Ab initio studies on the structural and magnetic properties of FeCu superlattices

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FeCu superlattices with bcc and fcc structures are studied by means of the self-consistent full-potential linearized augmented-plane-wave method under the generalized gradient approximation with full lattice relaxation. By total-energy minimization, the lattice constants in their ground states are determined. The concentration dependences of the volume and moment are discussed, and fairly good agreements are obtained between the theory and the experiment. [S0163-1829(99)13029-7]

FeCu systems have received much attention both experimentally and theoretically. Although neither intermediate phase nor intermetallic compound exists naturally in the equilibrium phase diagram, the metastable and homogeneous alloys of Fe-Cu systems can be formed over the entire range of concentrations by mechanical alloying as well as sputtering.[1,2] It has been reported[1] that the $Fe_{1-x}Cu_x$ alloy has a single bcc phase for $0<x<0.4$, a mixture of bcc and fcc phase for $0.4<x<0.6$, and a single fcc phase for $0.6<x<1.0$, and magnetic properties show very interesting dependence on the concentrations x. One of the phenomena discovered in those systems, i.e., the concentration dependence of the magnetovolume effect, has long been the subject of theoretical researchs. However, due to the difficulties in describing a disordered system within the framework of *ab initio* calculations, most previous theoretical calculations have been performed based on some empirical models.[3]

Most recently, Serena and García[4] studied the magnetism of FeCu metastable alloys by *ab initio* calculations. However, without lattice relaxation in their study, no information can be obtained related to the magnetovolume effect. In this paper, we study the magnetovolume effect in FeCu systems through *ab initio* approach with full lattice relaxation. Following the same ideas proposed by Serena and García in Ref. 4, we choose six ordered systems to simulate the $Fe_{1-x}Cu_x$ alloys with five concentrations: bcc Fe ($x=0$), bcc Fe_3Cu ($x=0.25$), tetragonal B_2- and $L1_0$-ordered superlattices (both for $x=0.5$), $FeCu_3$ with $AuCu_3$ structure ($x=0.75$), and fcc Cu ($x=1$). Although some of those ordered structures do not exist naturally in equilibrium, these hypothetical model structures are used in theoretical calculations, and we will show such simulation is meaningful to the study of magnetovolume effect. On the other hand, a large number of experimental results for Fe/Cu multilayers[5–10] have revealed that the Fe/Cu multilayers may be ordered in fcc-like superlattices when epitaxially grown on Cu(100),[5–9] and in bcc-like superlattices when epitaxially grown on bcc Fe(100).[10] Therefore, present *ab initio* results may also offer more information on such experiments.

All the calculations reported in this paper are performed by using the self-consistent full-potential linearized augmented-plane-wave (FLAPW) method[11] under the generalized gradient approximation (GGA) in a scalar relativistic version without spin-orbit coupling. The lattice structure is treated as a simple *cubic* supercell, and the muffin-tin radii of Cu and Fe are set equal and in contact. Within the muffin-tin spheres, lattice harmonics with angular momentum l up 8 are used to expand the charge density, the potential, and the wave functions. The Brillouin-zone sampling is performed using $40\sim156$ special k points in the irreducible Brillouin zone. The energy cutoff constant $R_{MT}K_{max}=8.0$ is fixed[12] in the present numerical calculations. We have adopted the Perdew *et al.* exchange-correlation functionals[13] in the GGA calculations, and also the Perdew-Wang exchange-correlation functionals[14] for the local spin-density approximation (LSDA) calculations for comparison. Since GGA gives more accurate lattice constant than LSDA compared to the experimental data of bcc Fe and fcc Cu (see Table I), in the studies reported below, GGA is adopted throughout for all systems.

In order to find the ground-state spin configurations and the equilibrium volumes of these systems, the total energies are calculated as the functions of the volume in paramagnetic (PM), antiferromagnetic (AF), and ferromagnetic (FM) states. It is found that the most stable magnetic states are

TABLE I. Calculated equilibrium lattice constants a (Å), and magnetic moments $M(\mu_B)$, for bcc Fe, Fe_3Cu, FeCu and fcc FeCu, $FeCu_3$, Cu ordered systems obtained with GGA or LSDA.

System	Method	State	a(Å)	$M(\mu_B)$
bcc Fe	LSDA	FM	2.768	2.09
	GGA	FM	2.843	2.20
	Expt.	FM	2.866	2.22
bcc Fe_3Cu	GGA	FM	2.888	2.43
bcc FeCu	GGA	FM	2.900	2.62
fcc FeCu	GGA	FM	3.637	2.67
fcc $FeCu_3$	GGA	FM	3.631	2.72
fcc Cu	LSDA		3.524	
	GGA		3.616	
	Expt.		3.615	

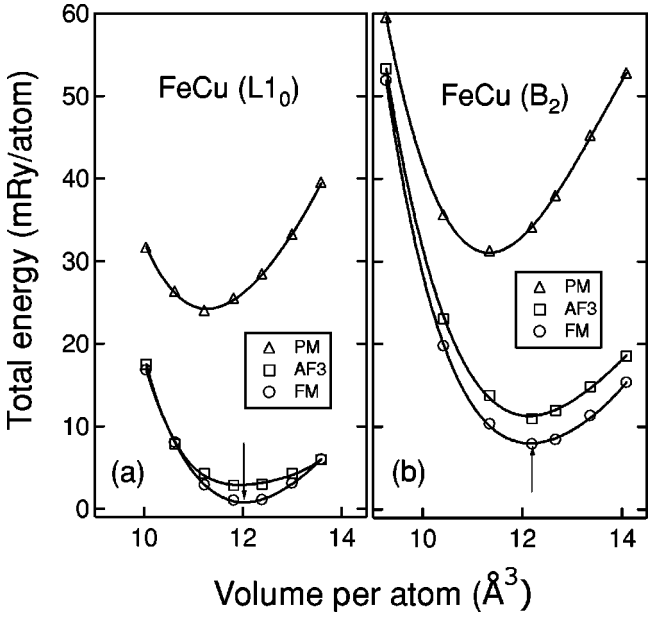

FIG. 1. Total energy as a function of atomic volume in the paramagnetic (PM), ferromagnetic (FM), and antiferromagnetic (AF3) states: (a) for the $L1_0$ FeCu alloy; (b) for the B_2 FeCu alloy. Arrows indicate the equilibrium volumes.

FM. As an example, the calculated total energies are shown in Fig. 1 as the functions of atomic volume in the PM, AF3 (i.e., the case of interlayer AF coupling), and FM state[15] for $L1_0$- and B_2-ordered superlattices, respectively. It is noted that according to the present calculation, the $L1_0$ structure is energetically more stable than the B_2 one with 8-mRy energy difference per atom. This has been confirmed experimentally where $Fe_{50}Cu_{50}$ alloy favors the fcc structure,[2] and the experimental value of lattice constant 3.639 Å^2 is found very close to our calculated value 3.637 Å (see Table I).

According to the *ab initio* calculations, the ground-state lattice constants and magnetic moments of all the ordered structures considered here are obtained. In Fig. 2, the volumes and moments are then plotted as the functions of the Cu concentration x, where the $Fe_{1-x}Cu_x$ alloy is divided into two phase regions, i.e., bcc one on the Fe-rich side and fcc one on the Cu-rich side. We can see that as x increases, the local moment at Fe site increases from $2.2\mu_B$ of the bcc bulk Fe to $2.72\mu_B$ in fcc $FeCu_3$ superlattice[16] as shown in Fig. 2(a). This is due to the reduced symmetry and loss of magnetic neighbors with increasing x. Both effects usually lead to a narrower $3d$ bandwidth with larger local density of states (DOS) at E_F (see Fig. 3) and hence a larger moment.[17,18] Simultaneously, as shown in Fig. 2(b), the equilibrium volumes of FeCu systems in FM states are expanded compared to corresponding PM states, although the volumes in PM states are almost equal to the averaged values of the bcc Fe (PM) and fcc Cu (dotted line). Moreover, the equilibrium volumes in FM states are further expanded compared to the simple dilute law of $Fe_{1-x}Cu_x$ alloy (dashed line) due to the magnetovolume effect.

Because of the absence of the equilibrium-ordered FeCu alloys, we do not have direct experimental data to compare with. However, we found that the volume dependence of the magnetization energy is almost quantitatively identical for all ferromagnetic structures (see Fig. 4 and the discussion in the next paragraph). This independence provides evidence that the magnetovolume effect is of a short range (even intra-atomic) origin, and shows that a comparison of our calculation with existing data of disordered alloy could be meaningful. The experimental data of $Fe_{1-x}Cu_x$ disordered alloys[1] are thus plotted in Fig. 2 for comparison. It can be clearly seen that over the entire range of concentrations, present *ab initio* results for ordered superlattice are in fairly good agreement with the experimental data for magnetic moments and the equilibrium volumes. The only exception arises for the magnetic moment in fcc region ($0.5<x<1$), where the experimental values are obviously smaller than the present numerical results. This is possible, since in the highly diluted case some Fe atoms or clusters may lose their magnetization in the disordered fcc FeCu alloys[19] due to segregation fluctuation and thermal fluctuation, while the present results are for ordered FeCu alloys, and all Fe atoms possess enhanced moments.

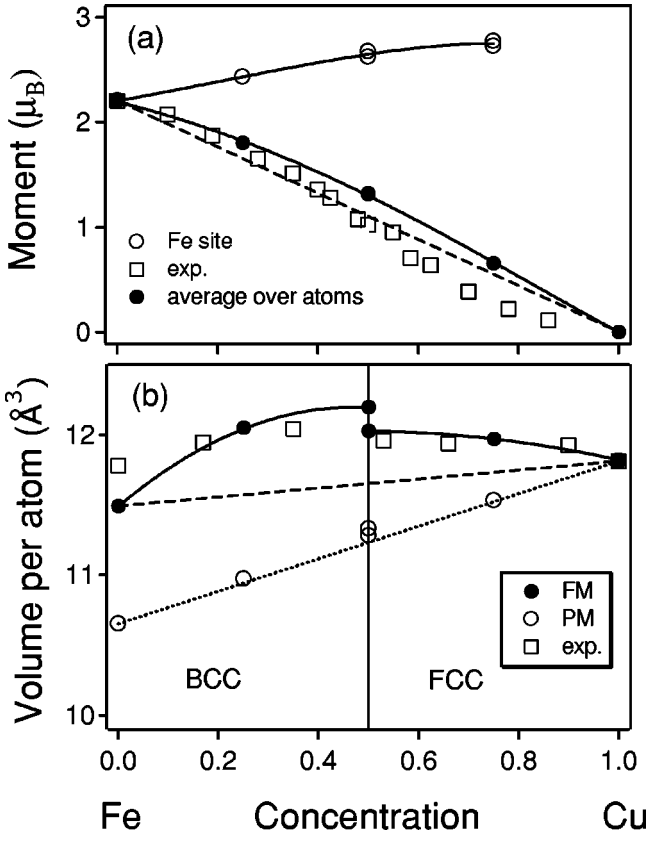

FIG. 2. Concentration dependences of volume and moment for FeCu alloy. □ indicates the experimental data of the FeCu alloy given by Ushida *et al.* (Ref. 1). The dashed line indicates the value estimated by simple dilution law, solid and dotted lines are drawn as a guide to the eyes according to present calculation.

As mentioned above, in Fig. 2(b), the equilibrium volumes of $Fe_{1-x}Cu_x$ systems in PM states coincide with the dilute law (dotted line) fairly well, which means that the volume expansions in the FM state are *essentially* induced by the magnetization effect. In Fig. 4, to clear this point, the volume dependences of the magnetization energy (approximated by $E_{FM}-E_{PM}$) are represented for several systems. We can see that the magnetization energy of Fe are decreasing functions of the volume, so that the magnetic states are more stable than the PM ones with the equilibrium volumes

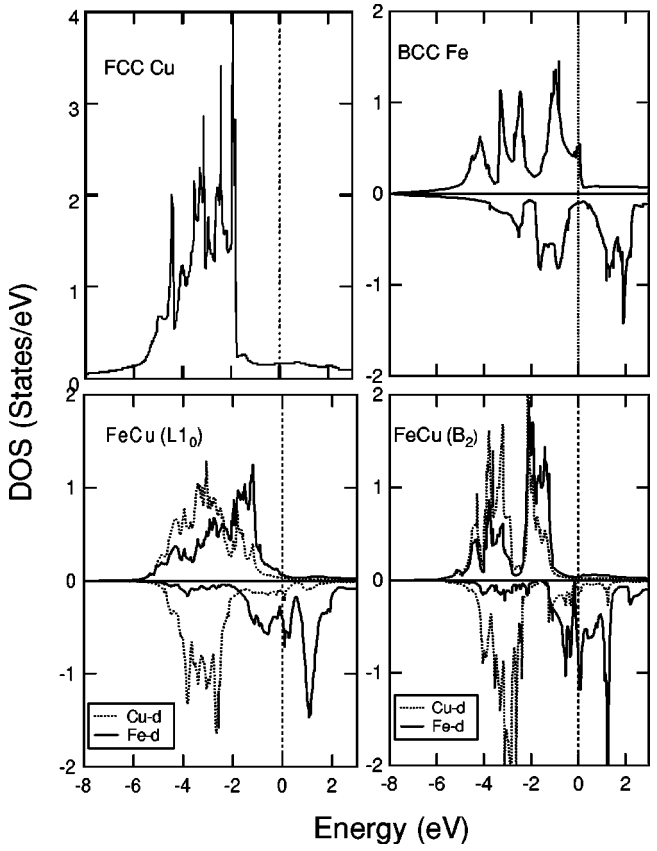

FIG. 3. Total and partial electronic DOS of up spins and down spins for FeCu superlattice, together with fcc Cu and bcc Fe.

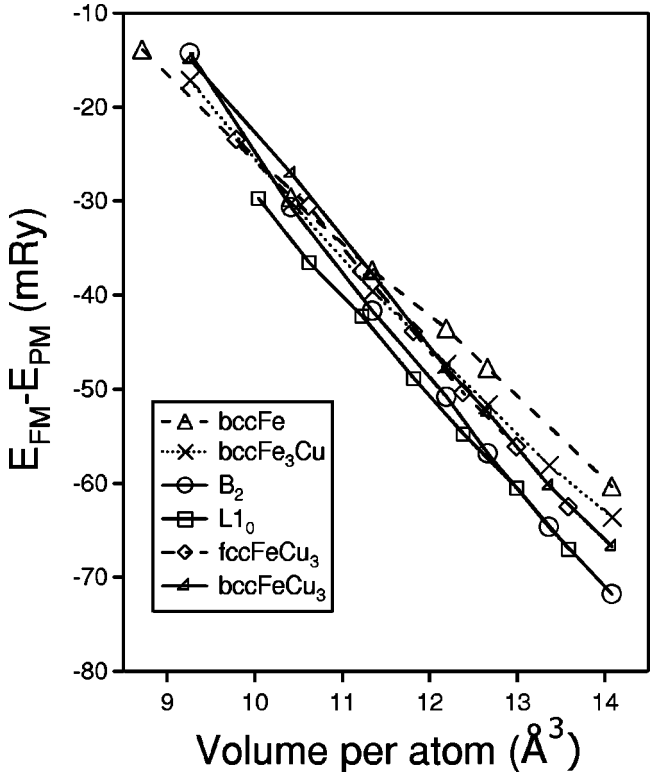

FIG. 4. Calculated magnetization energy per Fe atom as a function of atomic volume.

being expanded compared with those in PM states. The most striking character shown in Fig. 4 is that the magnetization energy exhibits very similar volume dependences for these distinct structures, and the results for fcc and bcc $FeCu_3$,[16] $L1_0$ and B_2 FeCu are almost equal, especially in the large volume region, exhibiting a single atomic behavior. Actually, according to the Ising model that usually works well for such systems,[20] we have $E_{FM}-E_{PM}\simeq E_M-\frac{1}{2}\Sigma_j J_{0,j}$, where E_M is the single-atomic term and $\{J_{0,j}\}$ are the exchange integrals. Since $\{J_{0,j}\}$ are usually only about 1 mRy, the dependence shown in Fig. 4 could be interpreted as, to the first-order approximation, that the magnetization energy only depends on the concentration x and does not depend sensitively on the distributions of the magnetic atoms. It is indicated that the magnetovolume effect is indeed a *local* magnetic effect governed by short-range interactions,[3] so that a comparision between the theoretically *ordered* model systems with experimentally *disordered* alloys on such an effect, if the model systems are selected enough approaching the real system,[21] could be meaningful.

In summary, we have examined the magnetic properties of the ordered $Fe_{1-x}Cu_x$ systems in some special x points ($x=0.25,0.5,0.75$) by using the self-consistent FLAPW method under the GGA with lattice parameter relaxation over a wide range. These superlattices are found to have a ferromagnetic ground state with enhanced moment at Fe site and expanded volume. These theoretical results are discussed in connection with the magnetovolume effect in the Fe-Cu alloy. Good agreement is found between the theoretical results and the experimental results for the Fe-Cu alloy.

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