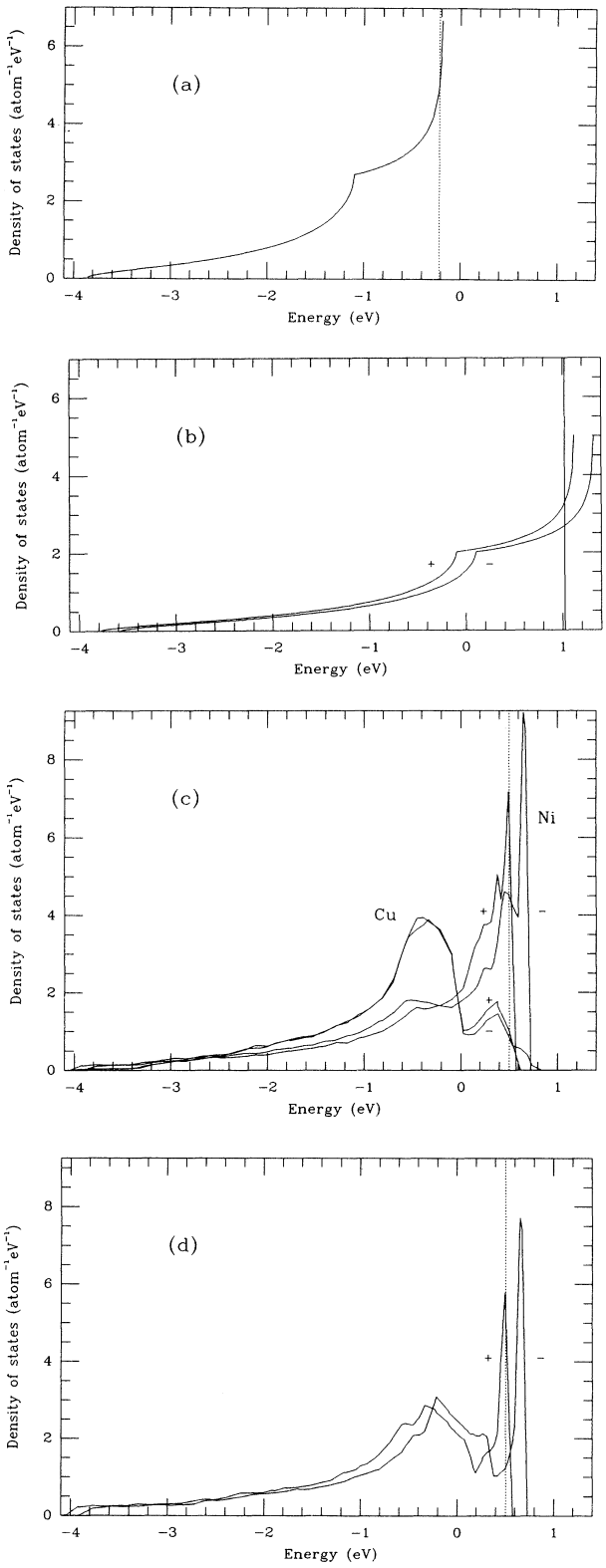

FIG. 1. Local densities of states on (a) bulk Cu, (b) bulk Ni, "+" indicates majority states and "−" minority ones, (c) Cu and Ni interfaces for a Cu/Ni superlattice with $N_{Cu} = N_{Ni} = 3$, (d) intermediate Ni layer for the same superlattice. Broken line gives the position of the Fermi level.

TABLE V. Same as Table IV but as a function of the number of Cu layers for a fixed number of Ni layers. $N_{Ni} = 3$.

		N_{Cu}=1		N_{Cu}=2		N_{Cu}=3		N_{Cu}=4		N_{Cu}=5	
	i	$\Delta\eta_i$	m_i	$\Delta\eta_i$	m_i	$\Delta\eta_i$	m_i	$\Delta\eta_i$	m_i	$\Delta\eta_i$	m_i
Cu	1	0.28	0.04	0.26	0.05	0.16	0.05	0.19	0.05	0.20	0.04
	2					0.17	−0.02	0.03	−0.00	0.07	−0.02
	3									−0.11	−0.04
Ni	1	−0.11	0.79	−0.32	0.88	−0.34	0.86	−0.3	0.86	−0.28	0.87
	2	−0.06	0.67	0.11	0.53	0.19	0.49	0.16	0.49	0.13	0.49
		$\overline{m}_{Ni}$=0.76		$\overline{m}_{Ni}$=0.80		$\overline{m}_{Ni}$=0.76		$\overline{m}_{Ni}$=0.77		$\overline{m}_{Ni}$=0.75	

ent values of N_{Cu}. The results obtained are practically independent of the number of Cu layers.

To understand the origin of the increased magnetization at the interfaces we show in Fig. 1 the partial densities of states for pure Cu and Ni and those corresponding to a superlattice with N_{Ni}=3 and N_{Cu}=3. We see that in the superlattice the partial densities of states on Ni are higher at the Fermi level than in the bulk, and this explains the increased magnetization that we obtain at the interface. However, this result could be due either to the different bandwidths of the two materials or to symmetry. To separate these two effects we calculated this same last example taking $t_{CuCu} = t_{CuNi} = t_{NiNi}$. From the results obtained, shown in Table VI, it is seen that the increase in the magnetization is nearly independent of the differences in the d-band widths and is due, essentially, to the form of the local densities of states and to the position of the Fermi level. These are intrinsic properties of the structure and symmetry of the superlattice within the model we are using.

The local densities of states on the second Ni layer present a deep valley. Although the Fermi level falls on a peak of the majority spin bands both for the interface and second Ni layer, in this last case it falls in the valley of the minority spin band. This gives rise to a decrease of the second layer magnetization with respect to the interface and bulk values.

To study the magnetization on Ni layers when they are in contact with a transition metal having less d electrons we have studied a superlattice system of the V/Ni-type, assuming for V, for the ease of calculation, also the fcc structure. For the V-type atoms we set $\eta_V^0 = 3.6$, $\varepsilon'_V - \varepsilon'_{Ni} = 2.23$ eV, $t_{VV} = 0.4$ eV. In Table VII we show the results obtained for $N_V = 3$, $N_{Ni} = 3$ and $N_V = 3$, and $N_{Ni} = 5$. Contrary to what happens in the Ni/Cu case, magnetism goes down at the interface and increases in the internal layers. In this case Ni receives electrons and the partial density of states at the interfaces shown in Fig. 2 does not have an abrupt edge at the Fermi level, therefore, the density of states is lower and this explains the decrease of the magnetization at the interface. On the other hand the Fermi level falls on a peak of the partial density of states of the second Ni layer. When N_{Ni} increases the internal layers become more similar to those of pure Ni and the previous effect is not so pronounced as is the case for $N_V = 3$, $N_{Ni} = 5$.

TABLE VI. Layer magnetizations for two systems having $t_{NiNi} = t_{CuCu} = t_{CuNi}$.

		$N_{Cu}=N_{Ni}=3$		$N_{Cu}=N_{Ni}=4$	
	i	$\Delta\eta_i$	m_i	$\Delta\eta_i$	m_i
Cu	1	0.12	0.06	0.13	0.07
	2	0.14	−0.00	0.04	−0.03
Ni	1	−0.26	0.82	−0.26	0.94
	2	0.14	0.48	0.09	0.50
		$\overline{m}_{Ni}$=0.75		$\overline{m}_{Ni}$=0.74	

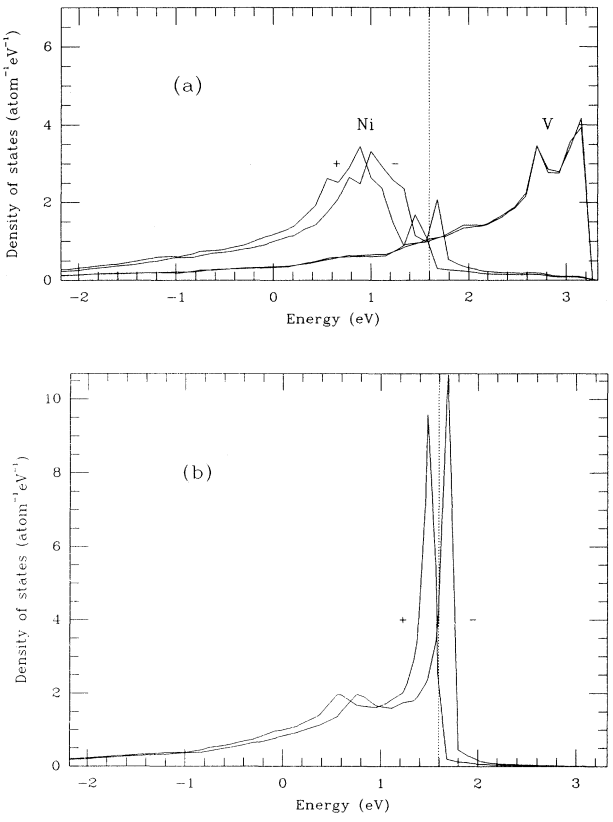

FIG. 2. Local densities of states for a V/Ni-type superlattice with $N_{Ni} = N_V = 3$ (a) V and Ni interfaces, (b) intermediate Ni layer.

TABLE VII. Layer magnetizations for a V/Ni-like superlattice for two different compositions and modulations.

		$N_V=3$, $N_{Ni}=3$		$N_V=3$, $N_{Ni}=5$	
	i	$\Delta\eta_i$	m_i	$\Delta\eta_i$	m_i
V	1	−0.45	−0.02	−0.52	−0.01
	2	0.19	−0.02	0.25	−0.00
Ni	1	0.49	0.33	0.55	0.2
	2	−0.27	1.47	−0.11	0.7
	3			−0.1	0.54
		$\overline{m}_{Ni}=0.69$		$\overline{m}_{Ni}=0.46$	

VI. DISCUSSION

We have calculated in this work the charge transfer profiles in Ni/Cu-like superlattices grown along the [111] direction. As a first approximation, the *s*-band occupation is held fixed so that we have taken into account only the *d*-band contribution. The *d* orbitals have been replaced by five degenerate *s* orbitals. We have also calculated the layer magnetizations as a function of the number of Ni layers in each unit cell.

We have shown that in the case of a superlattice, when using a tight-binding approach, it is necessary to take into account the long-range electrostatic effects due to charge transfers from one metal to the other. We have treated these transfers self-consistently by introducing a Madelung term in the diagonal elements of the Hamiltonian. Doing this we obtain an oscillating damped charge transfer profile, which ensures bulk *d* occupations in layers sufficiently apart from the interfaces. This same kind of behavior has been found by Leuken *et al.* performing *ab initio* electronic structure calculations on Nb/Zr multilayer systems.[9] Our results do not depend strongly on the number of layers or compositions of the superlattice, but the average charge transfer diminishes as the modulation length increases.

By not taking into account the *d*-orbital symmetry we overestimate in this work the value of the density of states of Ni at the Fermi level. As the value of U, within our model, is of the order of $1/[n(E_F)]_{Ni}$ this leads, probably, to an overestimation of charge transfers, but the trends and relative values should not change when introducing *d*-orbital symmetry.

Within our model it is difficult to imagine a coherent set of parameters that would give a uniform distribution of charge transfers in the superlattice as suggested by Huberman and Grimsditch in Ref. 4 in order to explain the origin of the supermodulus effect. We have also shown that the variation of the electronic properties with tensions, taken into account by changing the values of the hopping integrals, seems to be small.

With respect to the magnetization we obtain for the Ni/Cu superlattices an enhancement of the Ni magnetization at the interfaces. We show that this is due to a symmetry effect that increases the density of states at the Fermi level within our model. It is therefore opposite to *s-d* hybridization, which rounds off the densities of states, as has been shown by Victora, Falicov, and Tersoff for several systems which do not have the superlattice symmetry.[7]

Comparison with experiment is not simple. The early results of Thaler, Ketterson, and Hilliard[17] show an increase in magnetization of Ni in modulated Cu/Ni structures, but later experiments by Zheng *et al.*[18] give the opposite results. However, in these samples the interfaces were not sharp and therefore the symmetry argument should not hold. Recent results for Cu/Co superlattices,[19] with sharper interfaces, give no change for the magnetic moment of the Co atom with respect to bulk Co. Also, there is an important decrease in the Curie temperature for thin layers of a magnetic material that may have influenced the experimentals results.

We are aware that taking a fixed magnetic split, Δ, as suggested in Ref. 11 from molecular calculations with a full Hamiltonian may not be equivalent to a self-consistent solution of the model Hamiltonian having $\Delta = \frac{Um}{5}$. In future work we plan to check this assumption and also to include in our model s-d hybridization, the symmetry of the different *d* orbitals and also interfacial diffusion.

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[1] See, for instance, *Physics, Fabrication and Applications of Multilayered Structures*, edited by P. Dhez and C. Weisbuch (Springer, Berlin, 1989); *Metallic Superlattices (Artificially Structured Materials)*, edited by T. Shinjo and T. Takada, in No. 49 of *Studies in Physical and Theoretical Chemistry* (Elsevier, Amsterdam, 1987).

[2] W. M. C. Yang, T. Tsakalakos, and J. E. Hilliard, J. Appl. Phys. **48**, 876 (1977); A. Moreau, J. B. Ketterson, and J. Mattson, Appl. Phys. Lett. **56**, 1959 (1990); J. Mattson, R. Bhadra, J. B. Ketterson, M. B. Brodsky, and M. Grimsditch, J. Appl. Phys. **67**, 2973 (1990); J. R. Dutcher, S. Lee, J. Kim, G. I. Stegeman, and C. M. Falco, Phys. Rev. Lett. **65**, 1231 (1990); D. Baral, J. B. Ketterson, and J. E. Hilliard, J. Appl. Phys. **57**, 1076 (1985).

[3] B. Y. Jin and J. B. Ketterson, Adv. Phys. **38**, 189 (1989).

[4] M. Grimsditch, Superlatt. Microstruct. **4**, 677 (1988); M. L. Huberman and M. Grimsditch, Phys. Rev. Lett. **62**, 1403 (1989).

[5] T. Jarlborg and A. J. Freeman, J. Appl. Phys. **53**, 8401 (1982).
[6] I. K. Schuller (unpublished).
[7] J. Tersoff and L. M. Falicov, Phys. Rev. B **26**, 6186 (1982); R. H. Victora, in *Magnetism in Low Dimensional Systems*, edited by J. L. Morán-López and L. M. Falicov (Springer, Berlin, 1985).
[8] S. Blügel, B. Drittler, R. Zeller, and P. H. Dederichs, Appl. Phys. A **49**, 547 (1989).
[9] H.v. Leuken, A. Lodder, M. T. Czyżyk, F. Springelkamp, and R. A. de Groot, Phys. Rev. B **41**, 5613 (1990).
[10] C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. IV, p. 227.
[11] F. Liu, M. R. Press, S. N. Khanna, and P. Jena, Phys. Rev. B **39**, 6914 (1989).
[12] V. Massidda, Physica **95B**, 317 (1978); Physica **103B**, 365(E) (1981).
[13] R. Hoffmann, J. Chem. Phys. **39**, 1397 (1963).
[14] J. Giner, F. Brouers, F. Gautier, and J. van der Rest, J. Phys. F **6**, 1281 (1976).
[15] O. K. Andersen, O. Jepsen, and D. Goetzel, in *Highlights of Condensed Matter Theory* (North-Holland, Amsterdam, 1985).
[16] V. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).
[17] B. J. Thaler, J. B. Ketterson, and J. E. Hilliard, Phys. Rev. Lett. **41**, 336 (1978).
[18] J. Q. Zheng, J. B. Ketterson, C. M. Falco, and I. K. Schuller, J. Appl. Phys. **53**, 3150 (1982).
[19] A. Cebollada, J. L. Martínez, J. M. Gallego, J. J. de Miguel, R. Miranda, S. Ferrer, F. Batallán, G. Fillion, and J. P. Rebouillat, Phys. Rev. B **39**, 9726 (1989); C. M. Schneider, P. Bressler, P. Schuster, J. Kirschner, J. J. de Miguel, and R. Miranda, Phys. Rev. Lett. **64**, 1059 (1990).