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Electronic structure and magnetism of Fe–Ge interfaces

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Abstract. The local electronic density of states (LDOS) has been calculated for Fe–Ge(110), Fe–Ge(111) and Fe–Ge(100) interfaces and neighbouring atomic planes using the recursion method. Interface states are found to exist within the mutual gaps of the constituent atoms and strongly depending on the local atomic environments. The most excess LDOSs are found for Fe–Ge(111) interface and the least for Fe–Ge(110). The magnetic moments for Fe atoms are found to decrease when the Fe layer approaches the interface boundary, which is in accord with the experiments. The electron spin polarization parameters evaluated from the LDOS are qualitatively consistent with experimental measurements.

1. Introduction

Metal-semiconductor interfaces continue to be of scientific and technological interest. The properties of the metal–Si interface has been extensively studied owing to its importance in applications. As Ge provides an important alternative to Si and Fe–Ge multilayers can be used as a neutron polarizer and also the narrower energy gap of Ge might result in new characteristics of the metal–Ge interface, the interest of scientists in the study of the Fe–Ge interface properties is obvious.

Pickett and Papaconstantopoulos [1] have calculated the local electronic density of states (LDOS) of the Fe–Ge(110) interface with the parametrized tight-binding method. They used a superlattice atomic model with a unit cell containing 50 atoms. Their results showed that plenty of interface states exist. In the following we shall present our results of electronic structure and magnetism for Fe–Ge(110), Fe–Ge(111) and Fe–Ge(100) interfaces. We use the recursion method developed in [2–4]. We find that the interface states strongly depend on the local atomic environment and that the Fe layer at the interface is not magnetically dead. The Fe layer adjacent to Ge has its magnetic moment decreased by 6–8% compared with the bulk value. The reduction in magnetic moment for the interface Fe arises primarily from the electron transfer from the majority spin band to the minority spin band and the changes in the shape of the Fe LDOS. In addition, we find that the electron spin polarization (ESP) parameters are positive and qualitatively consistent with experiments.

In section 2 of this paper we describe the atomic configuration at the interface and cite the tight-binding parameters from the literature. In section 3 we present the results and discuss them. In section 4 we draw conclusions.

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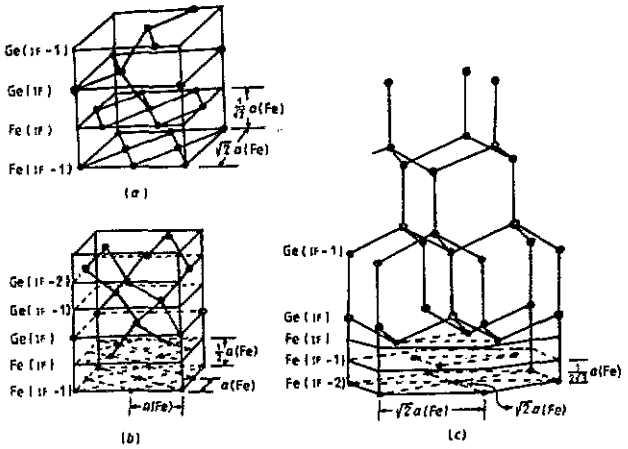

Figure 1. Atomic positions at ideal Fe–Ge interfaces for (*a*) Fe–Ge(110), (*b*) Fe–Ge(100) and (*c*) Fe–Ge(111) intefaces where *a*(Fe) denotes the lattice constant of BCC Fe: ●, Fe; ⊙, Ge.

Table 1. Cluster size and the number of atomic planes.

Interface	Cluster size	Number of Fe layers	Number of Ge layers
Fe–Ge(110)	1078	8	14
Fe–Ge(111)	1008	9	12
Fe–Ge(100)	1015	8	14

2. Interface model and parameters

Assume that the interfaces are ideal and that no relaxation and no reconstruction have taken place (i.e. no movement of atomic planes normal to the interfaces nor parallel to it). The lattice constant of BCC Fe is a_0(Fe) = 2.866 Å, and that of Ge is a_0(Ge) = 5.658 Å; the small (1.3%) lattice mismatch between Fe and Ge is neglected.

Even for the ideal assumption, the registry of the Fe and Ge planes must be assigned. The model suggested in [1] is assumed as follows: Fe atoms will 'bond' with Ge in the usual tetrahedral configuration, i.e. Fe atoms are at positions which Ge atoms would occupy if one more plane of Ge atoms were added to the Ge slab. Fe atoms also occupy the 'interstitial' sites in this layer. Placing Fe atoms at both the diamond lattice sites and its interstitial sites gives the BCC Fe lattice. The interface atomic positions are shown in figure 1.

Table 1 shows the cluster size (in number of atoms) and the number of atomic planes.

The two-centre tight-binding parameters were cited from [1]. In our calculation, 4s and 4p orbitals for Fe atoms are omitted because the main contribution to the electronic density of states (DOS) comes only from its five 3d orbitals. Therefore for the starting state the orbitals of the central atom of the layer considered, i.e. five 3d orbitals xy, yz, zx, $x^2 - y^2$ and $3z^2 - r^2$ for Fe and three 3p orbitals x, y and z and one s orbital for Ge,

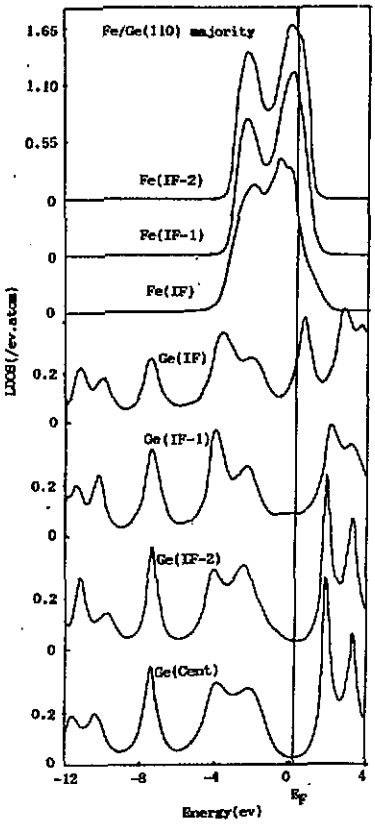

Figure 2. The majority LDOS per atom on several Fe and Ge layers near the Fe–Ge(110) interface.

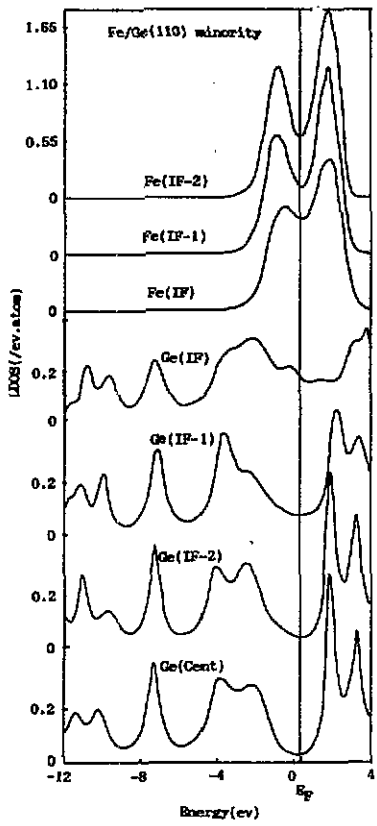

Figure 3. As in figure 2 but for the minority spin.

are taken in consideration. It should be noted that the self-energy parameters were adjusted (for Fe upwards by 0.25 eV and for Ge downwards by 0.25 eV) to keep the central layer of Fe and Ge charge neutrality, respectively, and also to keep the Fermi energy located at the dip of the minority spin which makes the ferromagnetic state of Fe stable [5].

The coefficients a_n and b_n of the continued fraction are calculated up to the fifteenth level; in our experience, calculation beyond this level is not necessary.

The generalized square root termination is adopted for Ge and the quadrature termination is used for Fe. The reason for the latter choice is to search for the main feature of the DOS.

3. Results and discussion

The calculated results of the LDOS of several layers of the Fe–Ge(110) interface for majority spin are shown in figure 2. Fe(IF) signifies the Fe atom at the interface layer and Fe(IF − 1) that at the next below the Fe(IF) layers (see figure 1). The LDOSs of the

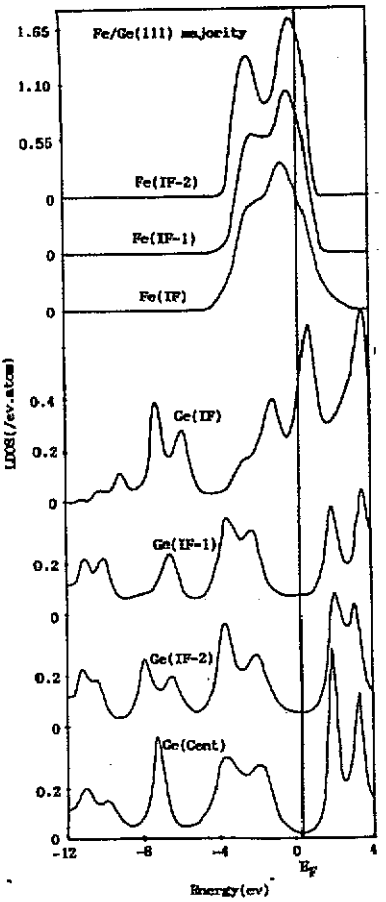

Figure 4. The majority LDOS per atom on several Fe and Ge layers near the Fe–Ge(111) interface.

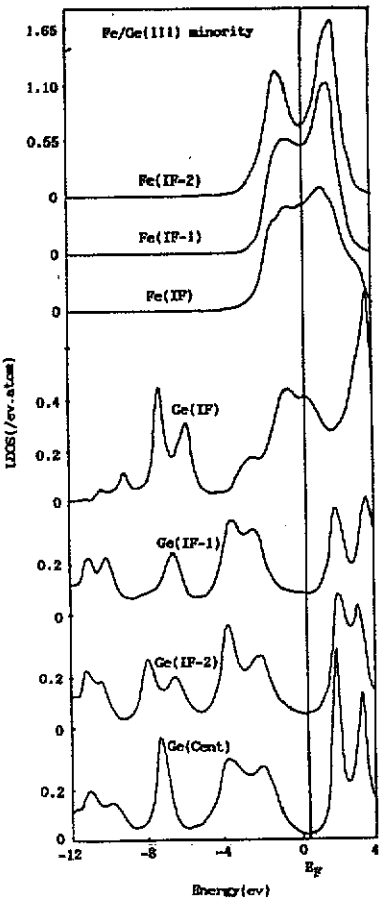

Figure 5. As in figure 4 but for the minority spin.

Fe–Ge(110) interface for minority spin are shown in figure 3. The LDOS of Fe–Ge(111) for majority and minority spin are shown in figures 4 and 5 respectively; those of Fe–Ge(100) are shown in figures 6 and 7 respectively. The vertical lines indicate the positions of the Fermi level E_F.

3.1. Discussions of the results for the Fe–Ge(110) interface for the majority and minority spins

The following characteristics of the LDOS should be noted as the Ge layer goes from the interface to the central layer.

(1) For the majority spin (see figure 2) the LDOS in the central layer is very close to that of bulk Ge (compared with, for example, [6]). Two obvious peaks for Ge(Cent) are located near -7 eV and above E_F, respectively.

(2) The intensities of these two peaks decrease for Ge(IF), and a large excess LDOS (the LDOS exceeding that of the central layer) occurs for Ge(IF) where the fundamental

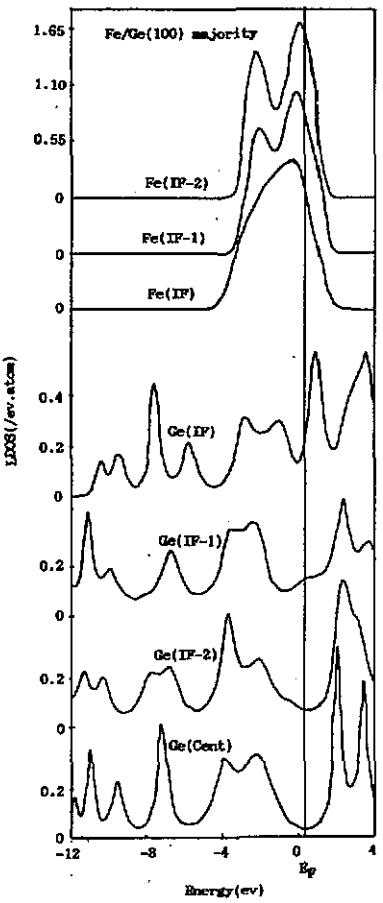

Figure 6. The majority LDOS per atom on several Fe and Ge layers near the Fe–Ge(100) interface.

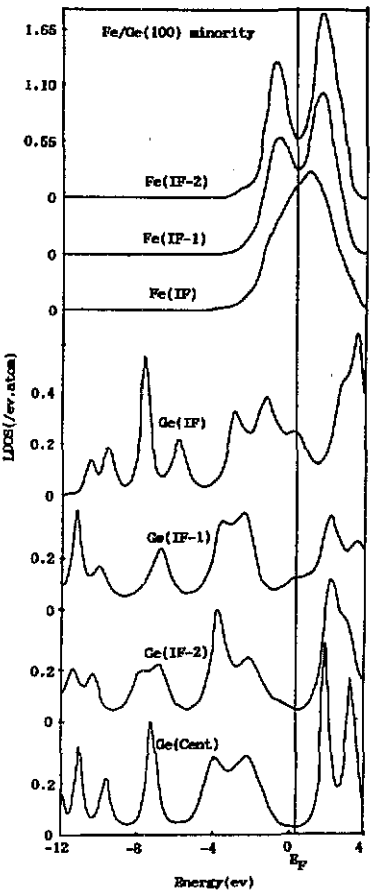

Figure 7. As in figure 6 but for the minority spin.

gap and the conduction band occur for Ge(Cent). The excess LDOS although comparatively small, also exists in other ranges: between −4 and −3 eV, between −9 and −8 eV and between −12 and −11 eV.

(3) For Ge(IF − 1), some excess LDOS occur near E_F, 2.5 eV, −3.5 eV and −11.5 eV.

(4) Less LDOS occurs for Ge(IF − 2) than for the first two Ge layers above, but the excess LDOS near −11 eV for Ge(IF − 2) is more than that for Ge(IF − 1).

(5) The deeper-energy part of the curve for Ge(IF − 1) is similar to that for Ge(Cent), while that for Ge(IF − 2) is different from that for Ge(Cent).

The phenomena above are explained as follows: the reduced symmetry due to existence of interface causes the LDOS of the interface layer to differ from that of the bulk-like central layer. The interaction of the s and p orbitals of Ge with the d orbitals of Fe in the interface layer form bonding atoms. It is commonly observed that at the metal–insulator interfaces there exists 'metal-induced gap states' [7]. The farther the Ge layer is from the interface, the less the excess LDOS is. In other energy ranges the existence of the excess LDOS for the Ge atom is related to the interaction of the atom with the

environment. The similar local environments of Ge(Cent) and Ge(IF − 1) leads to little excess LDOS for Ge(IF − 1) below −6 eV. Although the Ge(IF − 2) layer is farther from the interface than Ge(IF − 1) is, the atomic environment of Ge(IF − 2), which is more similar to Ge(IF) results in more excess LDOS in a deeper-energy range for Ge(IF − 2) in comparison with Ge(IF − 1).

The LDOS of the Fe layers for majority spin shows a typical two-peak structure and has a sharp upper band edge characteristic. The LDOS for the interface Fe(IF) layer differs dramatically from that for the Fe(IF − 2) layer (see figure 2); owing to the reduced symmetry and the interaction with Ge, the characteristic two-peak d-band structure (pseudogap between −1 and −2 eV) is almost lost and the LDOS curve becomes rounded because of the interaction with the Ge conduction band at the interface. In addition, the width of the LDOS of the Fe(IF) layer increases to 1.32 Ryd from 0.60 Ryd for the Fe(IF − 2) layer owing to the Fe–Ge interaction.

For the minority spin there exist common gaps, called the mutual gaps (a pseudogap for Fe), for both the elements within the fundamental gap of Ge (see figure 3). Many interface states appear near E_F and decay more slowly into Ge than into Fe, reflecting the wider band width of sp wavefunctions in contrast with the localized d wavefunctions. In fact, from our calculation, the LDOS for Fe(IF − 2) is nearly the same as for bulk-like Fe(Cent). Similar to the majority-spin case, the LDOS below −6 eV for minority spin on Ge(IF − 1) is analogous to that for Ge(Cent). Except for Ge(IF) the LDOS results for two kinds of spin are similar for each Ge layer and become identical for Ge(Cent). This is because the central layer Ge(Cent) is little influenced by Fe. The curve shapes of the corresponding Fe layers for two kinds of spin are also similar. That for majority spin is easily obtained by a translation of the corresponding minority-spin curve by 1.9 eV or so towards the right except for the band width which in the latter case is somewhat wider.

Comparing the LDOS of the Fe–Ge(110) interface with that in [1], we can see that the band width for Fe is narrower because we omitted the 4s and 4p orbitals for Fe in our calculation. The peak near E_F for minority Ge(IF) is less obvious than that in [1], which may occur for the same reason. The LDOS of the Fe–Ge(110) interface for both majority and minority spins are generally similar to that shown in [1]. The small difference in the details of features is probably caused by the different calculation method and the different cluster size used.

3.2. Comparison of the electronic DOS for three interfaces: Fe–Ge(111), Fe–Ge(100) and Fe–Ge(110)

In figures 4–7 are shown the results of the LDOS for the Fe–Ge(111) and Fe–Ge(100) interfaces for the majority and minority spins. Excess LDOS and interface states near E_F and in other energy ranges are found for Ge(IF) for the majority and minority spins, respectively. The sequence in order of decreasing excess LDOS or interface states is Fe–Ge(111), Fe–Ge(100) and Fe–Ge(110).

If we only consider the Ge surface, the atoms are incompletely coordinated and at least one orbital should be directed outwards from the surface. At the Fe–Ge interface, because of existence of transition-metal atoms with their relatively narrow d band, lobes of Fe atomic orbitals can be considered to be available for bonding with Ge. So Fe atoms at the interface may form a 'bond' with Ge in the usual tetrahedral configuration. There is only one Fe–Ge nearest neighbour for Fe–Ge(110) interface, two for Fe–Ge(100) and three for Fe–Ge(111) (see figure 1). Therefore there are the most excess LDOS or interface states near E_F for Fe–Ge(111), and the least for Fe–Ge(110).

The coordinations of the central-layer Ge atom for the three cases may be unified through transformation of axes and their LDOSs should be very similar. This has really been verified by our calculation except for small differences in the deeper-energy range. The cause lies in the small different total numbers of atoms and the different numbers of atoms along the x, y and z directions far from the central atom, which causes the continued fraction at the high level to be different.

In addition it can be seen from figures 2–7 that, with increasing coordination number of Ge atoms, the pseudogap of the Fe atoms at the interface disappears.

3.3. The distribution of the local magnetic moment near the Fe–Ge interface

The values of the local magnetic moment m of Fe atoms on the ith layer can be calculated with the integrated DOS:

$$m_i = \tfrac{1}{2}\left(\int_{-\infty}^{\infty} f(E)n^+(E)\,\mathrm{d}E - \int_{-\infty}^{\infty} f(E)n^-(E)\,\mathrm{d}E\right) = [N^+(E_F) - N^-(E_F)] \tag{1}$$

where $f(E)$ is the Fermi distribution, n^+ and n^- are the LDOS for the majority and the minority spin, respectively, and $N^+(E_F)$ and $N^-(E_F)$ are the corresponding values integrated up to E_F. The approximate relationship (1) become exact at low temperatures and then N^+ and N^- are the electron occupation numbers. In our calculation of the LDOS for Fe, the contribution of the sp electrons of Fe atoms have been neglected. This is justified as it was pointed out by Kuhnen *et al* [8] that the magnetic moment due to p electron equals merely about 0.5% of that caused by d electrons and the contribution of s electrons is even less.

The local magnetic moment calculated for Fe and Ge layers together with the values of electron occupation number are presented in table 2. For comparison in table 2 are also shown the experimental values of m for α-Fe and hexagonal FeGe compound.

It can be seen in table 2 that there is charge transfer from Fe to Ge (about 0.2 electron) occurring at the interface layer. The charge transfer is in contradiction to related experimental phenomena [11]. This may be caused by the non-self-consistency of the method [2]. As in [1], to eliminate the charge transfer effect, the results can be improved by shifting the Fe self-energy downwards 0.1 eV and the Ge self-energy upwards 0.4 eV at the interface. The results are also shown in table 2.

In an earlier experiment, Lieberman *et al* [12, 13] found the so-called 'magnetic dead layers' at surface for Fe, Co and Ni films. However, further experiments [14, 15] did not support the suggestion of Lieberman *et al*. The LCAO self-consistent calculation by Wang and Freeman [16, 17] and the LAPW calculation by Jepsen *et al* [18] showed that the Ni(001) and Fe(001) surfaces are not magnetically dead. Up to now, experiments have been done on many materials (Fe, Co, Ni and alloys) in different forms [19–21] but yielded inconclusive results.

Our calculation (see table 2) indicates that the Fe interface is not magnetically dead but that there exists a general tendency for the magnetic moment to decrease as the Fe atomic layer approaches the interface. We find a reduction in the Fe magnetic moment at the interface of about 6–8% per atom compared with the Fe(IF − 2) layer which is close to the bulk value. This decreasing tendency is in accordance with the experimental results as pointed out in [1]. In addition, as the Mössbauer experimental hyperfine field is proportional to the magnetic moment of this Mössbauer atom in the first-order approximation, Shinjo [22] found that the hyperfine field of the interface Fe layer of a

Table 2. The electronic numbers (unit charge) and magnetic moments $m(\mu_B)$ of interface atoms before and after shift in the self-energy. The experimental values of $m = 2.21$ for α-Fe and $m = 1.85$ for hexagonal FeGe are taken from [9, 10].

		Unshifted				Shifted			
		IF	IF − 1	IF − 2	Cent	IF	IF − 1	IF − 2	Cent
Fe(110)	$N^+(E_F)$	3.94	4.06	4.06		4.00	4.06	4.07	
Fe(110)	$N^-(E_F)$	1.88	1.96	1.93		1.99	1.97	1.93	
Fe(110)	m	2.06	2.10	2.13		2.01	2.09	2.14	
Ge(110)	$N^+(E_F)$	2.11	2.00	2.00	2.00	1.96	1.98	2.00	2.00
Ge(110)	$N^-(E_F)$	2.15	2.01	2.00	2.00	2.06	2.00	2.00	2.00
Ge(110)	m	−0.04	−0.01	0.00	0.00	−0.10	−0.02	0.00	0.00
Fe(111)	$N^+(E_F)$	3.90	4.08	4.07		3.97	4.08	4.07	
Fe(111)	$N^-(E_F)$	1.91	1.93	1.94		2.02	1.94	1.94	
Fe(111)	m	1.99	2.15	2.13		1.95	2.14	2.13	
Ge(111)	$N^+(E_F)$	2.09	2.02	2.00	2.00	1.92	1.99	2.00	2.00
Ge(111)	$N^-(E_F)$	2.18	2.03	2.00	2.00	2.07	2.02	2.00	2.00
Ge(111)	m	−0.09	−0.01	0.00	0.00	−0.15	−0.03	0.00	0.00
Fe(100)	$N^+(E_F)$	3.95	4.06	4.09		4.01	4.06	4.09	
Fe(100)	$N^-(E_F)$	1.85	1.93	1.92		1.98	1.94	1.92	
Fe(100)	m	2.10	2.13	2.17		2.03	2.12	2.17	
Ge(100)	$N^+(E_F)$	2.08	2.02	2.00	2.00	1.94	1.97	2.00	2.00
Ge(100)	$N^-(E_F)$	2.16	2.04	2.00	2.00	2.05	2.02	2.00	2.00
Ge(100)	m	−0.08	−0.02	0.00	0.00	−0.11	−0.05	0.00	0.00

Fe–Cu film decreased by 10–15% compared with the 'bulk' value which is about 340 kG [23].

After shifting the self-energy of the interface atom we can see there is a small amount of electron transfer from the majority-spin state to the minority-spin state. The interaction between the Fe d band and the Ge conduction band makes the majority d band of Fe(IF) wider and makes the dip in the minority Fe(IF) shallower or lost, which removes some of the occupied states of Fe in the majority band. The electrons removed from the majority-spin band will fill the minority-spin band to keep the layer-by-layer neutrality. Therefore, the magnetic moment of Fe(IF) is reduced.

From figures 2–7, it is shown that the shape of the Fe LDOS at the interface changes dramatically compared with that of Fe(IF − 2) and becomes rounded; in particular it loses the two-peak structure as well as the sharp upper band edge characteristic of the ideal Fe d band. For a rounded band there is less tendency for the magnetization to saturate (one spin band completely full) than in a band with a sharp edge. This may give rise to the reduced magnetic moment of Fe(IF) as seen in figures 2–7 and table 3. In addition, at the interface the states at E_F have reduced the local d character owing to the interaction with the Ge conduction band. The local effective exchange potential felt by a state is roughly proportional to its local d character; thus the local effective exchange potential becomes weaker and this also leads to a reduced moment at the interface. To our knowledge there are no quantitative experimental results up to now on the distribution of magnetic moment near 'ideal' Fe–Ge interfaces. However, comparing

Table 3. Electron spin polarization parameter $P(hkl, E_F)$ and the LDOS $n^+(E_F)$ for Fe interface atoms. For P^{exp} see [15].

		$n^+(E_F)$	$n^-(E_F)$	P^{calc} (%)	P^{exp} (%)	$P^{calc\,a}$ (%)
(110)	IF − 2	1.61	0.64	+43.1		
(110)	IF − 1	1.66	0.74	+38.3	+13	
(110)	IF	1.09	0.90	+9.6		
(100)	IF − 2	1.62	0.59	+46.6		
(100)	IF − 1	1.36	0.89	+20.9	+14 ± 2	−50 to −70[a]
(100)	IF	0.78	1.13	−18.3		
(111)	IF − 2	1.62	0.65	+42.7		
(111)	IF − 1	1.35	1.04	+13.0	+31 ± 2	
(111)	IF	1.04	1.00	+2.0		

[a] The P-value of the Fe(100) surface, calculated in [24, 25].

the theoretical magnetic moment values of Fe(IF − 2) and Fe(IF) layers with the similar experimental data for α-Fe and the hexagonal compound FeGe, respectively, as seen in table 2, we can conclude that our calculated results are reasonable, while the inconsistency of the increasing tendency of Fe layers approaching the interface with the experimental data remains to be clarified.

3.4. The electron spin polarization at the Fe–Ge interface

The ESP as a function of the surface indices (hkl) and energy E is defined as

$$P(hkl, E) = [n^+_{hkl}(E) - n^-_{hkl}(E)]/[n^+_{hkl}(E) + n^-_{hkl}(E)] \qquad (2)$$

where n^+ and n^- have the same meanings as above. Only the value of P at $E = E_F$ is physically significant. These calculated values are shown in table 3, where also are presented the similar experimental results obtained by the electron capture spectroscopy (ECS) technique [15]. Our calculation showed that P values are positive except for the Fe(IF) of the (100) interface. Noting that it is difficult to obtain an ideal interface, our results must be considered rather satisfactory and in qualitative agreement with the experimental ECS measurements. Other measurements at the surface of a polycrystalline evaporated Fe film found the ESP of electrons near the Fermi level to be +54% [26] and +44% [22].

4. Conclusions

We performed a calculation of the electonic structure for ideal Fe–Ge(110), Fe–Ge(111) and Fe–Ge(100) interfaces and discussed the distribution of magnetic moments of several Fe layers near interfaces. The following results were obtained.

(1) There are obvious differences between the electronic states of the interface and those of the bulk system. The interface states which exist on the interface layer atom are related to the atomic local environment (ALE). The greater the differences between the ALEs of the interface atom and the central-layer atom, the more abundant are the interface states.

(2) The Fe atomic magnetic moment decreases as the Fe layer approaches the interface layer. The reduction is caused by the electron transfer from the majority-spin states to the minority-spin states and by the changes in the LDOS curves at the interfaces. This is in agreement with neutron scattering, x-ray scattering and Mössbauer experiments.

(3) From the evaluation of the ESP parameters for several Fe layers near the Fe–Ge interface, we found qualitative agreement with some surface ESC and other measurements.

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