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Superlattices and interfaces X/Cu (X = Fe, Co, Ni): Calculation and interpretation of magnetic properties.

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ABSTRACT. I study the different magnetic behaviors of Fe, Co and Ni with respect to bulk properties when forming superlattices with Cu and when one monolayer is deposited on Cu(001). I perform spin polarized calculations using a self-consistent tight binding Hamiltonian and obtain the contribution to the magnetic moment coming from the different orbital symmetries. This information is nowadays experimentally available. I show that the magnetic properties studied can be explained by a qualitative analysis using model paramagnetic densities of states. The distinct magnetic behaviors are essentially due to band filling.

RESUMEN. Se estudian las diferencias en el comportamiento magnético de Fe, Co y Ni cuando forman superredes con Cu y cuando una monocapa se deposita sobre Cu(001) con respecto a los sólidos puros en la fase fcc. Se utiliza un hamiltoniano de enlaces fuertes autoconsistente y se obtiene la contribución al momento magnético de las diferentes simetrías orbitales. Esta información puede obtenerse actualmente con métodos experimentales. Se demuestra que las propiedades magnétics estudiadas pueden ser explicadas a través de un análisis cualitativo utilizando densidades de estados paramagnéticas. Se encuentra que las diferencias en el comportamiento magnético de Fe, Co y Ni en los sistemas estudiados se deben especialmente al llenado de la banda *d*.

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1. INTRODUCTION

Calculations of magnetic properties for X/Cu (X = Fe, Co, Ni) superlattices and interfaces grown in the (001) and (111) directions have been performed with the aim of giving a simple interpretation to the different behaviors observed.

A Hubbard tight binding Hamiltonian in the unrestricted Hartree-Fock approximation with s, p and d orbitals parametrized to the pure materials is used as it is the simplest Hamiltonian which can account for the studied magnetic properties providing simple interpretations and direct comparison with bulk properties. The method of calculation used in this work has been well described and succesfully applied to the study of superlattices, surfaces and overlayers in Refs. 1, 2 and 3 respectively. The splitting

between the majority and minority d-bands is related in these calculations to an effective exchange parameter J through the expression

$$\varepsilon_{id-} - \varepsilon_{id+} = JM_{id} \tag{1}$$

where M_{id} is the magnetization of the d orbitals on site i [4].

I perform calculations for 3X/3Cu superlattices and find that fcc Fe layers in contact with Cu behave as low-dimensional systems thus favoring the appearance of magnetism. In the case of Ni the hybridization with Cu lowers the magnetic moment and in the Co/Cu superlattice (SL) the magnetic moment of Co is similar to its bulk value. Detailed studies of M in the 2X/2Cu superlattices as a function of J are compared with the M *vs.* J plots for the corresponding transition metal bulks.

To simulate the overlayers on the Cu substrate I also study X/5Cu/X slabs looking for the contribution to the d-orbital occupation and magnetic moment coming from the different orbital symmetries. These quantities are now available from experience [5] by x-ray magnetic circular dichroism (XMCD) spectroscopy and may be related to magnetic anisotropy. I find that in the case of Fe the d-orbital magnetization is greater for orbitals with $m = 0$ than for those with $m = 2$ while the opposite holds for Ni (m is the L_z quantum number with z axis perpendicular to the surface). Experimental results also show different orientations of the easy axis of M for Fe and Ni monolayers on Cu(001) [6].

Based on a qualitative analysis of paramagnetic model densities of states I show that the distinct magnetic behaviors of the systems studied are due essentially to band filling.

2. Results and discussion

2.1. 3X/3Cu superlattices (X = Fe, Co, Ni)

The results for 3X/3Cu superlattices (X = Fe, Co and Ni) grown in the fcc (111) and (001) directions are shown in Table I. The magnetic moments obtained within this model for the bulk materials in the fcc ferromagnetic phase are given for comparison in the last row of the Table. For all superlattices studied there exists a ferromagnetic solution but for the 3Fe/3Cu system we find also a phase with antiferromagnetic coupling between planes within the Fe slab. We see that making SL's with Cu favors the appearance of magnetism in Fe (fcc), has almost no effect in Co and diminishes the magnetic moment per atom of Ni in 3Ni/3Cu SL with respect to bulk Ni. The case of Fe/Cu SL was extensively discussed in a previous work [1] where calculations for 2Fe/2Cu, 3Fe/3Cu SL and for 2Fe, 3Fe free standing slabs were performed finding that the superlattices behave as low-dimensional systems. In the case of Cu/Ni SL it is the hybridization between Ni-d and Cu-sp bands which rounds off the sharp peak at the top of the d band of fcc bulk Ni and determines the decrease of the magnetic moment at the Ni interfaces. In the case of 3Co/3Cu SL an intermediate situation is present and the magnetic moment is almost the same as in the bulk.

These results show good agreement with experiments [8] and available *ab initio* calculations [9]. For example, in the case of 3Ni/3Cu(111) and (001) SL we obtained at the Ni interface layer the same 30% reduction of the magnetic moment with respect to the bulk

TABLE I. Magnetizations (μ_B) for 3X/3Cu(111) SL and 3X/3Cu(001) SL for X = Fe, Co and Ni. $\langle M_X \rangle$ is the average magnetic moment per X atom in a 3X/3Cu SL (the corresponding values for the bulk fcc phase obtained in our calculations are given for comparison). The exchange integrals J_i were fitted to give the bulk magnetization values of Fe(bcc), Ni(fcc) and Co(fcc) and taken from Ref. 7 for Cu.

		3X/3Cu superlattices			
		X = Fe		X = Co	X = Ni
		Ferri	Ferro	Ferro	Ferro
	layer	M	M	M	M
(111)	Cu_{I-1}	-0.01	-0.01	-0.02	-0.01
	Cu_I	0.01	0.01	-0.01	-0.01
	X_I	2.39	2.63	1.63	0.40
	X_{I-1}	-1.46	2.34	1.55	0.60
		$25\langle M_{Fe}\rangle$=1.11	$\langle M_{Fe}\rangle$=2.54	$\langle M_{Co}\rangle$=1.59	$\langle M_{Ni}\rangle$=0.46
(001)	Cu_{I-1}	-0.02	-0.01	-0.02	-0.01
	Cu_I	0.02	0.03	0.00	-0.01
	X_I	2.49	2.73	1.73	0.42
	X_{I-1}	-1.67	2.29	1.46	0.58
		$\langle M_{Fe}\rangle$=1.11	$\langle M_{Fe}\rangle$=2.60	$\langle M_{Co}\rangle$=1.64	$\langle M_{Ni}\rangle$=0.46
			Bulk fcc (Ferromagnetic phase)		
			$\langle M_{Fe}\rangle$=0	$\langle M_{Co}\rangle$=1.58	$\langle M_{Ni}\rangle$=0.60

value than Freeman *et al.* with the spin-polarized self-consistent linear muffin-tin orbital (LMTO) method. Experimental measurements performed by Xiao *et al.* in Cu/Ni SL and by Sill *et al.* in Cu/Ni/Cu sandwiches as a function of the number of Ni layers show also a reduction of the magnetic moment per Ni atom, $\langle M_{Ni} \rangle$, that is consistent with a reduction of the magnetic moment at Ni interface layers. Fu *et al.* performed spin polarized full-potential linear augmented-plane-wave (FPLAPW) calculations for Cu/5Fe/Cu(001) sandwiches and obtained solutions with ferro and antiferromagnetic coupling between planes and a similar behavior of the layer magnetic moments than we obtained with our parametrized tight binding hamiltonian. For example, in the case of the ferromagnetic solution they found a magnetic moment of 2.6 μ_B for the Fe interface layer (I) and 2.23 μ_B for the sub-interface layer $(I-1)$. The last example I would like to mention is the experimental study performed by Cebollada *et al.* on Co/Cu(001) SL where they shown that Co layers have almost the same magnetic moment than bulk fcc Co.

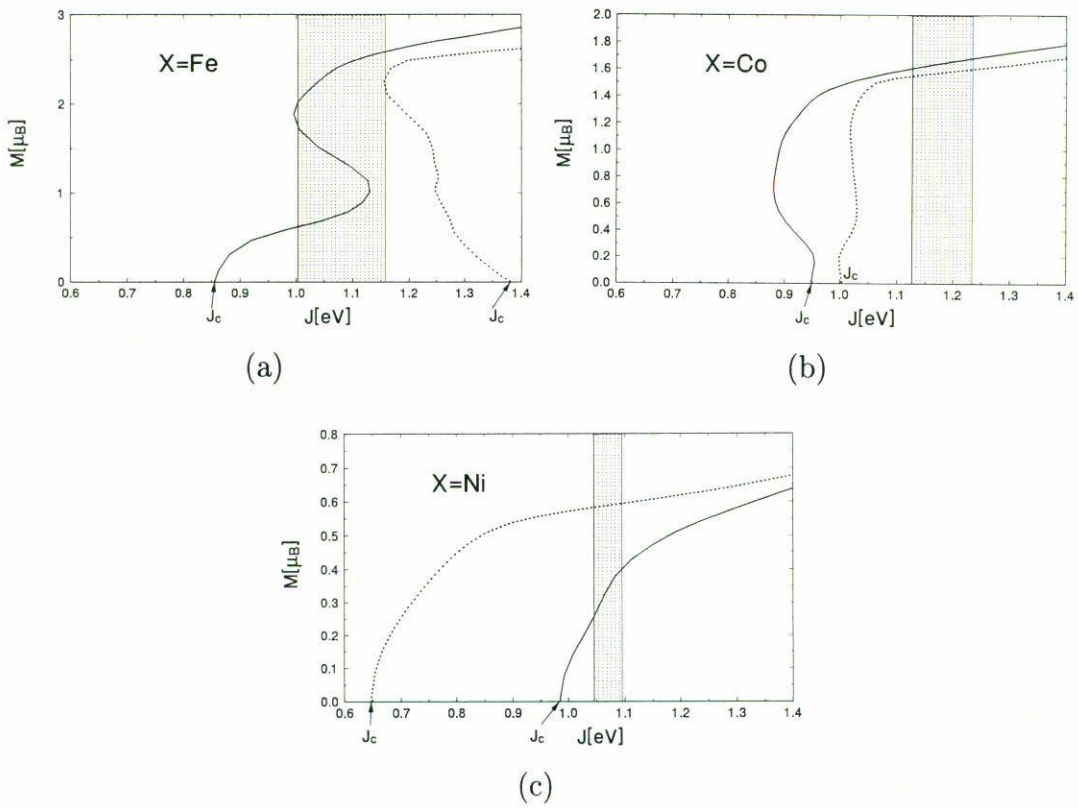


FIGURE 1. Magnetization per X atom as a function of parameter J in a 2X/2Cu(111) SL (continuous line) and in the corresponding X fcc bulk material (broken line) for (a) X = Fe, (b) X = Co and (c) X = Ni. J_c is the inverse of the paramagnetic LDOS of X-d orbitals at the Fermi level.The dashed region indicates a reasonable range of variation for parameter J in our model. The values used in Table I are the upper limits.

2.2. M_X *vs.* J IN 2X/2Cu SUPERLATTICES (X = Fe, Co, Ni)

To study the dependence of these results on parameter J I focused on the SL's 2X/2Cu which have only one magnetic atom per unit cell. The curve M *vs.* J gives additional information and is useful to predict the behavior of the system under volume changes. Fig. 1a shows that 2Fe/2Cu SL favors the appearance of magnetism in Fe (fcc) since ferromagnetic solutions exist in the superlattice for values of J much smaller than for bulk fcc Fe. In particular $J_c(SL) < J_c(\text{bulk})$. In Fig. 1c the opposite holds and the magnetic moment per atom of Ni suffers a substantial reduction in 2Ni/2Cu SL with respect to bulk Ni. In the case of Fig. 1b one sees that magnetic solutions appear for lower values of J in 2Co/2Cu SL than in Co fcc bulk but in the range of interest saturation is almost reached in both cases and there are no significant differences in the magnetic moment per Co atom.

Concerning changes in volume, for any one of the systems of Fig. 1, a lattice expansion would give rise to a decrease in bandwidth and a new plot of M *versus* J would be shifted

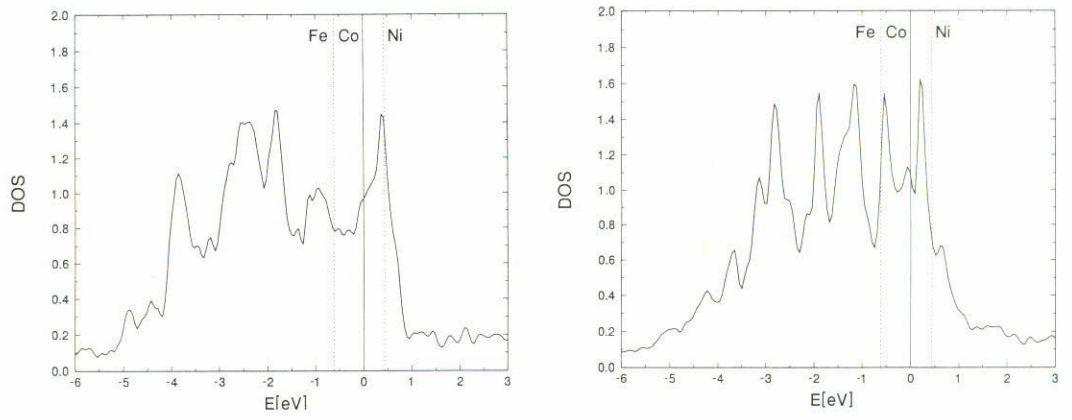


FIGURE 2. Densities of states per spin of the paramagnetic phases for (a) fcc Co and (b) Co in 2Co/2Cu SL. Energies are referred to Co Fermi level. Dotted lines indicate the Fermi level position for band fillings corresponding to Fe and Ni.

to smaller values of J, thus giving larger values of M for the same J. Small changes in volume may trigger important changes in the magnetic state in 2Fe/2Cu SL and may modify the value of the magnetic moment in 2Ni/2Cu but no important changes are expected in the behavior of 2Co/2Cu SL. Within the expected range of variation of parameter J in the model, 2X/2Cu SL show the same qualitative behavior of M as the 3X/3Cu SL.

The relevant features of all the curves of Fig. 1 may be understood by qualitative inspection of the paramagnetic DOS, N(E), of bulk fcc Co and the LDOS of Co in the 2Co/2Cu SL shown in Fig. 2. The positions of the Fermi levels for band fillings corresponding to Fe, Co and Ni are shown. For the bulk

$$N(E_F^{\mathrm{Fe}}) < N(E_F^{\mathrm{Co}}) < N(E_F^{\mathrm{Ni}}) \tag{2}$$

while for superlattices

$$N(E_F^{\mathrm{Fe}}) > N(E_F^{\mathrm{Co}}) > N(E_F^{\mathrm{Ni}}) \tag{3}$$

This is related to the ordering of the points labelled as J_c in Fig. 1. Since, in the Stoner model, $J > J_c$ gives a sufficient condition for the appearance of a ferromagnetic phase, inequalities (2) and (3) help to explain the different magnetic behavior of X/Cu superlattices with respect to X-bulk materials.

In Ref. 10 was shown for the Stoner model that from the shape of the paramagnetic density of states one may even infer the stable ($dM/dJ > 0$) or unstable ($dM/dJ < 0$) solutions in an M *vs.* J plot. In that case, for a rigid band splitting Δ between majority and minority bands the magnetization, $M(\Delta)$, is given by the area below N(E) from $E_F - \Delta/2$ to $E_F + \Delta/2$. If T(Δ) is the area of the trapezium defined by the points $N(E_F+\Delta/2)$, $N(E_F-\Delta/2)$, $E_F-\Delta/2$ and $E_F+\Delta/2$ then stable ferromagnetic solutions are expected if $T(\Delta) < M(\Delta)$. This analysis based in the Stoner model is very useful to

TABLE II. Occupations and magnetizations per orbital at the X layer in $s'/X/5Cu/X/s'$ slabs for X = Fe, Co and Ni. The exchange integrals J_i were taken as in Table I.

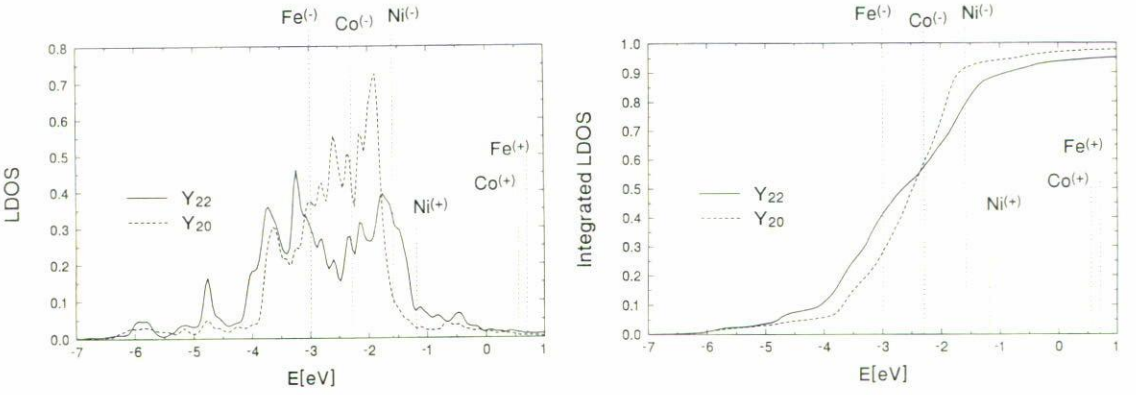
	s'/X/5Cu/X/s' Slabs					
	X = Fe		X = Co		X = Ni	
	n	M	n	M	n	M
Y_{22}	1.37	0.52	1.53	0.37	1.66	0.08
Y_{21}	1.26	0.63	1.42	0.46	1.74	0.04
Y_{20}	1.25	0.70	1.59	0.36	1.86	0.02
d	6.52	3.00	7.48	2.02	8.67	0.27
sp	1.10	−0.04	1.08	−0.02	1.02	−0.01
TOT	7.62	2.96	8.56	2.00	9.69	0.26
s'	0.34	−0.06	0.39	−0.04	0.35	0.00

understand qualitatively the curves of Fig. 1 based on those of Fig. 2. For example, in the case of 2Fe/2Cu SL the stable region for $M < 1$, the unstable one for $1 < M < 2$ and the stable one for $M > 2$ may be explained by inspection of Fig. 2b. For increasing values of Δ, $T(\Delta)$ is smaller, larger and smaller again than $M(\Delta)$. Actually, this analysis based on paramagnetic Co-bands works even quantitatively in this case and shows that band filling is the relevant parameter in this description.

2.3. X MONOLAYER ON Cu(001) (X = Fe, Co, Ni)

For the case of an X-monolayer deposited on Cu(001) for X = Fe, Co and Ni I looked at the contribution to the magnetic moment and d-orbital occupation coming from different orbital symmetries. I performed calculations of $s'/X/5Cu/X/s'$ slabs where s' is an extra s-type orbital added to account for the spill-over at the surface [2]. In these slab calculations, instead of introducing a Madelung term in the Hamiltonian, the site energies of the s' orbitals and of the s, p and d orbitals of the X layers are shifted in a similar way as was done in Ref. 3. In the present case the shift is taken as the difference between the Fermi levels of bulk Cu and $s'/2X/s'$ slab. For the five d-orbitals the same band splitting is considered (expression (1)) as I am interested here in a qualitative discussion. To check this approximation for the case of surfaces I did self-consistency for each d-orbital and obtained that average self-consistency gives the correct trends.

In Table II d-orbital occupations and magnetizations are shown. The total d-magnetization of Fe and Co corresponds to the saturation value as in the case of free-standing monolayers. In the case of Ni the magnetization suffers a drastic reduction with respect to its saturation value ($1\mu_B$) as a consequence of hybridization with the substrate. In the case of Fe the orbitals with $m = 2$ are more ocuppied and have a smaller magnetization than those with $m = 0$ and the opposite holds in the case of Ni. The different band filling of Fe and Ni gives rise to this effect and it can also be explained in terms of model densities of states.



(a) (b)

FIGURE 3. (a) Y_{22} and Y_{20} components of the density of states per spin for Co in the paramagnetic phase of s'/Co/5Cu/Co/s' slab and (b) the corresponding integrated densities of states. Vertical dotted lines indicate the energies that give d-band occupations corresponding to majority (+) and minority (−) bands of s'/X/5Cu/X/s' slabs in the ferromagnetic phase (see text). Origin of energies is arbitrary.

As in the previous case the relevant features of Table II may be understood by qualitative inspection of paramagnetic Co LDOS. In Fig. 3, I plot the Y_{20} and Y_{22}-Co partial densities of states of the system s'/Co/5Cu/Co/s' in the paramagnetic phase and the corresponding integrated densities of states. Co parameters are used and Fe and Ni are simulated by only changing the occupation in the Co-d band. The vertical lines indicate the energies for which the integrated LDOS of paramagnetic Co d-band gives occupations corresponding to the majority and minority X-d bands of ferromagnetic s'/X/5Cu/X/s' slabs. In a qualitative discussion we may disregard majority bands since they are almost full. Looking at the minority ones it is clear that for occupations smaller than that of Co, the Y_{22} band will be more occupied than the Y_{20} one and that for larger occupations the opposite holds. The main reason for this effect is that the Y_{22} band originates from orbitals in the plane (d_{xy} and $d_{x^2-y^2}$) and the LDOS is wider and lower than the one corresponding to the Y_{20} band whose charge distribution points out of the plane of X atoms. Actually Table II and Fig. 3b contain "quantitatively" the same information (with a precision of 0.02).

Recently some sum rules have been derived [11] that connect the XMCD-intensities with the expectation value of the magnetic dipole operator $\langle \mathbf{T} \rangle$ of valence electrons ($\mathbf{T} = \mathbf{S} - 3\hat{\mathbf{r}}(\hat{\mathbf{r}}.\mathbf{S})$). $\langle \mathbf{T} \rangle$ is related to the anisotropy of the charge distribution. With the results of Table II we obtain for $7\langle T_z \rangle$ the values of $0.29\hbar$, $0.08\hbar$ and $-0.10\hbar$ for Fe, Co and Ni monolayers on Cu(001) respectively. $\langle T_z \rangle$ has the same sign for Fe and Co and opposite for Ni. Although the relation between $\langle T_z \rangle$ and magnetic anysotropy is still a matter of discussion [5, 12], it is interesting to note that both magnitudes experiment the same change of sign.

3. CONCLUSIONS

Calculations of magnetic properties of X/Cu superlattices and of X monolayers on Cu (001) were performed for X = Fe, Co and Ni. A self-consistent Hubbard tight binding Hamiltonian with s, p and d orbitals parametrized to the pure materials was used. The results obtained are in agreement with available experimental results and *ab initio* calculations and may be summarize as follows: making SL's with Cu favors the appearance of magnetism in Fe (fcc), has almost no effect in Co and diminishes the magnetic moment per atom of Ni in Ni/Cu SL's with respect to bulk Ni. In the case of X monolayers on Cu (001) I have looked at the contribution to the X d-orbital magnetization coming from the different orbital symmetries and found that in the case of Fe the dominant contribution comes from orbitals whose charge distribution points out of the plane of Fe atoms while the opposite holds for Ni. Based on a qualitative analyses of paramagnetic LDOS I conclude that band filling is the relevant quantity to understand the differences in the magnetic behavior of X/Cu SL with respect to bulk materials. It is also relevant to understand the anisotropy of the d charge density in thin films and overlayers. Only one model LDOS for Fe, Co and Ni accounts for a qualitative description of low dimensional magnetic properties, which can now be experimentally observed.

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