Electronic structure of a ferromagnetic-metal–insulator superlattice

E. de Jonge, P. K. de Boer, and R. A. de Groot
Electronic Structure of Materials, Research Institute for Materials, Toernooiveld 1, 6525 ED, Nijmegen, The Netherlands
(Received 16 April 1999)

Electronic structure calculations on superlattices of iron on one side and alloys of Ge, GaAs, and ZnSe on the other side are reported. A very large spin polarization of conduction electrons is found, which is of opposite sign compared to the spin polarization of conduction electrons in bulk iron. The occurrence of almost 100% spin polarization is dependent on the thickness and composition of the insulator layer and on the thickness of the iron layer. [S0163-1829(99)13731-7]

I. INTRODUCTION

The possibilities of making multilayer materials has led to various new and unexpected phenomena. Early work has concentrated on multilayer materials based on various semiconductors;[1] later work also included multilayers made out of metallic constituents. In this field special attention is focused on the so-called ''giant'' magnetoresistance.[2] Multilayers consisting of a ferromagnetic and a nonmagnetic metal can show large, negative magnetoresistances. This occurs if the thickness of the nonmagnetic metal is such that the ferromagnetic layers couple antiferromagnetically and are forced in a ferromagnetic orientation by an external applied magnetic field. A natural extension is to consider multilayers of metals and semiconductors. In this paper, a systematic study is reported on the multilayer system Fe/Ge(GaAs)(ZnSe), i.e., multilayers consisting of iron and admixtures of Ge, GaAs, and ZnSe. The motivation of this work is as follows. Recently much higher magnetoresistances were obtained in the manganites systems (colossal magnetoresistance).[3] An explanation exists[4–6] based on the half-metallic nature of the manganites,[5–7] but other explanations have been proposed as well.

The fact that entropy is the driving force in the colossal magnetoresistance makes the effect extremely temperature dependent, the magnetoresistance strongly peaking at the Curie temperature, which is usually below room temperature. Both effects hamper applications. Returning to the giant magnetoresistance in metallic multilayers, an essential ingredient in any explanation is the asymmetry towards conduction for the two spin directions of the magnetic layer. The ultimate asymmetry is provided by half-metallic materials. This has motivated various experimental studies based on the archetype HMF, NiMnSb.[8] Difficulties in preparing stoichiometric interfaces hamper progress in this field, however.[9] Some time ago, attention was focused on half-metallic properties of interfaces between a ferromagnetic metal and an insulator.[10] The purpose of this study is to investigate under which conditions reasonable volumes of half-metallic behavior can be induced in multilayer systems consisting of a ferromagnetic metal and a semiconductor/insulator with the hope of combining the relative temperature independence of the giant magnetoresistance with (part of) the size of the colossal magnetoresistance.

The motivation of the Fe/Ge(GaAs)(ZnSe) is as follows. Two quantities have to be optimized in order to obtain the desired effect: the value of the interface showing a high degree of spin polarization as well as the thickness of the insulating layer in order to obtain a (weak) antiferromagnetic coupling between the iron layers without an applied magnetic field. This requires two degrees of freedom. Since Ge and GaAs as well as GaAs and ZnSe can be mixed in two continuous series with the band gap continuously increasing in going from Ge towards ZnSe, this band gap is the second degree of freedom in this study. The lattice parameters are hardly affected by this substitution and match almost perfectly to that of Fe, so that there is hope these systems will be realizable experimentally. The only computational studies we are aware of is the calculation of Butler *et al.*[11] on the Fe/GaAs/Fe system and the Fe/Ge/Fe system.

II. DETAILS OF THE CALCULATIONS

Electronic structure calculations were performed using the localized spherical wave (LSW) method, based on density-

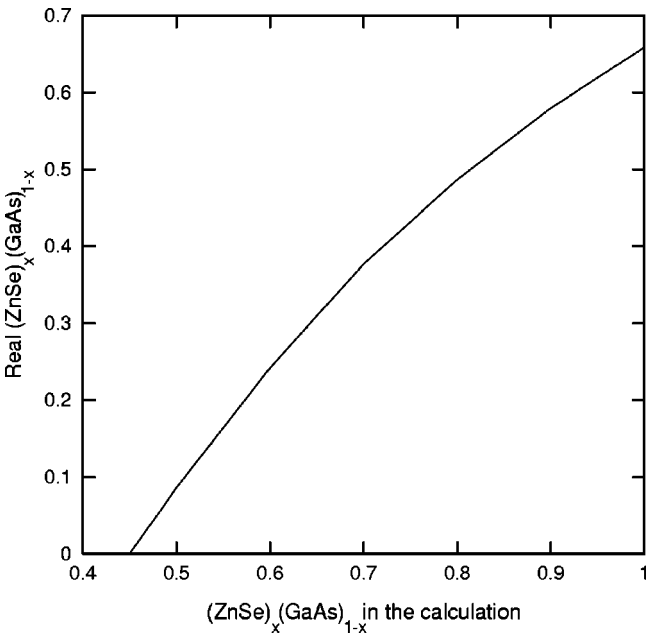

FIG. 1. Relation between real composition in $(GaAs)_{1-x}(ZnSe)_x$ and composition in a calculation using the virtual crystal and LDA approximations leading to identical band gaps.

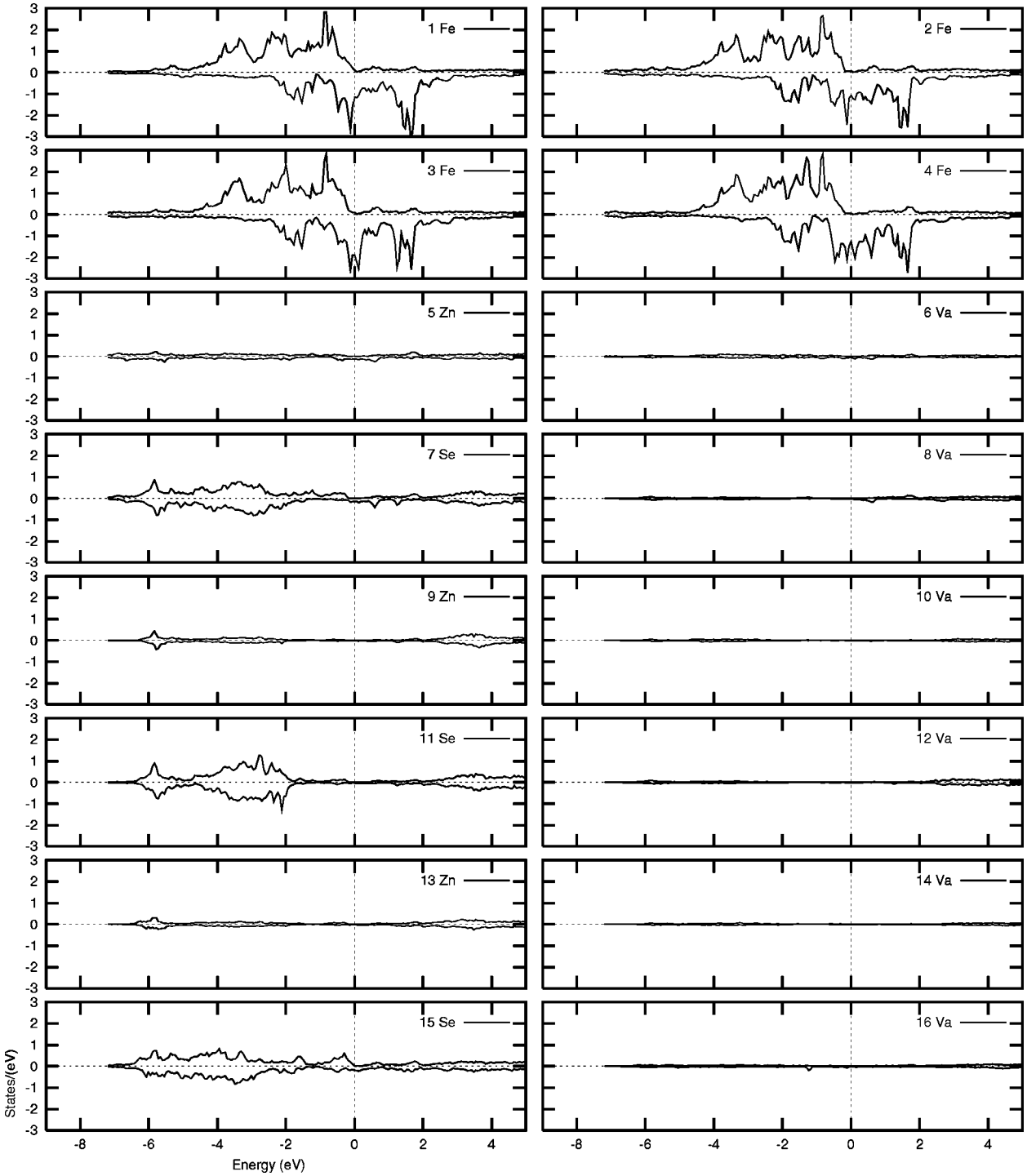

FIG. 2. Local density of states for the $Fe_2/(ZnSe)_3$ multilayer system with ferromagnetic coupling.

functional theory in the local-density approximation (LDA). The effect of the substitution of GaAs in Ge and ZnSe in GaAs was taken into account by the application of the virtual crystal approximation. This implies that for the semiconducting/insulator layer various members of the continuous series *AB* were considered, where *A* is an atom of nuclear charge $(32-x)$, and *B* an atom with nuclear charge $(32+x)$, i.e., $x=0$ corresponds to Ge, $x=1$ to GaAs, and $x=2$ with ZnSe . It is well known that LDA underestimates the band gap in semiconductors. This seriously hampers studies of the type presented here. However, the fact that a continuous series exists comes to the rescue. The calculated band gap for a certain x equals the experimental band gap at a lower x (Fig. 1). Hence, in first approximation, the effect of the LDA can be transformed in a rescaling of the concentration x.

Unless specified differently, the values of x mentioned are the ones corresponding to the value used in the calculation. Layers were stacked along the (100) direction for both the bcc iron and the zinc-blende semiconductor. Since only semiconductor layers of stoichiometric composition are considered, two different interfaces exist in each multilayer system considered: one which has an anion-terminated semiconductor in contact with iron while the other has an interface

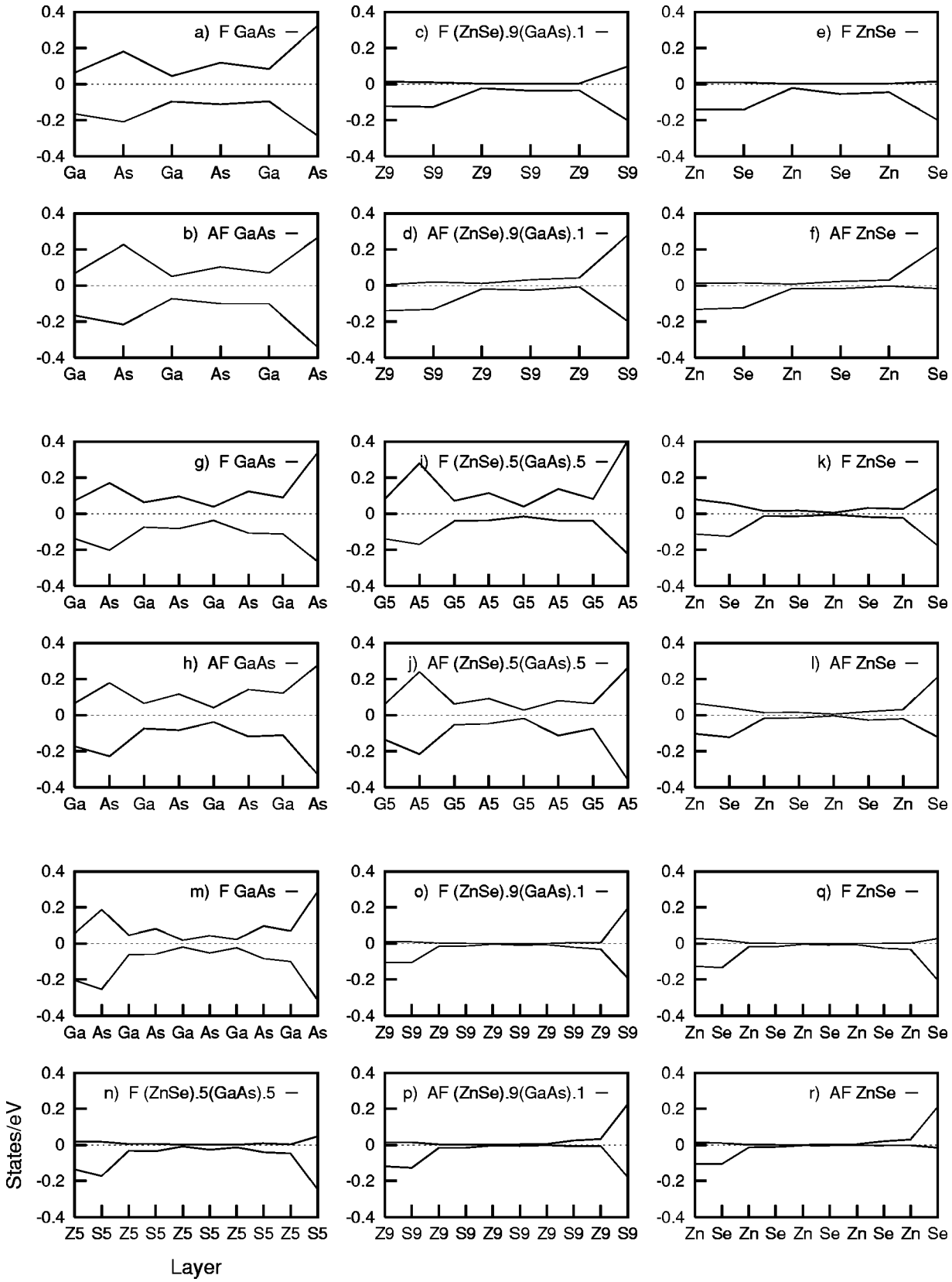

FIG. 3. Density of states at the Fermi energy in the semiconductor region of various multilayers. *Z*9, *S*9, *Z*5, and *S*5 denote atoms with nuclear charge 30.1, 33.9, 30.5, and 33.5, respectively.

with the cation in contact with the iron. Multilayer systems, considered here, consisted of 2 monolayers of iron (each containing two iron atoms) and three, four, or five layers of semiconductor (each containing two monolayers of the two constituents of the semiconductor). In this paper $Fe_2/(ZnSe)_3$, for instance, denotes a multilayer with a unit cell consisting of 2 monolayers Fe and three layers (6 monolayers) ZnSe. In order to allow for an antiferromagnetic cou-

TABLE I. Total energies of some relevant superlattices.

Spacer	E_{AF} (Ry)	E_F (Ry)	ΔE (Ry)
6 ML			
ZnSe	−70964.024401	−70964.020011	−0.004390
$(ZnSe)_{0.9}(GaAs)_{0.1}$	−70930.379317	−70930.350105	−0.029212
GaAs	−70716.694902	−70716.703990	+0.009088
8 ML			
ZnSe	−87843.048012	−87843.043800	−0.004212
$(ZnSe)_{\frac{1}{2}}(GaAs)_{\frac{1}{2}}$	−87645.224178	−87645.398787	+0.174609
GaAs	−87513.072485	−87512.864283	−0.208202
10 ML			
ZnSe	−104722.054582	−104722.049378	−0.005204
$(ZnSe)_{0.9}(GaAs)_{0.1}$	−104666.556084	−104666.550895	−0.005189

pling of the iron layers, the unit cells were doubled, leading to unit cells of 16, 20, and 24 monolayers. In order to avoid large overlaps between Wigner-Seitz spheres in the semiconductor, empty spheres were included here. In the construction of the LSW basis, spherical waves were augmented by solutions of the scalar relativistic radial equations with angular momentum up to and including $l=2$ for all atoms and $l=1$ for the empty spheres. The internal l summation used to augment the central Hankel function at surrounding atoms was extended to $l=3$ for all atoms and $l=2$ for the empty spheres. The 3*d* states of Zn deserve special attention. The spurious self-interaction in the LDA approximation positions these states much too high in energy. As a consequence, the hybridization with the valence band is too strong, leading to a further reduction of the band gap in ZnSe. In order to avoid this unphysical interaction, we prefer to treat the 3*d* states as core states and have used 4*d* states of Zn as basis functions instead.

III. RESULTS

In order to avoid unnecessary repetition, we will discuss the electronic structure of one multilayer system in some detail and focus on the relevant differences with the other systems only.

The local density of states of the $Fe_2/(ZnSe)_3$ ferromagnetic multilayer system is shown in Fig. 2. The presence of the ZnSe neighboring the iron has changed the magnetic properties of the iron. The Fermi-energy in bulk iron intersects the *d* bands for both spin directions. As a result, iron is weakly magnetic, and the density of states of the majority electrons at the Fermi energy exceeds that of the minority electrons. The lower coordination of neighboring iron at the interface leads to an increased exchange splitting of the iron. As a consequence, the iron in the multilayer system has the properties of a strong magnet: the majority *d* band is filled, and the density of states at the Fermi energy is primarily determined by the minority electrons. This is directly reflected by the interactions with the neighboring ZnSe layers (5–8 and 13–16). A finite density of states in the majority spin direction exists, but the density of states of the minority electrons greatly exceeds this. This asymmetry is even larger in the central ZnSe layer (9–12), where the density of states at the Fermi level is even smaller for the majority spin direction.

In Fig. 3 the density of states at the Fermi energy for $Fe_2/(GaAs)_3$ [ferromagnetic (F) and antiferromagnetic (AF)], $Fe_2/((ZnSe)_{0.9}(GaAs)_{0.1})_3$ (F and AF), $Fe_2/(ZnSe)_3$ (F and AF), $Fe_2/(GaAs)_4$ (F and AF), $Fe_2/((ZnSe)_{0.5}(GaAs)_{0.5})_4$(F and AF), $Fe_2/(ZnSe)_4$ (F and AF), $Fe_2/(GaAs)_5$ (F), $Fe_2((ZnSe)_{0.5}(GaAs)_{0.5})_5$ (F), $Fe_2/((ZnSe)_{0.9}(GaAs)_{0.1})_5$ (F and AF), and $Fe_2/(ZnSe)_5$ (F and AF) are shown as a function of the monolayer.

The following conclusions can be drawn: Systems with GaAs as semiconductor hardly show any spin polarization at the interface (a,b,g,h,m). Also, the type of magnetic ordering (ferro- or antiferromagnetic) of the iron layers has very little influence on the density of states of the spacer layer. This situation is different for the other systems. Comparing the systems with three semiconductor layers, a much larger asymmetry is found for the $(ZnSe)_{0.9}(GaAs)_{0.1}$ system *(c,d)* as well as a clear influence of the type of the magnetic ordering. The differences are even stronger in the ZnSe system *(e,f)*: the polarization at the interface is further enhanced and the density of states for the majority spin direction in the central semiconductor layer is reduced by a factor of 3. Surprisingly enough, the systems with four semiconducting layers show much less polarization at the Fermi energy, even in the case of $(ZnSe)_{0.5}(GaAs)_{0.5}$ *(i,j)* and ZnSe *(k,l)*. Much larger *a* symmetries are found in the systems with five semiconductor layers: with the exception of GaAs, which still does not show any spin polarization whatsoever, for $((ZnSe)_{0.5}(GaAs)_{0.5})$, $((ZnSe)_{0.9}(GaAs)_{0.1})$, and ZnSe the density of states for the majority-spin direction for the central layers in the ferromagnetic systems is virtually zero.

IV. RELATIVE STABILITY OF THE MAGNETIC SOLUTIONS

In order to obtain any magnetoresistance, the iron layers have to order antiferromagnetically in the absence of an external magnetic field. Table I summarizes the total energies of the ferro- and antiferromagnetically coupled configurations for some relevant systems. The following conclusions

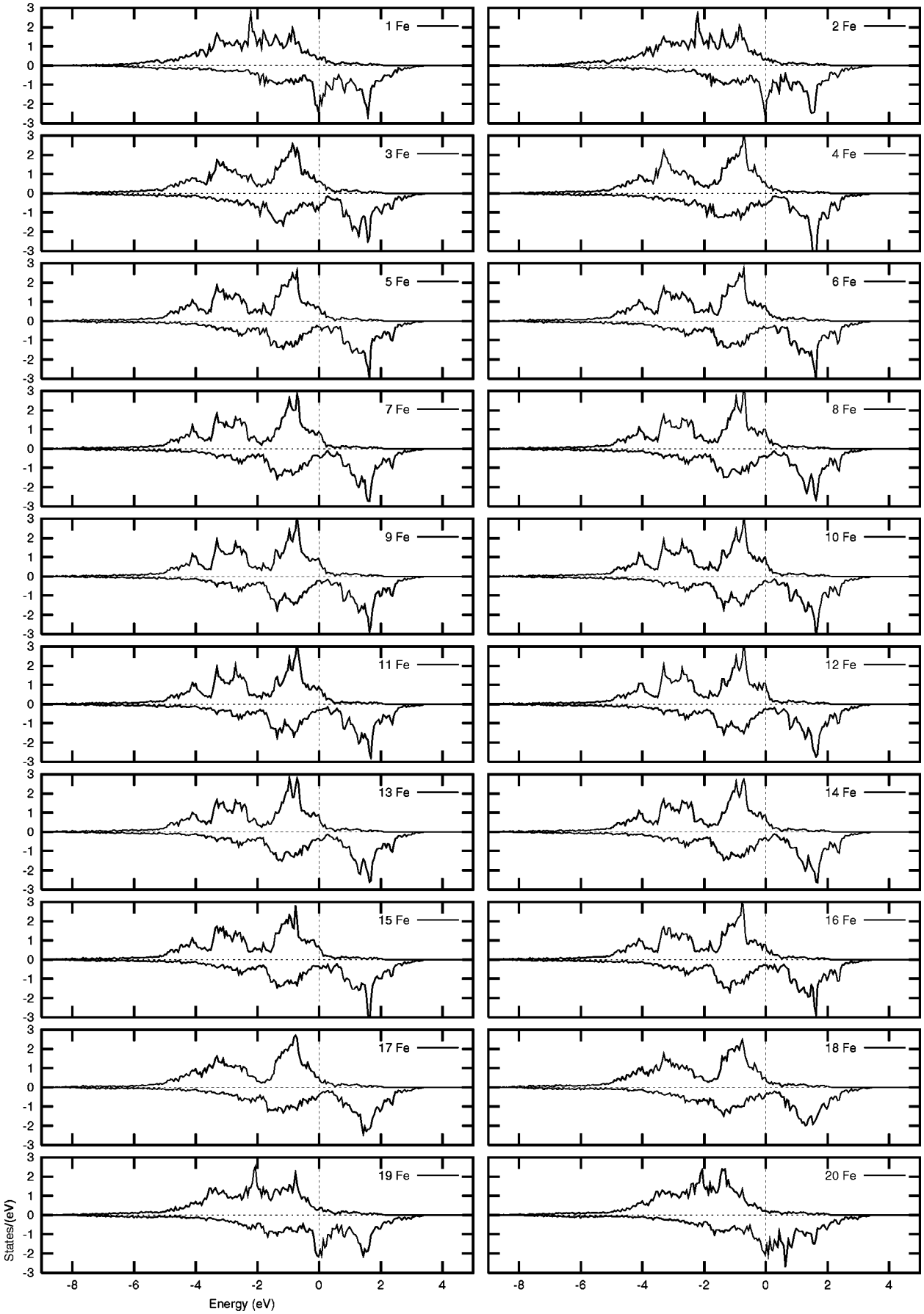

FIG. 4. Local density of states for the iron in a 10/10 Fe/ZnSe ''multilayer.'' 1 and 2 refer to iron atoms neighboring the Se-terminated ZnSe layer; atoms 19, 20 are neighboring the Zn-terminated part of the ZnSe layer.

can be drawn. In the case of ZnSe, the antiferromagnetic configuration is always more stable as compared with the ferromagnetic configuration. The energy differences between the two configurations are hardly dependent on the thickness of the semiconductor layer, i.e., these systems behave very different from the metallic multilayers, where an oscillatory behavior of the exchange coupling is found as a function of spacer thickness.

In the case of GaAs, a reversal of the sign of the exchange coupling is found with the ferromagnetic configuration more stable in the case of three semiconductor layers. It should be noted that due to the much smaller band gap of GaAs; the entire semiconductor behaves as a genuine metal. Also the case of $(ZnSe)_{0.5}(GaAs)_{0.5}$ is noteworthy in the case of four semiconductor layers: the ferromagnetic configuration is very much more stable in contrast with ZnSe and GaAs for the same semiconductor thickness.

V. RELATION WITH INTERFACES

The multilayer systems considered in the previous sections were based on a layer thickness of two for the magnetic metal, iron. Thus, both layers have an interface with the semiconductor, and the electronic structure of them is basically different from bulk iron. The question arises, how the properties of these multilayers compare with systems with a large magnetic metal thickness, i.e., the limit of a single Fe/semiconductor interface. In order to investigate this question, systems with five layers ZnSe (10 monolayers) and six (or 10 ML) iron were investigated. Figure 4 shows the local density of states (DOS) of the iron part of the system. The central iron atoms show a DOS that strongly resembles bulk iron (9–12). Ingoing towards the interface (1,2 and 19,20), the reversal of the polarization of the density of states at the Fermi energy takes place, as was the case in the systems with two iron layers. But it does not lead to a strong magnetic behavior of the interface iron as it did in the multilayer system. As a result, the extreme spin polarization of the semiconductor layer is *not* found in the calculation for the interface: Fig. 5 compares the spin polarization of the conduction electrons in the two cases. The reason for this strong dependence of the electronic structure of the semiconductor on the layer thickness of the ferromagnetic metal is the different charge transfer in the two cases. With two Fe layers the iron layer adjacent to selenium has a charge of 0.337,[12] while the iron layer adjacent to zinc has a charge of 0.220. With thicker iron layers the charge-per-iron layer shows an oscillatory behavior towards the bulk. In the case of 6 ML iron, the iron layer adjacent to selenium has a charge of 0.473, the next Fe-0.095 followed by -0.001 electrons; the corresponding numbers for the iron layers adjacent to zinc are 0.321, -0.123, and 0.005, respectively. The iron layers adjacent to selenium and zinc show a slightly larger charge transfer (approximately 0.1 electron per layer) in the interface system compared to the multilayer. This difference is responsible for the fact that holes in the majority 3*d* bands remain, and the interaction of these holes with the ZnSe diminishes the strong spin polarization of the conduction electrons in the ZnSe layer. This situation is qualitatively the same as described by Butler *et al.*[11] for the case of a tunnel structure of nine layers of Ge or GaAs sandwiched between two half-infinite units of iron. The difference in charge transfer between the multilayer and the interface is small but results in a strong difference in spin polarization at the Fermi energy in the ZnSe layer. As a consequence, it is expected that spin-polarization experiments will show a rather large dependence on the applied bias voltage. Such a strong dependence was recently found in a FM metal-insulator junction.[13]

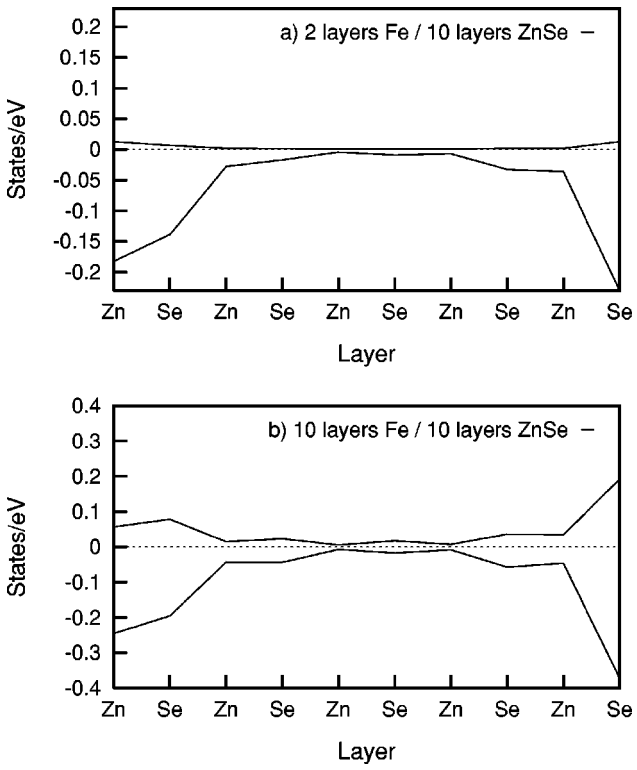

FIG. 5. Spin-resolved density of states at the Fermi energy in the ten layer ZnSe multilayer system, (a) with two Fe layers, (b) with ten Fe layers.

VI. CONCLUDING REMARKS

The results presented here confirm the observations by Butler *et al.*[11] that the properties of an interface between iron and various semiconductors are different from the bulk properties of its constituents, and the interpretation of spin-dependent transport should be based on the interface properties. A first observation is that the spin polarization of the electrons at the Fermi energy is reversed as compared with bulk iron. A substantial enhancement of the spin polarization at the interface can be achieved in the case of ZnSe. This calculational result should correspond with a real band gap of $(GaAs)_{0.35}(ZnSe)_{0.65}$. However, since this composition corresponds to the end of the series considered here,[14] it cannot be excluded that pure ZnSe would work equally well. The effect of the layer thickness of the semiconductor shows a maximal effect for 10 ML. It is unexplained, why 8 ML semiconductor thickness performs so much more poorly as 6 ML thickness. All ZnSe systems considered prefer an antiferromagnetic ordering between the Fe layers. A dramatic effect is found in the influence of the thickness of the Fe layer on the spin-polarization at the interface: only thin layers (2 ML) show the enhancement of the spin polarization of the conduction electrons.

[1] L. Esaki, Curr. Sci. **69**, 240 (1995).
[2] M. N. Baibich, M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).
[3] R. M. Kusters, J. Singleton, D. A. Keen, R. McGreevy, and W. Hayes, Physica B **155**, 362 (1989).
[4] P. K. de Boer, H. van Leuken, R. A. de Groot, T. Rojo, and G. E. Barberis, Solid State Commun. **102**, 621 (1997).
[5] P. J. M. Bastiaansen and H. J. F. Knops, J. Phys. Chem. Solids **59**, 297 (1998).
[6] P. K. de Boer and R. A. de Groot, Comput. Mater. Sci. **10**, 240 (1998).
[7] W. E. Pickett and D. J. Singh, Phys. Rev. B **53**, 1146 (1996).
[8] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).
[9] C. T. Tanaka, J. Nowak, and J. S. Moodera, J. Appl. Phys. **81**, 5515 (1987); M. C. Kautzky, F. B. Mancoff, J.-F. Bobo, P. R. Johnson, R. L. White, and B. M. Clemens, *ibid.* **81**, 4026 (1997).
[10] R. A. de Groot, Physica B **172**, 45 (1991).
[11] W. H. Butler, X. G. Zhang, Xindong Wang, Jan van Ek, and J. M. Muelaren, J. Appl. Phys. **8**, 5519 (1997).
[12] The charge on an atom cannot be defined in a unique way. Here we use the charge within the Wigner-Seitz sphere. Since all radii for iron were equal (and equal to that of pure iron), these numbers are meaningful. The charges quoted here are averages over the inequivalent irons within a layer.
[13] M. Sharma, S. X. Wang, and J. H. Nickel, Phys. Rev. Lett. **82**, 616 (1999).
[14] The study could be extended beyond ZnSe in considering a virtual crystal approach for a mixture of ZnSe and CuBr. However, in the case of CuBr the 3*d* states certainly cannot be treated as core electrons. Thus, a self-interaction corrected calculation would be required here, which for systems of this size is currently out of reach.