PHYSICAL REVIEW B VOLUME 34, NUMBER 12 15 DECEMBER 1986

Electronic structure of the Fe/Ge(110) interface

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(Received 6 August 1986)

Ge and bcc Fe have lattice spacings which are well matched, and therefore these elements present an excellent prototype system to study magnetic effects at a metal-semiconductor interface. We study the electronic structure of the (110) Fe/Ge interface using a parametrized tight-binding approach. The necessary tight-binding parameters were determined by fitting to first-principles band structures of Ge, spin-polarized bcc, Fe, and a CsCl-structure FeGe compound. We have implemented a generalized Slater-Koster scheme suitable to handle arbitrary atomic geometries, which allows the number of layers of each material to be increased easily to study convergence of interface properties. We find that seven layers of Fe and eleven layers of Ge are necessary to identify unambiguously the interface bands in this system. The Fe minority-spin projected band structure has a large gap around the $\overline{M}$ point which spans the fundamental gap in Ge; there are eight interface bands which lie in this mutual gap. For the majority-spin electrons we also find a large density of interface resonances just above the Fermi level which are strongly localized on the Ge atoms at the interface. These results are consistent with the reactive nature of this interface seen in experimental studies.

I. INTRODUCTION

Metal-semiconductor interfaces display physical and chemical properties[1-3] which have stimulated many experimental and theoretical studies. Properties of great interest include the Schottky barrier height (which determines the electrical behavior), the interfacial morphology, and the stability of the interface against chemical reaction and interdiffusion. Because of technological interest and the wealth of experience silicon interfaces have been the most widely studied. However, germanium provides an important alternative, since clean Ge surfaces are also readily obtainable and the smaller energy gap of Ge may provide access to desired characteristics in a new range of energy or temperature. Furthermore, since for many applications a clean, nearly-lattice-matched interface is desired, the different lattice constant of Ge may prove useful in itself.

In this paper we report a study of the electronic structure of the (110) Fe/Ge interface. In addition to the properties mentioned above, the presence of a magnetic material introduces the possibility of studying magnetic behavior at interfaces. Prinz and collaborators[4,5] have reported the growth (by molecular-beam epitaxy at elevated temperature) of single-crystal (110) Fe films on GaAs and subsequent measurement and description[6] of the magnetic properties of the film. It was found,[7] however, that Fe films grown on (110) Ge are heavily intermixed with Ge, even to a thickness of several tens of layers. It can be inferred that the Fe/Ge interface is considerably more reactive and therefore prone to intermixing than is the Fe/GaAs interface.

The morphology of Fe/Ge interfaces is also of interest due to the use of Fe/Ge multilayers as neutron polarizers. The multilayers studied by Majkrzak *et al.*[8,9] and Lynn *et al.*[10] were made by sputter deposition and, although the Fe layers showed strong (110) texture, the Ge layers were amorphous. Neutron and x-ray scattering studies support (i) a compression of (110) Fe planes near the interface, (ii) a number of FeGe alloy planes with varying degrees of relative concentration, and (iii) a decrease in moment from the center of the Fe layers to the interface. Upon annealing, increased interdiffusion is found. These results are consistent with the picture of the Fe/Ge interface as reactive and perhaps metastable, i.e., prone to intermixing. Although these multilayers serve as useful neutron polarizers, more nearly ideal abrupt crystalline interfaces could improve their performance.

The phase diagram[11] of the Fe_xGe_{1-x} system displays a rich assortment of crystallographic and magnetic phases. Again, this proclivity of Fe and Ge to form compounds is consistent with the tendency toward intermixing at the interface. It is unclear to what extent intermixing begins to destroy the magnetism. Hexagonal FeGe is antiferromagnetic with a moment[12] close to the bulk moment of $\sim 1.85\mu_B$, while amorphous Fe_xGe_{1-x} alloys show a greatly reduced moment[13] near $x \sim 0.5$.

In the present study we determine the electronic structure of the unrelaxed abrupt (110) Ge/Fe interface utilizing a superlattice geometry. We find eight well-defined minority interface bands which lie in a mutual gap near the Fermi level E_F in the (110) projected band structures. For the majority spin a large density of interface resonances also occurs near E_F. This large density of states near E_F at the interface suggests that energy can be gained by relaxing, reconstructing or intermixing, any of which could serve to reduce the number of occupied states at high energy.

II. METHOD OF CALCULATION

Although self-consistent first-principles calculations are the method of choice for interface calculations, their use here is not feasible. For the (110) Fe/Ge interface each layer of Fe requires four atoms and our tests indicate that seven layers are necessary to separate the two interfaces in the unit cell sufficiently to identify interface states unambiguously. Taking into account the Ge as well, for which about eleven layers are needed, the calculations will require 40–50 atoms in the unit cell. Such calculations are beyond the capabilities even of present supercomputers with current algorithms.

For this reason the present calculations were done with the parametrized tight-binding method as proposed by Slater and Koster.[14] A new and general computer code was written[15] which allows an arbitrary unit cell and provides for the periodic repetition of the unit cell in zero, one, two, or three dimensions. The code allows for either an orthogonal or non-orthogonal basis set, but for simplicity is restricted to a two-center representation of hopping integrals and wave-function overlaps. The code was tested by comparing with existing programs[16] for several simple structures and obtaining identical results.

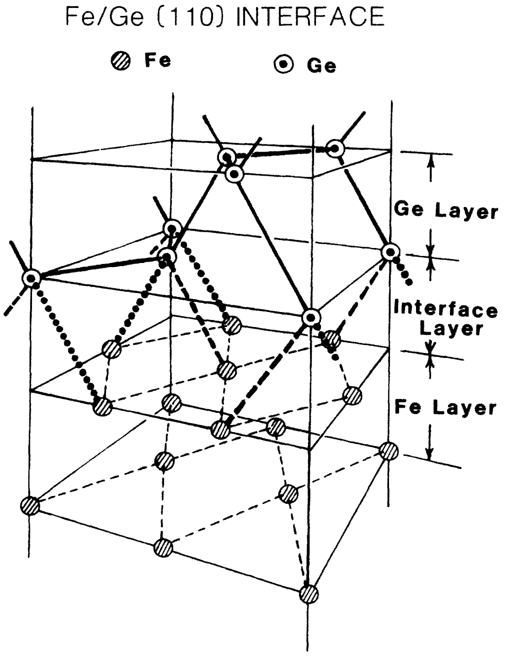

FIG. 1. Atomic positions at the ideal Fe/Ge(110) interface. Bold dashed lines (bold dotted lines) denote the Fe-Ge bonding (nonbonding) nearest-neighbor distances across the interface, as discussed in the text.

TABLE I. Fe and Ge two-center parameters (eV).

	Fe		
	Majority	Minority	Ge
s	5.54	5.67	−6.09
p	14.82	14.68	1.17
$d(t_{2g})$	−1.08	0.77	
$d(e_g)$	−1.34	0.39	
$ss\sigma$	−1.76	−1.80	−1.86
$sp\sigma$	2.36	2.35	1.90
$pp\sigma$	3.50	3.52	2.79
$pp\pi$	0.33	0.36	−0.93
$sd\sigma$	−0.83	−0.97	
$pd\sigma$	−1.15	−1.32	
$pd\pi$	0.24	0.29	
$dd\sigma$	−0.62	−0.72	
$dd\pi$	0.37	0.45	
$dd\delta$	−0.04	−0.04	
$ss\sigma$	−0.40	−0.41	0.04
$sp\sigma$	0.89	0.97	−0.20
$pp\sigma$	2.29	2.48	0.28
$pp\pi$	0.56	0.50	−0.08
$sd\sigma$	−0.48	−0.55	
$pd\sigma$	−0.74	−0.89	
$pd\pi$	−0.04	−0.06	
$dd\sigma$	−0.37	−0.46	
$dd\pi$	0.08	0.08	
$dd\delta$	0.01	0.02	
$ss\sigma$	0.22	0.22	0.05
$sp\sigma$	−0.34	−0.31	0.09
$pp\sigma$	−0.68	−0.58	0.02
$pp\pi$	0.24	0.21	0.04
$sd\sigma$	−0.01	0.00	
$pd\sigma$	−0.01	0.03	
$pd\pi$	−0.03	−0.05	
$dd\sigma$	0.02	0.03	
$dd\pi$	0.05	0.00	
$dd\delta$	0.08	−0.01	

For the Fe/Ge interface we have chosen to parametrize the host materials with a third-neighbor orthogonal representation.[16] A non-orthogonal representation could have been chosen at the expense of including many more (overlap) parameters. The third-neighbor fit, however, gives an excellent fit to the host bands. For Fe we have used the fit to self-consistent augmented-plane-wave calculations; the rms difference between *ab initio* and fit eigenvalues is 0.04 eV over the lowest six bands. For Ge we have used a fit to empirical pseudopotential results modifying the form factors of Chelikowsky and Cohen[17] due to our omission of the spin-orbit interaction. Our pseudopotential

TABLE II. Fe-Ge two center parameters (eV).

$ss\sigma$	−1.98
$sp\sigma$	−0.20
$ps\sigma$	3.98
$pp\sigma$	1.26
$pp\pi$	−1.94
$ds\sigma$	−1.06
$dp\sigma$	−1.19
$dp\pi$	0.49

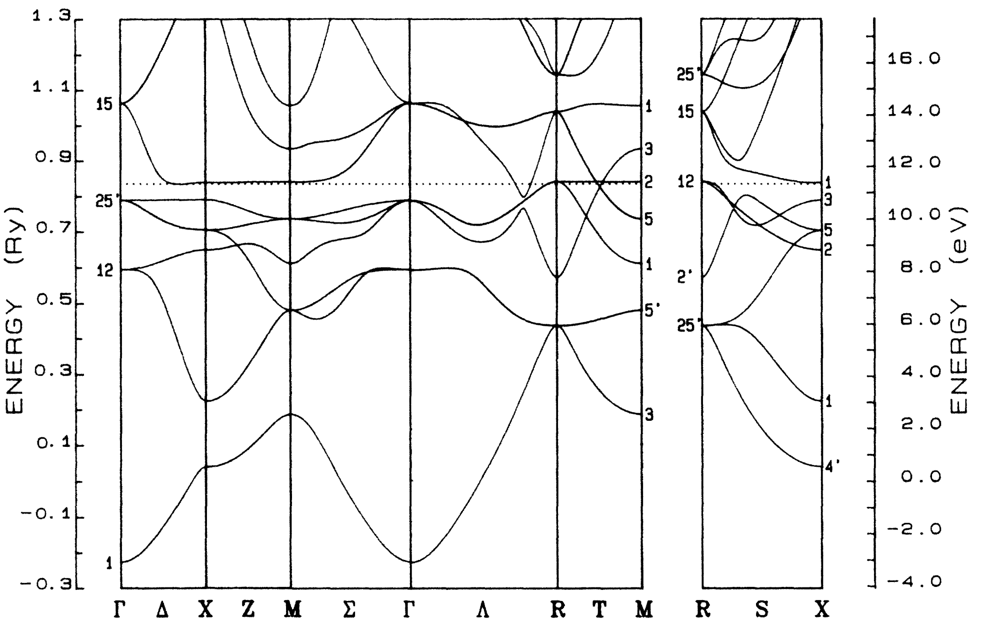

FIG. 2. Energy bands of hypothetical $B2$ structure FeGe compound along high-symmetry directions.

form factors are $V(\sqrt{3})=-0.231$, $V(\sqrt{8})=0.019$, and $V(\sqrt{11})=0.053$, all in Ry. In our fit the rms difference is 0.20 eV for the valence band and 0.74 eV for the lowest two conduction bands. These Fe and Ge parameters[16] are given in Table I.

The choice of Fe-Ge and Ge-Fe parameters depends on the geometrical arrangement of atoms at the interface. Even for the abrupt, unrelaxed (110) interface which we consider in this paper, the registry of the Fe and Ge planes must be assigned. We make the natural assumption that Fe atoms will "bond" with Ge in the usual tetrahedral configuration, i.e., Fe atoms sit at positions which Ge atoms would occupy if one more (110) plane of Ge atoms were added to the Ge slab. Fe atoms also occupy the "interstitial" sites in this layer, since the number density of Fe atoms is twice that of Ge atoms. (Put another way, placing Fe atoms at both the diamond lattice sites and its interstitial sites gives the bcc Fe lattice.) The interface atomic structure is shown in Fig. 1. The small (1.3%) lattice mismatch $[a_0(\mathrm{Fe})\approx\frac{1}{2}a_0(\mathrm{Ge})]$ between Fe and Ge is neglected in this study.

With this choice of geometry the Fe-Ge nearest-neighbor distances are equal to the Fe-Fe and Ge-Ge nearest-neighbor distances in the bulk. To determine the Fe-Ge parameters we first carried out self-consistent augmented-plane-wave calculations for an artificial $B2$-(CsCl-) structure FeGe compound with the desired nearest-neighbor distance. The calculated bands were fit with a nearest-neighbor two-center tight-binding model and the corresponding Fe-Ge parameters, given in Table II, have been used in our interface calculations. We have not attempted to determine any second or third neighbor Fe-Ge parameters. From the rapid decrease with distance in the Ge parameters (Table I) we expect these Fe-Ge parameters to be small.

The energy bands and density of states (DOS) of $B2$-structure FeGe obtained from our fit are shown in Figs. 2–4. The low-lying states are dominated by s-like Ge states. The energy levels in the range 0.4–1.0 Ry are composed of hybridized Fe d and Ge p states with the Fe d states being the dominant component. The flat bands along the Δ, Z, and T directions result in a pronounced peak in the DOS just above E_F. This peak has Fe e_g character and may be indicative of possible magnetic

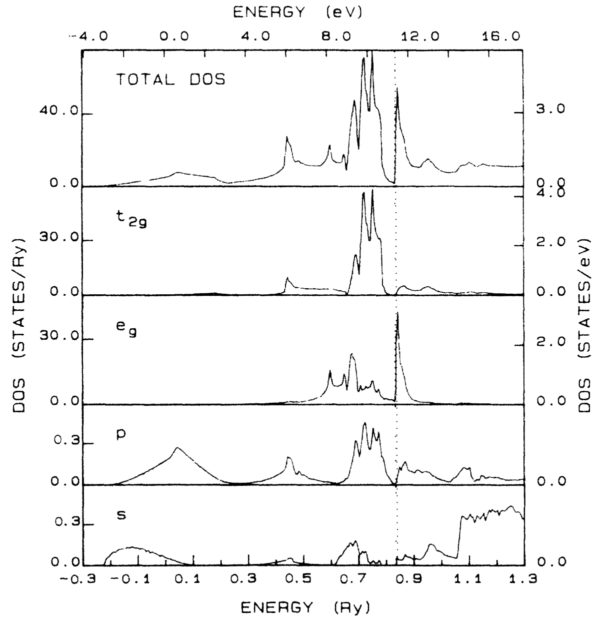

FIG. 3. Total DOS, and l-decomposed DOS on the Fe atom, of $B2$ FeGe.

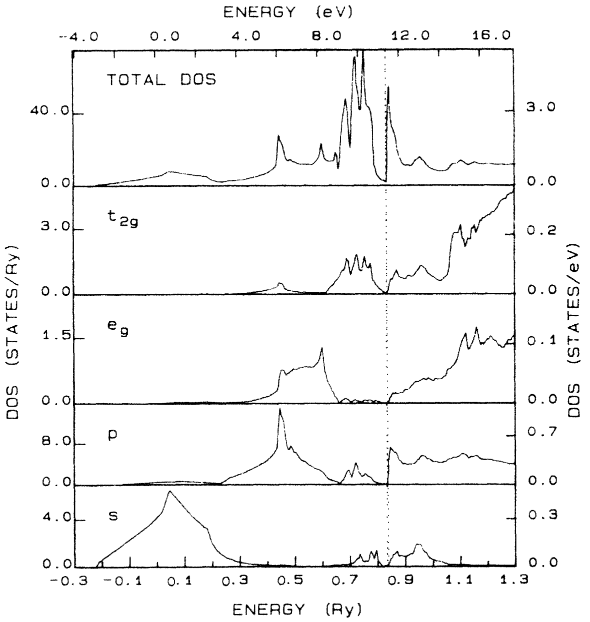

FIG. 4. Total DOS, and l-decomposed DOS on the Ge atom of $B2$ FeGe.

behavior in this structure, which we have constrained to be paramagnetic. If this $B2$ FeGe could be formed and remained paramagnetic, slight doping could change the value of the DOS $N(E_F)$ by an order of magnitude.

Some features of the interface atomic geometry should be pointed out. First, the (110) interface requires two Ge atoms per layer and four Fe atoms per layer. Since it is necessary to include several layers of each material to separate the interfaces enough to identify interface bands, the rather large number of atoms precludes the use of first-principles methods, as already noted. For example, we have found it necessary to use seven layers of Fe and eleven layers of Ge (a total of 50 atoms) to isolate the interface bands. This large unit cell has necessitated our use of this parametrized method to investigate the electronic structure.

Secondly, since we are not using a self-consistent method the Schottky barrier height cannot be determined. The limited experimental information[18] suggests that the Fermi level E_F of Fe lies near the middle of the Ge gap. Therefore we have aligned the Fe and Ge bands so E_F lies 0.35 eV above the valence-band maximum (VBM) of Ge; the VBM of Ge has been taken as the zero of energy for the present calculation.

Thirdly, the lack of self-consistency can manifest itself in unphysical charge transfer between atoms near the interface. If one simply uses the parameters in Tables I and II and calculates the charge and moment on each atom, the "unshifted" results of Table III are obtained. The charge transfer, nearly 0.3 electron from Fe to Ge across the interface, is in contradiction both with the known Fe-Ge phases,[11] which appear to have covalent or metallic bonding rather than ionic, and with experimental data on amorphous $\mathrm{Fe}_x\mathrm{Ge}_{1-x}$ alloys which show no detectable charge transfer.[13] We have compensated for this unphysical charge transfer by shifting the on-site energies of atoms near the interface. To approach charge neutrality it is necessary to shift Fe on-site energies downward and Ge on-site energies upward. The shifts we have chosen (after testing several values) and the resulting charges and moments are also shown in Table III. This procedure has been used previously[19] for calculations on Fe surfaces.

The results of Table III include the distinction between the two chemically distinct Fe sites in each layer. The Fe sites can be classified according to whether they would be occupied or unoccupied if the Fe layers were successively replaced by Ge layers. The dashed interface bonds in Fig. 1 connect Ge atoms to Fe atoms at sites which would be occupied if the Fe layer were replaced by a Ge layer, i.e., this Fe site completes the standard fourfold coordination

TABLE III. Atomic charges Q (units of e) and moments μ (units of μ_B) at the Fe/Ge(110) interface before shifting, and after shifting on-site energies by ΔE (eV).

	Unshifted		Shifted		Amount of shift
	Q	μ	Q	μ	ΔE
$\mathrm{Fe}^{b}_{\mathrm{IF}-3}$	8.02	2.08	8.01	2.08	
$\mathrm{Fe}^{\mathrm{nb}}_{\mathrm{IF}-3}$	8.01	2.08	8.00	2.08	
$\mathrm{Fe}^{b}_{\mathrm{IF}-2}$	8.02	2.09	8.02	2.10	
$\mathrm{Fe}^{\mathrm{nb}}_{\mathrm{IF}-2}$	8.02	2.08	8.02	2.09	
$\mathrm{Fe}^{b}_{\mathrm{IF}-1}$	7.99	2.16	7.97	2.20	
$\mathrm{Fe}^{\mathrm{nb}}_{\mathrm{IF}-1}$	7.97	2.18	7.96	2.22	
$\mathrm{Fe}^{b}_{\mathrm{IF}}$	7.66	2.33	8.00	2.19	−0.20
$\mathrm{Fe}^{\mathrm{nb}}_{\mathrm{IF}}$	7.72	2.38	7.98	2.28	−0.15
$\mathrm{Ge}_{\mathrm{IF}}$	4.28	−0.07	4.03	−0.11	0.30
$\mathrm{Ge}_{\mathrm{IF}-1}$	4.10	0.01	4.03	0.00	0.10
$\mathrm{Ge}_{\mathrm{IF}-2}$	4.00	0.00	4.00	0.00	
$\mathrm{Ge}_{\mathrm{IF}-3}$	4.01	0.00	4.00	0.00	

of the interface Ge atom, and we refer to it as the "bonding" Fe site Fe^{b}. The dotted interface bonds in Fig. 1 connect interface Ge atoms to Fe atoms at the "nonbonding" site Fe$^{\mathrm{nb}}$.

Several features can be noted from Table III. Before shifting, only the Fe atoms at the interface (IF), Fe$_{\mathrm{IF}}$, and the Ge atoms on the first two layers, Ge$_{\mathrm{IF}}$ and Ge$_{\mathrm{IF}-1}$, show appreciable deviations from neutrality. It was found to be necessary to shift each of these atomic on-site energies to achieve near neutrality. In addition to achieving the desired degree of atomic neutrality, the shifts served to reduce the enhanced moment on the Fe$_{\mathrm{IF}}$ atoms but slightly increased the moment on the Fe$_{\mathrm{IF}-1}$ atoms and the small negative moment on the Ge$_{\mathrm{IF}}$ atom. The shifts also acted to decrease the difference between Fe^{b} and Fe$^{\mathrm{nb}}$ atoms within each layer, with the only remaining significant distinction being the difference in moment on the Fe$_{\mathrm{IF}}$ layer ($\Delta\mu=0.09\mu_B$). Some small distinctions between the Fe$^{b}_{\mathrm{IF}}$ and Fe$^{\mathrm{nb}}_{\mathrm{IF}}$ sites will also be discussed in Sec. III.

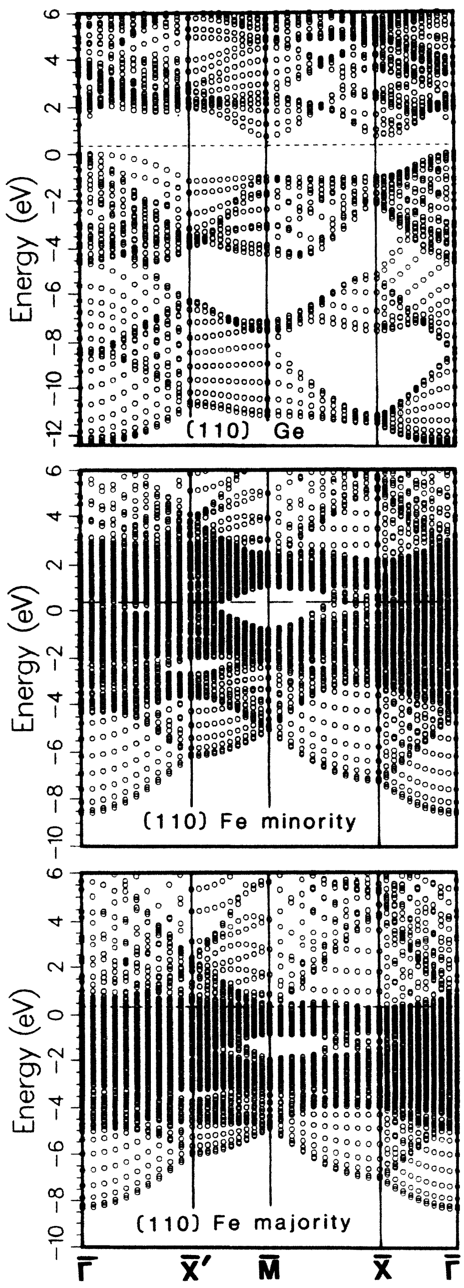

FIG. 5. The (110) projected band structures of Ge (top panel), Fe minority (middle panel), and Fe majority (bottom panel) plotted on identical energy scales. The zero of energy is taken to be the valence-band maximum of Ge, while the dotted line denotes the Fermi level of Fe.

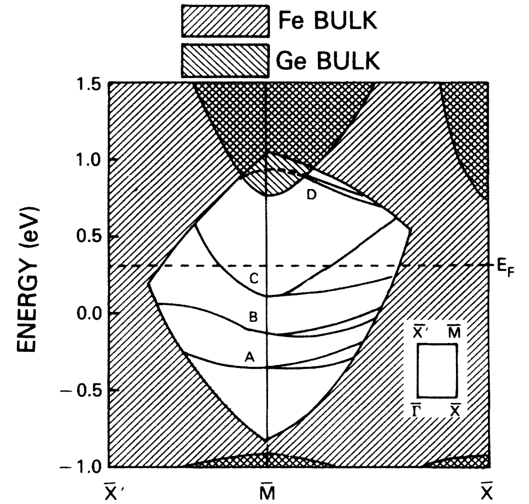

FIG. 6. The spectrum of interface bands A,B,C,D (see text) near $\bar{M}$ in the mutual gaps of Fe and Ge. E_F denotes the Fermi level of Fe.

III. RESULTS

True interface states can exist only within a mutual gap in the projected band structures (PBS) of both components. The PBS's of Ge and Fe (both spins) are presented in Fig. 5. Of greatest interest are mutual gaps within the fundamental gap of Ge, since partially filled interface bands can only occur there. The only significant gap in Fe occurs around the $\bar{M}$ point in the middle of the d bands. In the majority bands this gap falls between 1 and 2 eV below E_F. In the minority bands, however, this gap spans the Ge gap, giving rise to a rich spectrum of interface states which are discussed below. There is, in addition, a small gap 3.5 eV (majority) and 2.5 eV (minority) below E_F around $\bar{X}$ which does not overlap with any gap in Ge.

An enlargement of the mutual gap in the minority bands is given in Fig. 6. There are three interface bands (A,B,C) and one interface resonance (D) at $\bar{M}$. Each is doubly degenerate and remains so along $\bar{M}-\bar{X}'$, but splits along the $\bar{M}-\bar{X}$ direction. Bands A and B are occupied and D is unoccupied, while band C is only partially occupied and forms two pieces of Fermi surface involving only interface states.

The interface states are primarily Fe-like, but it should be kept in mind that there are twice as many Fe atoms as Ge atoms at the interface. The characters of the states at $\bar{M}$ are as follows. Band A, at $E_F-0.7$ eV, is approxi-

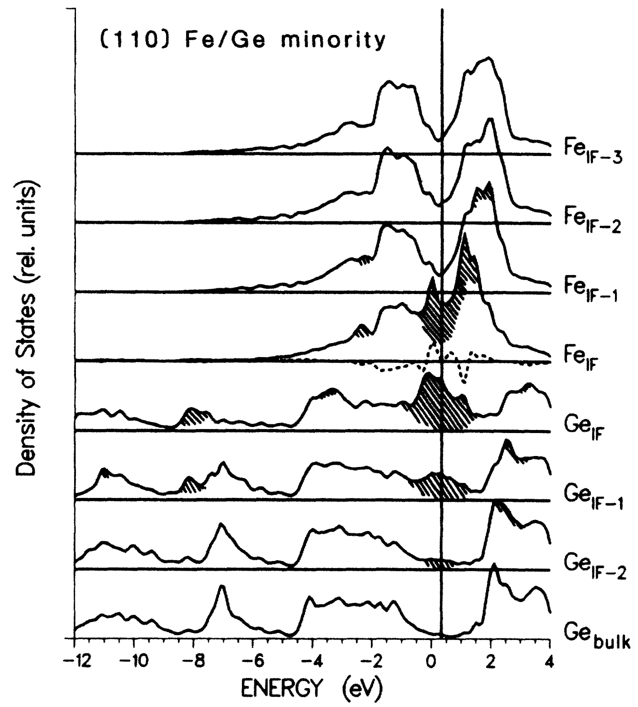

FIG. 7. The minority local density of states (LDOS) per atom on several Fe and Ge layers near the Fe/Ge(110) interface. The hatched region indicates interface states, i.e., where the LDOS exceeds the bulk DOS. $\mathrm{Ge}_{\mathrm{bulk}}$ indicates an average over the interior five layers of Ge. The dotted line on the $\mathrm{Fe}_{\mathrm{IF}}$ layer indicates the difference between the LDOS on the $\mathrm{Fe}_{\mathrm{IF}}^{b}$ and $\mathrm{Fe}_{\mathrm{IF}}^{\mathrm{nb}}$ sites. Note: the LDOS for the Ge layers have been multiplied by two for easier comparison.

mately 22% each of Fe^{b}, $\mathrm{Fe}^{\mathrm{nb}}$, and Ge on the respective interface layers and reflects primarily Ge-Fe ($pd\sigma$) bonding. Band B, at $E_F-0.45$ eV, is extremely strongly confined to the Fe interface layer, with 50% $\mathrm{Fe}_{\mathrm{IF}}^{\mathrm{nb}}$ and 30% $\mathrm{Fe}_{\mathrm{IF}}^{b}$ character. It has almost no charge on the $\mathrm{Ge}_{\mathrm{IF}}$ layer and only 5% on the $\mathrm{Ge}_{\mathrm{IF}-1}$ layer. Band C, at $E_F-0.2$ eV, is 20% $\mathrm{Fe}_{\mathrm{IF}}^{\mathrm{nb}}$, 30% $\mathrm{Fe}_{\mathrm{IF}}^{b}$, and 25% $\mathrm{Ge}_{\mathrm{IF}}$. Resonance D is somewhat more diffuse, with almost 50% $\mathrm{Fe}_{\mathrm{IF}}$ (mostly nonbonding), 6% $\mathrm{Ge}_{\mathrm{IF}}$, and 6% $\mathrm{Ge}_{\mathrm{IF}-1}$. None of the interface bands show much Fe d_{xy} (in-plane) character, indicating that the interface counterparts of surface "dangling bonds" are most important in forming these interface states.

The minority local densities of states (LDOS's) for several planes are shown in Fig. 7. The excess LDOS (where the LDOS exceeds the bulk DOS, shown as shaded areas) appears near the Fermi level as expected from Fig. 6, and decays more slowly into the Ge, with its wide-band sp wave functions, than it does into Fe with its localized d functions. There is little excess LDOS elsewhere in the minority bands.

The majority LDOS, shown in Fig. 8, shows large regions of excess LDOS in spite of the lack of mutual gaps in the projected DOS. A large excess LDOS occurs on Ge in its fundamental gap, reflecting the "metal-induced gap states"[20] commonly observed at metal-insulator interfaces. In addition, the Fe "pseudogap" at −1 to −2 eV is washed out considerably on the interface layer.

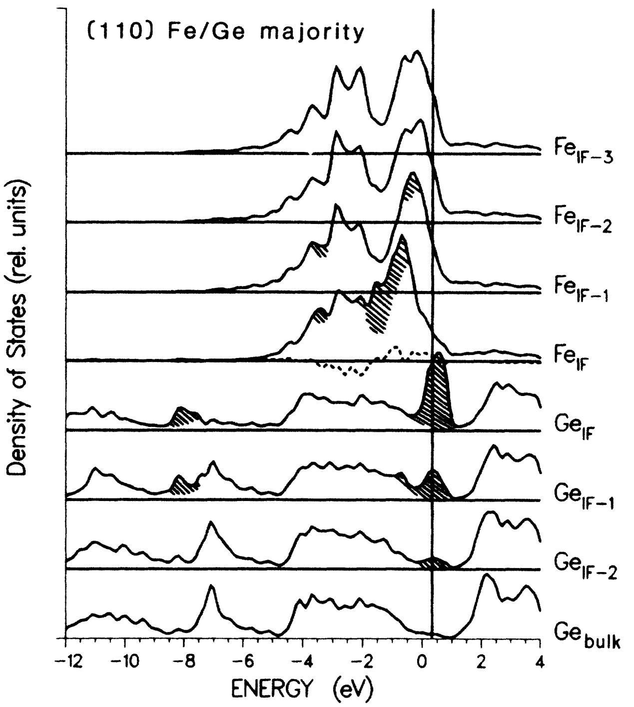

FIG. 8. As in Fig. 7, but for the majority spin.

IV. DISCUSSION

Qualitatively the changes we have found in the LDOS at the interface were to be expected. The separation between bonding and antibonding peaks in the d density of states in bcc transition metals is known to develop only when the atom is surrounded by its first *two* coordination shells. The Fe atom at the interface has only half of its first two bcc shells occupied by Fe atoms, so the bonding-antibonding distinction should not be fully developed. This is observed in both spin directions. Similarly, it takes several shells of neighboring Ge atoms to impose the "gap" on the central atom, so it is understandable to find a large LDOS in the gap on the interface Ge atom which extends two layers further into the Ge.

What is unusual about these results is the rich spectrum of *eight* minority interface states in the mutual gap near $\overline{M}$, and the large majority LDOS on the Ge atom at the interface. The very large interface DOS at E_F for the abrupt interface, encourages the system to gain electronic energy by relaxing or by intermixing to form a disordered layer or an interfacial compound, thereby lowering the DOS at E_F, while the interface Fermi surface arising from interface band C could drive a periodic distortion. As mentioned in the Introduction, an abrupt Fe/Ge interface has not yet been fabricated. However, we are not aware of any experimental study of this system which has investigated an extensive range of deposition conditions.

The Yb/Ge(111) interface is one metal-Ge interface which has been studied carefully. Deposition of Yb onto the cleaved Ge(111) surface results[21] in a reacted Yb-Ge phase 2–3 monolayers thick, which subsequently limits further Yb-Ge interdiffusion. This behavior is typical of rare-earth–Si interfaces as well, although germanium tends to form broader interfacial phases than does Si.

Our theoretical results are consistent with, and even suggestive of, intermixing of Fe and Ge at the interface as has been observed.[8–10] An important question to address is what form this intermixing takes in the Fe-Ge system. Several possibilities exist: (1) Fe atoms diffuse into the Ge lattice via the interstitial sites in the diamond lattice, (2) Fe atoms diffuse into the Ge by reaction (bonding) with Ge neighbors, with, for example, fluorite structure $FeGe_2$ local coordination, (3) interchange of Fe and Ge atoms occurs in successive layers, or (4) formation of a disordered Fe-Ge region at the interface occurs. The results of Prinz and Krebs[7] indicate that intermixing occurs over many tens of layers when deposition is carried out well above room temperature; beyond that little is known. For the related Ni/Si interface Hamann and Mattheiss[22] reported first-principles total-energy calculations on thin slabs which indicate the "reacted" form of Ni in Si, i.e., strong Ni-Si bonding, is energetically more favorable than the nonbonding interstitial form of Ni in Si. This argues against diffusion of Ni into Si via the interstitial sites. Whether the same result would hold for Fe in Ge is not known. It should be noted, however, that Ni/Si interfaces can be made which are highly ordered and rather abrupt, quite different than the few results reported on Fe/Ge interfaces so far.

ACKNOWLEDGMENTS

The authors are grateful to G. A. Prinz and J. J. Krebs for valuable discussions and a critical reading of the manuscript. This work was supported in part by Office of Naval Research, Contract No. N0014-83-WR-30007.

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