



# High pressure stability of the monosilicides of cobalt and the platinum group elements



J.A. Hernandez<sup>a,\*</sup>, L. Vočadlo<sup>b</sup>, I.G. Wood<sup>b</sup>

<sup>a</sup> Laboratoire de géologie de Lyon, CNRS UMR 5276, École Normale Supérieure de Lyon, Université Claude Bernard Lyon 1, 46 Allée d'Italie, 69364 Lyon Cedex 07, France

<sup>b</sup> Department of Earth Sciences, University College London, WC1E 6BT, UK

## ARTICLE INFO

### Article history:

Received 3 September 2014

Received in revised form 6 November 2014

Accepted 11 November 2014

Available online 18 December 2014

### Keywords:

Transition metal monosilicides

Phase transition

Electronic structure

High pressure

First-principles calculations

## ABSTRACT

The high pressure stability of CoSi, RuSi, RhSi, PdSi, OsSi, IrSi and PtSi was investigated by static first-principles calculations up to 300 GPa at 0 K. As found experimentally, at atmospheric pressure, CoSi, RuSi and OsSi were found to adopt the cubic  $\varepsilon$ -FeSi structure ( $P2_13$ ) whereas RhSi, PdSi, IrSi and PtSi were found to adopt the orthorhombic MnP ( $Pnma$ ) structure. At high pressure, CoSi, RuSi and OsSi show a phase transition to the CsCl structure ( $Pm\bar{3}m$ ) structure at 270 GPa, 7 GPa and 6 GPa respectively. RhSi and IrSi were found to transform to an  $\varepsilon$ -FeSi structure at 10 GPa and 25 GPa. For PdSi and PtSi, a transformation from the MnP structure to the tetragonal CuTi structure ( $P4/nmm$ ) occurs at 13 GPa and 20 GPa. The pressure dependence of the electronic density of states reveals that RuSi and OsSi are semiconductors in the  $\varepsilon$ -FeSi structure and become metallic in the CsCl structure. RhSi and IrSi are metals in the MnP structure and become semimetals in their high pressure  $\varepsilon$ -FeSi form. CoSi in the  $\varepsilon$ -FeSi configuration is a semimetal. PdSi and PtSi remain metallic throughout up to 300 GPa.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Transition metal monosilicides have been well studied at ambient conditions due to their special thermoelectric properties and resistance against oxidation. In Earth sciences, FeSi and NiSi have been recently investigated in order to better understand the Fe–Ni–Si alloys identified as possible compounds in the Earth's core. The presence of light elements such as silicon is necessary to match the observed seismic waves velocities such as those in the Preliminary Reference Earth Model (PREM [1]); silicon is also consistent with geochemical constrains [2–4]. In previous simulations on FeSi and NiSi, athermal calculations showed that FeSi adopts an  $\varepsilon$ -FeSi structure (space group  $P2_13$ ) up to 13 or 40 GPa depending the authors, before adopting a CsCl structure ( $Pm\bar{3}m$ ) at higher pressure [5,6]. In contrast, NiSi crystallizes in the MnP structure ( $Pnma$ ) up to 21 GPa, transforms with pressure  $P$  to a  $Pm\bar{3}m$  structure for  $21 < P < 264$  GPa and finally adopts a CsCl structure above 264 GPa [7]. However, for NiSi, other phases (such as  $\varepsilon$ -FeSi), predicted to be potentially stable [8] because of the very small enthalpy differences between the different structures in the first principles calculations, have also been observed experimentally [9]. In order to understand better the reasons for the contrasting

behaviour of FeSi and NiSi at high pressure, we have investigated the stability of CoSi (because cobalt is located between iron and nickel in the periodic table of elements) and also the behaviour of the monosilicides of the platinum group elements to investigate whether similar behaviour to that of the 3d transition metals is found for elements with occupied 4d and 5d orbitals.

Like FeSi, RuSi and OsSi adopt an  $\varepsilon$ -FeSi structure at 0 GPa and 0 K. Their electronic structures show that FeSi and RuSi are semiconductors with relatively small energy gaps (0.26 eV for RuSi) and that OsSi is a degenerate semiconductor [10]. RuSi was found to transform from the  $\varepsilon$ -FeSi structure to the CsCl structure at 13–15 GPa, making it a good nonmagnetic analogue of FeSi [11,12]. More diversity appears between CoSi, RhSi and IrSi. In the ground state, CoSi adopts the  $\varepsilon$ -FeSi crystal structure but is a semimetal [13]; its high residual resistivity makes it a good material for thermoelectric applications [14]. RhSi and IrSi are metals adopting the MnP crystal structure with space group  $Pnma$  which can be interpreted as a distorted form of the hexagonal NiAs structure ( $P6_3/mmc$ ) [15,16]. The pressure dependence of the electronic band structure of RhSi shows the crossing of the Fermi energy in the  $\Gamma$ – $Z$  direction between 10 GPa and 25 GPa [17]. More recently, Wang et al. [18] have shown that RhSi presents a phase transition between the MnP structure and the  $\varepsilon$ -FeSi structure at 5.9 GPa. Like NiSi, which is used for contact applications in semiconductor devices, PdSi and PtSi have also been well studied both

\* Corresponding author.

E-mail address: [jeanalexis.hernandez@ens-lyon.fr](mailto:jeanalexis.hernandez@ens-lyon.fr) (J.A. Hernandez).

experimentally and theoretically at zero pressure; for example, they have applications in electronics in Schottky diodes used in infrared detectors [19].

In this paper, we have investigated the stability of seven structures for each of the monosilicides of the elements highlighted in Table 1.

These structures are as follows: (i) the cubic CsCl structure with space group  $Pm\bar{3}m$ ; (ii) the  $\epsilon$ -FeSi structure ( $P2_13$ ) which is also cubic; (iii) the hexagonal  $\alpha$ -WC-type structure ( $P6m2$ ); (iv) the  $Pbma$  structure as described by Vočadlo et al. [8]; (v) the orthorhombic MnP structure ( $Pnma$ ); (vi) the “anti-MnP structure” obtained by exchanging the positions of the metal atoms and the silicon atoms of the MnP structure; and (vii) the orthorhombic  $Pmmn$  structure as described by Wood et al. [7] which constitutes a high pressure form of NiSi. We have also calculated the electronic structure and the density of states for each silicide, since analysis of the electronic structure of any new high pressure phases might allow a better understanding of the differences and similarities of the behaviour of the different silicides. Finally, a high pressure study of these materials was of interest as high pressure phases can sometime be stabilized in microfilms offering potential applications if electronic properties are discovered.

## 2. Computational details

We performed athermal calculations using the code VASP (Vienna ab initio simulation package [20]) based on density-functional theory (DFT [21,22]) which solves the Schrödinger equation with an approximation for the exchange–correlation energy. This method uses a pseudopotential description of the core–electron interactions and describes the interactions between the valence electrons explicitly. The wavefunctions are described by a sum of plane-wave functions. We performed the calculations on the HEC-ToR facility located at the University of Edinburgh. For all our calculations we chose the general gradient approximation (GGA) with Perdrew–Wang 91 pseudopotentials (PW91 [23]).

### 2.1. Self-consistent calculations

For each monosilicide, the convergence in energy of each structure was tested by increasing the cutoff energy and the size of the Monkhorst-type k-points grid [24]. Convergence to the required

**Table 1**  
Part of the periodic table of elements containing the transition metals we used in our study (in bold).

Period	Group		
	VIII	IX	X
4	Fe	Co	Ni
5	<b>Ru</b>	<b>Rh</b>	<b>Pd</b>
6	<b>Os</b>	<b>Ir</b>	<b>Pt</b>

precision ( $<1$  meV atom $^{-1}$ ) for all six platinum group monosilicides in all seven structures was achieved with a cutoff energy of 1000 eV and a k-points grid size of  $8 \times 8 \times 8$ ; for CoSi the required precision was reached with a cutoff energy of 800 eV and a k-point grid of  $6 \times 6 \times 6$ . Simulations were performed on decreasing volumes (increasing pressure) with the relaxed structure of the previous volume being used as the starting point for the next simulation. The calculations were performed so as to retain the starting symmetry but allowing transformations to higher symmetries.

In order to determine the relative stability of the high pressure phases, we fitted the internal energy per atom  $E$  versus volume per atom  $V$  to a third order Birch–Murnaghan equation of state (BMEOS3 [25]). The resulting bulk modulus,  $K_0$ , pressure derivative,  $K'_0$ , and volume per atom at 0 GPa,  $V_0$ , were then used to calculate the pressure,  $P$ , and the enthalpy per atom,  $H$ . The calculation of  $H$  is sufficient to determine the stability, because at 0 K,  $H$  is equal to the free Gibbs energy,  $G$ . Thus, the structure with the lowest enthalpy is thermodynamically the most stable.

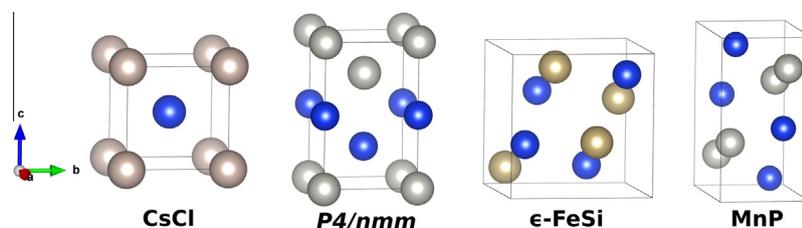
### 2.2. Electronic structure

To calculate the electronic density of states (DOS) and the partial density of states (pDOS) we used the procedure described above except for an increased k-points grid of  $21 \times 21 \times 21$ ; in deriving the DOS an increment of 0.05 eV for the semiconductors and an increment of 0.2 eV for the metals was used.

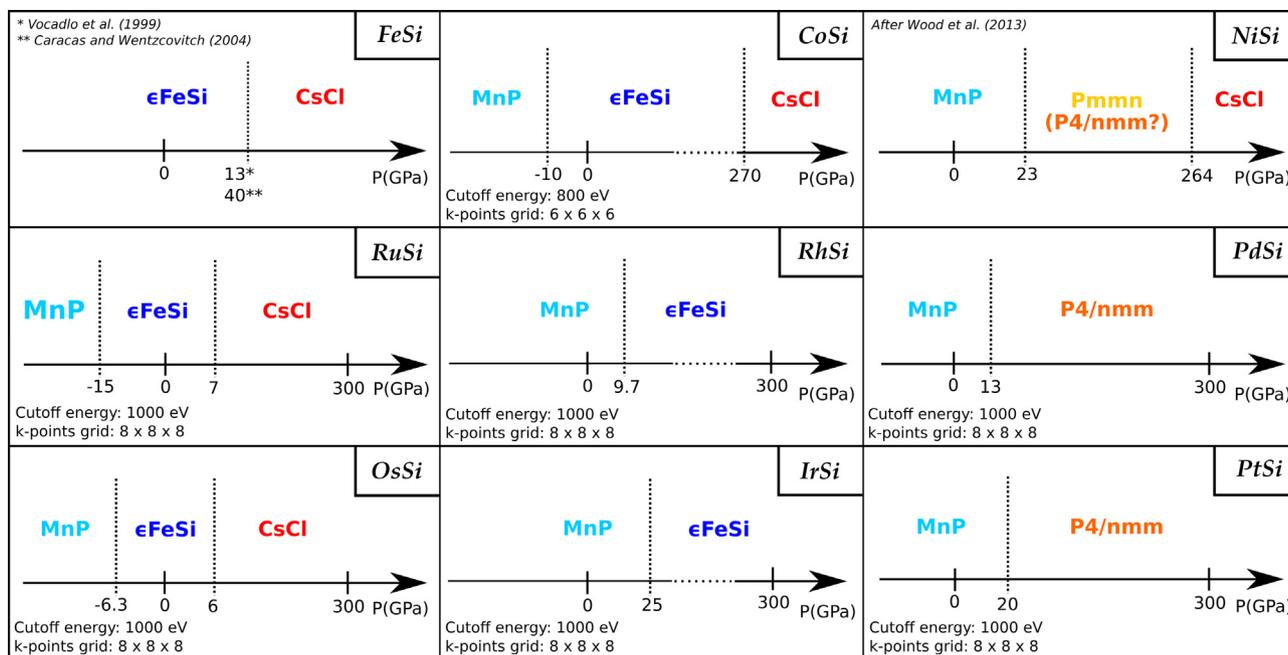
## 3. Results and discussion

### 3.1. Structural properties

We found that at 0 GPa, CoSi, RuSi and OsSi adopt an  $\epsilon$ -FeSi structure and that RhSi, PdSi, IrSi and PtSi adopt an MnP structure, which is in agreement with previous studies [16,26]. When considering the difference in behaviour shown by FeSi and NiSi, we found that CoSi has only one phase transition at high pressure, between the  $\epsilon$ -FeSi and CsCl structures, occurring around 270 GPa; thus CoSi behaves similarly to FeSi but the transition is at a much higher pressure. RuSi and OsSi were found to show the same phase transition at roughly 6–7 GPa for both compounds. This transition pressure is similar to, but slightly lower than, that found previously for RuSi (Ref. [11] found 13 GPa). RhSi and IrSi were found to transform from the MnP structure to the  $\epsilon$ -FeSi structure at 10 GPa and 25 GPa respectively. The phase transition in RhSi is consistent with the computational studies of Wang et al. [18] who found the same phase transition at 5.9 GPa, and Altintas [17] who observed an intersection of the Fermi energy for  $P > 10$  GPa between  $\Gamma - Z$  direction in the electronic structure of RhSi in the MnP configuration. The final two silicides studied, PdSi and PtSi, behave similarly to each other, with a phase transition from the MnP structure to the tetragonal  $P4/nmm$  (CuTi) structure at 13 GPa and 20 GPa



**Fig. 1.** Representation of the most stable structures encountered in our study. The darker (blue) spheres represent the silicon atoms and the lighter (grey) spheres represent the transition metal atoms. The frontward (red), rightward (green) and upward (blue) arrows indicate respectively the directions of the  $a$ ,  $b$  and  $c$  axis for each unit-cell. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Summary of the monosilicides stability at 0 K and up to 300 GPa. Negative pressures are presented here to highlight a possible phase transition sequence MnP- $\epsilon$ -FeSi-CsCl for RuSi, OsSi, CoSi, RhSi, and IrSi.

respectively. Although simulations were not performed starting with  $P4/nmm$  symmetry, the space group  $P4/nmm$  is a supergroup of both  $Pmnn$  and  $Pbmal$  and transitions to structures with this symmetry occurred independently from both the  $Pmnn$  and  $Pbmal$  starting symmetries. This tetragonal structure is commonly reported as the CuTi-type structure described by Karlsson [27]. It is essentially the same structure as the  $Pmnn$  structure reported for NiSi [7] but with the unit-cell parameters  $a$  and  $b$  equal to each other. Fig. 1 shows the unit-cells of the stable structures adopted by the monosilicides.

**Table 2**  
Unit-cell parameters of MSi (with M the transition metal) at 0 GPa.

M	Structure		$a$ (Å)	$b$ (Å)	$c$ (Å)
Co	$\epsilon$ -FeSi	GGA	4.439		
Co	$\epsilon$ -FeSi	LDA [28]	4.442		
Co	$\epsilon$ -FeSi	Exp. [29]	4.438		
Co	CsCl	GGA	2.787		
Ru	$\epsilon$ -FeSi	GGA	4.753		
Ru	$\epsilon$ -FeSi	Exp. [16]	4.73		
Ru	CsCl	GGA	2.945		
Ru	CsCl	Exp. [16]	2.909		
Os	$\epsilon$ -FeSi	GGA	4.794		
Os	$\epsilon$ -FeSi	Exp. [16]	4.729		
Os	CsCl	GGA	2.960		
Rh	MnP	GGA	5.590	3.124	6.428
Rh	MnP	GGA [18]	5.606	3.105	6.455
Rh	MnP	LDA [17]	5.475	3.036	6.312
Rh	MnP	Exp. [30]	5.552	3.069	6.374
Rh	$\epsilon$ -FeSi	GGA	4.732		
Rh	$\epsilon$ -FeSi	GGA [18]	4.734		
Ir	MnP	GGA	5.593	3.276	6.344
Ir	MnP	Exp. [16]	5.558	3.211	6.273
Ir	$\epsilon$ -FeSi	GGA	4.781		
Pd	MnP	GGA	5.648	3.474	6.193
Pd	MnP	Exp. [30]	5.614	3.386	6.149
Pd	$P4/nmm$	GGA	3.402		5.060
Pt	MnP	GGA	5.690	3.637	6.001
Pt	MnP	Exp. [30]	5.582	3.596	5.926
Pt	$P4/nmm$	GGA	3.460		5.003

Fig. 2 summarizes the thermodynamically stable phases for each monosilicide up to 300 GPa. This figure implicitly shows the different evolutions with pressure of the coordination number of the transition metal. In FeSi, RuSi, OsSi, and CoSi, the transition metals adopt a 7-fold coordination due to the  $\epsilon$ -FeSi structure and an 8-fold coordination in the CsCl structure. In RhSi and IrSi, the transition metals are in 6-fold coordination (MnP structure) and 7-fold coordination at higher pressure. Lastly, in PdSi and PtSi, the transition metals remain in 6-fold coordination throughout (MnP and CuTi structures). Clearly, the coordination of the transition metals in our monosilicides decreases with increasing group number and, in some cases, increases with pressure.

Table 2 lists the unit-cell parameters of the structures of each monosilicide at 0 GPa, obtained from a simulation at  $V = V_0$ . The

**Table 3**  
Calculated parameters of the equations of state of MSi (with M the transition metal).

M	Structure	$K_0$ (GPa)	$V_0$ (Å <sup>3</sup> at <sup>-1</sup> )	$K'_0$	$E_0$ (eV at <sup>-1</sup> )
Co	CsCl	202	10.824	4.72	-6.5950
Co	$\epsilon$ -FeSi	217	10.942	4.44	-6.8065
Co	$\epsilon$ -FeSi [31]	221		4.66	
Ru	CsCl	270	12.750	4.29	-7.8802
Ru	CsCl [11]	233	12.805	4.32	-7.854
Ru	CsCl [32]	250 ± 15	12.321	6.71	
Ru	$\epsilon$ -FeSi	227	13.363	4.51	-7.9015
Ru	$\epsilon$ -FeSi [11]	202	13.420	4.49	-7.8673
Ru	$\epsilon$ -FeSi [32]	215 ± 15	13.015	7.63	
Os	CsCl	295	12.979	4.57	-8.6605
Os	$\epsilon$ -FeSi	233	13.703	4.91	-8.6915
Rh	MnP	191	14.030	4.56	-7.1302
Rh	MnP [18]	208.7	14.05	4.82	
Rh	$\epsilon$ -FeSi	229	13.247	4.57	-7.0873
Rh	$\epsilon$ -FeSi [18]	230.4	13.27	4.79	
Ir	MnP	194	14.533	4.81	-7.7874
Ir	$\epsilon$ -FeSi	258	13.630	4.51	-7.6714
Pd	MnP	140	15.258	4.57	-5.8436
Pd	$P4/nmm$	156	14.628	4.60	-5.8009
Pt	MnP	212	15.414	3.72	-6.3958
Pt	$P4/nmm$	180	14.967	4.72	-6.3306

values obtained for the cell parameters in this study are always higher than the experimental data, as expected from the use of GGA. All simulations were performed with spin polarization, although no magnetic moments remained after energy minimization for any of the structures simulated.

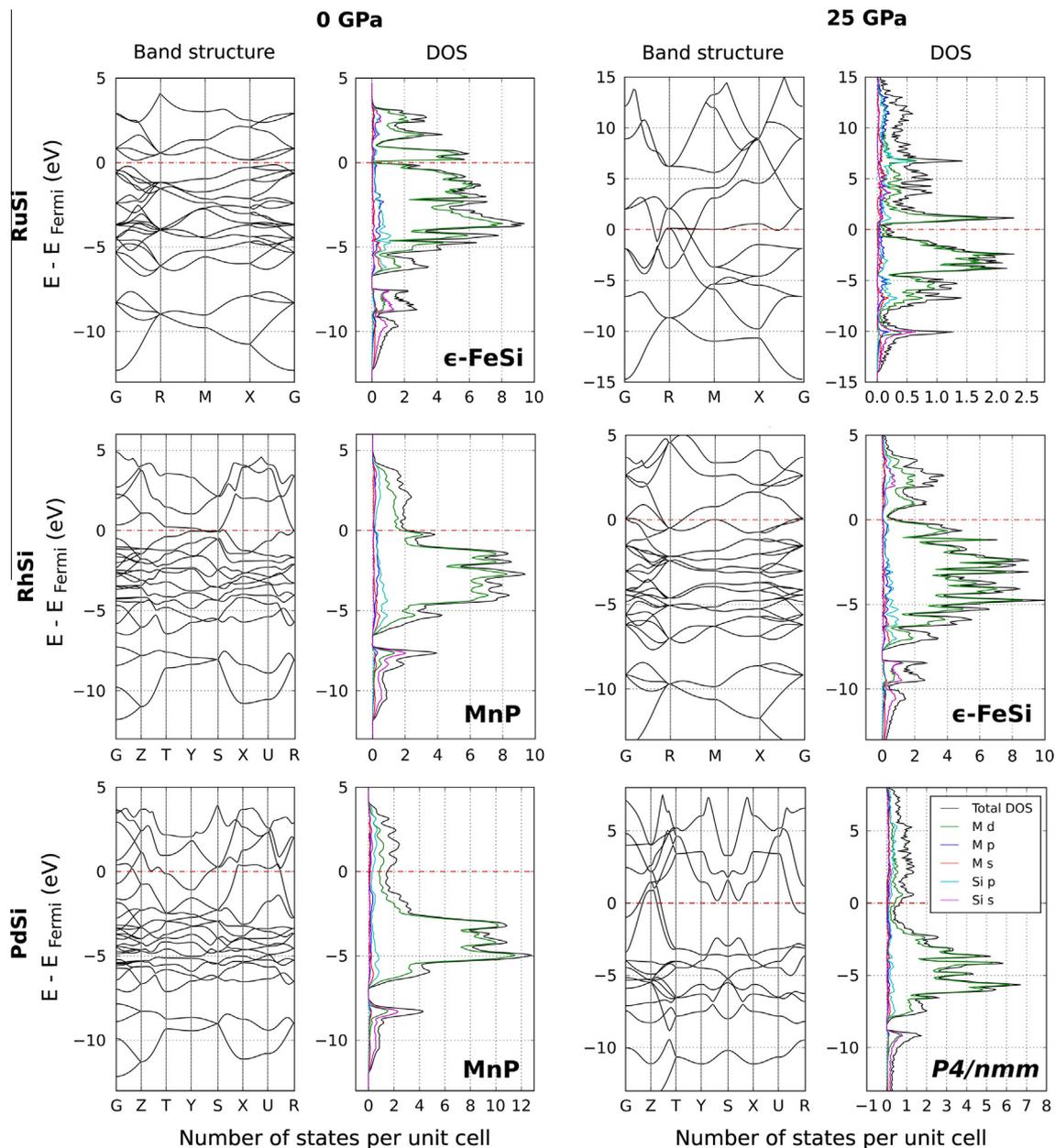
### 3.2. Equations of state

The equation of state parameters (see Table 3) are from fitting the  $E$  versus  $V$  curve to a BMEOS3 up to 300 GPa [5].

The results for CoSi and RuSi are in agreement with previous theoretical studies [31,32]. For some structures there is no comparison data available in the literature. In general, the agreement with experiment, where available, is very good [32].

### 3.3. Electronic structure calculations

We have calculated the DOS and pDOS of the monosilicides at different pressures. Because the electronic properties are directly linked to the structure adopted by the material, we observe important changes in the electronic behaviour, notably around the Fermi energy. The DOS at 0 GPa are in agreement with the results of Yarmoshenko et al. [30] with a first group of valence electrons between  $\sim -15$  eV and  $\sim -8$  eV (relative to the Fermi energy), mainly composed of the silicon's  $s$  states. A second group is observed between  $\sim -8$  eV and the Fermi energy, which is largely composed of the transition metal's  $nd$  electrons (where  $n$  is the period of the transition metal) hybridized with the silicon's  $p$  electrons. The last group constitutes the conduction band for which the DOS depends much more on the crystal structure. Thus,



**Fig. 3.** Electronic band structures and DOS of RuSi, RhSi and PdSi at 0 GPa and 25 GPa. The total DOS is represented in black and the partial DOS as indicated in the legend of the DOS of PdSi at 25 GPa. It appears that RuSi, which is a semiconductor in the  $\varepsilon$ -FeSi structure at 0 GPa, becomes metallic in its CsCl high pressure structure. RhSi is metallic in the MnP structure at 0 GPa and becomes a semimetal in its  $\varepsilon$ -FeSi high pressure structure. Lastly, PdSi remains a metal in its low pressure MnP structure and in its high pressure  $P4/nmm$  structure.

the comparison between the electronic DOS at 0 GPa and at 25 GPa shows that the hybridization between the silicon's s and p electrons and the transition metal's d electrons observed at ambient conditions by Yarmoshenko et al. [30] persists when the pressure increases. Moreover for the same structure, the ranges of energies occupied by the electrons increase and the electronic bands become wider when the pressure increases, implying a stronger delocalization of the electrons and a higher conductivity for the material.

In detail, we found that in the pressure range of stability of the  $\varepsilon$ -FeSi structure, RuSi and OsSi were respectively a semiconductor and a degenerate semiconductor with band gaps respectively of 0.27 eV and 0.53 eV at both 0 GPa and 5 GPa. These results are in good agreement with experiment which proposed a gap of 0.26 eV for RuSi and a non-determined but larger than 0.26 eV value for OsSi [33]. In their high pressure CsCl form, RuSi and OsSi become metallic with a relatively low electronic density at the Fermi energy (see Fig. 3 for RuSi). It was previously shown that CoSi is a semimetal at ambient conditions [10]. We add that it remains a semimetal up to at least 50 GPa, with a very low electronic density near to the Fermi energy. RhSi and IrSi are metals in the MnP configuration but become semimetallic when they adopt the  $\varepsilon$ -FeSi structure (see Fig. 3 for RhSi). In the case of RhSi, these results are consistent with previous studies [18,34]. Lastly, PdSi and PtSi remain metals whatever the pressure and the structure adopted (see Fig. 3 for PdSi). Only the DOS of RuSi, RhSi, and PdSi are represented in Fig. 3 because the behaviour of OsSi, IrSi and PtSi follow the same trends overall. The DOS of PdSi and PtSi in the MnP structure present good similarities with the DOS of NiSi in the same structure calculated previously by Connétable and Thomas [35]. The electronic behaviour of CoSi in the  $\varepsilon$ -FeSi structure is very similar to that of RhSi in the same structure. The main difference is the absence of a band gap between the lowest energy group of valence electrons containing the 3s electrons of Si and the upper group. We observe also that for the same structure and the same pressure, the localization of the d electrons in the 4d transition metal monosilicides is stronger than in the 5d ones. This trend has already been reported by Imai and Watanabe [10] and persists when the pressure increases.

#### 4. Conclusion

The athermal high pressure study of the stability and the electronic structure of cobalt monosilicide and the monosilicides of the platinum group elements extends the results of previous theoretical and experimental studies at 0 GPa and ambient conditions [7,10,11,16,26,30,32]. RuSi and OsSi adopt the same low pressure ( $\varepsilon$ -FeSi) and high pressure (CsCl) structures as FeSi, and show relatively comparable semiconductor electronic behaviour. We predict that CoSi has a phase transition from the  $\varepsilon$ -FeSi structure to the CsCl structure around 270 GPa and remains a semimetal at least up to 50 GPa. RhSi and IrSi are found to follow a similar behaviour with a phase transition from the orthorhombic MnP structure to the cubic  $\varepsilon$ -FeSi structure at 10 GPa and 25 GPa respectively. Both are metallic in the MnP structure and become semimetals in the high pressure phase. PdSi and PtSi adopt the MnP structure up to 13 GPa and 20 GPa respectively, and a tetragonal  $P4/nmm$  structure at higher pressure. They remain metals whatever the structure adopted. The electronic properties of the transition metal monosilicides studied show stronger localization of the d electrons in 4d metals than in 5d metals, and the hybridization between the silicon's 3s and 3p electrons with metal's nd electrons, observed by Imai and Watanabe [10] and Yarmoshenko et al. [30] seems to persist at high pressure.

It would be highly desirable to confirm the results of our computer simulation study by high pressure, high temperature exper-

iments, since we have found that temperature is significant in determining the phase relations in NiSi ([7–9,36]). In particular, studies of PdSi and PtSi may show a transition to a truly tetragonal phase rather than the orthorhombically distorted variant seen in NiSi ([7]). However, for some phases, e.g. CoSi, the pressure required to observe any phase transitions may be prohibitively high. Alternatively, some of these high pressure phases have already been synthesised at ambient conditions by epitaxial growth or in a SiC matrix (Refs. [37,38] for CoSi with a CsCl structure) allowing convenient experimental analysis of their transport properties.

#### Acknowledgments

The authors are grateful to the UK supercomputing facility HEC-ToR and to the French regional council of Rhône-Alpes for financial support.

#### References

- [1] A.M. Dziewonski, D.L. Anderson, Preliminary reference earth model, *Phys. Earth Planet. Inter.* 25 (1981) 297–356, [http://dx.doi.org/10.1016/0031-9201\(81\)90046-7](http://dx.doi.org/10.1016/0031-9201(81)90046-7).
- [2] F. Birch, Elasticity and constitution of the earth's interior, *J. Geophys. Res.* 57 (1952) 227–286, <http://dx.doi.org/10.1029/JZ057i002p00227>.
- [3] F. Birch, Density and composition of the mantle and core, *J. Geophys. Res.* 69 (1964) 4377–4388, <http://dx.doi.org/10.1029/JZ069i020p04377>.
- [4] J.P. Poirier, Light elements in the earth's outer core: a critical review, *Phys. Earth Planet. Inter.* 85 (1994) 319–337, [http://dx.doi.org/10.1016/0031-9201\(94\)90120-1](http://dx.doi.org/10.1016/0031-9201(94)90120-1).
- [5] L. Vočadlo, G.D. Price, I.G. Wood, Crystal structure, compressibility and possible phase transition in  $\varepsilon$ -FeSi studied by first-principles pseudopotential calculations, *Acta Crystallogr. Sect. B* 55 (1999) 484–493, <http://dx.doi.org/10.1107/S0108768199001214>.
- [6] R. Caracas, R. Wentzcovitch, Equation of state and elasticity of FeSi, *Geophys. Res. Lett.* 31 (2004) L20603, <http://dx.doi.org/10.1029/2004GL020601>.
- [7] I.G. Wood, J. Ahmed, D.P. Dobson, L. Vočadlo, High-pressure phase transitions and equations of state in NiSi. iii. A new high-pressure phase of NiSi, *J. Appl. Crystallogr.* 46 (2013) 14–24, <http://dx.doi.org/10.1107/S0021889812047085>.
- [8] L. Vočadlo, I.G. Wood, D.P. Dobson, High-pressure phase transitions and equations of state in NiSi. i. Ab initio simulations, *J. Appl. Crystallogr.* 45 (2012) 186–196, <http://dx.doi.org/10.1107/S0021889812000337>.
- [9] O.T. Lord, L. Vočadlo, I.G. Wood, D.P. Dobson, S.M. Clark, M.J. Walter, High-pressure phase transitions and equations of state in NiSi. ii. Experimental results, *J. Appl. Crystallogr.* 45 (2012) 726–737, <http://dx.doi.org/10.1107/S0021889812016809>.
- [10] Y. Imai, A. Watanabe, Electronic structures of platinum group elements silicides calculated by a first-principle pseudopotential method using plane-wave basis, *J. Alloys Comp.* 417 (2006) 173–179.
- [11] L. Vočadlo, G.D. Price, I.G. Wood, Structures and physical properties of  $\varepsilon$ -FeSi and CsCl-type RuSi studied by first-principles pseudopotential calculations, *Acta Crystallogr. Sect. B* 56 (2000) 369–376, <http://dx.doi.org/10.1107/S0108768199016420>.
- [12] E.G. Moroni, W. Wolf, J. Hafner, R. Podloucky, Cohesive, structural, and electronic properties of Fe–Si compounds, *Phys. Rev. B* 59 (1999) 12860–12871, <http://dx.doi.org/10.1103/PhysRevB.59.12860>.
- [13] D. Shinoda, S. Asanabe, Magnetic properties of silicides of iron group transition elements, *J. Phys. Soc. Jpn* 21 (1966) 555, <http://dx.doi.org/10.1143/JPSJ.21.555>.
- [14] C.S. Lue, Y.K. Kuo, C.L. Huang, W.J. Lai, Hole-doping effect on the thermoelectric properties an electronic structure of CoSi, *Phys. Rev. B* 69 (2004) 125111, <http://dx.doi.org/10.1103/PhysRevB.69.125111>.
- [15] L. Schellenberg, J.L. Jorda, J. Muller, The rhodium-silicon phase diagram, *J. Less-Common Met.* 109 (1985) 261–274, [http://dx.doi.org/10.1016/0022-5088\(85\)90058-X](http://dx.doi.org/10.1016/0022-5088(85)90058-X).
- [16] W.L. Korst, L.N. Finnie, A.W. Searcy, The crystal structures of the monosilicides of osmium, iridium and ruthenium, *J. Phys. Chem.* 61 (1957) 1541–1543, <http://dx.doi.org/10.1021/j150557a020>.
- [17] B. Altintas, A comparative study on electronic and structural properties of transition metal monosilicides, CrSi (B20-type), RhSi (B20-type), RhSi (B31-type) and RhSi (B2-type), *J. Phys. Chem. Solids* 72 (2011) 1325–1329, <http://dx.doi.org/10.1016/j.jpcs.2011.07.027>.
- [18] J.J. Wang, X.Y. Kuang, Y.Y. Jin, C. Lu, X.F. Huang, Theoretical investigation on the structural phase transition, elastic properties and hardness of RhSi under high pressure, *J. Alloys Comp.* 592 (2014) 42–47, <http://dx.doi.org/10.1016/j.jallcom.2014.01.012>.
- [19] R.D. Schinella, W.H. Herndon, Methods for forming metal/metal silicide semiconductor device interconnect system, US Patent 3,777,364, 1973.

- [20] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B* 54 (1996) 11169–11186, <http://dx.doi.org/10.1103/PhysRevB.54.11169>.
- [21] P. Hohenberg, W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* 136 (1964) B864–B871, <http://dx.doi.org/10.1103/PhysRev.136.B864>.
- [22] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, *Phys. Rev.* 140 (1965) A1133–A1138, <http://dx.doi.org/10.1103/PhysRev.140.A1133>.
- [23] J.P. Perdrew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation, *Phys. Rev. B* 46 (1992) 6671–6687, <http://dx.doi.org/10.1103/PhysRevB.46.6671>.
- [24] H.J. Monkhorst, J.D. Pack, Special points for brillouin-zone integrations, *Phys. Rev. B* 13 (1976) 5188–5192, <http://dx.doi.org/10.1103/PhysRevB.13.5188>.
- [25] F. Birch, Finite elastic strain of cubic crystals, *Phys. Rev.* 71 (1947) 809–824, <http://dx.doi.org/10.1103/PhysRev.71.809>.
- [26] K. Göransson, I. Engström, B. Nöläng, Structure refinements for some platinum metal monosilicides, *J. Alloys Comp.* 219 (1995) 107–110, [http://dx.doi.org/10.1016/0925-8388\(94\)05046-5](http://dx.doi.org/10.1016/0925-8388(94)05046-5).
- [27] N. Karlsson, An X-ray study of the phases in the copper-titanium system, *J. Inst. Metals* 79 (1951) 391–405.
- [28] J. Teyssier, R. Viennois, J. Salamin, E. Giannini, D. van der Marel, Experimental and first principle calculation of  $\text{Co}_x\text{Ni}_{(1-x)}\text{Si}$  solid solution structural stability, *J. Alloys Comp.* 465 (2008) 462–467, <http://dx.doi.org/10.1016/j.jallcom.2007.10.139>.
- [29] B. Boren, *Arkivfor kemi, Mineralogi och Geologi* 1 (1933) 1–28.
- [30] Y.M. Yarmoshenko, S.N. Shamin, L.V. Elokhina, V.E. Dolgih, E.Z. Kurmaev, S. Bartkowski, M. Neumann, D.L. Ederer, K. Göransson, B. Nöläng, I. Engström, Valence band spectra of 4d and 5d silicides, *J. Phys.: Condens. Matter* 9 (1997) 9403, <http://dx.doi.org/10.1088/0953-8984/9/43/023>.
- [31] Y. Liu, S.N. Li, Z.Z. Wang, Theoretical studies of elastic and thermodynamic properties of cubic B20 CoSi, *Physica B* 407 (2012) 4700–4705, <http://dx.doi.org/10.1016/j.physb.2012.08.028>.
- [32] B. Buschinger, W. Guth, M. Weiden, C. Geibel, F. Steglich, V. Vescoli, L. Degiorgi, C. Wassilew-Reul, RuSi: metal-semiconductor transition by change of structure, *J. Alloys Comp.* 262–263, [http://dx.doi.org/10.1016/S0925-8388\(97\)00389-7](http://dx.doi.org/10.1016/S0925-8388(97)00389-7).
- [33] H. Hohl, A.P. Ramirez, C. Goldmann, G. Ernst, E. Bucher, Transport properties of RuSi, RuGe, OsSi, and quasi-binary alloys of these compounds, *J. Alloys Comp.* 278 (1998) 39–43, [http://dx.doi.org/10.1016/S0925-8388\(98\)00584-2](http://dx.doi.org/10.1016/S0925-8388(98)00584-2).
- [34] N.K. Niranjana, First principles study of structural, electronic and elastic properties of cubic and orthorhombic RhSi, *Intermetallics* 26 (2012) 150–156, <http://dx.doi.org/10.1016/j.intermet.2012.03.049>.
- [35] D. Connétable, O. Thomas, First-principle study of the structural, electronic, vibrational, and elastic properties of orthorhombic NiSi, *Phys. Rev. B* 79 (2009) 094101, <http://dx.doi.org/10.1103/PhysRevB.79.094101>.
- [36] O.T. Lord, E.T. Wann, S.A. Hunt, A.M. Walker, J. Santangeli, M.J. Walter, D.P. Dobson, I.G. Wood, L. Vocadlo, G. Morard, M. Mezouar, The NiSi melting curve to 70 GPa, *Phys. Earth Planet. Inter.* 233 (2014) 13–23, <http://dx.doi.org/10.1016/j.pepi.2014.05.005>.
- [37] D. Walter, I.W. Karyasa, Synthesis and characterization of cobalt monosilicide (CoSi) with CsCl structure stabilized by a  $\beta$ -SiC matrix, *Z. Anorg. Allg. Chem.* 631 (2005) 1285–1288, <http://dx.doi.org/10.1002/zaac.200500050>.
- [38] H. von Känel, C. Schwarz, S. Goncalves-Conto, E. Müller, L. Miglio, F. Tavazza, G. Malegori, New epitaxially stabilized CoSi phase with the CsCl structure, *Phys. Rev. Lett.* 74 (1995) 1163–1166, <http://dx.doi.org/10.1103/PhysRevLett.74.1163>.