

Acta Crystallographica Section B

**Structural  
Science**

ISSN 0108-7681

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# Structures and physical properties of $\epsilon$ -FeSi-type and CsCl-type RuSi studied by first-principles pseudopotential calculations

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An investigation of the relative stability of the two known polymorphs of RuSi, having the  $\epsilon$ -FeSi and CsCl structures, has been made by first-principles pseudopotential calculations. The resulting cell volumes and fractional coordinates at  $P = 0$  are in good agreement with experiment. Application of high pressure to the  $\epsilon$ -FeSi phase of RuSi is predicted to produce a structure having almost perfect sevenfold coordination. However, it appears that RuSi having the CsCl-type structure will be the thermodynamically most stable phase for pressures greater than 3.6 GPa. Fitting of the calculated internal energy *versus* volume to a fourth-order logarithmic equation of state led to values (at  $T = 0$  K) for the bulk modulus,  $K_0$ , of 202 and 244 GPa for the  $\epsilon$ -FeSi and CsCl phases, respectively, in excellent agreement with experiment. Band-structure calculations for both phases are also presented.

Received 16 August 1999  
Accepted 15 December 1999

## 1. Introduction

In a recent paper (Vočadlo *et al.*, 1999) we have used first-principles pseudopotential calculations to examine the stability and physical properties of the sevenfold-coordinated  $\epsilon$ -FeSi structure relative to various hypothetical polymorphs, concluding that a CsCl-type structure would be the thermodynamically most stable phase for pressures greater than 13 GPa (a similar transition pressure,  $\sim 15$  GPa, has also been reported recently by Moroni *et al.* 1999). However, FeSi with the CsCl structure has not yet been observed in bulk material, experimental studies to date having failed to detect any phase transitions from the  $\epsilon$ -FeSi form under conditions of high pressure and temperature (Knittle & Williams, 1995; Guyot *et al.*, 1997), although it has been reported in thin films of FeSi grown on silicon substrates (von Känel *et al.*, 1992, 1994; Kafader *et al.*, 1993; Dekoster *et al.*, 1997). The compressibility of FeSi is of considerable interest to Earth scientists, silicon being a possible alloying element in the Earth's outer core. There is, however, considerable disagreement between the values of the bulk modulus,  $K_0$ , determined by experiment; these range from 209 (6) to 115 GPa, although it seems that the most likely value is  $\sim 170$ –175 GPa, results of 172 (3), 176 (3) and 173 GPa having been reported by three separate research groups using different methods (see Vočadlo *et al.*, 1999, for further details). A number of calculations of  $K_0$  at  $T = 0$  K have been made recently using both the local density approximation (LDA) and the generalized gradient approximation (GGA), leading to values of 230 GPa (LDA) and 195 GPa (GGA) (Qteish & Shawagfeh, 1998); 227 GPa (GGA) (Vočadlo *et al.*, 1999); 209 GPa (GGA) (Moroni *et al.*,

1999); 220 GPa (LDA) (Jarlborg, 1999). Zinoveva *et al.* (1974) and Sarrao *et al.* (1994) reported that  $K_0$  was strongly temperature dependent between 0 and 300 K, but even after allowing for this the results of the calculations [with the possible exception of the GGA result of Qteish & Shawagfeh (1998)] appear to lie at the extreme end of the spread of experimental values.

Ruthenium silicide, RuSi, provides an interesting analogue of FeSi, with, however, the important difference that two polymorphs can be synthesized, one having the  $\varepsilon$ -FeSi structure and the other having the CsCl structure, both of which persist at room temperature and pressure (Buddery & Welch, 1951; Weitzer *et al.*, 1988; Göransson *et al.*, 1995). In contrast with earlier observations by Weitzer *et al.* (1988), Buschinger, Geibel *et al.* (1997) reported that a phase transition between the two structures, probably of first order, occurs at 1578 K; annealing below this temperature (*e.g.* at 1563 K) was found to reduce greatly the amount of CsCl-type material in a multiphase sample, whereas annealing at 1623 K produced little effect on the ratio of the two phases, observations which were taken to indicate that the CsCl-type was the more stable at high temperatures and that the phase transition was rather sluggish. The stoichiometry of the initial sample was also found to influence the material formed; in samples with excess Ru, the CsCl-type phase was predominant, whereas samples deficient in Ru showed a mixture of both RuSi phases and of Ru<sub>2</sub>Si<sub>3</sub>. The standard enthalpy of formation of RuSi has been measured at 1400 and 1473 K (Topor & Kleppa, 1988) but, unfortunately, only for the CsCl phase. The crystal structure of the  $\varepsilon$ -FeSi phase of RuSi at room pressure and temperature has been determined from Rietveld refinement of multiphase X-ray powder data by Göransson *et al.* (1995). A number of physical properties of RuSi have also been measured recently, including the compressibility of both phases up to  $\sim 40$  GPa, determined by angle-dispersive X-ray powder diffractometry with a diamond-anvil cell at the ESRF, Grenoble (Buschinger, Guth *et al.*, 1997), values of  $255 \pm 15$  and  $215 \pm 15$  GPa being reported for the CsCl-type and  $\varepsilon$ -FeSi-type materials, respectively (note that the paper by Buschinger, Guth *et al.*, 1997, contains a number of misprints in which these compressibility values are transposed). No evidence of pressure-induced phase transitions were found in this investigation. The electrical properties have been investigated by Buschinger, Geibel *et al.* (1997), Buschinger, Guth *et al.* (1997) and Hohl *et al.* (1998), who found the CsCl-type material to be metallic and the  $\varepsilon$ -FeSi-type to be a narrow-gap semiconductor, the size of the band gap being given as 0.2–0.3 eV (Buschinger, Guth *et al.*, 1997) and 0.26 eV (Hohl *et al.*, 1998). In this respect the observed properties of CsCl-type RuSi may differ from those expected for CsCl-type FeSi, in which band-structure calculations indicate either a narrow gap (Girlanda *et al.*, 1994; Vočadlo, Price & Wood, unpublished) or a pseudogap (Moroni *et al.*, 1999) at the Fermi level. Similarly, the magnetic susceptibility of the two compounds is different;  $\varepsilon$ -FeSi shows strongly temperature-dependent paramagnetism below room temperature (Paschen *et al.*, 1997) whereas, in all three studies of  $\varepsilon$ -FeSi-type RuSi, small temperature-inde-

pendent diamagnetism was observed (Buschinger, Geibel *et al.*, 1997; Buschinger, Guth *et al.*, 1997; Hohl *et al.*, 1998).

A detailed discussion of the  $\varepsilon$ -FeSi crystal structure (Pauling & Soldate, 1948) has been given by Wood *et al.* (1996) and Vočadlo *et al.* (1999) and it will, therefore, be described only briefly here. The structure is cubic,  $P2_13$ ,  $Z = 4$ , with both Fe and Si atoms lying on threefold axes, occupying the  $4(a)$  ( $x, x, x$ ) sites. In an idealized  $\varepsilon$ -FeSi structure,  $x_{\text{Fe}} = +0.15451$  and  $x_{\text{Si}} = -0.15451$ ; each atom then has as its primary coordination seven equidistant atoms of the other kind, with six equidistant atoms of its own kind as next-nearest neighbours. The value of  $x$  required to produce this ideal sevenfold coordination is given by  $x = 1/4\tau$ , where  $\tau$  is the golden ratio  $(1 + 5^{1/2})/2$  (Wells, 1956). In real  $\varepsilon$ -FeSi structures both atoms are slightly displaced from their ideal positions, producing subtly different coordination. In the case of RuSi (Göransson *et al.*, 1995), these displacements are slightly larger than in FeSi, with  $x_{\text{Ru}} = +0.1284$  (7) and  $x_{\text{Si}} = -0.1643$  (11); the seven nearest-neighbour coordination distances for both Ru and Si atoms are then 2.383, 2.395 ( $\times 3$ ) and 2.706 Å ( $\times 3$ ), with six equal next-nearest-neighbour distances of 2.879 Å around the Ru atoms and of 2.926 Å around the Si atoms. The  $\varepsilon$ -FeSi structure may be regarded as being derived from that of rock salt by displacement of both atoms along  $\langle 111 \rangle$  directions (Mattheiss & Hamann, 1993; Wood *et al.*, 1996) and thus continuous transitions to either the sixfold-coordinated NaCl structure or (*via* the NaCl structure) to the eightfold-coordinated CsCl structure are, in principle, possible. However, it has been found that for FeSi the calculated free energy difference (at  $P = 0$  and  $T = 0$ ) between the  $\varepsilon$ -FeSi and NaCl structures is large, being in the range 1.4–1.6 eV per FeSi unit (Mattheiss & Hamann, 1993; Vočadlo *et al.*, 1999; Moroni *et al.*, 1999) and thus a transition between  $\varepsilon$ -FeSi-type and CsCl-type phases in FeSi or RuSi would seem to require a high activation energy.

The present computer simulation study of RuSi was carried out with the intention of addressing four main points. Firstly, examination of the calculated relative stabilities of  $\varepsilon$ -FeSi-type and CsCl-type RuSi would provide a good test of the validity of the conclusions we had drawn with respect to the stability of various hypothetical phases of FeSi (Vočadlo *et al.*, 1999). Secondly, our calculation of the compressibility of FeSi had produced a value which did not seem to be in agreement with experiment; similar calculations of compressibility of the two RuSi phases would provide a check on the methodology. Thirdly, it was of interest to examine the response to pressure of the atomic coordinates of the  $\varepsilon$ -FeSi phase of RuSi and the accuracy to which the reported crystal structure could be reproduced. Finally, RuSi is of some interest to physicists as it provides a non-magnetic reference system to FeSi, a material with unusual electrical and magnetic properties; no band-structure calculations for the two RuSi phases have been reported and these might, therefore, be of some value.

The calculations for RuSi presented here utilize a pseudopotential method, resulting in a significant reduction in computational requirements from those required for all-electron methods and thereby allowing efficient calculation of the internal energy of the  $\varepsilon$ -FeSi-type and CsCl-type phases of

RuSi for a range of values of pressure,  $P$ , and volume,  $V$ . Incorporation of the effect of atomic vibrations due to temperature would, however, be both extremely difficult and computationally very expensive and so this has not been attempted in the present calculations; these are, therefore, effectively all at 0 K and thus only the  $P, V, 0$  section of the  $P, V, T$  phase diagram is accessible. This is a drawback of the present study since it means that we are unable to address directly the stability of the two RuSi polymorphs at high temperature or to make comparisons with the high-temperature experimental data (we are similarly unable to study the effects of small changes in the stoichiometry). In view of the known insensitivity of the structure of FeSi itself to changes in temperature (Watanabe *et al.*, 1963), we believe that this limitation is much less important when addressing the relative stability, with respect to pressure, of the RuSi polymorphs at room temperature. However, a similar analogy with FeSi, for which the effect of thermal activation on some of the physical properties is known to be large (due to the narrow band gap), suggests that neglect of temperature might lead to errors when calculating even such quantities as the elastic constants (Zinoveva *et al.*, 1974; Sarrao *et al.*, 1994).

## 2. Calculation method

The calculations presented here are based on density functional theory within the generalized gradient approximation using ultrasoft non-norm-conserving Vanderbilt pseudopotentials, implemented in the computer program *VASP* (Vienna *ab initio* simulation package; Kresse & Furthmüller, 1996*a,b*). Since the details of this approach have been described in the paper by Vočadlo *et al.* (1999), only a brief summary will be given here.

In this method the valence orbitals are expanded as plane waves and the interactions between the core and valence electrons are described by pseudopotentials. For Ru a [Kr] core was assumed, with valence electrons  $5s^1 4d^7$ , for Si an [Ne] core was assumed, with valence electrons  $3s^2 3p^2$ . Details of the construction of the pseudopotentials used in the present work are given by Kresse & Hafner (1994) and Moroni *et al.* (1997). When using *VASP*, the ground state is calculated exactly for each set of ionic positions and the electronic free energy is taken as the quantity to be minimized. Relaxation of atomic coordinates and axial ratios is allowed by the program; when performing such operations these parameters are changed iteratively so that the sum of the lattice energy and electronic free energy converges to a minimum value.

The calculations discussed below were carried out using the primitive unit cells of the  $\epsilon$ -FeSi- and CsCl-type structures. An appropriate number of sampling points in reciprocal space to be used in the calculations had been determined during our investigation of the FeSi polymorphs. For the energy–volume calculations, similarly spaced grids of  $k$ -points were used,  $5 \times 5 \times 5$  for the  $\epsilon$ -FeSi-type and  $11 \times 11 \times 11$  for the CsCl-type, leading to 11 and 56  $k$ -points, respectively, in the symmetry-irreducible volume of the Brillouin zone. For the calculations of the electronic density of states (DOS), finer grids ( $9 \times 9 \times 9$

for the  $\epsilon$ -FeSi-type;  $15 \times 15 \times 15$  for the CsCl-type) were used, with sampling intervals of approximately 0.06 and 0.03 eV in energy.

The procedure adopted to determine the equations of state was to use *VASP* to calculate the internal energy ( $E$ ) of the crystal at a set of chosen volumes ( $V$ ). For the CsCl modification there are no parameters to relax. In the case of the  $\epsilon$ -FeSi-type structure the fractional coordinates of both Ru and Si were allowed to vary. Although no symmetry constraints were imposed during the relaxation of these coordinates, they retained the symmetry of the space group to at least five significant figures. When calculating the electronic density of states for the relaxed RuSi structure, however, the coordinates were returned to their exactly correct symmetrical form as this greatly increases the speed and accuracy of the calculations. Since  $T = 0$ , the pressure ( $P$ ) at any point on the  $E$  versus  $V$  curve may be found using the standard thermodynamic result  $P = -(\partial E/\partial V)_{T=0}$ , the actual values being determined by fitting the  $E$  versus  $V$  curve to a fourth-order logarithmic equation of state (see below). Knowing  $P, V$  and  $E$ , the enthalpy  $H$  may be calculated. Since  $T = 0$ , the enthalpy is equal to the Gibbs free energy,  $G$ , and thus the most stable phase at any given pressure may be determined; for the special case of ambient pressure ( $P \simeq 0, T = 0$ ),  $G = E$  and the relative stability of the different polymorphs can be determined simply from the positions of the minima in the  $E$  versus  $V$  curves.

## 3. Results and discussion

### 3.1. Properties at $P = 0$

Fig. 1 shows the internal energy,  $E$ , versus volume,  $V$ , curves for the two RuSi polymorphs considered. The full lines shown in the figure were obtained by fitting the data to a fourth-order logarithmic equation of state, of the form

$$E = V_0 \{ p[\ln(V_0/V)]^2 + q[\ln(V_0/V)]^3 + r[\ln(V_0/V)]^4 \} + E_0$$

where

$$p = K_0/2, \quad q = K_0(K'_0 - 2)/6,$$

$$r = K_0[1 + (K'_0 - 2) + (K'_0 - 2)^2 + K_0 K''_0]/24,$$

$V_0$  and  $E_0$  are the volume and internal energy at  $P = 0$ .  $K_0$  is the (isothermal) bulk modulus (since  $T = 0$  K, the adiabatic and isothermal bulk moduli will be equal) and  $K'_0$  and  $K''_0$  are its first and second derivatives, respectively, with respect to pressure. This equation of state has been found recently to give a significantly better fit to the results of energy–volume calculations than the commonly used third-order Birch–Murnaghan equation (Vočadlo *et al.*, 2000) indicated by the dashed line in Fig. 1(*b*). The results obtained from fitting the equations of state are shown in Table 1. Clearly, when  $P = 0$ , RuSi with the  $\epsilon$ -FeSi structure is the more stable of the two polymorphs. The energy difference between this structure and the CsCl modification (0.013 eV atom<sup>-1</sup>) is, however, much

**Table 1**

Crystal structures and physical properties of  $\epsilon$ -FeSi- and CsCl-type RuSi.

(a) Internal energies and structural parameters at  $P = 0$ .

		$E_0$ (eV atom <sup>-1</sup> )	$V_0$ (Å <sup>3</sup> atom <sup>-1</sup> )	Cell (Å)	Relaxed coordinates
$\epsilon$ -FeSi-type	Present work†	-7.8673 (1)	13.420 (1)	4.7528 (2)	$x_{\text{Ru}} = 0.1293$ $x_{\text{Si}} = -0.1626$
	Experimental values		12.986–13.044‡	4.701–4.708‡	$x_{\text{Ru}} = 0.1284$ (7)§ $x_{\text{Si}} = -0.1643$ (11)§
CsCl-type	Present work†	-7.854 (1)	12.805 (4)	2.9476 (3)	
	Experimental values		12.283–12.359‡	2.907–2.913‡	

† The values of  $E_0$  and  $V_0$  were found by fitting to a fourth-order logarithmic equation of state (for details see text). Figures in parentheses are estimated standard deviations applying to the least significant figures. It should be noted, however, that these are derived solely on the basis of the goodness of fit to the chosen equation of state and take no account of errors in the simulation process. ‡ Weitzer *et al.* (1988), Göransson *et al.* (1995), Buschinger, Geibel *et al.* (1997) and Hohl *et al.* (1998). § Göransson *et al.* (1995).

(b) Compressibilities and their derivatives.

		$K_0$ (GPa)	$K_0'$	$K_0''$ (GPa <sup>-1</sup> )
$\epsilon$ -FeSi-type	Present work†	(ln 4) 202.1 (1) (BM3) 202 (3)	5.411 (8) 4.49 (4)	-0.0601 (5)
	Experimental values‡	215 (15)	7.63	
CsCl-type	Present work†	(ln 4) 243.6 (5) (BM3) 233 (2)	4.800 (5) 4.32 (3)	-0.0284 (3)
	Experimental values‡	255 (15)	6.71	

† Values labelled ln 4 and BM3 were obtained by fitting to fourth-order logarithmic and third-order Birch–Murnaghan equations of state, respectively (for details see text). The comment above with regard to the estimated standard deviations is equally applicable to this section. ‡ Buschinger, Guth *et al.* (1997).

smaller than that found for FeSi (0.042 eV atom<sup>-1</sup>) as might be expected from the experimental observation that both phases of RuSi exist at room temperature and pressure. The experimental values of the lattice parameters given in the literature vary from about 2.907 to 2.913 Å for the CsCl phase and 4.701 to 4.708 Å for the FeSi phase (Weitzer *et al.*, 1988; Göransson *et al.*, 1995; Buschinger, Geibel *et al.*, 1997; Hohl *et al.*, 1998). The values obtained in the present study, 2.948 and 4.753 Å, are in good agreement with experiment, differing by only about 1.2% for the CsCl and 1.0% for FeSi phases, respectively; however, in contrast with our previous results for FeSi itself in which the cell parameters were underestimated, in the case of RuSi VASP provides an overestimated cell. The predicted fractional coordinates for the  $\epsilon$ -FeSi phase at  $P = 0$  are  $x_{\text{Ru}} = 0.1293$  and  $x_{\text{Si}} = -0.1626$ , which are in excellent agreement with the experimental results of Göransson *et al.* (1995) who obtained values of  $x_{\text{Ru}} = 0.1284$  (7) and  $x_{\text{Si}} = -0.1643$  (11). As in the case of FeSi, it appears, therefore, that the pseudopotential method is able not only to determine correctly the stable polymorph at ambient pressure, but also to reproduce the observed crystal structure with an accuracy approaching that to which it has been determined experimentally.

Figs. 2 and 3 show the calculated electronic density of states (DOS), the local density of states associated with each of the atoms in the structure (LDOS) and the number of states (NOS) for the  $\epsilon$ -FeSi and CsCl phases of RuSi. These calculations indicate that the  $\epsilon$ -FeSi phase is a narrow-band-gap semiconductor. A value for the band gap of 0.20 eV was obtained from a calculation using a  $7 \times 7 \times 7$   $k$ -point grid and

an energy-sampling interval of 0.02 eV, in good agreement with the experimental results of Buschinger, Guth *et al.* (1997) and Hohl *et al.* (1998), who obtained values of 0.2–0.3 eV and 0.26 eV, respectively. Calculation of the density of states for such materials involves a compromise between smoothness and resolution unless unfeasibly fine sampling intervals are used; those shown in Fig. 2 were obtained using a  $9 \times 9 \times 9$   $k$ -point grid and an energy sampling interval of 0.06 eV, which produced a value of 8.86 eV for the Fermi level,  $E_F$ , and a slightly reduced band gap. The form of the DOS for the  $\epsilon$ -FeSi phase of RuSi is qualitatively similar to that of FeSi itself (Vočadlo *et al.*, 1999). VASP allows projection of the LDOS so as to discriminate between electrons with  $s$ -,  $p$ - and  $d$ -like character. It can be

seen from Fig. 2(b) that the DOS around  $E_F$  is dominated by the contribution from the Ru  $d$ -electrons. There is, however, a significant Si  $p$ - and  $d$ -electron contribution (Fig. 2c) in the range from about 0 to 7 eV below  $E_F$ , indicating a high degree of covalency in the bonding. As expected for a semiconductor, the NOS (Fig. 2d) is horizontal at  $E_F$ .

It can be seen from Fig. 3 that our calculations indicate that the CsCl phase is metallic, in agreement with the experimental data of Buschinger, Geibel *et al.* (1997), Buschinger, Guth *et al.* (1997) and Hohl *et al.* (1998). The DOS (Fig. 3a) is qualitatively similar to that expected for CsCl-type FeSi. However, in the case of FeSi the DOS falls either to zero (Girlanda *et al.*, 1994; Vočadlo, Price & Wood, unpublished) or very close to zero (Moroni *et al.*, 1999) at  $E_F$ , whereas for RuSi there is merely a pronounced dip in the density of states around the Fermi level (calculated to lie at 9.94 eV). It should be noted that this dip is also present in the DOS of the  $\epsilon$ -FeSi phase, where it lies about 1 eV above  $E_F$ . Once again, the DOS near  $E_F$  is dominated by the Ru  $d$ -electrons (Fig. 3b), but with significant Si  $p$ - and  $d$ -electron contributions (Fig. 3c).

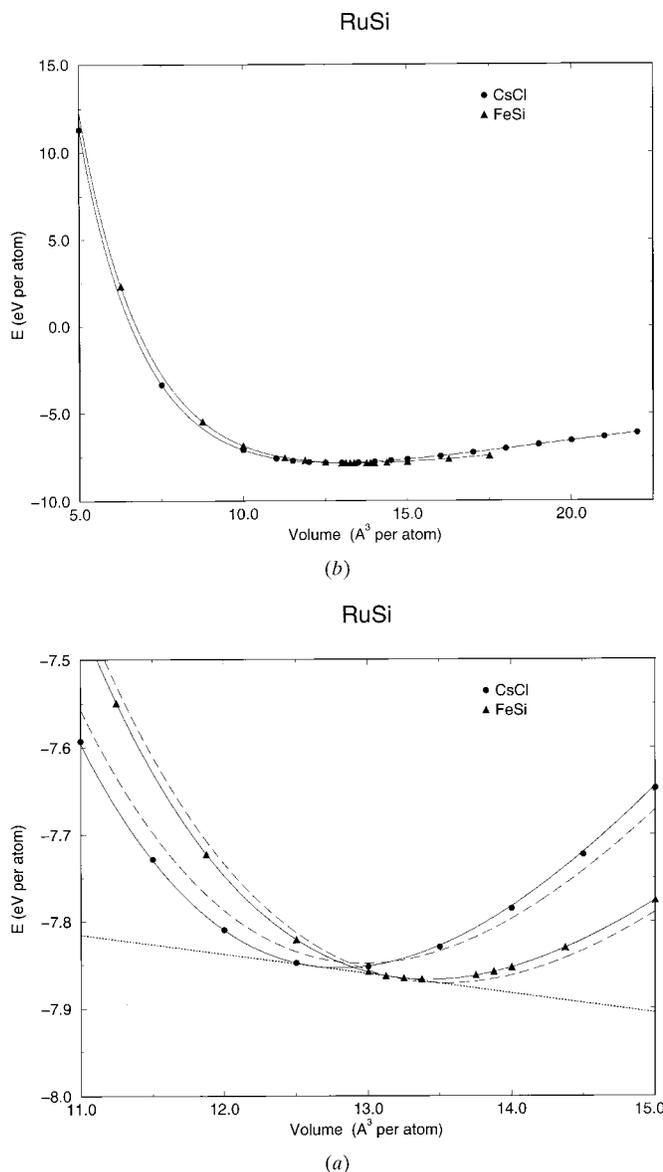
### 3.2. Behaviour at high pressure

Fig. 4 shows the effect of pressure on the fractional coordinates  $x_{\text{Ru}}$  and  $x_{\text{Si}}$  of the  $\epsilon$ -FeSi phase of RuSi (for comparison the results of our previous calculations for FeSi are also shown). In all cases the Ru and Si coordinates were relaxed from a starting structure with ideal sevenfold coordination, *i.e.* from  $x = \pm 1/4\tau$  ( $\pm 0.15451$ ). In no case was there any tendency towards relaxation away from the  $\epsilon$ -FeSi structure, the beha-

viour seen being very similar to that found previously for  $\epsilon$ -FeSi itself. As  $P$  increases, the magnitudes of the two coordinates become more equal and closer to the value required for an ideal sevenfold-coordinated structure, although the asymptotic trend appears to be towards a slightly lower value. At extreme pressures ( $\sim 900$  GPa,  $a = 3.684$  Å)  $|x_{\text{Ru}}| = |x_{\text{Si}}| = 0.1528$  and the two atoms then lie  $0.006$  Å away from their ideal positions. It is probable that this slight departure from

the ideal sevenfold-coordinated structure represents a real effect, rather than an artefact of the pseudopotential method, since it appears to follow the trend established at low pressures. Possibly, it reflects the fundamentally non-spherical atoms required by the geometry of the bonding (Pauling & Soldate, 1948; Vočadlo *et al.*, 1999).

Although RuSi with the  $\epsilon$ -FeSi structure shows no indication of instability at high pressures, it can be seen from Fig. 1 that the CsCl phase has the lower free energy at high pressures. Any straight line on Fig. 1 represents a locus of constant pressure,  $P$ , constant enthalpy,  $H$ , and (since  $T = 0$ ) constant Gibbs free energy,  $G$ , lines with steeper negative slopes having higher values of these quantities (see Vočadlo *et al.*, 1999 for further discussion). The dotted straight line shown in Fig. 1(b), which corresponds to a pressure of 3.6 GPa, is the common tangent to the  $E$  versus  $V$  curves of the two RuSi polymorphs. For pressures above and below 3.6 GPa, therefore, the CsCl and  $\epsilon$ -FeSi structures will, respectively, be the more stable. The value of the transition pressure was obtained by inspection of the calculated  $H$  versus  $P$  curves for the two phases. In comparison with our previous results for FeSi (Vočadlo *et al.*, 1999), RuSi has a much lower transition pressure (3.6 GPa as opposed to 13 GPa) and a smaller difference in internal energy at  $P = 0$  ( $0.013$  eV atom $^{-1}$  as opposed to  $0.042$  eV atom $^{-1}$ ), in accordance with the observation that both phases of RuSi are stable at room temperature and pressure.



**Figure 1**  
 (a) Internal energy versus volume for the  $\epsilon$ -FeSi and CsCl phases of RuSi. Calculated values are indicated by points; the full lines show fits of the data to a fourth-order logarithmic equation of state (for details see text). (b) Internal energy versus volume around  $P = 0$ . The full and dashed lines were obtained by fitting the data to fourth-order logarithmic and third-order Birch–Murnaghan equations of state, respectively. The common tangent to the curves for the two structures, shown as a dotted line, indicates that the CsCl phase will be stable for pressures greater than 3.6 GPa (for details see text).

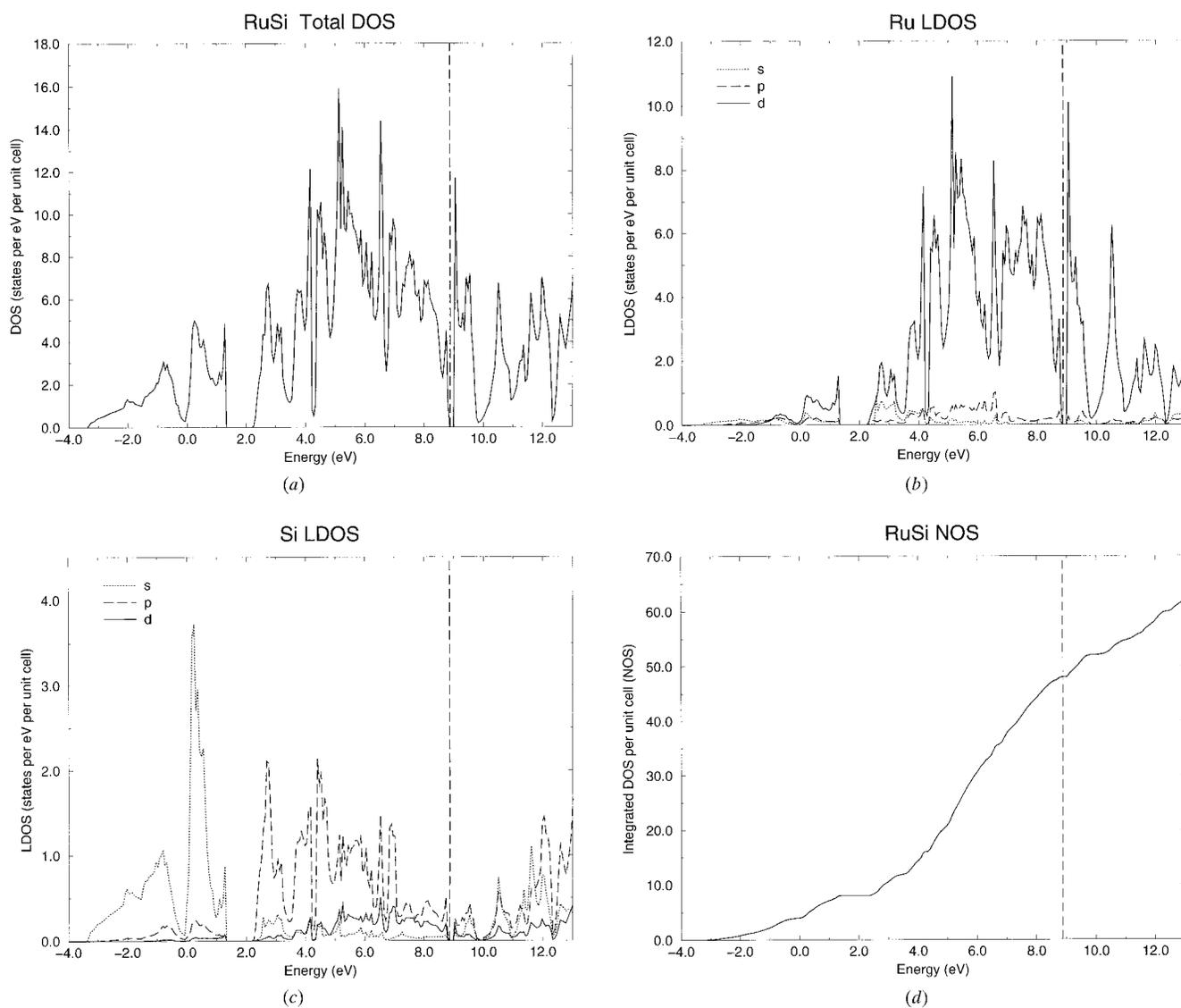
### 3.3. Compressibility

Table 1 shows the values of the bulk modulus,  $K_0$ , and its first- and second-pressure derivatives,  $K_0'$  and  $K_0''$ , obtained from fitting the  $E$  versus  $V$  curve to a fourth-order logarithmic equation of state ('ln 4', see above). The table also shows the values of  $K_0$  and  $K_0'$  obtained by fitting to the more commonly used third-order Birch–Murnaghan equation ('BM3'; see Vočadlo *et al.*, 1999, for details). Application of the two equations of state to our results led to identical values of  $K_0$  for the  $\epsilon$ -FeSi phase [ln 4: 202.1 (1) GPa; BM3: 202 (3) GPa] and values which differed by only 10 GPa (4%) for the CsCl phase [ln 4: 243.6 (5) GPa; BM3: 233 (2) GPa; it should be noted that the standard deviations quoted for the present study are derived solely on the basis of the goodness of fit to the chosen equation of state and take no account of any systematic errors in the simulation process]. The agreement with experiment is also extremely good, Buschinger, Guth *et al.* (1997) having obtained  $215 \pm 15$  GPa and  $255 \pm 15$  GPa for the  $\epsilon$ -FeSi-type and CsCl-type materials, respectively. The values of  $K_0'$  agree less well, both between the two different equations of state used in the present study and between this study and the experimental values. However, this probably simply reflects the greater sensitivity of this parameter to changes in the model and to errors in the data. For the  $\epsilon$ -FeSi phase we obtained values for  $K_0'$  of 5.411 (8) (ln 4) and 4.49 (4) (BM3) and, for the CsCl phase, 4.800 (5) (ln 4) and 4.32 (3) (BM3), the corresponding experimental values (Buschinger, Guth *et al.*, 1997) being 7.63 and 6.71.

3.4. General remarks

From the discussion above it appears that the expected high-pressure behaviour and properties of RuSi and FeSi should be quite similar. Our calculations for RuSi reproduce the results of the crystal structure refinement very well and are consistent with the measured electrical properties of both phases of the material and with the observed greater stability of the CsCl phase relative to the  $\epsilon$ -FeSi phase. As suggested previously (Vočadlo *et al.*, 1999), it seems quite probable, therefore, that bulk samples of the CsCl-type phase of FeSi might be synthesized under conditions of high  $P$  and  $T$ . It is most interesting that our calculated compressibility value for the  $\epsilon$ -FeSi phase of RuSi appears to be in far better agreement with experiment than was our result for FeSi itself. This indicates that there do not, therefore, appear to be any general

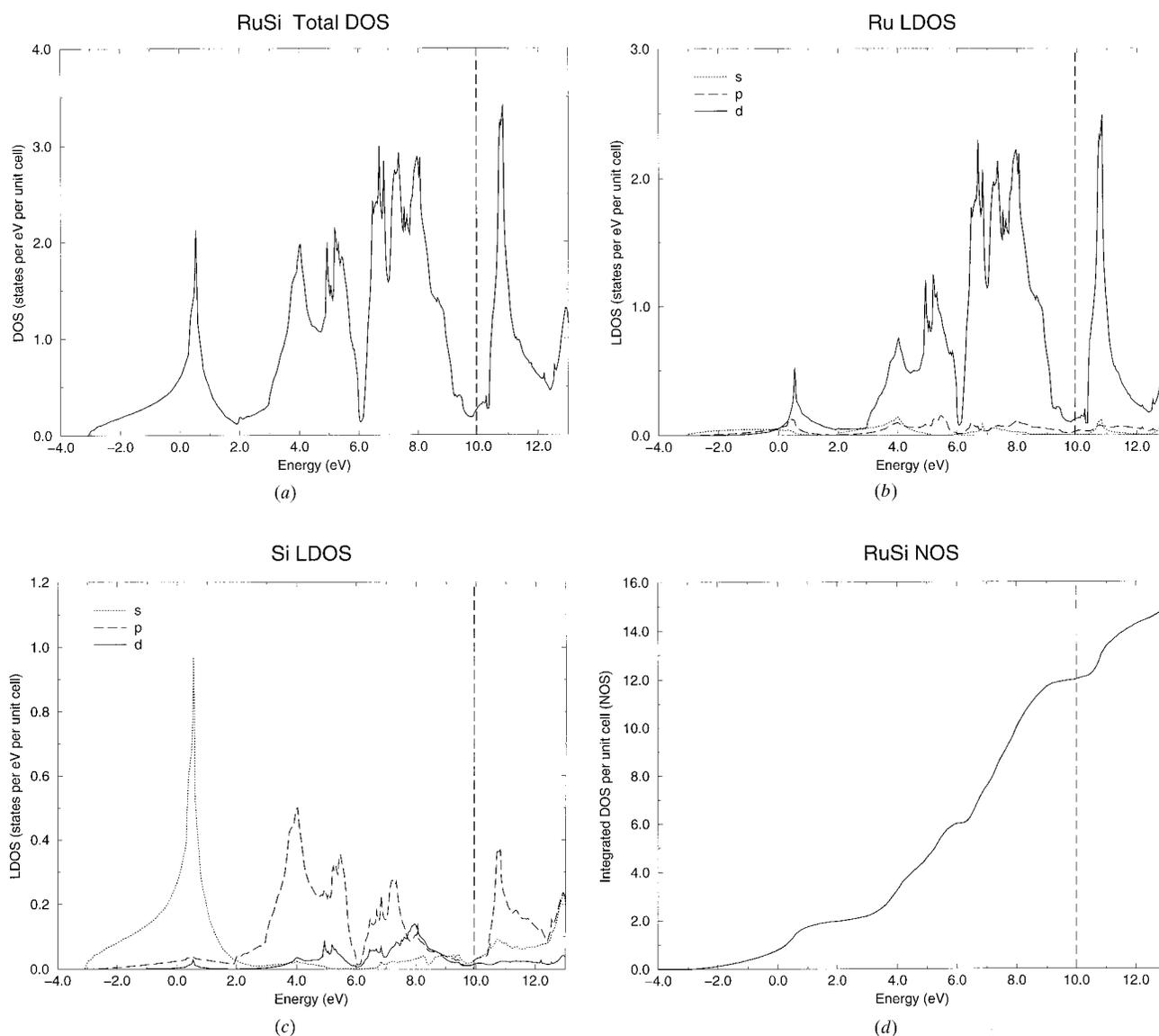
flaws in our calculations when applied to materials with this rather unusual structure. In our previous paper it was suggested that the discrepancy in the values of  $K_0$  might arise from small variations in stoichiometry of the FeSi samples used in the experiments, which could significantly affect the results. Although this suggestion is not without merit, bearing in mind the known sensitivity of the RuSi phases to small variations in composition, it is perhaps unlikely, since three research groups using material from different sources were able to obtain measured values of  $K_0$  for FeSi that are in almost exact agreement (Sarrazo *et al.*, 1994; Ross, 1996; Guyot *et al.*, 1997). A possibly significant difference between our calculations for the two compounds is that in the case of FeSi the unit-cell volume at  $P = 0$  was underestimated, whereas for RuSi it was overestimated, overestimation of  $V_0$  being the more common occurrence when using the GGA and VASP;



**Figure 2** Electronic density of states calculations for the  $\epsilon$ -FeSi phase of RuSi. (a) Total density of states (DOS). (b) Local DOS (LDOS) for Ru. (c) LDOS for Si. (d) Total number of states (NOS). The position of the Fermi level,  $E_F$ , is indicated by a vertical dashed line. Note that NOS is horizontal at  $E_F$ , indicating that the material is non-metallic. Core electrons are excluded from the calculation.

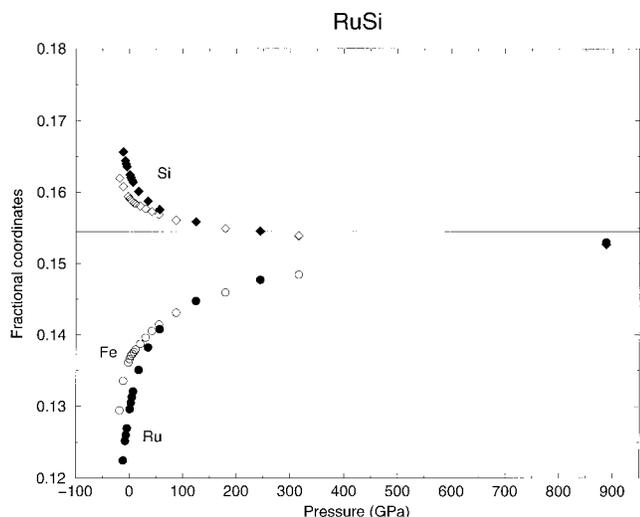
the reason for this difference is not, at present, clear. A similar underestimate of the cell volume was reported by Moroni *et al.* (1999) using the GGA and in all of the results obtained using the LDA (Qteish & Shawagfeh, 1998; Moroni *et al.*, 1999; Jarlborg, 1999). Qteish & Shawagfeh (1998), when using the GGA, did obtain an overestimated cell and it is probably significant that this calculation led to the lowest reported value of  $K_0$ . Important differences between RuSi and FeSi are found in their magnetic properties, with the  $\epsilon$ -FeSi phase of RuSi showing temperature-independent diamagnetism and FeSi itself showing unusual temperature-dependent paramagnetism. There is, however, no indication from neutron diffraction at liquid-nitrogen temperature that FeSi has a ground state which is magnetically ordered (Watanabe *et al.*, 1963), and neutron scattering studies of diffuse magnetic

intensity (Shirane *et al.*, 1987; Tajima *et al.*, 1988) seem to agree well with the behaviour expected on the basis of temperature-induced paramagnetism, as proposed originally by Jaccarino *et al.* (1967). In this model, FeSi is assumed to have a non-magnetic ground state, with thermal excitation of electrons across a narrow band gap to states which are paramagnetic. In our calculations for FeSi no net magnetic moment was found and so it seems unlikely that neglect of magnetism provides an explanation of the discrepancy in  $K_0$ , unless the material has an undetected antiferromagnetic phase existing in a temperature range below that studied by Watanabe *et al.* (1963). Recently, Sluchanko *et al.* (1998) detected an anomalous contribution to the Hall coefficient below 7 K, which it was suggested might arise from an electronic phase transition to a state with a spin-density wave. Inclusion of magnetism in



**Figure 3**

Electronic density of states calculations for the CsCl phase of RuSi. (a) Total density of states (DOS). (b) Local DOS (LDOS) for Ru. (c) LDOS for Si. (d) Total number of states (NOS). The position of the Fermi level,  $E_F$ , is indicated by a vertical dashed line. Note that NOS is not horizontal at  $E_F$ , indicating that the material is metallic. Core electrons are excluded from the calculation.



**Figure 4** Fractional coordinates of the Ru and Si atoms (solid symbols) as a function of pressure (for convenience  $|x_{\text{Si}}|$  is plotted). The open symbols show the corresponding results for FeSi (Vočadlo, Price & Wood, 1999). The value of  $x$  required for the ideal sevenfold-coordinate structure is shown by the horizontal line.

our *ab initio* calculations, if required, could produce a softer material (*i.e.* a decreased value of  $K_0$ ) since, although it will lower the internal energy for values of  $V$  corresponding to low pressures and hence increase the corresponding values of  $P$  [ $= -(\partial E/\partial V)$ ], this effect might be offset by a concomitant increase in  $V_0$ . The origin of the poor agreement between the experimental and calculated bulk moduli of FeSi, therefore, remains unresolved.

Technical assistance from G. Kresse is gratefully acknowledged. We should also like to thank M. Gillan for helpful discussions.

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