Origin and nature of the band gap in β-FeSi$_2$

Leo Miglio and Giovanna Malegori

Dipartimento di Fisica dell'Università di Milano, via Celoria 16, I-20133 Milano, Italy

The recent interest in β-FeSi$_2$, the semiconductor phase of metallic iron silicides, is related to the nature of its gap. By semiempirical tight-binding calculations we investigate the formation of the gap and the changes in the cohesion energy when the original calcium-fluorite structure (bulk unstable and metallic) is distorted into the β phase. We find out that the latter corresponds to an indirect semiconductor, but minor deformations of the structure turn the gap into a direct one.

Metallic silicides play an increasingly important role in the fabrication of microelectronic devices, due to their large compatibility with silicon integration technology. In the past five years, however, particular attention has been devoted to iron silicides, since there exists one semiconductor stable phase, namely, β-FeSi$_2$, which could be employed for optoelectronic devices. Actually, this material is interesting also from a fundamental point of view, since its mainly metallic texture allows for the appearance of several epitaxial phases on silicon. Some of them are bulk stable [such as the orthorhombic phase (β) below 940 °C and the tetragonal phase (α) at higher temperatures], some others just exist in thin-film configuration [pseudomorphic phases, such as fluorite (γ) and defective (d) (CsCl) Fe$_{0.5}$Si], as a result of the small misfit to the substrate lattice parameter.[1] However, the constitutional pd bonding between silicon and the transition metal still displays a sizable amount of directional, covalent character and this is probably the reason why semiconductive gaps may appear depending on the atomic configuration, as is the case with β-FeSi$_2$. The latter corresponds to a distortion of the CaF$_2$ (γ) structure—essentially a secondary coordination transformation—which reduces the volume per formula unit (f.u.) from 39.12 Å^3 to 37.62 Å^3, by rearranging 16 f.u. in the orthorhombic cell.[2]

Very recently, several improvements in the growth technique of iron disilicides have been reported in literature, which include molecular-beam epitaxy, allotaxy, and chemical vapor deposition.[3] Still, the possibility of employing β-FeSi$_2$ for optoelectronic devices has been questioned by one first-principles calculation, showing that an indirect gap as large as 0.78 eV is present, which is slightly smaller than the direct one (0.85 eV),[4] as confirmed by the recent findings in absorption and luminescence measurements.[5] In addition, the dimensions of the orthorhombic cell[2] ($a = 9.86$ Å, $b = 7.79$ Å, $c = 7.83$ Å) provide a bad match with silicon, generating misfit dislocations at the interface and the appearance of different domains in the films, so that it is not easy to obtain epitaxial samples with good crystalline quality at macroscopic size.[6]

Despite these shortcomings, the question of the gap nature is still very open, due to the great technological interest and to the tiny difference between indirect and direct gaps, which appears to be vanishingly small in very

recent photothermal-deflection-spectroscopy measurements at 77 K.[7] The latter feature is probably generated by the flatness of the lowest conduction bands and by their strong coupling with the lattice distortions, as suggested in Ref. 4. Therefore, it seems worthwhile to investigate whether small structural changes may reverse the gap nature. Due to the large size of the unit cell, a systematic analysis of the electronic structures and the relative stability of different configurations is presently outside the capabilities of first-principles methods, and for this reason we implemented a semiempirical tight-binding (TB) scheme. It is demonstrated to be highly transferable from one structure to another and more accurate in the predictions of the electronic features than the common standard for tight-binding methods.[8]

In this paper, we report our results of the total energy, the electronic density of states (DOS), and the band-gap diagram for a continuous distortion of the γ structure into the β phase and for small hydrostatic deformation of the latter. They show that the nature of the gap is very structure sensitive and that a slight decrease in the first-neighbor distance induces a change in the nature of the gap, from indirect to direct, so that a clear indication for renewed efforts in the epitaxial tailoring of this material is obtained.

Our method is grounded on the partition of the cohesive energy of the solid into a band-structure term E_{bs}, as originated by a reciprocal-space summation over occupied tight-binding states $\varepsilon_{n,k}$ (n is the band index, k is the wave vector) and a repulsive contribution E_{rep}, which is generated by a summation of one short-range, two-body potential $\phi(r_{ij})$ on the relevant shell of neighbors (j):

$$E = E_{bs} + E_{rep} = \sum_{n,k} \varepsilon_{n,k} + \sum_{i<j} \phi(r_{ij}) . \tag{1}$$

E_{bs} is negative (i.e., attractive) and takes into account the electronic features, as provided by a Slater-Koster (SK) parametrization of the TB matrix,[9] involving s and p orbitals for silicon and s, p, and d orbitals for iron. We obtain the configurational dependence of this term by scaling the radial part of the SK parameters $H_{ll'}$ with interatomic distance r_{ij}, following the Harrison rules:[10]

$$H_{ll'}(\mathbf{r}_{ij}) = H_{ll'}(\mathbf{r}_{ij}^0) \cdot (r_{ij}^0/r_{ij})^{n_{ll'}} , \tag{2}$$

where $l, l' = s, p, d$ orbital and $n_{ll'} = 2$, 3.5, or 5 if none,

TABLE I. Koster-Slater parameters $H_{ll'm}$ along with those of the repulsive potential (see text).

(eV)	$ss\sigma$	$sp\sigma$	$pp\sigma$	$pp\pi$	$sd\sigma$	$pd\sigma$	$pd\pi$	$dd\sigma$	$dd\pi$	$dd\delta$	ψ (keV)	m
Fe-Si	−1.087	1.598	3.439	−0.458								
Si-Fe	−1.087	1.660	3.439	−0.458	−1.579	−1.302	0.622				0.532	6.554
Si-Si	−0.895	1.209	1.848	−0.539							0.138	4.768
Fe-Fe	−0.142	0.267	0.755	−0.053	−0.088	−0.207	0.086	−0.121	0.049	−0.011	2.049	8.341

Fe	$E(s)$	$E(p)$	$E(d)$	Si	$E(s)$	$E(p)$
(eV)	4.730	6.029	−1.582	(eV)	−3.925	4.044

one, or both orbitals are d-like, respectively. In our case the TB elements have been mainly fitted to the full-potential linear augmented-plane-wave (FLAPW) bands of the fluorite structure, but for the Fe-Fe hopping terms, which are adjusted to the corresponding ones for (CsCl)FeSi.[11] In the the latter structure they play an important role, since the iron sites are in second-neighbor position, which correspond to a reduced interatomic distance with respect to fluorite, as is the case for a few iron pairs in β-FeSi$_2$ (see the note in Ref. 2). In detail, 52 states at five symmetry points of the Brillouin zone (BZ) are fitted for γ-FeSi$_2$ and 34 states at four symmetry points are considered for (CsCl)FeSi (Table I). Particular emphasis is given to the reproduction of the DOS features near the Fermi level (E_f), which follow very satisfactorily the FLAPW results, but for the overestimated localization of silicon s states at very low energy.[8] Charge-transfer effects on the diagonal elements of the TB Hamiltonian are taken into account by a site renormalization with a Hubbard parameter $U_{Si}=U_{Fe}=0.5$ eV. Still, this procedure is important only when the coordination number is changed.

The repulsive term in (1), E_{rep}, phenomenologically represents the quantum-mechanical interaction between occupied orbitals, so that the summation of $\phi(r_{ij})$ is extended up to third-neighbor Fe-Fe pairs, as for TB hopping elements. We have chosen a simple two-body form,

$$\phi(r_{ij}) = \phi_{\alpha,\beta}(r_{ij})^{-m_{\alpha,\beta}} ,$$ (3)

which, however, discriminates the metallic pairs from the silicon ones (α=Si, β=Fe). The four repulsive parameters, $\phi_{Si,Si}$, $\phi_{Fe,Fe}$, $m_{Si,Si}$, $m_{Fe,Fe}$ are obtained by imposing the equilibrium and stability conditions at the experimental lattice constant and the FLAPW bulk modulus of γ-FeSi$_2$ and (CsCl)FeSi, where the Si-Fe parameters are fixed to be the geometric average of the prefactors and the algebraic average of the exponents (Table I).

In Fig. 1 we report the modification of the DOS for a progressive distortion of the fluorite (γ) structure into the β one. We have considered a supercell of 48 atoms which corresponds to four conventional fcc cells (16 unit cells) for the γ phase and to one orthorhombic cell for the β one, integrating the bands over 576 k points in the irreducible part of the BZ. Our molecular-statics calculation is performed at 11 atomic configurations (here only six are displayed), which are generated by a linear interpolation of the atomic positions and cell dimensions between the two phases. ε is the configurational parameter

that quantifies this distortion, ranging from 0 at γ to 1 at β. Considering the small size of the atomic displacements we believe our linearization of the transformation path to be appropriate, as confirmed by the total-energy results of Fig. 2 (top panel), where a smooth, monotone decrease is found from γ to β. Here, the absence of any activation barrier is consistent with the fact that no relevant bond breaking occurs in the structural phase transition and the epitaxial metastability of the γ phase in thin-film configuration on Si(111) should only be addressed to interface contributions. The difference in cohesion energy between the two phases (0.46 eV/f.u.) is confirmed by the
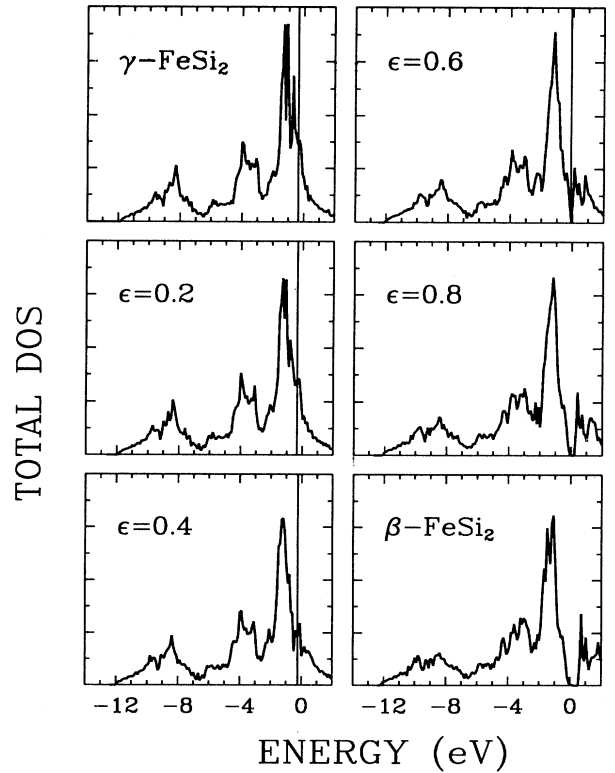

FIG. 1. Electronic density of states of FeSi$_2$ for a progressive distortion of the fluorite (γ) phase into the orthorhombic (β) one. ε is the corresponding configurational parameter (see text) and the vertical bar indicates the position of the Fermi level for metallic structures.
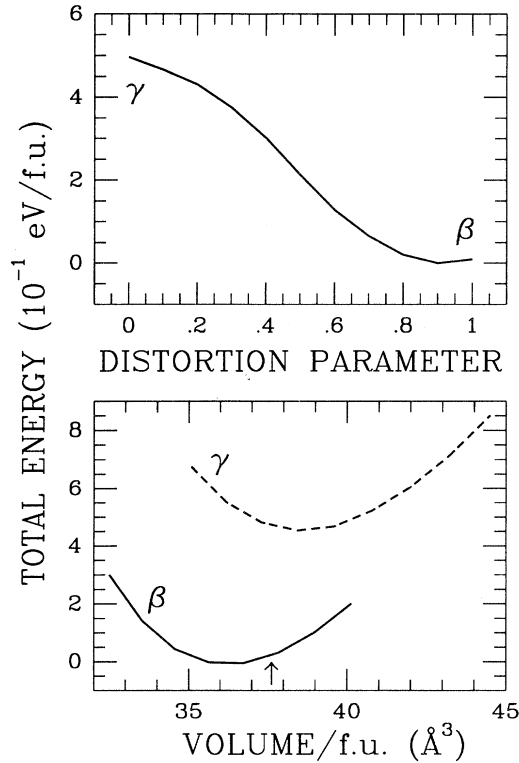
FIG. 2. Tight-binding total energy for the same structural distortion of Fig. 1 (top panel) and for the hydrostatic deformations of the two phases (bottom panel). $\varepsilon = 1$ and the arrow indicate the experimental configuration for the ρ structure.

FIG. 3. Progressive opening of the band gap in β-FeSi$_2$ (see text) for $\varepsilon = 0.7$ (a), $\varepsilon = 0.9$ (b), and $\varepsilon = 1$ (c), as plotted along $\langle 111 \rangle$ and $\langle 001 \rangle$ directions.

bottom panel of Fig. 2, where we plot the total energy vs hydrostatic changes of the volume. It agrees fairly well with preliminary, still-unpublished linear-muffin-tin orbital (LMTO) predictions (0.59 eV/f.u.).[12]

Getting back to Fig. 1, we note that a progressive shift to higher energies of the nonbonding pd-like peak generates the appearance of the gap at $\varepsilon = 0.7$. In the experimental structure $\varepsilon = 1$ we find a DOS which correctly displays the same line shape of the LMTO calculation for the β phase.[4] In addition, our estimation of the energy gap at Γ is 0.52 eV [see Fig. 3(c)], which is lower than the experimental value (0.85 eV); still, it lies within the range of local-density-approximation predictions (0.5–0.8 eV.[4] We also find a slightly lower indirect gap along the $\langle 111 \rangle$ direction, in accordance with Ref. 4. The latter result is very remarkable, since our method is not self-consistent, so that the nature and the size of the gap in the β phase is demonstrated to be entirely structure originated.

This is confirmed by the fact that getting back towards the fluorite structure the gap turns out to be direct at $\varepsilon = 0.9$ [Fig. 3(b)], where we actually find the minimum of the total (distortion) energy, and maintain this nature up to its disappearance at $\varepsilon = 0.7$ [Fig. 3(a)]. It is our opinion that the driving mechanism for the modification of the lowest conduction-band dispersion originates from the fact that first-neighbor Fe-Si pairs are getting closer in the transformation from β to γ (despite the volume increase[2]), so that the overlap interactions between them
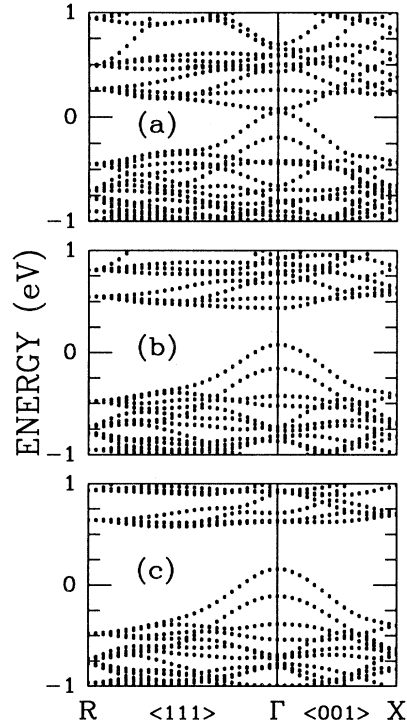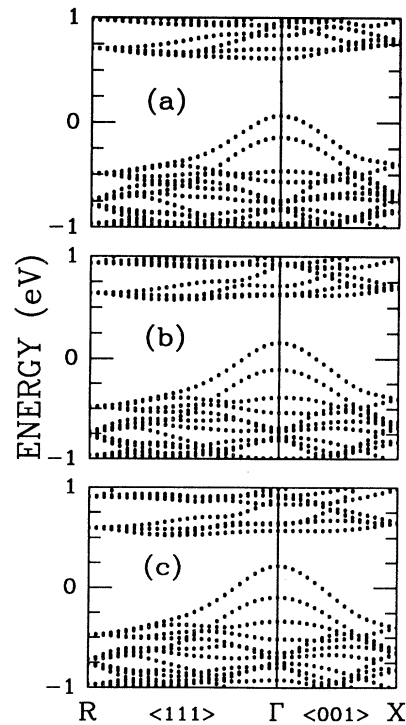

FIG. 4. The same as in Fig. 3 for a hydrostatic compression by 3.8% (a) and dilatation by 3.6% (c) of the experimental configuration (b).

are larger. In fact, when the β structure is hydrostatically compressed from the experimental value (V/f.u. = 37.62 Å^3) to the minimum of total energy (V/f.u. = 36.18 Å^3) the gap turns into a direct one [see Figs. 4(b) and 4(a), respectively] and the opposite trend is found for the expansion to V/f.u. = 38.98 Å^3 [Fig. 4(c)].

We do not expect the structural shrinking with very low temperatures to be enough to drive the β phase towards our equilibrium structure, which displays a direct gap. Actually, the experimental findings,[5,7] indicate a

steeper rise of the indirect gap with respect to the direct one as the temperature decreases; still, at 77 K this effect is not sufficient to reverse the gap nature. However, a clear indication emerges within the accuracy of our semiempirical approach that induced lattice distortions are critically important in β-FeSi$_2$. To this end, a careful tailoring of the substrate lattice parameter could improve the coherency of the epitaxial growth and, in turn, both the crystalline quality of the film and the amount of (helpful) strain in it.

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[3]For a general overview of the methods, see Part II of *Silicides,*

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