PHYSICAL REVIEW B VOLUME 42, NUMBER 11 15 OCTOBER 1990-I

Electronic structure of β-FeSi$_2$

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(Received 11 April 1990; revised manuscript received 15 June 1990)

Ab initio calculations of the electronic structure of β-FeSi$_2$ show that this material, in agreement with experiment, is a semiconductor. The calculated hole and electron masses of the band-edge states are $\simeq 0.8m_0$. A particularly strong coupling of the band-edge states to the lattice is suggested. This may cause the mobilities, even in pure β-FeSi$_2$ samples, to be very low at ambient temperature.

I. INTRODUCTION

Transition-metal disilicides, MSi$_2$, attract an increasing interest as potential constituents in microelectronic and optoelectronic devices. Several of the MSi$_2$ compounds can be grown[1] epitaxially on Si. For example, NiSi$_2$ and CoSi$_2$, which assume the fluorite structure, have lattice constants that almost match that of Si, and since they are metallic they are well suited in forming structurally very perfect[1] metal-semiconductor contacts (Schottky junctions) with Si. A considerable experimental[1] and theoretical[2] effort has lately been devoted to the study of these systems. FeSi$_2$ would also, as will be shown below, have been metallic if its crystal structure had been the same as that of CoSi$_2$ and NiSi$_2$. As will be shown, this hypothetical FeSi$_2$ phase is highly unstable, and an energy-lowering distortion drives the system into the complex β structure,[3] in which FeSi$_2$ develops a gap in the electronic spectrum.[4] Very few MSi$_2$ that are semiconductors are known; apart from FeSi$_2$, only OsSi$_2$ and CrSi$_2$, to our knowledge, are known to exhibit a forbidden gap. Due to its semiconducting property, it has been suggested that β-FeSi$_2$ will be well suited to combine the benefits of silicon-based digital technology with new optoelectronic devices, optical fiber links, electro-optic interconnects, and infrared detector arrays. Consequently, studies of epitaxy of β-FeSi$_2$ on Si surfaces have been undertaken.[5]

II. BAND STRUCTURES

The band-structure calculations are performed within the density-functional theory,[6] and we use the local-density approximation (LDA). The LDA parametrization by von Barth and Hedin[7] is applied. The one-particle wave equation is solved self-consistently by means of the scalar-relativistic[8] linear muffin-tin orbital (LMTO) method.[9]

A. Fluorite structure

The fluorite structure can be viewed as a fcc Bravais lattice with four basis atoms (e.g., for NiSi$_2$), one Ni in (0,0,0), two Si in $(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$ and $(\frac{3}{4},\frac{3}{4},\frac{3}{4})a$, and one "empty sphere" (E) in $(\frac{1}{2},\frac{1}{2},\frac{1}{2})a$. The E sphere is introduced in order to optimize the LMTO method.[10] We have repeated the calculation of Ref. 10 for NiSi$_2$ and CoSi$_2$ in order to compare to the band structure for FeSi$_2$ in the (hypothetical) fluorite structure. Figure 1 shows the density of states (DOS) for the three compounds. As one would expect, the general shapes of these DOS functions are very similar. The major difference relates to the Fermi-level (E_F) position. In NiSi$_2$ and CoSi$_2$, E_F is above or close to the top of the M-d regime, but in FeSi$_2$, E_F falls right in a very sharp and strong peak of the Fe-d-DOS. A projection onto cubic harmonics shows that it has E_g character (x^2-y^2, $3z^2$-1). At first it was puzzling that the origin in **k** space of this peak could not be estimated by plotting the band structure as done in Fig. 2 along selected symmetry lines. No region of flat bands near E_F is found (Fig. 2). If, however, we consider the bands along lines lying in the hexagonal Brillouin-zone face as in Fig. 3, a completely different picture emerges. In large regions very flat bands of Fe $d(E_g)$ character are found near E_F, and in the regime above E_F the band structure along these lines exhibits a large gap (which does not extend throughout the zone, cf. Fig. 2).

The fact that E_F is located in the strong DOS peak [Fig. 1(c)] indicates that the fluorite form of FeSi$_2$ is highly unstable; the system can lower its energy by undergoing a transition that causes this peak to split. A splitting could be obtained if FeSi$_2$ would spin polarize. We therefore allowed for spin polarization but forced first the crystal structure to remain as that of CaF$_2$. Indeed, a ferromagnetic moment, $0.3\mu_B$/f.u. (f.u. being the formula unit), develops and the total energy is lowered.

The ferromagnetic fluorite form of FeSi$_2$ is still metallic, and nature prefers to split the strong DOS peak by distorting the crystal structure in such a way that the E_g peak splits into two, one above E_F and one below. This distortion may be viewed as a solid-state analogue to the Jahn-Teller effect. The stable crystal structure, the β phase, is easily seen[3] to deviate from the CaF$_2$ only through small deformations and rotations of the cubic cages in the fluorite structure.

B. Band Structure of β-FeSi$_2$

The band structure of FeSi$_2$ is orthorhombic, $a = 7.791$ Å, $b = 7.883$ Å, and $c = 9.863$ Å (in contrast to Ref. 3, Dusausoy *et al.* we take $\hat{z}$ along the longest edge and $\hat{x}$ along a). The primitive cell contains 16 Fe atoms, grouped in two sets of 8 Fe (1) and 8 Fe(2), i.e., there are only two different *types* of Fe sites. There are also only two kinds of Si atoms, Si(1) and Si(2), but there are 16 atoms of each type. The primitive cell thus contains 48 atoms, 16 Fe and 32 Si. The coordinates of these are all given by Dusausoy *et al.*[3]

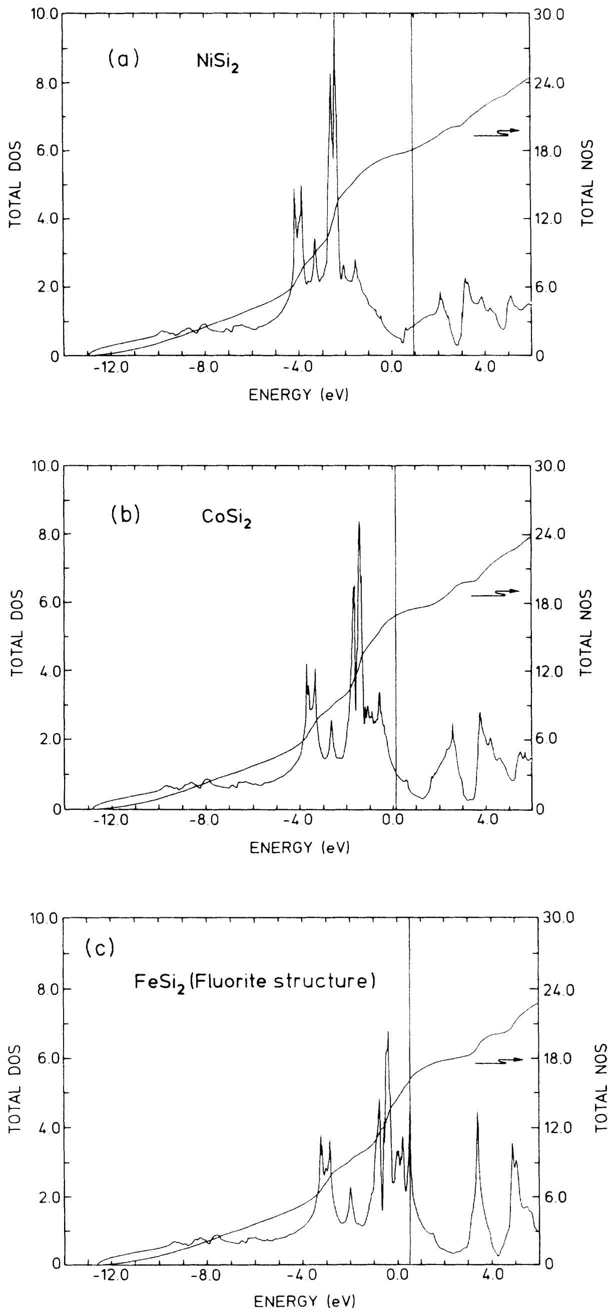

FIG. 1. Density of states functions calculated for (a) NiSi$_2$, (b) CoSi$_2$, and (c) FeSi$_2$, all in the fluorite structure (which for FeSi$_2$ is hypothetical). Density of states (DOS) and number of states (NOS) are in units of (electrons/eV) per formula unit (f.u.) and electrons/f.u., respectively. The Fermi level is indicated by a vertical line.

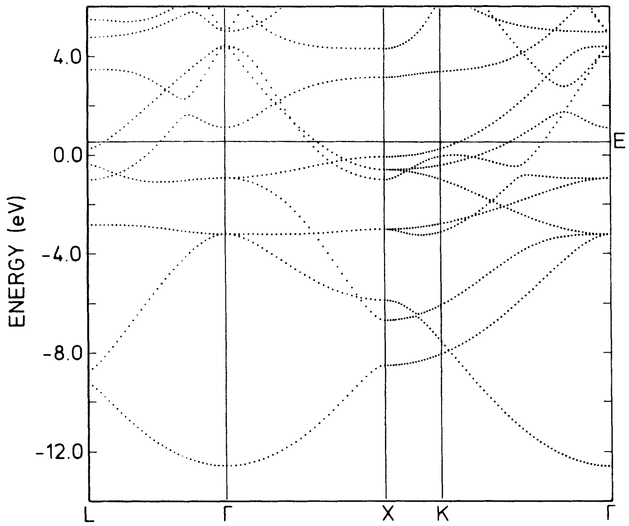

FIG. 2. Band structure of fluorite-FeSi$_2$ along symmetry lines in the first Brillouin zone.

As for the fluorite structure, the accuracy of the LMTO method is also optimized for the β structure by introduction of empty spheres. There are two types of symmetry-dictated empty-sphere positions, E_1 and E_2, eight of each type. The centers of the E_1 and E_2 spheres are in the centers of the empty "type-1 cubes," shown in Fig. 4, and of the empty "type-2 cubes" of Fig. 5 of Ref. 3 (Dusausoy *et al.*). The self-consistent LMTO calculation thus uses a primitive cell with a total of 64 "atoms," and since s, p, and d functions are included in the basis set, Hamiltonian and overlap matrices are of the size

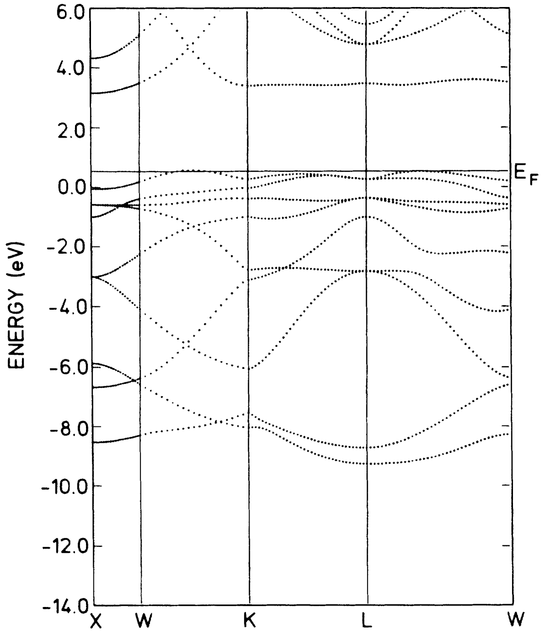

FIG. 3. Band structure of fluorite-FeSi$_2$ along lines lying in the hexagonal Brillouin-zone face.

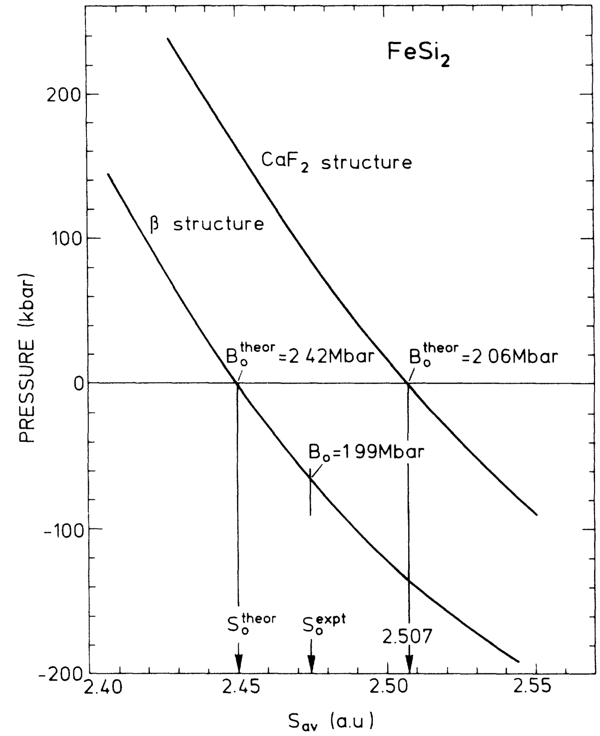

FIG. 4. Calculated variation of the pressure FeSi$_2$ with lattice spacing expressed via the average atomic-sphere radius, S_{av} (in units of bohrs). [(64)(4π/3)$S_{av}^3=abc$, the volume of the primitive cell]. S_0^{theor} and S_0^{expt} are the values corresponding to the theoretical and experimental equilibrium volumes, respectively, for the β-phase. The theoretical equation of state for the fluorite structure is shown for comparison. The bulk moduli calculated at the indicated volumes are denoted B_0. Those with superscripts theor are evaluated at the theoretical equilibrium volumes.

576×576. In spite of the fact that we need to introduce the E spheres, standard diagonalization procedures can easily be used because the LMTO uses a minimal basis set, resulting in this moderate size of the matrices.

Initial iterations were made by using only three special **k** points, but the last 10 iterations used **k** space sampling over 22 special points. The calculations were performed for six different volumes, specified through the average atomic-sphere radius, S_{av}, and Fig. 4 shows the calculated volume variation of the pressure as derived from the total energy. The minimum of the total energy is found for $S_{av}=2.45$ a.u., which deviates by less than 1% from the experimental value, 2.4715 a.u.

Figure 5 shows the total density of states, and it is seen that (even) the LDA band structure predicts β-FeSi$_2$ to be a semiconductor. The gap has opened as a consequence of splitting of the E_g peak in the fluorite-type DOS, and it is therefore not surprising that the band-edge states in β-FeSi$_2$ are mainly of Fe d character. It would then also be natural to assume that the bands at the valence-band maximum (VBM) and conduction-band maximum (CBM) should be quite flat, corresponding to a large (Fe d) effective mass.[11] The detailed band-structure calculation, though, shows (see Fig. 6) that there is some Si p admixture at the VBM and CBM, and that the band edges disperse corresponding to rather low effective-mass values. For the VBM and CBM states at Γ we get $m_h=0.85m_0$ and $m_e=0.80m_0$, m_0 being the free-electron mass. The nature of the gap in the band structure shown in Fig. 6 is indirect but the difference between the calculated direct (Γ) and indirect gaps is very small. Although an indirect gap, as found here, could explain a part of the absorption found for energies below the

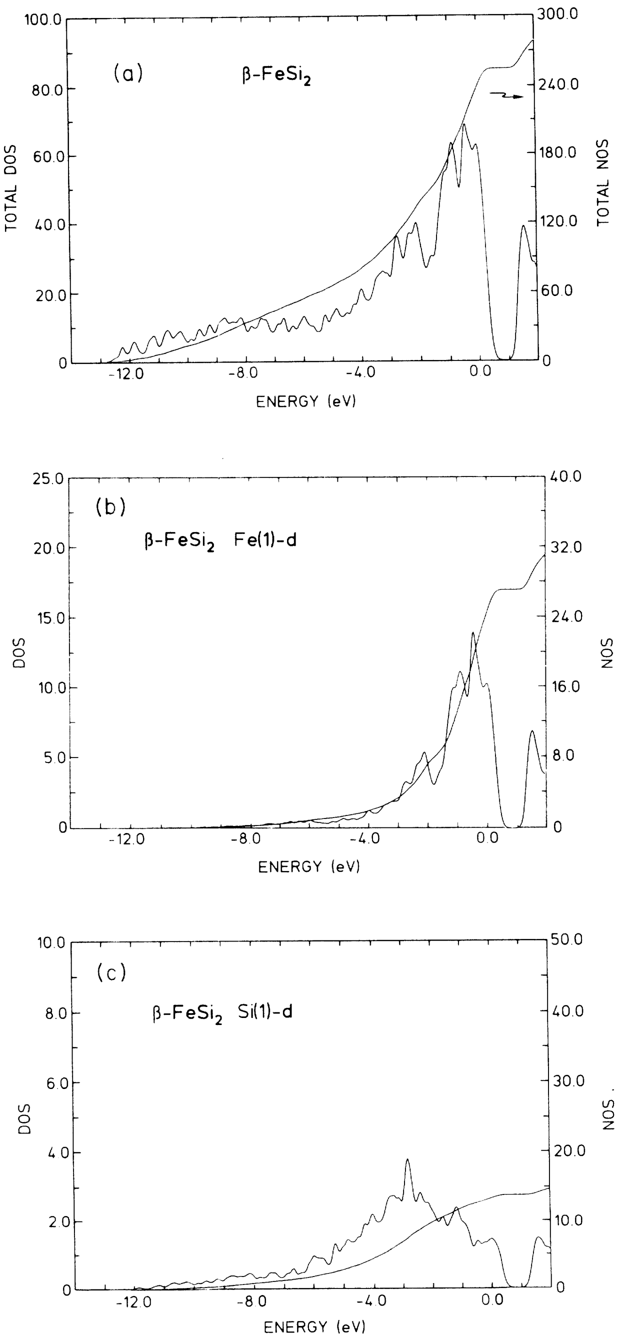

FIG. 5. Density-of-states (DOS) and number of states (NOS) functions for β-FeSi$_2$; (a) total, (b) Fe(1) d, (c) Si(1) p. In (a) the units are (electrons/eV)/cell and (electrons/cell), respectively. Those of (b) and (c) are similar, but per spin.

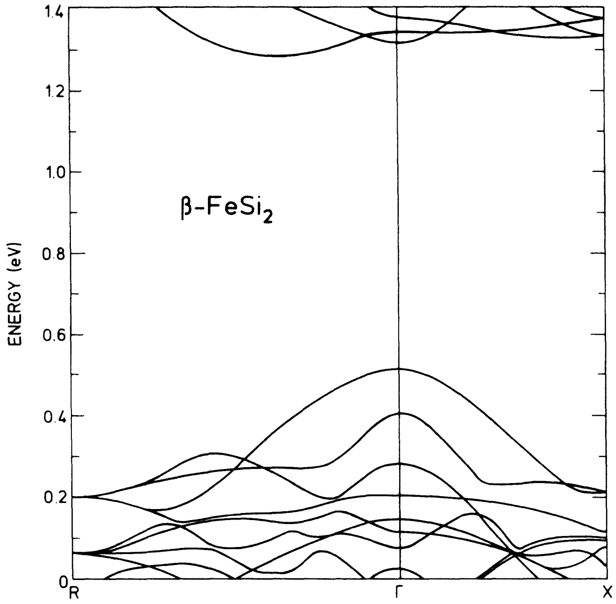

FIG. 6. Band structure (LDA) of β-FeSi$_2$ for energies close to the band gap. The ΓX line is along ⟨100⟩, ΓR along ⟨111⟩.

direct-gap transition energy, the accuracy of the present LDA calculation does not permit an unambiguous specification of the relative position of the Γ CBM and that at the $R\Gamma$ line.

The direct gap found experimentally[12] is 0.85 eV. The LDA calculation, Fig. 6, yields 0.80 eV. Usually the LDA band structures for semiconductors exhibit gaps that are 50–100 % too small (see, e.g., Ref. 13 and references given therein). Therefore the close agreement between the calculated LDA gap and experiment found here is very surprising. Although Ref. 14 might be relevant, the explanation is more likely to be related to a technical detail. During the preparation of the present paper, the author was informed that Eppenga[15] has also performed *ab initio* LDA calculations for β-FeSi$_2$. His DOS functions are similar to those presented here, except for the fact that a smaller gap, 0.44 eV, is found. The calculations of Ref. 15 are made by means of the augmented-spherical-wave (ASW) method, and since the ASW and LMTO schemes are very similar, one should expect the results to be identical. However, our LMTO calculations are made strictly within the atomic-spheres approximation (ASA), and do not include the so-called "combined-correction" term.[9] The ASW method as used by Eppenga does include this. In the case of GaAs, it was shown[13] that the combined correction reduces the gap, and this has also been observed for other sp^3-bonded zinc-blende-type semiconductors (the indirect gap of Si, though, is essentially unchanged). The important result, however, is that, whatever the level of sophistication of the band-structure scheme is, the LDA yields a gap of a significant width (0.5–0.8 eV), and the calculations allow us to describe the nature of the gap formation. The present calculation may differ from the best "true" LDA results, but since the gap is closer to the observed value, it may be more useful for calculations of effective band-edge masses and optical properties.

TABLE I. β-FeSi$_2$; the dominating occupancies (in %) of the valence-band maximum (VBM) and conduction-band minimum (CBM) states at $\mathbf{k}=0(\Gamma)$.

	VBM	CBM
Fe(1) *p*	11.2	1.4
Fe(1) *d*	8.8	23.6
Fe(2) *p*	4.2	
Fe(2) *d*	42.9	60.6
Si(1) *p*	18.0	2.5
Si(1) *d*	4.7	
Si(2) *s*		4.2
Si(2) p	3.1	
Si(2) *d*	4.3	

Experimental optical-absorption measurements[12] are claimed to yield the direct gap. If it were true (somewhat in conflict with the low mass values given above) that the CBM and VBM both were of Fe *d* character, then the transitions would be dipole forbidden. In order to examine this question, the wave functions at the band edges at Γ have been analyzed, and the site and projected occupation numbers are given in Table I. Note that the VBM has 11.2% Fe(1) *p* character and the CBM 23.6% Fe(1) *d*. Consequently, optical transitions are *not* forbidden, and in this respect the present LDA calculation also agrees with experiment.

So far, we have taken the experimental gap value to be 0.85 eV, but values up to 1.0 eV are also found in the literature.[16] In view of the spread in the experimental data it is not obvious which value one should associate with the $T=0$ gap, but presumably the room-temperature value of E_g is close to 0.9 eV. The magnitude of the linear temperature coefficient $dE_g/dT=-0.45$ meV K^{-1}, as measured by Waldecker *et al.*[17] is large, surprisingly large, as will be seen in Sec. III. If we assume that this value (measured for $700 < T < 1200$ K) also applies to the low-temperature regime, then E_g would extrapolate to 1.0–1.1 eV for $T \rightarrow 0$. Thus, this thermal effect on E_g implies that even if our LMTO-ASA calculation is considered, room is left for "LDA-errors." But it may be more important to note that $|dE_g/dT| \simeq 0.45$ meV K^{-1} is even larger than what is found for Si and Ge (0.3–0.4 meV K^{-1}). This points to a strong interaction between the band-edge states and the phonon system in β-FeSi$_2$. The following section discusses this suggestion.

III. MOBILITY AND ELECTRON-PHONON INTERACTION IN GAP-EDGE STATES

The mobilities measured (see Ref. 16) for holes (μ_p) and electrons (μ_n) in FeSi$_2$ are of the same order of magnitude. The values of (μ_n) and (μ_p) are small,[12,16] 0.3–4 cm^2 V^{-1} s^{-1}, i.e., much lower than the best values (several thousand) found in intrinsic conventional semiconductors (Si,Ge). The poor mobilities in FeSi$_2$ are not only due to the fact that band-edge masses are higher than in Si and Ge; we calculated the masses in $FeSi_2$ to be ≈ 0.8, i.e., large, but not a value which itself is "disastrously" high. It is often assumed that the mobility in $FeSi_2$ is predominantly limited by impurity scattering. One could then hope that improved sample preparation could increase the mobilities. There are reasons to believe, though, that this may not be the case, and it might well happen that $FeSi_2$ is characterized by an unusually strong electron-phonon scattering in the band-edge states. This suspicion naturally emerges when it is recalled that the formation itself of the gap is caused by a slight lattice distortion.

Assuming that the mobility (μ) is determined by scattering against acoustic phonons, and that the electronic band considered can be described by a parabola characterized by an effective mass m^*, μ is given by[18]

$$\mu = \text{const} \times \frac{s^2}{\bar{a}(m^*)^{5/2}} (k_B T)^{-3/2} , \tag{1}$$

where const is a prefactor depending on the mass density and natural constants, s is the sound velocity, $\bar{a}$ the band-edge acoustic-phonon deformation potential,[19] and k_B is Boltzmann's constant.

In Eq. (1), only $\bar{a}$ and m^* are state dependent, i.e., their values $\bar{a}_v, \bar{a}_c$ and m_h^*, m_e^* may be different at the valence- and conduction-band edges. Since these deformation potentials and effective masses also enter in the linear temperature coefficient of the gap, we can connect Eq. (1) to dE_g/dT. This thermal effect was described realistically by Fan[20] and more recently by Cardona *et al.*[21] For our purpose it is sufficient to consider dE_g/dT as consisting of the two terms

$$\frac{dE_g}{dT} = \left.\frac{\partial E_g}{\partial T}\right|_{\text{vib}} + \frac{\partial E_g}{\partial \ln V}\beta , \tag{2}$$

where the first term, caused by lattice vibrations, has the form

$$\left.\frac{\partial E_g}{\partial T}\right|_{\text{vib}} = -\text{const} \times (m_e^* \bar{a}_c^2 + m_h^* \bar{a}_v^2) , \tag{3}$$

[i.e., as Eq. (23) of Ref. 20], and the second describes the effect of the (static) thermal lattice expansion (β being the expansion coefficient). In Eq. (3), const denotes a positive quantity depending on natural and material parameters (cf. Ref. 20). The gap deformation potential is

$$\frac{\partial E_g}{\partial \ln V} = \bar{a}_c - \bar{a}_v . \tag{4}$$

For Si and Ge, Fan's calculations[20] suggest that the two terms in Eq. (2) are of similar magnitude. The last term is easily estimated, also for β-$FeSi_2$. We have calculated the gap for six different volumes, and it follows that, over the range considered, E_g varies almost linearly with volume, corresponding to $\partial E_g/\partial \ln V \simeq -1.4$ eV when evaluated at equilibrium. Taking β to be $\simeq 11 \times 10^{-6}$ K (the order of magnitude of the $CoSi_2$ value), the lattice expansion term in Eq. (2) is $\simeq -15$ μeV K^{-1}. This is ~ 10 times smaller than the Si value,[20] -178 μeV K^{-1}. Nevertheless, the measured (total) value of dE_g/dT is larger in magnitude for $FeSi_2$ than for Si. If the correct experimental value is -0.45 meV K^{-1}, it then follows that the electron-phonon scattering by far dominates over the thermal expansion term, and further that is "large." The gap deformation potential $dE_g/d\ln V = -1.4$ eV is smaller in magnitude than found for direct gaps in many III-VI semiconductors ($dE_g/d\ln V \simeq -7$ eV). Consequently, $\bar{a}_c$ and $\bar{a}_v$ in FeSi have almost the same values. Now this, together with the fact that we find $m_h^* \simeq m_e^*$, then implies that one should expect, according to Eq. (1), that the mobilities μ_n and μ_p are of similar magnitude, provided that we assume that lattice scattering dominates [i.e., that Eq. (1) is relevant]. As mentioned earlier, experiments do indeed show that $\mu_n \simeq \mu_p$. Since the samples actually used are considered to be rather impure, the electron-phonon scattering in $FeSi_2$ must, in order to be dominating as suggested here, be unusually strong.

Recent measurements,[12] carried out on samples with impurity concentrations so high that one normally should expect phonon scattering to be masked, have shown that, for T down to ~ 60 K, the mobilities in $FeSi_2$ vary with temperatures as $T^{-3/2}$, an observation which appeared very puzzling since this is the T dependence expected for *phonon* scattering [Eq. (1)]. The result however, is, fully consistent with the suggestions made above.

The idea of a particularly strong coupling of the band-edge states to the lattice in β-$FeSi_2$ is further substantiated by calculating the shifts in the energies induced by small changes in the atomic positions. A distortion, chosen such that the point-group symmetry is not altered, has been made by moving the Fe(2) atoms pairwise by equal amounts in opposite directions along $\hat{y}$ (in our coordinate system). Taking this displacement to be $0.01a/2$, i.e., $\simeq 0.4$ Å, and using the same potentials as for the undistorted case ("frozen-potential approximation"), we find that the three highest valence-band states shift by less than 0.3 mRy, whereas the conduction-band minimum (CBM) moves down by 31.1 mRy (0.423 eV), i.e., the gap is reduced by 0.42 eV or $\sim 50\%$. This illustrates the strong coupling to the lattice. Further, the result also shows that the atomic position must be extremely well defined if reliable calculations of the band-edge states are required. More interesting, it also illustrates that band-gap "tuning" can be made by doping in such a way that the lattice is distorted conveniently. Thus, in addition to the direct chemical tuning, a strong effect caused by the generation of internal strains is expected.

IV. DISCUSSION AND SUMMARY

The present LDA calculation shows, in agreement with experiment, that β-$FeSi_2$ is a semiconductor. The gap is found to be close to the measured value, 0.85 eV. Calculations were also performed for a hypothetical fluorite structure, and it was natural to describe the gap formation in β-$FeSi_2$ as being related to a crystal-structure distortion, i.e., a Jahn-Teller-type effect. Thus, we do not consider β-$FeSi_2$ as a Mott insulator like, for example, NiO. We have not here considered the α phase of $FeSi_2$, which is stable at high temperatures. This phase is metallic, and the crystal structure is tetragonal. Thus, FeSi$_2$ exhibits an insulator-metal transition when temperature is increased. The mechanism of this was discussed by Birkholz *et al.*[22] They argue that the transition upon cooling to the insulating phase of FeSi$_2$ is not a Mott transition, but that it is more appropriately described within the lattice-distortion model of Adler and Brooks.[23] This is consistent with the picture of the gap formation in β-FeSi$_2$, suggested by our calculations.

For the purpose of examining in more detail the properties of FeSi$_2$, in particular those important for device applications, we plan to consider the effects of doping. This is, for example, done by replacing a few of the Fe atoms by Co, but the calculations are complicated by the fact that the crystal structure relaxes, and the new equilibrium atomic coordinates must be determined by accurate (cf. Sec. III) force or total-energy calculations. As a first step in the direction towards such a more-complete description, we[24] have first studied Fe$_x$Co$_{1-x}$Si$_2$ alloys in the simpler fluorite structure and derived theoretical phase diagrams. These calculations are most realistic for the Co-rich range; the Fe-rich regime must be based on the β-type structure.

ACKNOWLEDGMENTS

The author is grateful to J. Derrien, N. Motta, A. Pasturel, and J. Werner for helpful discussions. Also, R. Eppenga is thanked for making his results available prior to publication (Ref. 15).

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[11] A very large mass would diminish the value of β-FeSi$_2$ as device material since this would strongly limit the carrier mobilities that could be obtained. As stressed in Sec. III, phonon scattering may strongly reduce the mobilities in β-FeSi$_2$ although the calculations indicate that the masses are relatively small ($\simeq 0.8 m_0$).

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[14] The gap in β-FeSi$_2$ differs in nature from those in "usual" compound semiconductors. In GaAs, for example, the gap is As *p* to (Ga,As) *s*. In β-FeSi$_2$ it is a *d-d* gap. One might speculate whether this gap, opened up by the Jahn-Teller-like effect, is directly related to the difference in total energy between two FeSi$_2$ phases, say, the β-FeSi$_2$ and fluorite-type FeSi$_2$. Since the density-functional theory yields total-energy differences correctly, it might then explain why also the *gap* in β-FeSi$_2$ would come out correctly.

[15] R. Eppenga, unpublished. This calculation (ASW) includes the "combined correction" (CC) term (see text and Ref. 9) which tends to reduce the gap. It does not, however, apply to "empty spheres," and a direct comparison to our LMTO-ASA is therefore not straightforward. A test calculation at Γ with LMTO+CC does seen to lead to a somewhat smaller gap, but a full calculation with CC has not been performed due to the slow convergence of the reciprocal-space summations of the CC term caused by the large number of atoms in the primitive cell.

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