Fe, Ru, and Os disilicides: Electronic structure of ordered compounds

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Electronic structure properties of MSi_2 , where M=Fe, Ru, or Os, in the orthorhombic β phase are investigated using the linear muffin-tin orbital method in the atomic sphere approximation. Selective substitution of Fe with Ru, Os, and Cr in β -FeSi₂ is also studied. These compounds are small-gap semiconductors with theoretical energy band gaps ranging from 0.06 to 0.50 eV, with the exception of the metallic Cr-substituted disilicides. Substitution of Ru or Os for Fe in β -FeSi₂ leads to a reduction of the gap width, an increase in volume of the unit cell, and a bulk modulus similar to or slightly smaller than for β -FeSi₂. Although the theoretical lattice constant of β -OsSi₂ agrees well with experiment, the calculated band gap (0.06 eV) is much smaller than the band gap in β -FeSi₂. This strongly contrasts with experimental observations that suggest a larger band gap in β -OsSi₂ (1.4 – 1.8 eV). Consideration of a proposed metastable monoclinic form of OsSi₂ does not remedy this discrepancy, since it is found to be a semimetal. [S0163-1829(96)02235-7]

I. INTRODUCTION

Two compounds with nominal composition FeSi₂ can be identified in the equilibrium Fe-Si-phase diagram.¹ The metallic high-temperature α -phase based on a tetragonal lattice forms at temperatures above 1255 K, and transforms into the semiconducting β -FeSi₂ for which the crystal structure has been resolved quite accurately.² The electronic properties of the one-face centered orthorhombic β phase (space group 64, Cmca, Pearson Symbol oC48, structure type FeSi₂) have been explored extensively over the past few years, especially in relation with its potential applications in microelectronic, optoelectronic, and thermoelectric devices. Many research groups were able to successfully grow the β phase using ion beam techniques,³ epitaxial growth on Si,⁴ or by depositing a thin iron film on Si, followed by annealing.⁵ Subsequent analysis of the samples confirmed the presence of β -FeSi₂ with a direct band gap of 0.85–0.90 eV.⁶ The existence of an indirect gap several hundredths of an eV smaller was deduced from optical linear transmittance experiments on β -FeSi₂ at low temperatures.⁷

Electronic structure calculations on the β -FeSi₂ phase have been performed by Eppenga⁸ and Christensen.⁹ Augmented spherical wave calculations performed by Eppenga resulted in a direct gap of 0.46 eV and an indirect gap of 0.44 eV. Eppenga also notes that oscillator strengths for optical transitions across the gap at Γ are small, but become significant around 0.77 eV which compares favorably with experimental data (0.85–0.90 eV). From linear muffin-tin orbital (LMTO) calculations Christensen deduced a band gap of 0.80 eV for β -FeSi₂. The equilibrium lattice constant he calculated is 1% smaller than the experimental value, while the bulk modulus is overestimated by about 20%. Christensen's calculations demonstrate the sensitivity of the states at the band edge to the atomic positions in the orthorhombic unit cell; minor displacements of Fe atoms in β -FeSi₂ lead to significant changes in the calculated band gap. More recently Eisebitt *et al.*¹⁰ compared results from soft x-ray experiments on α - and β -FeSi₂ to band structure calculations. Full-potential linear augmented plane wave (FLAPW) calculations for the β phase resulted in a band gap of 0.78 eV. From a semiempirical tight-binding study of the transformation from metallic fluorite-based FeSi₂ to semiconducting β -FeSi₂, Miglio and Malegori¹¹ estimated the width of the band gap to be 0.52 eV. Just very recently Filonov *et al.*¹² published results of a LMTO calculation with different atomic sphere radii for the different types of atoms. These authors find a quasidirect band gap of 0.74 eV at a point along the Γ -*Z* direction. Theoretical work therefore correctly establishes β -FeSi₂ to be a narrow-gap semiconductor with about the right lattice constant, bulk modulus, and band gap.

The motivation for the present work is twofold. First, doped β -FeSi₂ holds promise as a material with excellent thermoelectric properties, characterized by the figure of merit $Z = S^2 \sigma / \kappa$. Here S is the Seebeck coefficient, σ the electrical conductivity, and κ is the thermal conductivity. The temperature, T, at which the dimensionless quantity ZT reaches its maximum determines whether the material is more suitable for refrigerating or high-temperature generating applications. Theoretical models for the figure of merit of narrowgap semiconductors predict highest ZT at gap widths varying from 6 to 10 $k_B T$.^{13–15} Neglecting variation of the band gap with temperature, it is roughly estimated that β -FeSi₂ has an optimum (largest) ZT at temperatures just below the $\beta \rightarrow \alpha$ transition temperature. According to theoretical predictions, a narrower gap should lead to maximal ZT at lower temperatures, thereby altering the specifications of the thermoelectric device. Therefore, it is worthwhile to investigate ternary systems based on the β -phase, in which part of the iron atoms have been replaced. The substitution of Os for Fe in β -FeSi₂ is of particular interest since the (semiconducting) compound OsSi₂ (from now on referred to as

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 β -OsSi₂) is known to exist in a crystal structure of the β -FeSi₂ type.^{16,17}

The second motivation arises from interest in semiconducting disilicides for applications in micro- and optoelectronic devices. So far, only disilicides of Fe, Os, and Cr are known to be semiconductors. The prospect of being able to optimize the band gap of a disilicide with a particular application in mind is attractive. In the present work, the influence on the band gap of partial or complete substitution of Fe in β -FeSi₂ with Ru or Os is investigated theoretically. Also substitution of Cr (a potential *p*-type dopant) on the Fe sublattice, and the effect of substitution on equilibrium lattice parameters and bulk moduli for all these ordered compounds of the *o*C48 class are estimated.

The content of this paper is organized as follows. Section II gives a brief account of the computational procedure employed. In Secs. III and IV, the methodology is applied to the study of the electronic structure properties of α - and β -FeSi₂, β -OsSi₂, and a metastable monoclinic phase, referred to as m-OsSi₂. Since these four compounds have been synthesized and analyzed, calculated properties are compared with available experimental information. Overall satisfactory agreement leads to the conclusion that the theoretical approach used in this work gives a fair description of the electronic structure of these systems. In Sec. V results from band structure calculations for β -FeSi₂ and other oC48-based ordered compounds involving Ru, Os, and Cr are discussed. Although some of these compounds have not yet been synthesized in this particular structure, the aim here is to explore the effects of substitution of these three species in the Fe sublattice on electronic structure properties. It is found that partial or total substitution of Fe in β -FeSi₂ with Ru or Os preserves the small-gap semiconducting property. In all cases, the equilibrium lattice constant shifts to larger values, while the bulk modulus is similar or somewhat smaller than for β -FeSi₂. Finally, a summary of the main results of this work is presented in Sec. VI.

II. METHODOLOGY

The electronic structure calculations reported here were performed with the linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA).¹⁸ Exchange and correlation effects are treated within the local density approximation (LDA) of density functional theory.¹⁹ Although the LDA does not yield very accurate predictions for the band gap and, in general, underestimates the gap width, it is expected that the existence of a gap and trends in its width as a function of compound-composition are predicted correctly. Where appropriate, empty spheres were added in open interstitial regions in the crystal in order to reduce the overlap between adjacent atomic spheres. Self-consistent solutions to the Kohn-Sham equations are obtained for all electrons in the system using the exchange-correlation potential as parametrized by Hedin and Lundqvist.²⁰ The core electron states are obtained as solutions of the Dirac equation, and scalar relativistic terms are retained in the LMTO Hamiltonian for the band states. A set of 18 k points in the irreducible wedge of the one-face centered orthorhombic Brillouin zone was used in a temperature broadening integration scheme. It was verified that a higher number of k points did not significantly

TABLE I. Dimensions of the experimental unit cell for α -FeSi₂, the *o*C48-based compounds, and the monoclinic meta-stable OsSi₂ phase.

Compound	<i>a</i> /a.u.	<i>b/</i> a.u.	<i>c</i> /a.u.	β	Ref.
α -FeSi ₂	5.0834		9.7019		28
β-FeSi ₂	14.7229	14.8022	18.6384		2
β -OsSi ₂	15.3385	15.5392	19.1800		23
m-OsSi ₂	16.5729	5.6692	13.9462	118.5°	27

alter the band structure or the charge contained in the atomic spheres. The density of states (DOS) for the orthorhombic compounds was constructed using a denser grid of 40 k points. The irreducible part of the tetragonal Brillouin zone (for the α phase) was probed with a mesh of 112 k points in a tetrahedron integration scheme, while for the metastable monoclinic phase of OsSi₂ (hereafter referred to as *m*-OsSi₂) a set of 125 k points was used.

In the case of α -FeSi₂ pivotal energies for the *s*-, *p*-, and d-like muffin-tin orbitals on all atomic spheres were automatically adjusted to the center of gravity of the occupied part of the atom-angular momentum projected DOS in each iteration of the electronic structure calculation. The same procedure, when applied to the oC48 structure (e.g., β -FeSi₂) or *m*-OsSi₂, led to spurious solutions (the socalled ghost bands). Muffin-tin orbitals of *d*-type on Si and the empty spheres strongly hybridized with low-lying states in the valence band. Linearizing the d orbitals on Si and the empty spheres around the center of the canonical d band resolved this problem. Pivotal energies for the d states on the transition metal atoms were always adjusted to the center of gravity of the (atom projected) d band in each iteration towards self-consistency. Self-consistency was reached when the total energy had converged to a level of 10^{-2} mRy or better.

III. ELECTRONIC STRUCTURE OF FE DISILICIDES

In this section, the electronic structure of two Fe disilicide compound phases is discussed. Computed physical properties of the compounds are compared with available experimental data. Band structure and DOS from the present calculations are discussed in relation with previously published results.

A. α -FeSi₂

The high-temperature form of FeSi₂ is the tetragonal α -phase with three atoms per unit cell. This structure can be viewed as a tetragonally distorted *B*2 (CsCl-type) ordered structure where composition is attained by omitting one metallic layer every two layers along the [001] direction. In the unit cell the Fe atom is located at (0,0,0), while the Si atoms are at $(\frac{1}{2}, \frac{1}{2}, 0.27)$ and $(\frac{1}{2}, \frac{1}{2}, 0.73)$. One empty sphere per formula unit is placed at $(0,0,\frac{1}{2})$. A series of total energy calculations at fixed c/a ratio, but with varying lattice parameter a, resulted in an equilibrium value of $a_{eq}=5.19$ a.u., about 2% larger than the experimental value given in Table I. The computed bulk modulus at a_{eq} is 177 GPa, but no experimental value is available for the high-temperature phase. Figure



FIG. 1. Density of states (a) and band structure (b) of tetragonal α -FeSi₂.

1 shows the DOS and the band structure for the metallic α phase. There are several features to note from Fig. 1. A high DOS starting about 5 eV below the Fermi level corresponds to the energy region where Fe-*d* states hybridize with Si-*s* and *p* states. The very sharp peaks in the DOS correspond to *d*-like states that are localized as a result of the low coordination of the Fe atoms, e.g., Bloch states along Γ -*Z* in reciprocal space [see Fig. 1(b)]. The pseudogap at the Fermi energy indicates a relation with the low-temperature β phase through a structural transformation with FeSi₂ in the CaF₂ structure as an intermediate phase.²¹

Recently similar data derived from a calculation without any approximation to the shape of the crystal potential were published.¹⁰ Comparison with Fig. 1 demonstrates that the present LMTO-ASA calculations accurately reproduce the full-potential results. From this it is concluded that addition



FIG. 2. Projection of atomic positions (light: Si; dark: Fe) on the *a*-*c* plane of the simple orthorhombic unit cell of β -FeSi₂. Also shown are the lattice vectors $\frac{1}{2}(a+c)$ and $\frac{1}{2}(a-c)$ for the one-face centered unit cell.

of one empty atomic sphere per formula unit results in a reliable description of the electronic structure of α -FeSi₂.

B. β -FeSi₂

Fully self-consistent calculations have been performed for the orthorhombic compounds β -FeSi₂ and β -OsSi₂. These calculations were done using the one-face centered orthorhombic unit cell with face centering in the a-c plane (with lattice parameters a < b < c) (see Fig. 2). The cell contains a total of 24 atoms and eight empty spheres, grouped in seven different types of equivalent atomic spheres: four (four) atoms of type M_I (M_{II}), where M = Fe or Os, eight (eight) of type Si_I (Si_{II}) as defined in Refs. 2 and 4 (two and two) empty spheres of type E_I (E_{II} and E_{III}). The empty spheres are placed in the interstitial region, inside the distorted Si cubes that are not occupied by Fe atoms, as discussed in Ref. 2. The lattice parameters were taken from experiment^{22,17} and are given in Table I. The calculations were performed for the two compounds at various values of the lattice parameter a, but with fixed b/a and c/a ratios, and with internal parameters as quoted in Refs. 2 and 23 for β -FeSi₂ and β -OsSi₂, respectively. From a fit of the total energies at different unit-cell volumes to a Murnaghan equation of state,²³ theoretical equilibrium lattice parameters, a_{eq} , and bulk moduli at a_{eq} were obtained, and are presented in Table II. For both compounds the calculated lattice parameter differs from experiment by about one percent. The bulk modulus for β -FeSi₂ is also in good agreement with experiment. Christensen⁹ achieved excellent agreement for the lattice parameter of β -FeSi₂, while the bulk modulus was overestimated by about 20%. This discrepancy may be due to the fact that in Ref. 9 and also in the recent paper by Filonov et al.¹² the empty spheres of type E_{II} and E_{III} are treated as equivalent, thereby forcing incorrect symmetry on the charge distribution in the system. According to space group Cmca

TABLE II. Computed equilibrium lattice constants, a_{eq} , bulk moduli, *B* for various transition metal disilicides. Available experimental data are given in parentheses. Also listed are direct band gaps, Δ , at the points Γ and *Y* as well as the indirect band gaps $\Delta_{indirect}$ with the direction in reciprocal space given in parentheses.

	Equilibrium lattice	Bulk modulus	Δ at		$\Delta_{indirect}$	
	parameter	at a_{eq}	Г	Y	manoor	
Compound	$a_{\rm eq}/{\rm a.u.}$	B/GPa	eV		eV	
$\overline{\alpha}$ -FeSi ₂	5.19 (5.08)	177	metal			
β -FeSi ₂	14.62 (14.72)	203 (199)	0.51	0.58	0.44 $(\Gamma \rightarrow \Gamma - Z)$	
Ru _{1/2} Fe _{1/2} Si ₂	15.13	223	0.39	0.48		
$\operatorname{Fe}_{1/2}\operatorname{Ru}_{1/2}\operatorname{Si}_2$	15.07	168	0.52	0.71	0.31 $(Y \rightarrow \Gamma)$	
RuSi ₂	15.46	198	0.34	0.17		
$Os_{1/2}Fe_{1/2}Si_2$	15.26	145	0.57	0.53	0.50 $(\Gamma \rightarrow Y)$	
Fe _{1/2} Os _{1/2} Si ₂	15.20	197	0.37 0.65		0.34 $(\Gamma$ - $Z \rightarrow \Gamma)$	
β^* -OsSi ₂	15.61	203	0.30 0.42		0.30 $(\Gamma \rightarrow Y)$	
β -OsSi ₂	15.52 (15.34)	212	0.60 0.32		0.06 $(\Gamma \rightarrow Y)$	
<i>m</i> -OsSi ₂	16.44 (16.57)	222	semimetal			
$\operatorname{Cr}_{1/2}\operatorname{Fe}_{1/2}\operatorname{Si}_2$	14.87	184	metal			
$\frac{\mathrm{Fe}_{1/2}\mathrm{Cr}_{1/2}\mathrm{Si}_2}{2}$	14.82	184	metal			

(number 64), the E_{II} and E_{III} empty spheres occupy Wyckoff sites 4b and 4a, respectively. The inequivalence of these two sites leads to different charge distributions containing 1.63 electrons in each E_{II} empty sphere and 1.57 electrons in each E_{III} sphere. In a test calculation, in which E_{II} and E_{III} were forced to be equivalent, these empty spheres contain 1.72 electrons. Therefore, a significant amount of charge is redistributed as the incorrect constraint on the charge density is relaxed.

Figure 3 shows the band structures for the two transition metal silicides at the experimental crystal structure along high symmetry directions in the one-face centered orthorhombic Brillouin zone. For β -FeSi₂ an indirect gap of 0.44 eV was found between Γ and a point half way along Γ -Z. The lowest unoccupied states along Γ -Z are of predominantly d character on the two types of Fe, while at Γ the highest occupied state has mixed $Fe_{II}-d/Si_{I}-p$ signature. A direct gap of 0.51 eV at Γ is almost equal to the tight-binding result of Miglio and Malegori (0.52 eV), and consistent with the value reported by Eppenga (0.46 eV), but substantially smaller than Christensen's value of 0.80 eV, or the direct gap at Γ deduced from the band structure presented by Eisebitt et al. (0.92 eV). Eppenga reported an indirect gap along Γ -Z of 0.44 eV, which is identical to the present value. However, his band structure along Γ -Z differs from the one displayed in Fig. 3(a), possibly due to his neglect of scalarrelativistic effects in the Hamiltonian. As pointed out in Ref. 10, some care must be taken when comparing the dispersion relation in a one-face centered Brillouin zone with that in the simple orthorhombic zone. Figure 3(a) compares favorably with the band structure derived from a full-potential treatment (see Fig. 4 of Ref. 10), although some details differ (e.g., shape of the highest occupied band along Γ -Z, and precise position of the bands). The cause for the difference in band gap between the present result (0.44 eV) and the value reported by Eisebitt *et al.* (0.78 eV) may be due to the details of the electronic structure calculation (FLAPW versus LMTO-ASA).

Summarizing, the results for α -FeSi₂ and β -FeSi₂ are in good agreement with results from theoretical studies in the literature. The lattice constant for the α phase is about 2% too large. For β -FeSi₂ a_{eq} is 1% too small and the bulk modulus is in excellent agreement with experiment. In β -FeSi₂ the band gap is found to be indirect from Γ to a point along Γ -*Z* (0.44 eV). The direct gap at Γ is 0.51 eV wide.

IV. ELECTRONIC STRUCTURE OF OS DISILICIDES

A. β -OsSi₂

It is expected that the band structure for β -OsSi₂ [Fig. 3(b) is of similar quality, since the b/a and c/a ratios and the internal parameters which define the structure are close to those for β -FeSi₂. In comparing the band structures of the Os and Fe disilicides, one notes many features present in Fig. 3(a) that are also found in Fig. 3(b), but stretched along the energy axis. Since the electronic states around the band gap have large d components, the usual broadening of the d band when going from 3d to 4d and to 5d in the transition metal series is preserved in the electronic structure at the band edge for these disilicides. Further analysis showed that for β -FeSi₂ the lowest state with significant d character at the Γ point lies 6.6 eV below the top of the valence band, while for β -OsSi₂ this state is at 8.1 eV below the top of the valence band. This clearly reflects the width of the occupied part of the *d*-band in the pure metal, ~ 5.3 eV and ~ 8.5 eV for Fe and Os, respectively. In addition, estimates of *d*-band widths on the basis of the relevant LMTO potential parameters indicate that, at equal volume, the Os 5d states form a



FIG. 3. Band structure around the gap along high symmetry directions in the one-face centered orthorhombic Brillouin zone for (a) β -FeSi₂ and (b) β -OsSi₂. Labels for high symmetry points in reciprocal space are consistent with those given in Refs. 10 and 24.

much wider band than the Fe 4d states. Potential parameters for the metal s and p states as well as the states on Si are found to be very similar in the two compounds.

The band gap for β -OsSi₂ is indirect between Γ and Y, and is only 0.06 eV wide. At the points Γ and Y the width of



FIG. 4. Total and atom-decomposed density of states for β -FeSi₂ (thick) and β -OsSi₂ (thin).

the gap is 0.60 and 0.32 eV, respectively. When comparing to β -FeSi₂ the band structure has most noticeably changed around the point Y. A very dispersive feature at the bottom of the conduction band almost closes the gap. In β -FeSi₂ the same band is present at Y, but is much less dispersive. Closer investigation showed that, at Y, this band is for almost 85% of d character in the Fe-based compound, whereas for β -OsSi₂ admixture of s and p states on Si_{II} (25% altogether) and reduction of d character (to 25%) is observed. This enhancement of Si 3s and 3p character is reflected in the freeelectron-like shape of the lowest unoccupied band around Y, and is consistent with the larger spatial extent of the Os 5d orbitals. A self-consistent calculation including the effect of the spin-orbit interaction on the valence states did not significantly alter the situation for β -OsSi₂. The band gap was reduced to 0.05 eV, whereas the charges on the various types of atomic spheres differed by at most 3×10^{-4} or less with respect to the scalar relativistic band structure calculation. The small effect of spin-orbit coupling on the band gap is due to two factors. First, spin-orbit induced splittings are relatively small in low symmetry systems where crystal-field splittings already lift most of the degeneracies. Second, the states in the region of the gap have a significant amount of Si sp character and will, therefore, be less affected by spin-orbit effects.

In Fig. 4, the total and atom-decomposed DOS for β -FeSi₂ and β -OsSi₂ are compared. One immediately recognizes that the *d* band in the Os compound is much wider than in β -FeSi₂. Also clearly reflected in Fig. 4 is the fact

that the *d* character of the states at the band edge is strongly reduced in β -OsSi₂, not only with respect to FeSi₂, but also in comparison with the DOS on the Si atoms in β -OsSi₂. As a result, the dispersive states which are predominantly associated with the Si atoms significantly influence the band edge in β -OsSi₂, whereas in the Fe-based compound 3*d* states are dominant.

Temperature-dependent resistance measurements in Alcontaminated (1.5 at.%) β -FeSi₂ and β -OsSi₂ yielded band gaps of 0.88 eV and 1.8 eV, respectively.¹⁶ For the Oscompound, this compares well to the gap value of 1.4 eV obtained by Schellenberg *et al.*¹⁷ using a similar measurement. It is known that the LDA can underestimate band gaps by 50% or more. Therefore, a calculated gap of 0.44 eV versus an experimentally determined gap of 0.80–0.95 eV for β -FeSi₂ is not unreasonable. It is surprising, however, that the calculated band gap reduces from 0.44 to 0.06 eV on going from β -FeSi₂ to β -OsSi₂ whereas the experimental gap increases to 1.4–1.8 eV. It is not unusual to have an LDA error in the band gap of around 1.3 eV, as observed in the case of β -OsSi₂, but usually theory reproduces the correct trends in the gap width (see, e.g., Ref. 25).

A possible explanation for this discrepancy in the band gap of β -OsSi₂ may be found in considering a metastable form of this compound. In quenched Os-Si mixtures a monoclinic phase with nominal composition OsSi₂ has been described in the literature.^{26,17} In the next subsection a brief investigation of this phase, focusing on the band gap, will be presented.

B. Monoclinic *m*-OsSi₂

Table I lists the dimensions of the simple monoclinic unit cell of the metastable phase of OsSi₂, as given in Ref. 26. Later Schellenberg *et al.*¹⁵ deduced parameters that are very close to those in Table I (volume of the unit cell about 1% smaller). In both cases, the authors were unable to extract atomic positions from their x-ray diffraction measurements. The structure-type is consistent with the experimentally observed OsGe₂ compound,²⁷ a one-face centered monoclinic unit cell (space group C2/m, number 12) with six atoms in the unit cell. The six atoms are grouped in three types of different atomic sites: two equivalent Os atoms, two atoms of type Si_{I} , and two of type Si_{II} . The OsGe₂ structure is a relatively open structure. Planes with composition OsSi2 in a distorted-honeycomb arrangement are stacked along the b axis of the monoclinic unit cell, with large interstitial regions at the centers of the hexagons.

A series of four calculations have been performed at the experimental lattice parameters, but with the internal parameters which define the atomic positions in the unit cell chosen to be those of the $OsGe_2$ structure: (i) a standard LMTO-ASA calculation in which the total volume of the atomic spheres (of equal radius) matches the volume of the unit cell; (ii) a LMTO-ASA calculation with three additional empty spheres located at suitable positions in the unit cell to reduce the overlap of atomic spheres; (iii) a LMTO calculation similar to (ii) which also includes the so-called "combined correction" term in the LMTO Hamiltonian,¹⁸ accounting for the interstitial region in a perturbative manner; and (iv) a full-potential LMTO calculation.²⁸ For cases (ii) and (iii) an

automated procedure²⁹ was used to determine the three optimum empty sphere positions at $(\frac{1}{2},0,\frac{1}{2})$, (0.788,0,0.174), and (0.212, 0, 0.826) in units of (a, b, c). The ratio of atomic sphere to empty sphere radius was chosen to be 1.3.

Figure 5(a) shows the dispersion relation obtained from calculations (ii). Although there are significant differences in the results from (i) to (iv), the general features of the dispersion relation can be discussed with reference to Fig. 5(a). The loop Γ -X-Z- Γ in reciprocal space samples states associated with the two-dimensional honeycomb layers. In these directions the system exhibits a 3 - 4 eV energy band gap with relatively dispersionless bands of predominantly Os dcharacter at the band edge. The separation between the highest occupied and lowest unoccupied states at the Γ point increases as a function of pressure. At the same time the 5d-band width increases as a result of increased hybridization between Os 5d states. In terms of a bonding/antibonding model this means that the energy separation between bonding and antibonding combinations of 5d states increases faster with pressure than the increase in bandwidth does. In the Γ -Y direction, perpendicular to the Γ -X-Z- Γ loop, electronic states at the band edge that link the layers are probed. At Γ virtually unhybridized 5d states determine the electronic structure. Then, going towards Y, hybridization with 3p states on Si_I and Si_{II} sets in, resulting in dispersive bands. Further, it was found that adding the effects of spinorbit coupling to the Hamiltonian alters some details (degeneracies) in the band structure, but leaves the basic features largely unaffected.

Three energy regions can be distinguished in the occupied DOS of m-OsSi₂ [Fig. 5(b)]. At low energies (-14 to -8 eV) extended states built from atomic 3*s*- (Si) and 6*s*- (Os) states dominate the DOS. From -8 to -2 eV the 3*p* states on Si strongly hybridize with the Os 5*d*-states. Finally, an almost separated subband of states labeled with *k* vectors corresponding to directions perpendicular to the honeycomb planes is found between -2 eV and the Fermi level. As discussed earlier, the character of these states varies from almost pure Os-5*d* (at -2 eV) to Si-3*p*/Os-5*d* around the Fermi level.

Band structure calculations based on (ii), (iii), and (iv) yield a semimetal. The gap along the Γ -X-Z- Γ loop varies from 2.8 eV for (iii) to 3.1 and 3.4 eV for (ii) and (iv), respectively. In calculation (i) a band gap of about 1 eV opens up along Γ -Y. Inspection of the band structure revealed that all four calculations produce similar bands in the low energy region (below -6 eV). At energies closer to the highest occupied states, where the Os d band dominates the electronic structure, significant deviations from the fullpotential result (iv) were found. Especially in calculation (i) the *p*-*d* hybridization along Γ -*Y* is very different from (iv) with, for instance, the consequence that the dispersion of the highest occupied and lowest unoccupied bands is such that a band gap exists. Furthermore, the position on the energy scale of the localized d states along the Γ -X-Z- Γ loop is sensitive to the level of approximation to the shape of the crystal potential. The addition of three empty spheres to increase the packing fraction of the structure gives a band structure that compares favorably with the full-potential result from (v). As shown in Fig. 5(c), one finds similar dispersion of the bands although the position of the bands may



FIG. 5. Band structure along high symmetry directions in the one-face centered monoclinic Brillouin zone (a) and DOS (b) for m-OsSi₂ as obtained from an LMTO-ASA calculation including empty spheres and (c) the band structure from a full-potential LMTO calculation.

be shifted by tenths of an eV, and the overall bandwidth for (ii) is 0.4 eV smaller than for (iv). Addition of the so-called combined correction term to the LMTO Hamiltonian makes the bandwidth practically the same as found from calculation (iv), but does not systematically improve the position of the localized d states with respect to (ii).

Minimization of the total energy with respect to the volume of the unit cell in a calculation of the second type (LMTO-ASA with empty spheres) resulted in a lattice parameter slightly smaller than the experimental value (see Table II). The bulk modulus computed for monoclinic $OsSi_2$ is slightly larger than the one found for the orthorhombic (β) phase.

Since the positions of Os and Si in the monoclinic unit cell are not precisely known (internal parameters borrowed from OsGe₂), the influence of a small displacement (0.16 a.u. along the *a* direction, in the honeycomb plane) of the Os atoms was investigated in a test calculation. Overall, the characteristics of the band structure remain unchanged. The dispersion relation at the band edge along Γ -*Y* changes in such a way that a small gap (~0.1 eV) opens. Minor atomic rearrangements are not expected to lead to a large (> 1 eV) band gap.

In summary, the calculated equilibrium lattice constant for β -OsSi₂ is about 1% larger than the experimental value. Surprisingly, the experimentally observed increase in the width of the band gap going from β -FeSi₂ to β -OsSi₂ is not reproduced by the electronic structure calculations. LDA results indicate a very small indirect gap (Γ to Y) for β -OsSi₂. For crystals with large regions of interstitial space between the atoms, a LMTO-ASA calculation with empty spheres at suitably chosen positions gives a noticeable improvement over a calculation with only atomic spheres. As long as there is no need to calculate, for instance, forces on atoms or shear elastic constants, a calculation with empty spheres provides a fair approximation of the full-potential result. This is found to be the case for the monoclinic phase of OsSi₂, but also for disilicides based on the orthorhombic oC48 structure (see the previous section). Metastable monoclinic OsSi2 in the OsGe2 structure was found to be a semimetal and, therefore, does not offer an explanation for the experimentally observed band gap of 1.4-1.8 eV in a compound with nominal composition OsSi₂. Nevertheless, it is conceivable that precise knowledge of the atomic positions in *m*-OsSi₂ may alter the dispersion relation along Γ -Y in such a way that a gap opens up.

V. SUBSTITUTION OF RU, OS, AND CR IN β -FESI₂

The three transition metals Fe, Ru, and Os are in the same column of the Periodic Table and the valence electron count in each of the silicide compounds remains constant. One, therefore, expects to find similarities in the electronic structure for these metal disilicides. Cr, on the other hand, represents a *p*-type dopant in β -FeSi₂, since it has fewer valence electrons than Fe. Although at high Cr-concentration the semiconducting property of the compound will definitely vanish, it remains of interest to know how the equilibrium lattice constant and the bulk modulus are affected as a result of substitution with Cr. Prospects of p-type (Cr) doped β -FeSi₂ as a thermoelectric compound with a high figure of merit make the investigation of basic properties of Crsubstituted β -FeSi₂ worthwhile. The effects of partial or complete substitution of the Fe atoms in β -FeSi₂ with Ru, Os, or Cr are examined, with particular attention paid to changes in the lattice parameter, the bulk modulus, and the evolution of the LDA band gap.

Results presented in this section are all based on the β -FeSi₂ (*o*C48) structure. The atomic positions *b/a* and *c/a* remain unaltered throughout. For each of the compounds an energy-versus-volume curve was computed and the equilibrium lattice constant and the bulk modulus at equilibrium were determined.

The relaxation of atomic positions as a result of substitution with Ru, Os, or Cr is not accounted for. Since the crystal structure for both β -FeSi₂ and β -OsSi₂ are known experimentally, a series of calculations for OsSi2 but with the atomic positions of the β -FeSi₂ structure were performed to assess the sensitivity of the results to atomic relaxations. This hypothetical OsSi₂ phase is denoted as β^* -OsSi₂. At the theoretical equilibrium lattice constant the volume per atom for β - and β^* -OsSi₂ differs only by 2.2%. This is of similar magnitude to errors commonly found in LDA-based calculations of atomic volumes for complex structures. For instance, from Table II one infers for α -FeSi₂ an error of \sim 7% with respect to the experimental volume per atom, for β -FeSi₂ ~ 2% and for β -OsSi₂ about 3%. Similarly, the bulk moduli for β - and β^* -OsSi₂ differ only by about 4%, while for elemental transition metals an agreement with experiment within 10% is considered quite satisfactory.³⁰ Therefore, errors made in neglecting the slight atomic rearrangement when substituting Fe with Os in the β phase are well within the usual error bars for LDA-ASA-based electronic structure calculations. Since physical properties such as lattice constant and bulk modulus are greatly influenced by the electrostatic interaction between atomic spheres in the crystal, a look at the charges contained within the spheres is instructive. It is found that in both the β -OsSi₂ and β^* -OsSi₂ crystals the Os and Si atoms are charge deficient by about 0.8 and 0.5 electrons, respectively, while the empty spheres in the interstitial region contain 1.5-2.1 electrons. Although not identical, the distribution of charge over the atomic spheres exhibits the same characteristics in the two OsSi₂ compounds. This is consistent with the small differences in a_{eq} and B as found for the two forms of OsSi₂, since the crystal structure is very sensitive to the electrostatics associated with the distribution of charge over the atomic spheres.

Figure 6 shows the dispersion relation for β^* -OsSi₂ along high symmetry directions at energies in the vicinity of the gap. This band structure should be compared to Fig. 3(b) (β -OsSi₂ at a_{eq}). The band gap in Fig. 6 has widened (to 0.30 eV), and is direct at Γ . The indirect gap from Γ to Y is of equal magnitude. At lower energies the band structure in Fig. 6 differs from the one presented in Fig. 3(b), but the states at the band edge seem to be fairly robust against modest rearrangement of atoms and slight alteration of the b/aand c/a ratios.

For the mixed Fe-Ru and Fe-Os compounds the question still remains what will happen if only part of the Fe-atoms are replaced with larger atoms such as Ru or Os. A difference in local lattice relaxation around the large (Ru, Os) and smaller (Fe) metal atom may significantly alter the band structure. Nevertheless the mixed compounds are included in the present work, since the data quoted in Table II constitute a first exploration of some mechanical and semiconducting properties of these mixed compounds.

Substitution of Fe in β -FeSi₂ can occur at the two in-



FIG. 6. Band structure around the gap for one-face centered orthorhombic β^* -OsSi₂ at the calculated equilibrium lattice parameter.

equivalent sites Fe₁ and Fe₁₁. Both for substitution with Ru and Os three systems are considered, namely, (i) substitution at the Fe₁ site (denoted $M_{1/2}$ Fe_{1/2}Si₂), (ii) at the Fe₁₁ site (Fe_{1/2} $M_{1/2}$ Si₂), and (iii) at both sites. Equilibrium lattice constants, bulk moduli, and information about a possible band gap are gathered in Table II.

Replacement of Fe, a 3*d* transition metal atom, with its 4*d* or 5*d* isoelectronic counterpart, leads to an expansion of the lattice. Relative to β -FeSi₂ substitution on either of the two Fe-sites results in a 3% expansion of the lattice for Ru and about 4% for Os. Total replacement of Fe with Ru or Os approximately doubles these figures to 6% and 7%, respectively. In both cases substitution at site *I* leads to slightly larger expansion of the lattice. Comparison of total energies reveals that for both Ru and Os the Fe₁₁ site is energetically favored by 4 and 5 mRy per atom, respectively. This is probably due to the slightly larger distorted Si cube around the Fe₁₁ sites which can accommodate the bigger Ru or Os atoms more easily. Bulk moduli, *B*, for all compounds are found to be very similar with the exception of a high value for Ru _{1/2}Fe_{1/2}Si₂.

A direct gap at either Γ or *Y* is observed in all cases. Direct gaps, varying from 0.17 eV at *Y* for RuSi₂ to 0.53 eV at Y for Os_{1/2}Fe_{1/2}Si₂, are found to depend sensitively on the transition metal composition of the compound. With the exception of Ru_{1/2}Fe_{1/2}Si₂ and RuSi₂ the energy band gap is indirect, either between Γ and *Y* or between Γ and a point along Γ -*Z*. Since the equilibrium volumes for the compounds are different, it is hard to discern any trends in the

TABLE III. Net charges in the transition metal atomic spheres in oC48-based disilicides.

	Metal sites			
Compound	Fe ₁	Fe _{II}		
β-FeSi ₂	0.00	0.05		
$\operatorname{Fe}_{1/2}\operatorname{Ru}_{1/2}\operatorname{Si}_2$	0.00	0.59		
$Ru_{1/2}Fe_{1/2}Si_2$	0.53	0.05		
RuSi ₂	0.53	0.57		
$\operatorname{Fe}_{1/2}\operatorname{Os}_{1/2}\operatorname{Si}_2$	0.02	0.86		
$Os_{1/2}Fe_{1/2}Si_2$	0.80	0.07		
β^* -OsSi ₂	0.78	0.82		

value of the band gap from Table II. For instance, along the path $\text{FeSi}_2 \rightarrow \text{RuSi}_2 \rightarrow \text{OsSi}_2$, the gap is indirect (0.44 eV), becomes direct at *Y* (0.17 eV) and finally is indirect from Γ to *Y* (0.30 eV) again.

Increased overlap of 4d and 5d atomic states with respect to 3d is counterbalanced by a simultaneous increase in the equilibrium lattice constant. Table III shows the net charges in the transition metal atomic spheres. For Fe in any of the compounds the net charge deficiency varies from 0 to 0.07electrons. For Ru this ranges from 0.53 to 0.59 and for Os from 0.78 to 0.86 electrons. These numbers reflect the enhanced delocalization of the *d* electrons when going from the 3d to the 4d and to the 5d series. While the 3d state is almost entirely contained inside the atomic sphere, the 5d wave function significantly overlaps with neighboring atoms. Table IV systematically compares band gaps at three different volumes, namely the β -FeSi₂ equilibrium volume (corresponding to an atomic sphere radius of 2.47 a.u.), the β -OsSi₂ equilibrium volume (S = 2.60 a.u.) and a point half way between the two. Only compounds containing a single transition metal species are included in the table. Inspection of Table IV reveals that for the Ru and Os disilicides the gap width, Δ , slowly increases with increasing volume, whereas for β -FeSi₂ the magnitude of Δ decreases with increasing volume. Often the nature of the band gap changes with volume, too, e.g., from direct at Γ to direct at Y or from direct to indirect or vice versa. Table IV further lists gap deformation potentials, $\partial \Delta / \partial \ln V$, at Γ and at Y and for the direct or indirect band gap (last column). For β -FeSi₂ these crude estimates of the gap deformation potential are based on the calculations at S=2.47 and S=2.54 a.u., while for the $RuSi_2$ and $OsSi_2$, results at S=2.54 and S=2.60 a.u. were used.

The estimated gap deformation potential $\partial \Delta / \partial \ln V$ for β -FeSi₂ varies from -1.0 eV at *Y* to 1.1 eV at Γ . Values for $\partial \Delta / \partial \ln V$ deduced from calculations for *simple* orthorhombic β -FeSi₂ in Refs. 9 and 11 (-1.4 and -0.5 eV, respectively) are in qualitative agreement with this range. Interestingly, in β -FeSi₂ the band gap at Γ increases with increasing volume while the gap at *Y* decreases at the same rate, leading to a small, discontinuous effective value of $\partial \Delta / \partial \ln V$ over the indicated volume range. For RuSi₂, the band gap changes from direct at *Y* to direct at Γ . The gap deformation potential lies in the -4 to -1 eV range. A comparison of β^* -OsSi₂ with β -OsSi₂ shows that the gap is sensitive to atomic displacements, and even vanishes at low volume for β -OsSi₂. The

TABLE IV. Band gap Δ (direct or indirect) as a function of atomic sphere radius *S*. Also indicated are the high symmetry points that define the gap in the one-face centered orthorhombic Brillouin zone. Gap deformation potentials at Γ , *Y* and across the gap from Γ to *Y* and vice versa are given in the final four columns.

	Δ/eV			$\frac{\partial \Delta}{\partial \ln V} / \text{eV}$			
Compound	S = 2.47 a.u.	S = 2.54 a.u.	S = 2.60 a.u.	at Γ	at Y	$\Gamma \longrightarrow Y$	$Y \rightarrow \Gamma$
β -FeSi ₂	$ \begin{array}{c} \Gamma \!\rightarrow\! \Gamma \; (\simeq\! \Gamma \!\rightarrow\! Y) \\ 0.51 \end{array} $	$\begin{array}{c} Y \longrightarrow Y \\ 0.49 \end{array}$	$\begin{array}{c} Y \longrightarrow Y \\ 0.37 \end{array}$	1.1	-1.0	-0.3	0.4
RuSi ₂	$\begin{array}{c} \Gamma \longrightarrow Y \\ 0.23 \end{array}$	$\begin{array}{c} Y \longrightarrow Y \\ 0.24 \end{array}$	$\begin{array}{c} \Gamma \rightarrow \Gamma \\ 0.33 \end{array}$	-4.3	-1.1	-0.02	-5.4
β^* -OsSi ₂	$\Gamma \rightarrow Y$ 0.17	$\Gamma \rightarrow Y$ 0.26	$ \begin{array}{c} \Gamma \rightarrow \Gamma \ (\simeq \Gamma \rightarrow Y) \\ (S = 2.62 \text{ a.u.}) \\ 0.30 \end{array} $	-4.4	-0.8	0.4	-4.5
β-OsSi ₂	$\stackrel{\Gamma \to Y}{-}$	$\begin{array}{c} \Gamma \longrightarrow Y \\ 0.02 \end{array}$	$\begin{array}{c} \Gamma \longrightarrow Y \\ 0.06 \end{array}$	-1.0	0.2	0.3	-1.2

gap deformation potentials for these two systems are similar, however, and show similar signs and magnitude for the indirect Γ -*Y* gap. The gap deformation potentials in Table IV are small compared to those found for many semiconductors. Following Christensen's discussion⁹ of the temperature dependence of the band gap for β -FeSi₂, one is led to the conclusion that also for the Ru- and Os-based compounds quoted in Table IV the electron-phonon scattering contribution to $d\Delta/dT$ will overwhelm the effect of thermal expansion on the band gap.

The energy band gaps for all the β -FeSi₂-based compounds are of about the same order of magnitude (0.3 to 0.5 eV), which ranks these compounds among the small-gap semiconductors of interest in relation with optoelectronic and thermoelectric applications. Strong coupling of the states at the band edge to the precise atomic positions was already observed by Christensen⁹ and by Miglio and Malegori¹¹ in the case of β -FeSi₂. Here these ideas are stressed once more by the results for RuSi₂ and the two slightly different orthorhombic OsSi₂ crystalline phases.

Combination of the Δ_{indirect} , a_{eq} , and *B* values in Table II with the observation that substitution on the Fe_{II} site is energetically favored, leads to the conclusion that replacement of Fe with Ru or Os will induce a *reduction* of the band gap of up to 30% at 1:1 composition on the metal sublattice. The lattice constant is predicted to increase by 3–4 %, whereas the bulk modulus remains the same (Os) or decreases slightly (Ru).

The substitution of Fe₁ or Fe₁₁ with small amounts of Cr provides a case of *p*-type doping. Here, the electronic structure of two heavily doped Fe-Cr disilicides is investigated. Due to a reduced valence electron count in the system the semiconducting property of β -FeSi₂ vanishes. The lattice of Cr-substituted disilicides has expanded somewhat with respect to β -FeSi₂. For both systems a bulk modulus of B = 184 GPa was found, somewhat smaller than for undoped FeSi₂. At equilibrium the total energy for the system with Cr located at the more open Fe₁₁ sites is about 1 mRy per atom lower than for substitution at Fe₁. This is consistent with the fact that a Cr atom is slightly larger than Fe, but not as much as Ru or Os (Fe_{II} favored by 4 and 5 mRy, respectively). Therefore substitutional Cr-dopant atoms are expected to be primarily located at the Fe_{II} site in β -FeSi₂.

Summarizing, partial or total replacement of Fe atoms in the β -FeSi₂ structure with Ru or Os, followed by hydrostatic relaxation of the lattice, invariably results in a small-gap semiconductor. Gap deformation potentials are estimated to be relatively small for these materials (-0.2-1.3 eV). Adjustment of the atomic positions, in particular in the mixed Fe/Ru and Fe/Os disilicides, may affect the outcome, but a clear tendency towards semiconducting behavior has been established here. Substitution of Fe with Cr yields an electron deficient version of β -FeSi₂.

VI. SUMMARY

In this work, a series of transition metal disilicides involving Fe, Ru, Os, and Cr have been studied. These materials are of interest in view of their (potential) application in thermoelectric, microelectronic, and optoelectronic devices. Some of the phases studied have already been experimentally observed (α -, β -FeSi₂, β -OsSi₂, and metastable monoclinic OsSi₂). Other compounds have not been synthesized yet, and remain hypothetical at this stage.

The calculated DOS and band structure for the tetragonal α phase of FeSi₂ were found to be in excellent agreement with results from a full-potential method. This is encouraging, since the structure of α -FeSi₂ is relatively open, but satisfactory results are obtained if care is taken to obtain a reasonable partitioning of space. A theoretical estimate for the bulk modulus of 177 GPa was derived at the calculated equilibrium lattice constant (2% larger than the experimental value).

For orthorhombic β -FeSi₂ and β -OsSi₂ the calculated lattice parameters agree very well with the experimental values (error ~ 1%). Recognizing that three different types of

empty spheres (instead of two) need to be used in the β structure, close agreement between computed and experimental bulk modulus of β -FeSi₂ was obtained. An indirect band gap of 0.44 eV from Γ to a point along the Γ -Z direction was calculated for β -FeSi₂. The direct gap at Γ is 0.58 eV. These numbers are 30-50 % smaller than the experimental values, which is not unusual for electronic structure calculations based on the local density approximation of density functional theory. However, the difference between the magnitude of the direct and indirect band gaps, 0.07 eV, is consistent with the experimental observation that such a difference must be very small. Going from FeSi₂ to OsSi₂, a reduction of the band gap due to the more dispersive nature of the states at the band edge was observed. Basically this effect is caused by the widening of the *d* band when going from Fe to Os. Delocalized 5d states on Os strongly hybridize with 3s and 3p states on Si. In RuSi₂ and OsSi₂ this results in the appearance of strongly dispersive, freeelectron-like, features at the band edge. Therefore, experimental estimates for the gap in β -OsSi₂, which range from 1.4 to 1.8 eV, differ quite substantially from the computed indirect gap of 0.06 eV from Γ to Y. It is surprising that the experimentally observed increase in band gap width in going from β -FeSi₂ to β -OsSi₂ is not found in the calculations. Addition of the spin-orbit interaction to the Hamiltonian does not alter these findings. Altering the atomic positions and the lattice parameters to those of β -FeSi₂ opens the gap slightly (0.30 eV from Γ to Y). This demonstrates some sensitivity to the fine details of the crystal structure, but the delocalized character of the states at the band edge is not affected. Since the results for β -FeSi₂ are very reasonable, and the crystal structure of the orthorhombic OsSi2 compound is so closely related to the β -FeSi₂ structure, one wonders whether the experimentally observed band gap is really associated with β -OsSi₂. To address this issue, the electronic structure of a suggested monoclinic compound with nominal composition OsSi2 was investigated.

Metastable monoclinic OsSi2 with the atomic positions taken from the OsGe₂-type structure is a semimetal both at the level of a full-potential and of an atomic sphere-based treatment. However, in the latter approach it was necessary to insert empty atomic spheres in the interstitial region in order to achieve satisfactory agreement with the fullpotential result. The calculated lattice constant agrees well with the experimental value and the theoretical bulk modulus is similar to the one computed for orthorhombic β -OsSi₂. Although minor rearrangement of the Os positions in the $OsGe_2$ -type structure opened a narrow gap (0.1 eV), it is nevertheless concluded that metastable monoclinic OsSi₂, with the suggested internal parameters taken from OsGe₂, cannot account for the experimentally observed band gap (1.4-1.8 eV) in OsSi₂. Omission of empty spheres in the interstitial region resulted in a semiconductor. This implies a substantial error in the results with respect to both the calculation with empty spheres and the full-potential treatment.

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Taking the β -FeSi₂ structure as the starting point, a series of ordered compounds in which Fe atoms are partially or completely replaced with Ru or Os were studied. Equilibrium lattice constants and bulk moduli for this series of hypothetical compounds have been calculated. The substitution of half of the Fe atoms in β -FeSi₂ with Ru and Os resulted in a 3-4 % increase in the lattice parameter, whereas complete replacement of Fe more or less doubled these percentages. Bulk moduli at the equilibrium lattice constant vary from -25% to +10% relative to β -FeSi₂. With respect to the band gap in these disilicides the main conclusion drawn from the substitution study is that both the partially and fully Ru or Os substituted iron disilicides are small-gap semiconductors at the theoretical equilibrium lattice constant. The nature of the gap varies from direct at Γ or Y to indirect between Γ and Y or between Γ and a k point along the Γ -Z direction. Magnitudes of the gap vary from -60% to +15% when compared to β -FeSi₂. Estimates for the gap deformation potential range from -0.2 eV for β -FeSi₂ to 1.3 eV for RuSi₂. Combination of these small values with previously reported data for β -FeSi₂ suggests a strong coupling of the states at the band edge to the atomic positions in the unit cell of RuSi₂ and OsSi₂.

The results of this study strongly suggest that a solid solution of Fe, Ru, and Os on the metal sublattice potentially offers possibilities to fine tune the band gap in an orthorhombic disilicide of the β -FeSi₂ type. It is known that band gaps evaluated within the local density approximation are often underestimated. Nevertheless, the overall picture is expected to hold and empirical confirmation of the above observations is awaited.

Substitution of Fe₁ or Fe₁₁ with Cr yields an electron deficient metallic version of β -FeSi₂, corresponding to the high concentration limit of Cr as a *p*-type dopant. A minor expansion (~1.5%) of the lattice was calculated upon substitution with Cr, and the bulk modulus is reduced by about 10%. A comparison of the computed total energies for substitution at the Fe₁ and the Fe₁₁ site revealed that the latter is preferred invariably (for Cr, Ru, and Os by 1, 3, and 4 mRy, respectively). This is attributed to the slightly more open Si-cage around the Fe₁₁ site. As a consequence lattice relaxation will probably be important in the actual system.

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