Ferromagnetism in FeCu metastable alloys

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We present linearized augmented-plane-wave calculations for FeCu fcc and bcc metastable phases using the local-density approximation (LDA) as well as the local-spin-density approximation (LSDA). The nonpolarized density of states calculated within the framework of LDA together with the reformulated Stoner theory provide results in excellent agreement with those obtained from LSDA calculations. The magnetization is calculated for several alloy compositions—the magnetic moment per Fe atom is almost constant over a wide range of Fe content—in good agreement with recent experiments.

In the last few years, the preparation of metastable phases of fcc and bcc Fe-Cu alloys has been possible by mechanical alloying[1-3] as well as sputtering.[4,5] Both techniques have provided new perspectives of understanding mechanisms for producing magnetism as well as for growing new magnetic materials. However, the magnetic properties of these new metastable alloyed phases present singular features which are far from a whole explanation, and represent a research field in which an intensive work remains to be done. In particular, Chien *et al.*[4] have shown that the fcc phase can be grown by sputtering when the Fe fraction is smaller than 60%, while the bcc phase appears for Fe contents higher than 70%. At intermediate compositions both phases coexist. Uenishi *et al.*[2] and Sumiyama, Yoshitake, and Nakamura[6] have shown that the magnetic moment per Fe atom keeps a high value ($\sim 2.2\mu_B$) in a wide range of Fe content ($\geq 50\%$), but it falls to zero when the Fe fraction is below 20%. Also, recent magnetic measurements by Crespo and co-workers[7,8] on the fcc $Fe_{51}Cu_{49}$ samples have shown that this phase presents a wide variety of magnetic behaviors at several stages in the decomposition process by thermal treatments as well as the possible appearance of fcc Fe after spinodal decomposition. The aim of the present work is to shed some light on one of the features of these systems: the high magnetic moment found in bcc and fcc FeCu phases.

In order to analyze the magnetic behavior of these FeCu alloys, we have performed all-electron linearized augmented-plane-wave (LAPW) calculations of band structures and density of states (DOS) for Fe_xCu_{100-x} ordered alloys in both bcc and fcc phases and for some specific Fe concentrations x. The main part of the calculations were carried out by using the Soler-Williams[9] implementation of the APW method in its linearized version.[10] These calculations were performed within the framework of the local-density approximation[11] (LDA) and therefore we were not able to deal explicitly with spin-polarization effects, so that no exchange splittings or magnetic moments were obtained. However, the nonpolarized DOS can be correlated to the exchange splittings and magnetic moments through the Stoner theory.[12,13] In some specific cases, and in order to verify the validity of the previous approach (LDA calculations plus Stoner model), we have performed LAPW calculations by using a different program,[14] which includes the local-spin-density approximation[15] (LSDA), and therefore provides directly information about the magnetic features of the system.

Due to the repeated supercell scheme featuring the LAPW calculations, the simulation of bcc and fcc Fe_xCu_{100-x} ordered alloys involves serious difficulties when intermediate Fe fractions x are involved, since there is a huge number of nonequivalent atomic positions, turning a detailed description of the alloy structure into an unaffordable task. At this point a simplification is done by restricting ourselves to the study of five concentrations ($x=0$, 25, 50, 75, 100) for which there exist very simple ordered representations involving few atoms. In this way, the study of bcc and fcc phases has been carried out with small unit cells containing four atoms, reducing as much as possible the calculation resources. We used the same muffin-tin radii for both Fe and Cu species, $R_{\rm mt}=2.30$ a.u., and a plane-wave energy cutoff of $T_{\rm max}=10.0$ Ry has been considered in all the cases. Sampling grids ranging from 56 to 126 special points in the irreducible wedge of the Brillouin zone are used for the study of bcc and fcc structures. In order to test the validity of this set of parameters, we have calculated in the LD approximation the pure bcc Fe using the experimental lattice constant. We obtained a cohesive energy of 5.8 eV per atom and a density of states at the Fermi level of DOS $(E_F)=3.4$ states/eV per atom. Both quantities are in agreement with previous results of Moruzzi, Janak, and Williams.[16] After determining the DOS, we have included the polarization of the electrons using the Stoner scheme[12] by shifting rigidly the two half bands (up and down) a relative magnetic exchange energy of 2.2 eV, previously computed[16] within the LSDA. Once this rigid shift is applied, we have obtained a magnetic moment of $2.25\mu_B$ per atom which agrees well with the $2.15\text{-}\mu_B$ LSD result. Hence, this confirms that our calculated band structure describes the crucial features of the system and that can be applied to the description of our set of period-

ic Fe_xCu_{100-x} alloys. All the calculations for the fcc phase compounds were done assuming that the lattice constant a is identical to that of fcc Cu ($a=6.82$ a.u.), whereas for bcc phase compounds we took the bcc Fe lattice constant ($a=5.42$ a.u.), being both values very close to those found experimentally in Fe_xCu_{100-x} systems.[4]

In Figs. 1 and 2 we show the DOS for the Fe_xCu_{100-x} alloys in bcc and fcc phases, respectively, obtained from the nonpolarized LAPW calculations. Looking at the bcc series (Fig. 1), we notice that when bcc Fe samples are doped with Cu, the d-character peak close to the Fermi level diminishes and the bottom of the band suffers strong modifications due to the appearance of Cu deeper levels. For bcc $Fe_{50}Cu_{50}$ [Fig. 1(c)] two different atom arrangements were taken into consideration, showing a very different DOS profile, although the values of the DOS at E_F were similar. The situation in the fcc case (Fig. 2) is different. When the fcc Cu sample is doped with Fe, a strong peak corresponding to Fe states is developed near the Fermi level. The more surprising characteristic is that for the fcc compounds $Fe_{50}Cu_{50}$ and $Fe_{75}Cu_{25}$ the DOS at E_F presents a value higher than that calculated for fcc Fe. Furthermore, in the case of $Fe_{75}Cu_{25}$ the DOS at E_F is even larger than the value found for the pure bcc Fe. We have checked the influence of possible lattice constant changes for the case $x=75$, since for such Fe content an increase of 4% in the sample volume has been reported.[4] In both phases, bcc and fcc, a similar change in the volume per atom lead to an increase smaller than 3% in the DOS at E_F. Therefore, these small volume changes do not represent a large variation in the DOS near E_F, and they do not imply any qualitative change in the magnetic behavior we will discuss below.

Once the DOS curves have been evaluated, we will apply the Stoner model of ferromagnetism to our results, taking into account the recent generalization of this model.[17,18] Following this theory, the change in energy $\Delta E(m)$ when forming a ferromagnetic state with magnetic moment m is given by the sum of kinetic and exchange energy contributions[17]

$$\Delta E(m)=\frac{1}{2}\int_0^m \frac{\bar{m}}{\bar{N}(\bar{m},V)}d\bar{m}-\frac{1}{4}I_S m^2 , \tag{1}$$

where I_S is the so called generalized Stoner parameter,[19] and $\bar{N}(m,V)$ is the paramagnetic density of states averaged between the Fermi levels of spin-up $[E_F^u(m)]$ and spin-down $[E_F^d(m)]$ electrons corresponding to a system with magnetic moment m and a unit-cell volume V. $\bar{N}(m,V)$ can be evaluated according to

$$\bar{N}(m,V)=m/[E_F^u(m)-E_F^d(m)] . \tag{2}$$

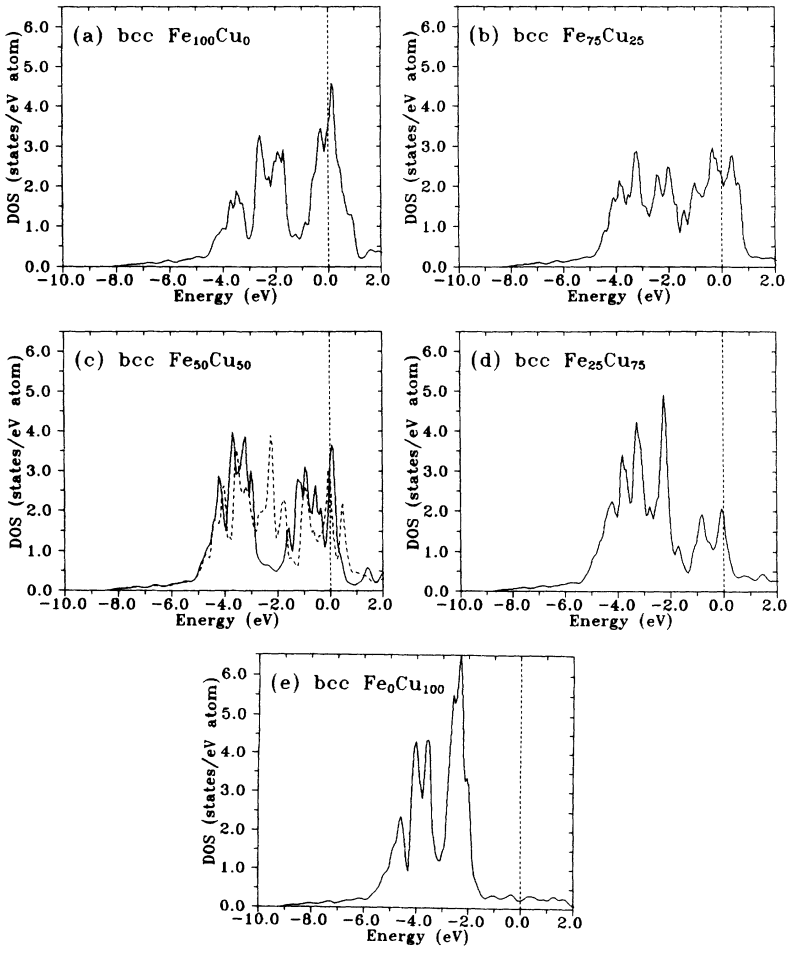

FIG. 1. Nonpolarized density of states (DOS) for bcc Fe_xCu_{100-x} alloys for $x=0$ (a), 25 (b), 50 (c), 75 (d), and 100 (e).

The Fermi levels $E_F^u(m)$ and $E_F^d(m)$ are determined from the nonpolarized density of states $N(E)$ through the equality

$$\int_{E_F}^{E_F^u(m)} N(E)dE = \int_{E_F^d(m)}^{E_F} N(E)dE = m/2 \ , \tag{3}$$

where E_F is the Fermi level for the nonpolarized (paramagnetic) system. If the relation

$$I_S\bar{N}(0,V) \geq 1 \tag{4}$$

is satisfied, then the nonmagnetic phase is not stable and a ferromagnetic state is formed.[17] The magnetic moment corresponding to this state is evaluated from the condition

$$I_S\bar{N}(m,V)=1 \ . \tag{5}$$

In principle, the Stoner constant I_S can be found in terms of a nonmagnetic system from the linear-response theory,[20] however, we have considered for Fe systems the value $I_S=0.068$ Ry obtained from different calculations.[17,18,20] Furthermore, we know that the Stoner constant is insensitive to changes in the unit-cell volume V and its value for Fe is only slightly influenced by the chemical environment.[18] Using Eqs. (1)-(5), we have determined if the Fe_xCu_{100-x} systems we have considered satisfy the Stoner criterion for ferromagnetism.

TABLE I. Magnetization of bcc and fcc Fe_xCu_{100-x} metastables alloys as a function of the Fe content. Nonmagnetic phases are labeled N.M.

	Magnetic moment per Fe atom (μ_B)	
Fe content at. %	bcc	fcc
0	N.M.	N.M.
25	N.M.	N.M.
50	2.10	2.18
75	2.32	2.30
100	2.30	2.42

In Fig. 3, we plot the value $I_S\bar{N}(0,V)$ as a function of Fe content for bcc and fcc systems. The results show that all the systems with $x \geq 50$ tend to develop a ferromagnetic state in both bcc and fcc phases. By applying Eq. (5) to the systems which tend to form such ferromagnetic state, we have determined their magnetic moments. Table I summarizes the values for the magnetic moment per Fe atom, noticing that in a wide range of Fe content, the Fe atom keeps a high value for this magnitude. For pure fcc Fe, these calculations are in agreement with previous results[17,18] in which the presence of a high-spin state for fcc Fe was reported (for the lattice constant we have studied). At this point we must emphasize that our calcula-

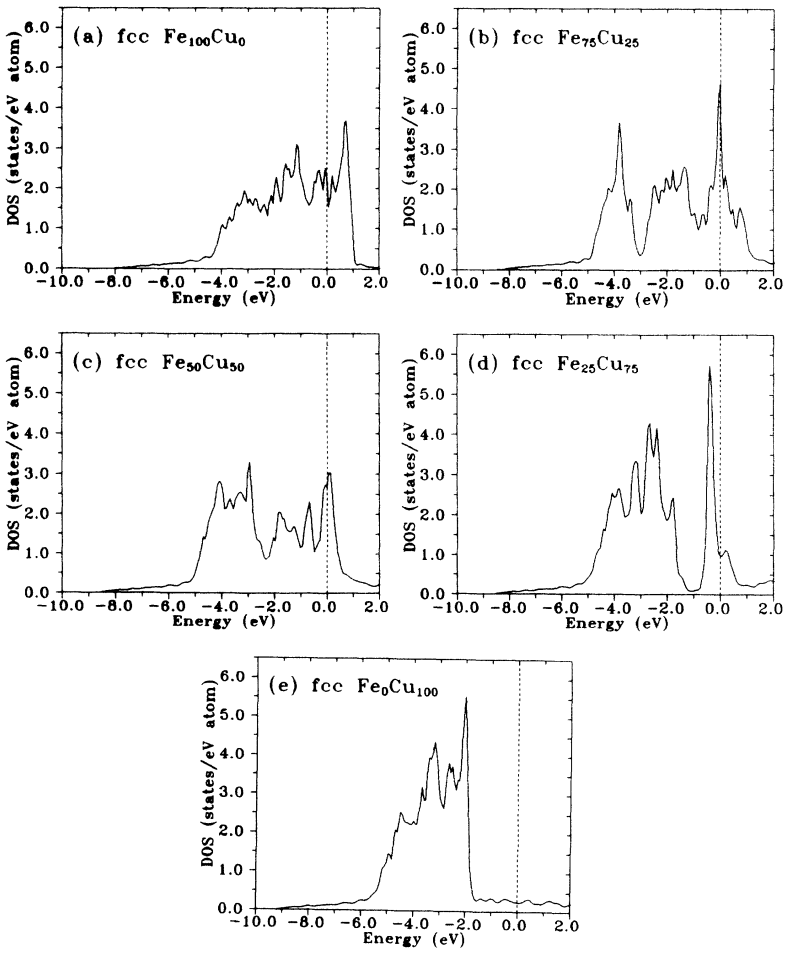

FIG. 2. Nonpolarized density of states (DOS) for fcc Fe_xCu_{100-x} alloys for $x=0$ (a), 25 (b), 50 (c), 75 (d), and 100 (e).

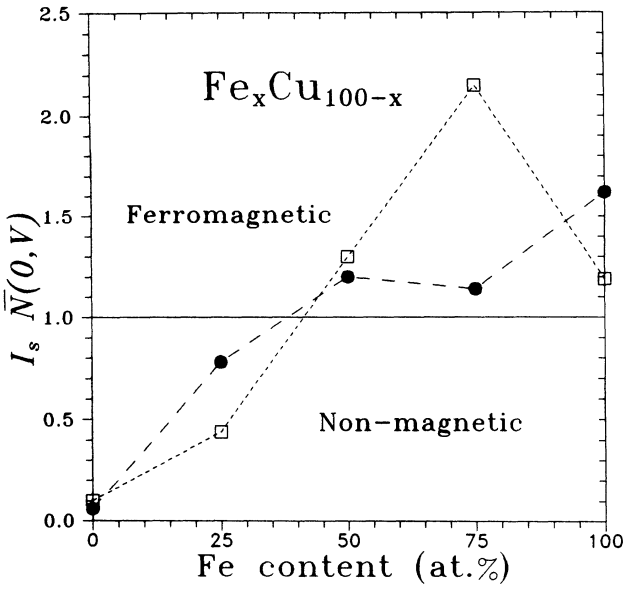

FIG. 3. $I_S\bar{N}(0,V)$ *versus* Fe content for bcc (black circles) and fcc (open squares) Fe_xCu_{100-x} systems. Lines connecting points are a guide for the eye. The horizontal line represent the cutoff frontier $[I_S\bar{N}(0,V)=1]$ between ferromagnetic and nonmagnetic behavior.

tions do not consider the possibility of antiferromagnetism, and, however, the calculated fcc Fe ground state has an antiferromagnetic structure.[21,22] A deeper analysis of this fact is out of the scope of the present work, and it does not impede discussing the experimental data, since at high Fe concentrations the FeCu system becomes bcc.

In order to verify the results concerning the fcc phase, we have performed preliminary LAPW (Ref. 14) studies for $Fe_{25}Cu_{75}$ and $Fe_{75}Cu_{25}$ within the LSDA. In these calculations we used the exchange-correlation potential of von Barth and Hedin[15] in the parametrization given by Moruzzi, Janak, and Williams.[16] We have found that the $Fe_{25}Cu_{75}$ configuration does not develop ferromagnetism and that, on the contrary, the $Fe_{75}Cu_{25}$ structure presents a ferromagnetic behavior. Figure 4(a) represents the total-energy curve as a function of the volume per atom for fcc $Fe_{75}Cu_{25}$. This curve shows that the experimental lattice constant we have used in our nonpolarized calculations (6.82 a.u.) is 3% higher than the LSDA equilibrium lattice constant (6.62 a.u.). In Fig. 4(b) we show the magnetic moment per Fe atom obtained from the polarized calculation. For the lattice constant we have taken into account that we get a magnetic moment per Fe atom of $2.30\mu_B$, in good agreement with the result we obtained from the application of the Stoner criterion to the nonpolarized system. Also, in this case we calculated directly an exchange splitting of 2.16 eV, which in combination with the magnetic moment previously shown gives a Stoner exchange constant of $I_S=0.069$ Ry, in excellent agreement with the value used above. This shows that the Fe Stoner constant does not depend dramatically on the Fe surrounding and that the Stoner criterion leads to the right results of comparable goodness to that found within LSDA calculations.

Although we have calculated the magnetic moment associated with several fcc and bcc FeCu configurations, our results do not take into account the alloy random character. We can incorporate the effect of randomness into the alloy composition by assuming that the lattice positions are to be occupied following a Poisson distribution which is dependent on the iron content of the alloy. This means that for a given average concentration x, it is possible to find small regions with different stoichiometric composition with a probability given by the corresponding Poisson distribution, and, furthermore, the magnetization of these small regions can be evaluated by interpolating from the results obtained for the representatives we have chosen for $x=0$, 25, 50, 75, 100 ordered alloys. Figure 5 summarizes the results for the magnetic moment of the Fe_xCu_{100-x} random alloys. Our main result is that the magnetic moment per Fe atom is almost in-

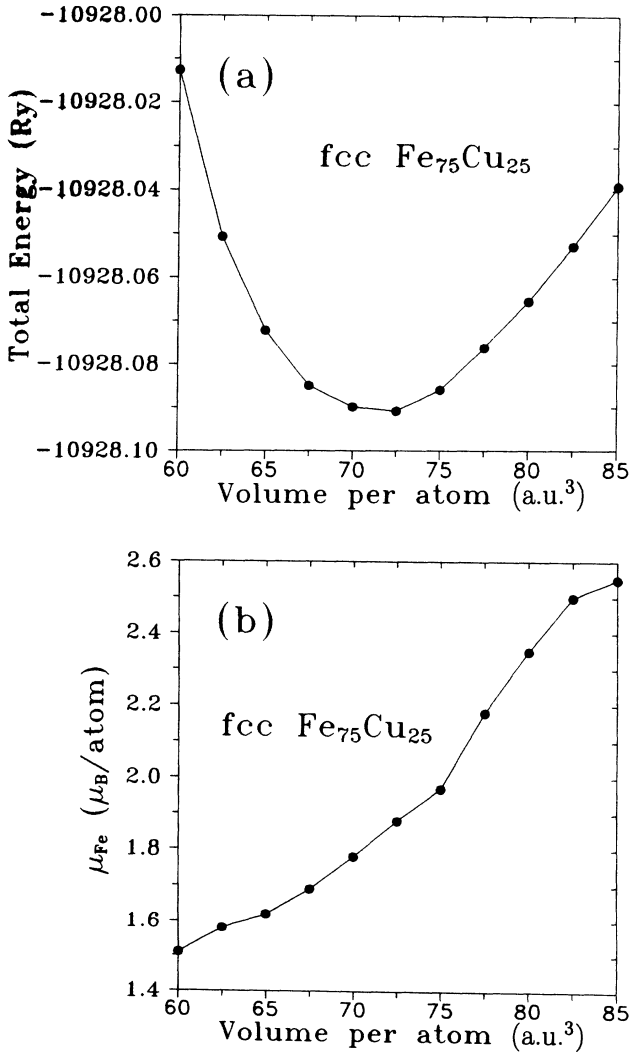

FIG. 4. (a) Total energy and (b) magnetic moment per Fe atom *versus* volume per atom for the $Fe_{75}Cu_{25}$ ordered alloy obtained from LSDA calculations (Ref. 14).

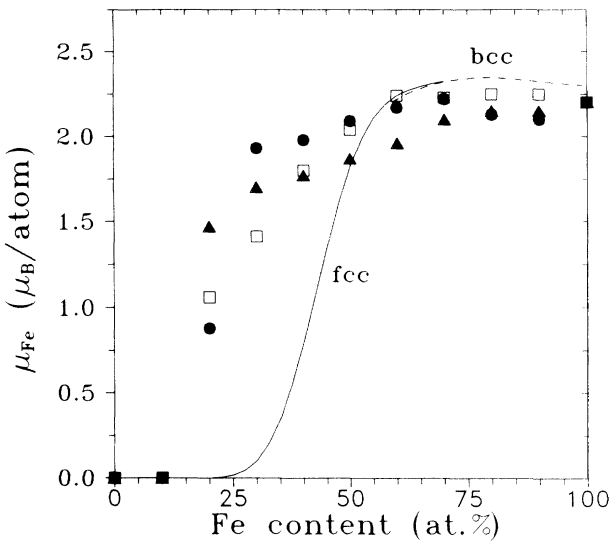

FIG. 5. Magnetic moment per Fe atom (μ_{Fe}) for bcc (dashed lines) and fcc (solid lines) Fe_xCu_{100-x} as a function of Fe content. Symbols denote experimental data (black dots from Ref. 2, triangles from Ref. 4, and squares from Ref. 6).

dependent of the Fe richness for a wide range of Fe content (up to 50%), in both bcc and fcc phases, in good agreement with different experiments.[2,4,6] However, within the region $x \leq 50\%$ the agreement is not so good, this being probably due to the bad representation we have account for alloys in which the Fe content is very low. At this point we should note that an isolated Fe atom into a fcc Cu sample presents a local magnetic moment close to $2.3\mu_B$ (with an exchange splitting close to 1.5 eV),[23] thus being possible that the formation of small Fe clusters at low Fe content (due to local fluctuations of Fe concentration) leads to magnetized samples whereas our calculation drastically cuts such a possibility due to the simple representation we have taken into account for $x = 25$. In order to increase the accuracy of our results at low Fe concentrations, more detailed calculations involving more complex structures are in progress.[24]

In conclusion, we have shown that the FeCu metastable alloys are magnetic in a wide range of Fe content ($x \geq 50$) even in the fcc phase formed below 70% Fe content. Furthermore we have estimated that the magnetic moment per Fe atom keeps a high value similar to that of pure bcc Fe within such concentration range. Although the approximations we used seem to be very simple (LDA calculation, Stoner criteria, mixing of magnetic moments through a Poisson distribution) we believe that the basic feature characterizing the magnetic structure relies on the high density of states at the Fermi level of the nonpolarized systems notices for some specific cases ($Fe_{75}Cu_{25}$ and $Fe_{50}Cu_{50}$). At the same time, the generalized Stoner model has been tested by comparing its results to LSDA calculations, obtaining a good agreement between these two different approaches. Although our results show good agreement with experimental data, more detailed and costly studies involving more configurations as well as magnetovolume effects have to be performed in order to cover the physical phenomena related to these new systems.

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