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Electronic and magnetic properties of Fe–Cu superlattices

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Abstract. The electronic and magnetic properties of Fe/Cu superlattices grown in the (111) direction, for which Fe takes the FCC structure, are studied with a parametrized tight-binding Hamiltonian. The splitting between majority and minority d bands is related to an effective exchange parameter J that we adjust to obtain within our model the bulk magnetization for BCC Fe. As the magnetization of bulk FCC Fe is very sensitive to this parameter we study the magnetic properties as a function of it. We find that the 2Fe/2Cu superlattice is possibly ferromagnetic and that 3Fe/3Cu has more than one stable state (paramagnetic, ferromagnetic or ferrimagnetic) with quite similar energies. As recent experimental results detect a small magnetic moment for this last superlattice, comparison with the calculations suggest that they are ferrimagnetic. Comparison with calculations for 2Fe and 3Fe FCC(111) free-standing slabs show that the 2Fe/2Cu and 3Fe/3Cu superlattices behave as low-dimensional systems, the effect of Cu being to slightly reduce the magnetic moment per atom of Fe with respect to a free-standing slab.

1. Introduction

The magnetic properties of artificially made metallic systems have attracted much attention in recent years [1] and particular interest has been focused on the Fe/Cu system. The small lattice mismatch at room temperature between FCC γ-Fe and Cu and the fact that they are mutually insoluble make this system favourable for epitaxial growth. Furthermore, the study of Fe/Cu superlattices is a way to study the magnetic properties of FCC Fe, as bulk FCC Fe is paramagnetic and only stable at high temperatures.

Controversial structural and magnetic properties of FCC Fe when grown on Cu as thin films or making multilayers have been reported [2, 3, 4, 5, 6]. A big experimental effort has been made lately [6] to determine if structural and magnetic properties are related to each other or not. Some authors believe that these contradictory results may be related to the transition from paramagnetic to different magnetic states of FCC Fe with increasing atomic volume predicted by theoretical calculations [7–10]. This transition occurs close to the atomic volume of Cu at $T = 0$. One may then foresee a delicate behaviour as a function of temperature: while increasing T decreases all forms of order, there is an opposite effect due to the increase in the atomic volume that favours magnetism.

The purpose of our work is to study the effect of dimensionality and hybridization at the interface with Cu in the magnetic properties of FCC Fe when forming ordered superlattices. We use a tight binding Hamiltonian with s, p and d orbitals parametrized to the pure materials as we believe that a tight binding Hamiltonian parametrized to fit bulk equilibrium properties of transition metals can be used to obtain qualitative information on the densities of states, magnetization and charge transfers in surfaces and superlattices. We consider the atomic

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volume of BCC Fe in all cases, bulk BCC, bulk FCC and superlattices, as we do not expect a tight binding calculation to be able to give the small differences in the equilibrium volume by energy minimization. The splitting between the majority and minority d bands is related in our calculations to an effective exchange parameter J, and when J is adjusted to give the bulk magnetization of BCC Fe ($J = J_0 = 1.16$ eV) we obtain that bulk FCC Fe is not ferromagnetic. We have not considered the antiferromagnetic or ferrimagnetic solutions of bulk FCC Fe. We should note that a small increase in the atomic volume gives rise in our calculation, as in most others, to the appearance of a ferromagnetic state of FCC Fe.

We perform a detailed study of the magnetization in the 2Fe/2Cu superlattice as a function of J and show that the low-dimensional structure of Fe in this superlattice favours the appearance of magnetism for values of J for which bulk FCC Fe is not ferromagnetic. However, the precise magnetic moment is difficult to establish. Finally we study the 3Fe/3Cu superlattice, allowing antiferromagnetic coupling between planes and obtain paramagnetic, ferromagnetic and ferrimagnetic solutions. The average magnetization value of the ferrimagnetic case seems to compare well with recent experimental results [6].

2. Method of calculation

We study superlattices (SL) of transition metals within a Hubbard tight binding formalism in the unrestricted Hartree–Fock approximation. Our aim is to obtain charge transfers and magnetic moment profiles, layer by layer, using s, p and d orbitals and also a Madelung correction. This last term avoids the dependence of charge transfer from one material to the other on the number of layers of each one. The Hamiltonian may be written as

$$H = \sum_{i,m,\sigma} \epsilon_{im\sigma} c^{\dagger}_{im\sigma} c_{im\sigma} + \sum_{i \neq j,m,m',\sigma} t^{mm'}_{ij} c^{\dagger}_{im\sigma} c_{jm'\sigma} - E_{dc} \tag{1}$$

where $c^{\dagger}_{im\sigma}$ ($c_{im\sigma}$) is the creation (annihilation) operator of an electron state on lattice site i, orbital type m and spin σ ($\sigma = 1$: majority, $\sigma = 2$: minority), $t^{mm'}_{ij}$ are the hopping matrix elements and $\varepsilon_{im\sigma}$ the diagonal matrix elements given by,

$$\varepsilon_{im\sigma} = \varepsilon^0_{im} + \sum_{m'} U_{imm'} \Delta n_{im'} + (-1)^{\sigma} \sum_{m'} \frac{J_{imm'}}{2} M_{im'} + \Delta\varepsilon_i^{(\mathrm{MAD})} \tag{2}$$

and

$$E_{dc} = \frac{1}{2} \sum_{im\sigma} (\varepsilon_{im\sigma} - \varepsilon^0_{im}) n_{im\sigma} \tag{3}$$

is the correction due to double counting in the Hartree–Fock approximation. $\Delta n_{im'}$ is the electronic occupation difference per layer and per orbital with respect to the bulk paramagnetic values, $M_{im'}$ is the magnetization, also per layer and per orbital and $n_{im\sigma}$ is the electronic occupation per layer, per orbital and per spin. $\Delta\varepsilon_i^{(\mathrm{MAD})}$ is a Madelung-type term per layer obtained by the procedure described in [11].

For ε^0_{im} and $t^{mm'}_{ij}$ we have used parameters given by Andersen from LMTO calculations for the pure paramagnetic materials [12]. We have taken for the screened Coulomb repulsion terms, $U_{imm'}$, those calculated in [13] for d–d interactions and $U_{ss} = U_{pp} = U_{sp}$, $U_{sd} = U_{pd}$. The relation U_{ss}/U_{dd} is taken from the corresponding atomic integrals. The exchange integral J, for d orbitals only, is the important parameter responsible for magnetic properties. For Fe it was fitted performing a calculation for BCC Fe using first and second-neighbour interactions so as to give the bulk magnetization of $2.2\mu_B$/Fe atom. We obtained $J = J_0 = 1.16$ eV and we take this value also for FCC Fe since it is not expected to change

significantly [8]. However, *ab initio* calculations for BCC Fe show that the majority band is narrower than the minority one and this enhances magnetism. As we do not consider spin dependent hoppings in our calculations our J value is an upper limit. The J value for Cu was taken from LMTO calculations of the Stoner parameter [12].

For the Fe/Cu superlattices we assume that Fe grows epitaxially on Cu and study the FCC(111) growth direction with perfect sharp interfaces. Only first-neighbour interactions were considered and the geometric mean of hopping integrals between Cu–Cu and Fe–Fe interactions was used for Cu–Fe interactions. We solve the Hamiltonian in reciprocal space with a unit cell of $n + m$ atoms for a SL nFe/mCu. The Brillouin zone is swept with 1000 random k points and the resulting levels broadened with a Gaussian as in reference [14] to obtain a better accuracy in the local densities of states $N_{im\sigma}(E)$ near the Fermi level. The Fermi energy is determined requiring global charge neutrality in the cell. We calculate the electronic occupations,

$$n_{im\sigma} = \langle c^{\dagger}_{im\sigma} c_{im\sigma} \rangle = \int_{-\infty}^{E_f} N_{im\sigma}(E)\, \mathrm{d}E \tag{4}$$

to obtain new site energies using expression (2) and the calculation is repeated iteratively until self-consistency in the $n_{im\sigma}$ is achieved. Finally we calculate the total energy,

$$E_T = \int_{-\infty}^{E_f} \left(\sum_{im\sigma} N_{im\sigma}(E) \right) E\, \mathrm{d}E - E_{dc}. \tag{5}$$

The precision in each one of the magnitudes calculated, in particular in total energy differences, was carefully studied considering different samplings in the Brillouin zone.

3. Results and discussion

In table I we show the parameters for Fe and Cu used in the present calculation, which correspond to the BCC ferromagnetic equilibrium density and to the FCC equilibrium density respectively. We assume the same atomic volume for Fe in the BCC and FCC structures and do not take into account the small mismatch of 1.5% between FE and Cu for the superlattice. The numerical errors involved in our calculation were analysed for bulk Fe and Cu considering ten samples of 1000 random k points each with a Gaussian broadening of 0.075 eV. We obtain errors in d-orbital occupation of $0.01e$ in magnetization of $0.03\mu_B$ and in total energy of 0.09 eV. However, if the same 1000 random k points are used for both phases of BCC Fe (paramagnetic and ferromagnetic) the energy difference per Fe atom of 0.56 eV has an error of 0.01 eV only.

The first problem studied was the magnetization of bulk FCC Fe as a function of parameter J, that controls magnetism. Figure 1 shows the magnetization and energy as a function of the parameter J for one set of 1000 random k points. To construct these curves the self-consistent procedure described in section 2 is not useful, as it does not give the unstable solutions ($\mathrm{d}M/\mathrm{d}J < 0$). We proceed as follows: since there is only one atom in the unit cell in this case and $J_{mm'} \neq 0$ only for $m = m' = d$, there is only one magnetization to determine self-consistently which enters the Hamiltonian through the expression:

$$\varepsilon_{d\sigma} = \varepsilon_d^0 + \sum_{m'} U_{dm'} \Delta n_{m'} + (-1)^{\sigma} \frac{\Delta}{2}$$

with $\Delta = J_{dd} M_d$. Giving a fixed value to Δ we determine self-consistently the $\Delta n_{m'}$. Then we calculate the output magnetizations $M_{m'} = n_{m'\uparrow} - n_{m'\downarrow}$ and obtain $J_{dd} = \Delta / M_d$, $M = M_d + M_{sp}$ and E_T with expression (5). The curves shown in figure 1 contain the

Table 1. Parameters used in the present calculation (eV) $U_{mm'} = U_{m'm}$, $U_{pp} = U_{sp} = U_{ss}$, $U_{pd} = U_{sd}$. $J_{mm'} = 0$ if $m, m' \neq d$. For BCC Fe first- and second-neighbour integrals are given. The repulsion parameters for the Madelung term were taken to be 2.67 eV both for Fe and Cu.

	ε_s	ε_p	$\varepsilon_d(T_{2g})$	$\varepsilon_d(E_g)$	ssσ	ppσ	ppπ	ddσ	ddπ
Cu	0.22	5.34	−4.41	−4.50	−1.00	1.78	−0.22	−0.41	0.17
Fe(FCC)	2.42	7.00	−2.07	−2.21	−1.04	1.83	−0.23	−0.70	0.30
Fe(BCC)	2.50	7.04	−2.00	−2.29	−1.28	2.15	−0.33	−0.80	0.39
					−0.44	0.85	−0.04	−0.37	0.07

	ddδ	spσ	sdσ	pdσ	pdπ	U_{ss}	U_{sd}	U_{dd}	J_{dd}
Cu	−0.01	1.33	−0.61	−0.83	0.20	1.00	1.20	3.01	0.70
Fe(FCC)	−0.03	1.38	−0.82	−1.10	0.26	0.75	0.97	2.33	1.16
Fe(BCC)	−0.04	1.66	−0.96	−1.28	0.36	0.75	0.97	2.33	1.16
	−0.00	0.62	−0.40	−0.56	0.06				

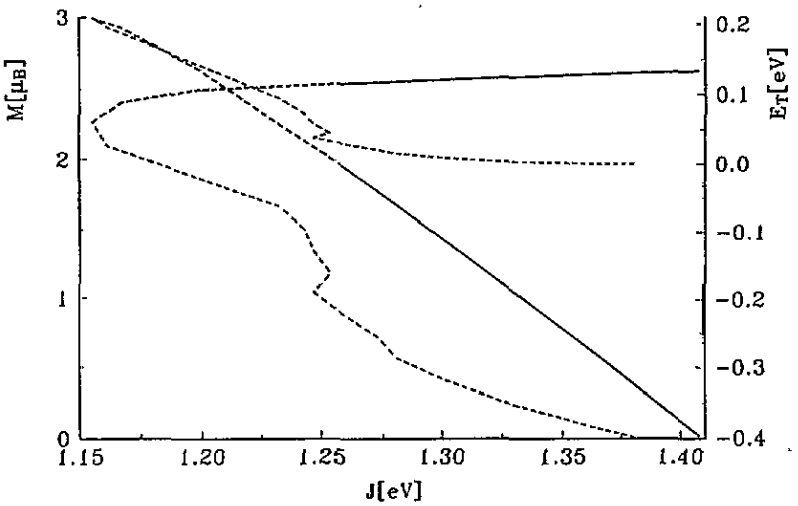

Figure 1. Magnetization and total energy for FCC Fe as a function of the parameter J. Full lines represent stable solutions and dotted lines unstable and metastable ones. For $J < J_{ST} = 1.26$ eV the stable solution is paramagnetic. Energies are referred to the paramagnetic phase. One should note that when the lattice parameter is increased by only 3% the whole figure is shifted to the left so that the ferromagnetic solution already appears for $J = 1$.

ferromagnetic solutions to the problem and were constructed giving different values to Δ in the range from 0 to 4 eV. The broken lines begin at $\Delta = 0$ and indicate the solutions with energy greater than the paramagnetic one. The full lines indicate the stable ferromagnetic solutions and begin for a value of $J = J_{ST} = 1.26$ eV. For $J < J_{ST}$ the stable solution is the paramagnetic one. Since J is at most J_0 in our model, as discussed before, we conclude that FCC Fe is not ferromagnetic in our approximation at the equilibrium density of BCC Fe. Other samples of 1000 k points give similar values of J_{ST} although the shape of the total curve may be somewhat different. Total energy calculations within a tight binding scheme may be questionable, but after a careful analysis of the results obtained we are fairly confident of the sign of the energy differences. For instance, we obtain the energy per atom of Fe in the paramagnetic FCC phase 0.3 eV higher than that of the ferromagnetic BCC phase.

The second problem studied was the superlattice 2Fe/2Cu. In figure 2 we show the

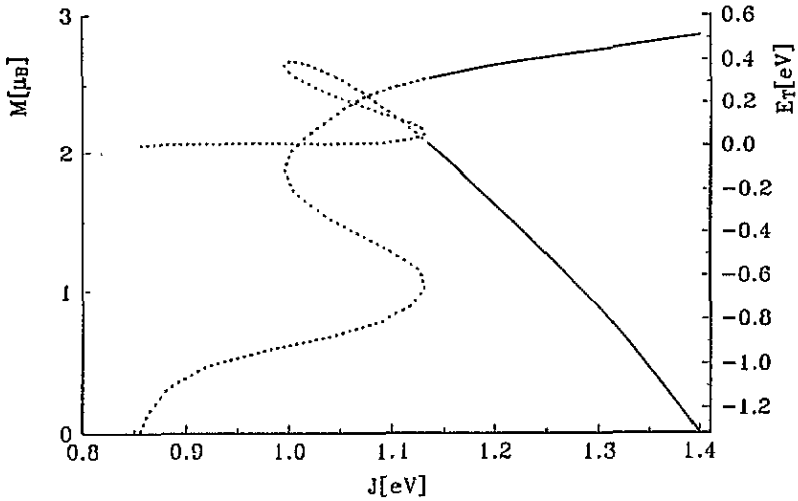

Figure 2. Same as figure 1 for the superlattice 2Fe/2Cu.

magnetization per atom of Fe as a function of J obtained by the same method described above. We would like to remark that in this case the ferromagnetic solutions exist for values of J much smaller than for bulk FCC Fe (figure 1). In particular, J_0 is of the order of J_{ST}, so that the superlattice has a larger probability of being ferromagnetic than bulk FCC Fe. Actually in the range 0.86 eV $< J <$ 1 eV there exist paramagnetic and ferromagnetic solutions which are almost degenerate in energy. From 1 eV to 1.13 eV there exist a low-spin solution and a paramagnetic one, with approximately the same energy and a high-spin solution which is less stable. Beyond $J_{ST} = 1.13$ eV the only ferromagnetic solution is clearly more stable than the paramagnetic one. We see that a small change in the parameter J gives in this case a large change in the magnetic moment (from $M < 1\mu_B$ to $M > 2.2\mu_B$). Small changes in the experimental conditions, for example the details of the epitaxial growth, could trigger important changes in the magnetic state. In fact, as in figure 1, a lattice expansion would give rise to a decrease in bandwidth and a new plot of M versus J in this case would be shifted to smaller values of J, thus giving larger M for the same J.

The 2Fe/2Cu superlattice behaves as a low-dimensional system, which favours the appearance of magnetism. To show this more clearly we plot in figure 3 the paramagnetic partial densities of states in the SL 2Fe/2Cu together with those of bulk FCC Fe and of a free-standing slab of two layers of Fe. There is a peak close to the Fermi level in the SL and in the slab but not in bulk FCC Fe. This peak will favour magnetism, as can be inferred from the simple Stoner criterion $N(E_f)J > 1$. The similarity between slab and SL is due to the small Fe-Cu interaction,

$$\varepsilon_d^{Fe} - \varepsilon_d^{Cu} = 2.32 \text{ eV} \gg dd\sigma^{Fe-Cu} = 0.53 \text{ eV}$$

To calculate the free-standing slab we use the same model but to account properly for the electron spill over we add a layer of s-type orbitals (s') at each side of the slab as explained in [15].

Finally we have studied the superlattice 3Fe/3Cu, allowing the system to develop antiferromagnetic order between planes. We also studied the 3Fe free-standing slab in the same conditions to compare with the SL. However, as in [15], instead of considering the Madelung correction in the slab case, we have shifted the site energies of the extra s'

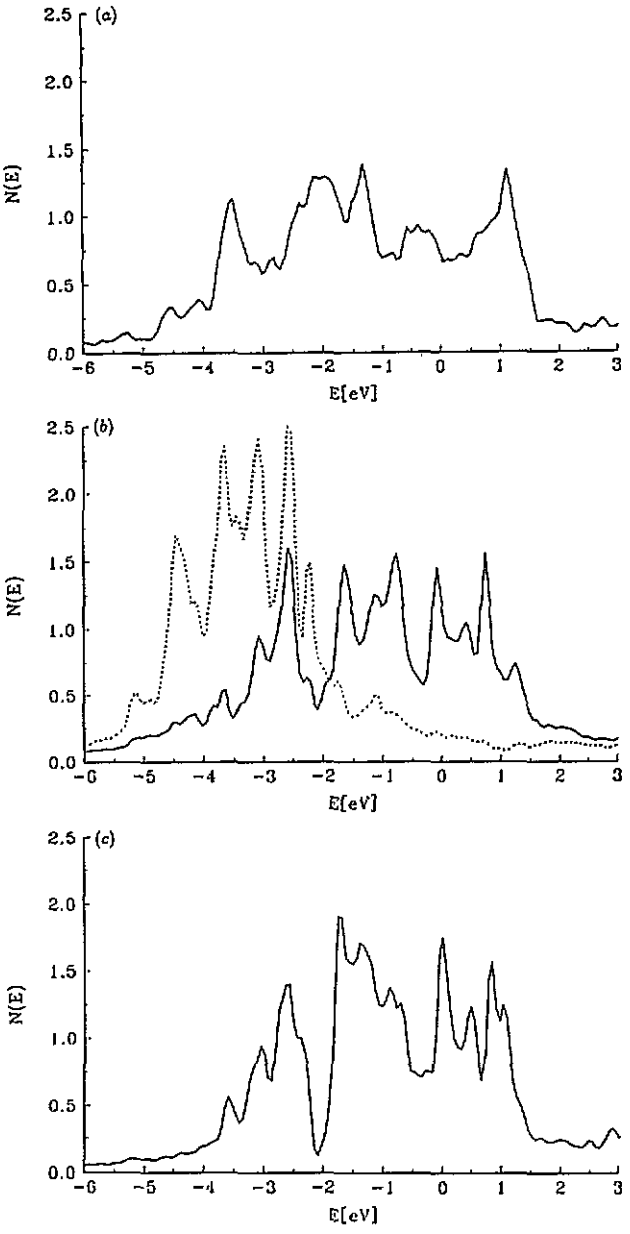

Figure 3. Densities of states per spin of the paramagnetic phases for *(a)* FCC Fe, *(b)* 2Fe/2Cu SL (full line: Fe, dotted line: Cu) and *(c)* 2Fe free-standing slab. Energies are referred to the Fermi level.

orbitals and the surface Fe orbitals by an amount equal to the difference between the Fermi levels of bulk FCC Fe and the bilayer. This simplifies the calculation and gives the same qualitative effect.

In table 2 we give the results for 2Fe/2Cu and 3Fe/3Cu superlattices and compare with those for the 2Fe and 3Fe slabs for J_0. The magnetic moments at the interfaces confirm quantitatively the similarity with the free-standing slabs, that is, the effect of low

Table 2. Charge transfers, magnetizations (μ_B) and total energies per Fe atom (eV) for 2Fe/2Cu, 3Fe/3Cu superlattices and 2Fe, 3Fe slabs for $J = J_0$. $\Delta E_T = E_T(\text{phase}) E_T(\text{para})$, Δn is the total occupation difference per layer with respect to the bulk paramagnetic value and Δn_d the corresponding difference for d orbitals only. S and I indicate surface and interface layers respectively.

System	Phase	ΔE_T	layer	Δn	Δn_d	M
Slab 2Fe	Para	0	s'	0.41		
			Fe	−0.41	−0.15	
	Ferro	−0.27	s'	0.42		−0.04
			Fe	−0.42	−0.12	2.88
2Fe/2Cu	Para	0	Cu	0.08	−0.05	
			Fe	−0.08	0.00	
	Ferro	−0.05	Cu	0.10	−0.03	0.00
			Fe	−0.10	−0.01	2.59
Slab 3Fe	Para	0	s'	0.41		
			Fe_S	−0.40	−0.11	
			Fe_{S-1}	−0.03	−0.01	
	Ferro	−0.20	s'	0.41		−0.03
			Fe_S	−0.44	−0.15	2.93
			Fe_{S-1}	0.06	0.07	2.44
	Ferri	−0.32	s'	0.43		−0.04
			Fe_S	−0.42	−0.14	2.64
			Fe_{S-1}	−0.02	0.01	−1.93
3Fe/3Cu	Para	0	Cu_I	0.07	−0.04	
			Fe_I	−0.13	−0.03	
			Fe_{I-1}	0.11	0.08	
	Ferro	−0.07	Cu_I	0.14	−0.01	0.00
			Fe_I	−0.35	−0.20	2.83
			Fe_{I-1}	0.41	0.31	2.09
	Ferri	−0.10	Cu_I	0.15	−0.01	0.01
			Fe_I	−0.31	−0.18	2.56
			Fe_{I-1}	0.33	0.24	−1.39

dimensionality inferred earlier. We see that the effect of Cu is to slightly reduce the value of the magnetic moment in the Fe layers with respect to the ones they would have in the corresponding free standing slab, as other authors have mentioned before [16, 17].

Even when the magnetic moments are very similar in the superlattices and in the slabs the energy differences between the magnetic solutions and the paramagnetic ones are smaller in the SL as a consequence of the positive energy contributions of sp Fe and Cu bands.

For the 3Fe/3Cu SL there exist three solutions (paramagnetic, ferromagnetic and ferrimagnetic), the ferromagnetic solution gives a high average magnetization ($2.58\mu_B$), much higher than the experimentally measured one. The antiferromagnetic solution gives an average magnetization of $1.24\mu_B$ comparable to the $0.88\mu_B$ extrapolated for $T = 0$ in [6] from magnetic measurements of a 3Fe/9Cu SL. In order to make this comparison, we verified that the number of Cu layers does not play an important role, by performing calculations for 2Fe/2Cu, 2Fe/4Cu and 2Fe/6Cu SL.

We have also calculated this SL for a smaller value of $J = 1$ eV which also gives a bulk magnetization value for BCC Fe compatible with experience and is closer to calculated values of J in the literature. There is no ferromagnetic solution in this case but the ferrimagnetic one persists and the average magnetization is $0.66\mu_B$, also comparable with experience.

Concerning charge transfers, we see a spill over of $0.4e$ in the free surfaces of the

slabs. In the superlattices the sp Cu orbitals receive a smaller charge of around 0.1e from Fe interface layers and there are charge oscillations inside the Fe slab. These are a consequence of the Madelung term and depend on the chosen value for the Madelung parameters, however the magnetizations are almost independent of these parameters. Charge oscillations are not present in the free-standing slab due to the simplified method used in the calculation.

We therefore conclude that the Fe/Cu superlattices allow the observation of low-dimensional FCC Fe magnetism, due to the small interaction between Fe and Cu. Magnetic solutions appear in our calculations for a reasonable range of values of J, but the energy differences between different magnetic states is very small. It is therefore understandable that small variations in the experimental conditions such as temperature may change the magnetic state.

References

[1] See for example,
Falicov L M *et al* 1990 *J. Mater. Res.* **5** 89
[2] Rau C , Schneider C , Xing G and Jamison K 1986 *Phys. Rev. Lett.* **57** 3221
[3] Macedo W A A and Keune W 1988 *Phys. Rev. Lett.* **61** 475
[4] Magnan H, Chandresis D, Villette B, Heckmann O and Lecante J 1991 *Phys. Rev. Lett.* **67** 859
[5] Tian D, Jona F and Marcus P M 1992 *Phys. Rev.* **45** 11216
[6] Cheng S F, Mansour A N, Teter J P, Hathaway K B and Kabacoff L T 1993 *Phys. Rev.* B **47** 206
[7] Moruzzi V L, Marcus P M, Schwarz K and Mohn P 1986 *Phys. Rev.* B **34** 1784
[8] Krasko G L 1987 *Phys. Rev.* B **36** 8565
[9] Moruzzi V L, Marcus P M and Kübler J 1989 *Phys. Rev.* B **39** 6957
[10] Haglund J 1993 *Phys. Rev.* B **47** 566
[11] Fabricius G, Llois A M and Weissmann M 1991 *Phys. Rev.* B **44** 6870
[12] Andersen O K, Jepsen O and Glötzel D 1985 *Highlights of Condensed Matter Theory* ed F Basani, F Fumi and M P Tosi (Amsterdam: North Holland) p59
[13] Bandyopadhyay T and Sarma D D 1989 *Phys. Rev.* B **39** 3517
[14] Fu C L and Ho K M 1982 *Phys. Rev.* B **28** 5480
[15] Fabricius G, Llois A M, Weissmann M and Khan A 1994 *Phys. Rev.* B **49** 2121
[16] Fu C L and Freeman A J 1987 *Phys. Rev.* B **35** 925
[17] Fernando G W and Cooper B R 1988 *Phys. Rev.* B **38** 3016