Crystal structure, compressibility and possible phase transitions in ε-FeSi studied by first-principles pseudopotential calculations

Lidunka Vočadlo, Geoffrey D. Price and I. G. Wood*

Research School of Geological and Geophysical Sciences, University College London, Gower Street, London WC1E 6BT, England. E-mail: wood@crystal.geol.ucl.ac.uk

Abstract

An investigation of the relative stability of the FeSi structure and of some hypothetical polymorphs of FeSi has been made by first-principles pseudopotential calculations. It has been shown that the observed distortion from ideal sevenfold coordination is essential in stabilizing the FeSi structure relative to one of the CsCl type. Application of high pressure to FeSi is predicted to produce a structure having nearly perfect sevenfold coordination. However, it appears that FeSi having a CsCl-type structure will be the thermodynamically most stable phase for pressures greater than 13 GPa. Fitting of the calculated internal energy *vs* volume for the FeSi structure to a third-order Birch–Murnaghan equation of state led to values, at $T = 0$ K, for the bulk modulus, K_0, and for its first derivative with respect to pressure, K_0', of 227 GPa and 3.9, respectively.

1. Introduction

Iron monosilicide (ε-FeSi) crystallizes with an unusual and intriguing structure (Pauling & Soldate, 1948). The space group is cubic, $P2_13$ ($Z = 4$) with both Fe and Si atoms occupying $4a$ (x, x, x) sites. In an idealized FeSi structure, as shown in Fig. 1(*a*), $x_{Fe} = +0.15451$ and $x_{Si} = -0.15451$; the primary coordination of each atom is then 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 τ is the golden ratio, $(1 + 5^{1/2})/2$ (see *e.g.* Wells, 1956). Dmitrienko (1994) has suggested that this structure may be considered as a crystalline approximate to an icosahedral quasicrystal. In the ideal sevenfold structure the seven atoms forming the primary coordination shell lie at seven of the twenty vertices of a regular pentagonal dodecahedron (Fig. 1*b*) with edges equal in length to $a/(\tau^2)$, where a is the cubic cell parameter. The atoms forming the nearest-neighbour coordination shell then lie at a distance $[a(3)^{1/2}]/2\tau$ from the central atom and have a closest separation from each other (equal to the distance of the next-nearest neighbour coordination) of a/τ, this length being the diagonal of the pentagons.

Inorganic structures in which the primary coordination results from occupation of the vertices of three of the five regular Platonic solids (*i.e.* the tetrahedron, cube and octahedron) are, of course, very common and it is of interest to find in FeSi a structure based on the fourth of these polyhedra, the pentagonal dodecahedron.

In the real FeSi structure, shown in Fig. 1(*c*) (Pauling & Soldate, 1948), both atoms are slightly displaced from their ideal positions, with coordinates $x_{Fe} = 0.137$ (2) and $x_{Si} = -0.158$ (4). This leads to nearest-neighbour distances for the primary coordination shell of both Fe and Si atoms of 2.294, 2.341 ($\times 3$) and 2.515 ($\times 3$) Å. The six next-nearest-neighbour Fe atoms surrounding each Fe atom lie at a distance of 2.753 Å, whereas the six Si atoms which are the next-nearest neighbours of each Si atom are at 2.781 Å. Thus, although both Fe and Si atoms are still in essentially the same environment, their coordination is subtly different. This feature is also revealed by calculation of the bond angles for the primary coordination shell; although the bond distances are the same for both atoms, the bond angles are not.

As discussed in some detail in an earlier paper (Wood *et al.*, 1996), it is possible to regard the FeSi structure as being derived from that of rocksalt by displacement of both atoms along ⟨111⟩ directions, and thus to envisage continuous phase transitions to either the sixfold coordinated NaCl structure or (*via* the NaCl structure) to the eightfold-coordinated CsCl type. The possibility of such phase transitions provided the impetus for us to carry out a study of FeSi by high-pressure neutron powder diffraction (Wood *et al.*, 1996). It was found that the structure was essentially invariant over the accessible pressure range (0–9 GPa), with no detectable tendency either towards, or away from, the ideal sevenfold-coordinated structure, a result which was confirmed by single-crystal X-ray diffraction using a diamond-anvil cell (Ross, 1996). Lattice-parameter measurements to much higher pressures (50 GPa) by powder X-ray diffraction (Knittle & Williams, 1995) did not suggest the presence of any structural phase transitions, even after laser-heating to about 1500 K at 49 GPa (the published data do, however, contain one point, at 36 GPa, which lies well away from the *PV* curve on which the rest of the data lie). Similarly, powder neutron diffraction studies

both above and below room temperature (Watanabe *et al.*, 1963) suggested that there was little change in the structure between 79 and 573 K. Recently, however, experiments on thin films of FeSi grown on silicon substrates (von Känel *et al.*, 1992; Kafader *et al.*, 1993; von Känel *et al.*, 1994; Dekoster *et al.*, 1997) have indicated the formation of a CsCl-type structure, stable for layers thinner than 890 Å, and it is known that RuSi undergoes a transition from an FeSi-type to a CsCl-type structure at 1578 (±15) K (Buschinger *et al.*, 1997).

The physical properties of ε-FeSi, and in particular its compressibility, are currently of interest to Earth scientists. Knittle & Williams (1995) obtained a value for the bulk modulus of 209 (6) GPa (using X-ray powder diffraction in a diamond-anvil cell to 50 GPa), which they considered to be sufficiently higher than that of iron [165 (4) GPa; Mao *et al.*, 1990] to eliminate the possibility that silicon might be a major alloying element in the Earth's outer core. However, other workers, using a variety of techniques, have generally determined the bulk modulus to be much less, *viz.* 172 (3) GPa (Guyot & Zhang, 1995; Guyot *et al.*, 1997; multi-anvil press to 10 GPa), 160 (1) GPa (Wood *et al.*, 1995; powder neutron diffraction to 9 GPa), 176 (3) GPa (Ross, 1996; single-crystal X-ray diffraction to 7 GPa), 115 GPa (Zinoveva *et al.*, 1974; ultrasonics), 173 GPa (Sarrao *et al.*, 1994; resonant ultrasound spectroscopy).

It is clear, therefore, that there are a number of aspects of the crystal structure and physical properties of FeSi that merit further study, namely: (i) the stability, at ambient pressure, of the sevenfold-coordinate FeSi crystal structure relative to that of other simple high-symmetry binary structure types, such as those of NaCl, CsCl and NiAs, in which all atoms are in sixfold or eightfold coordination; (ii) the extent to which distortion of the structure from the ideal sevenfold-coordinate form is important in determining its stability and the mechanism by which this distortion is brought about; (iii) the behaviour of the structure, and its stability relative to that of CsCl *etc.*, at high pressures; and (iv) the compressibility of the material, especially under conditions of high pressure.

Computer simulation provides a possible method with which to address these points, with the advantage that it is not constrained by the limitations of experiment. It should, perhaps, be mentioned at this stage that attempts to explain the structure and properties of FeSi in simple terms have had only limited success. Fig. 2, for example, shows the packing densities of the FeSi (ideal form), CsCl, NaCl and NiAs structures as a function of radius ratio **r**; it can be seen that for no value of **r** does the FeSi structure have the densest packing. The observed mean bond distance in FeSi is very close to the sum of the atomic radii derived from the structures of elemental Fe and Si, from which we conclude that an appropriate radius ratio might be about 0.95 (±0.01), with Fe as the larger atom. Thus, purely on the grounds of packing, it might be expected that FeSi should crystallize with the NiAs structure. Pauling & Soldate (1948) attempted to explain the observed FeSi structure by means of Pauling's resonating-valence-bond theory of metals (Pauling, 1948) and put forward some qualitative arguments as to why the FeSi structure might be preferred to that of NaCl, CsCl or NiAs. Although Pauling & Soldate's treatment of FeSi is, perhaps, not wholly convincing (requiring, for example, a somewhat arbitrary neglect of Si–Si interactions if an unacceptably high valence for Si is to be avoided), an interesting consequence of their analysis is that it would seem to imply that the small distortion of the FeSi structure from its ideal form is essential. Their theory requires each Si atom, for example, to use one of its four tetrahedral sp^3 bond orbitals to form a non-resonating single bond with the closest Fe atom at 2.29 Å; the other three orbitals
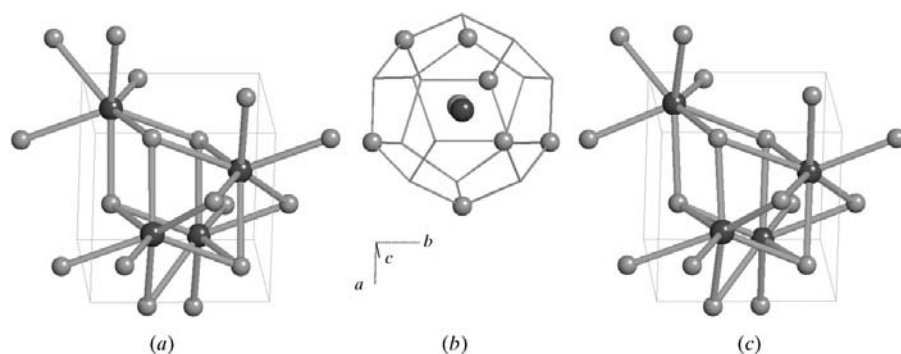

Fig. 1. The ideal (*a*) and actual (*c*) FeSi structures (the Fe atoms are represented by the larger, darker spheres). All atoms lie on threefold axes in the cubic unit cell. (*b*) shows the regular pentagonal dodecahedron surrounding the Fe atom at 0.15451, 0.15451, 0.15451 in the ideal sevenfold-coordinated structure, seven of the vertices being occupied by Si atoms, and also illustrates the displacement of this Fe atom seen in the actual structure (to 0.137, 0.137, 0.137), the displaced atom being represented by a lighter sphere. This displacement produces one short Fe—Si bond (along [111]), three equal intermediate bonds and three equal longer bonds. The displacements of the Si atoms from their positions in the ideal sevenfold-coordinated structure are much smaller, being less than those of the Fe atoms by about a factor of five.

then resonate between the three Fe atoms at 2.34 Å and the three Fe atoms at 2.52 Å, the latter set being less favoured.

Although computer simulations can now often provide reliable predictions of the structures and properties of simple inorganic materials, it is apparent that in the case of FeSi, a narrow band-gap semiconductor with a balanced interplay between itinerant and localized electronic states (Breuer *et al.*, 1997), empirical interatomic potential methods would provide a wholly inadequate tool; instead first-principles quantum-mechanical calculations must be used, in which the wave function of the valence and conduction electrons is calculated explicitly. A number of band-structure calculations for FeSi, using plane-wave (LAPW) and muffin-tin (LMTO) methods, have been made recently (Mattheiss & Hamann, 1993; Jarlborg, 1995, 1997), but these have been addressed almost exclusively towards interpreting the observed electrical and, especially, the unusual magnetic properties of the material. Mattheiss & Hamann (1993), however, did perform comparable LAPW calculations for FeSi with the atoms arranged as in NaCl, concluding that the preference for the observed structure was not driven by Fermi-surface effects, such as those found in systems showing charge-density-wave

Fig. 2. Hard-sphere volume packing densities for some simple *AB* structures as a function of the radius ratio, $\mathbf{r} = R_B/R_A$. The values for NiAs-I correspond to a structure in which the larger *A* atoms form two close-packed planes stacked directly above each other; the smaller *B* atoms then occupy interstices with trigonal prismatic coordination midway between the planes of *A* atoms. In NiAs-II, the *A* atoms form a hexagonal close-packed structure with the *B* atoms filling the octahedral interstices. In both the NiAs structures it is assumed that the planes of *A* atoms remain close-packed throughout; for values of **r** greater than those required to prevent 'rattling' of the *B* atoms, the two arrangements will have the same packing density. Note that the critical value of **r** required to prevent 'rattling' for the CsCl structure and for the ideal sevenfold-coordinated FeSi structures is identical [equal to $(3)^{1/2} - 1$]; this is a consequence of the geometry of the pentagonal dodecahedron, within which it is always possible to inscribe a cube of side equal in length to the diagonal of the pentagons.

distortions or Peierls transitions. The density of states near the Fermi level in FeSi is large, dominated by the Fe $3d$ component, and sensitive to small changes in the atomic positions. Band-structure calculations of FeSi in the CsCl modification have been made by von Känel *et al.* (1992) and by Girlanda *et al.* (1994); in both cases it was concluded that formation of this material as an epitaxic layer on Si is associated with a compressive strain, equivalent to an applied pressure of about 25 GPa. No calculations of FeSi with the NiAs structure have been reported.

In our present study we have used a pseudopotential method, in which approximations are made to describe the potential associated with the core electrons and only the electron density owing to valence and conduction electrons is explicitly calculated; this results in a significant reduction in computational requirements from that required for all-electron calculations, thereby enabling the phase diagram of the various hypothetical polymorphs of FeSi to be explored in detail. This method has recently been shown to be very successful in predicting the static properties and equation of state of solid iron (Vočadlo *et al.*, 1997). Incorporation of the effect of atomic vibrations owing to temperature is, however, a computationally very expensive process and so it has not been included in the present calculations; these are, therefore, effectively all at 0 K and thus in the present study only the $P,V,0$ section of the P,V,T phase diagram is accessible. In view of the apparent insensitivity of the FeSi structure to changes in temperature (Watanabe *et al.*, 1963) we do not believe that this is a serious limitation when addressing the relative stability of the different possible structures at room temperature. The effect of thermal activation on the physical properties of the material is, however, known to be large, owing to the narrow band gap, and thus the neglect of temperature may lead to serious errors when calculating even such quantities as the elastic constants, which are known to be quite temperature dependent (Sarrao *et al.*, 1994).
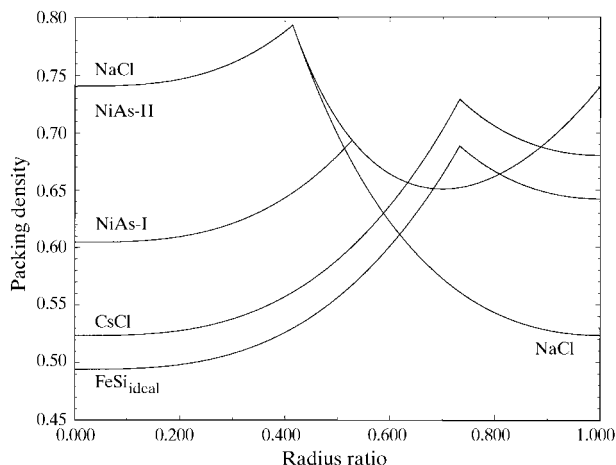
2. Calculation method

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*). 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 Fe, the $3p$ electrons were treated as valence electrons (*i.e.* an [Ne]$3s^2$ core was assumed), an assumption which was found to be essential for successful simulations of iron at high pressures (Vočadlo *et al.*, 1997); for Si an [Ne] core was assumed. The pseudopotential concept requires that the scattering properties of the pseudo-atom and of the

Table 1. *Predicted crystal structures and physical properties of hypothetical FeSi polymorphs*

The values of E_0, V_0, K_0 and K_0' were found by fitting to a third-order Birch–Murnaghan equation of state (for details see text).

	E_0 (eV atom^{-1})	V_0 (Å^3 atom^{-1})	Cell (Å)	Relaxed coordinates	K_0 (GPa)	K_0'
NaCl-type	−6.556	12.74	$a = 4.671$		163	3.9
NiAs-type	−7.137	11.39	$a = 2.736$ $c = 7.030$	$c/a = 2.570$	195	4.7
CsCl-type	−7.267	10.61	$a = 2.768$		226	5.4
FeSi$_{ideal}$ ($x = \pm 0.15451$)	−7.249	11.06	$a = 4.456$		224	4.5
FeSi$_{real}$	−7.309	11.11	$a = 4.463$	$x_{Fe} = 0.1367$ $x_{Si} = -0.1591$	227	3.9

exact atom are the same at a specified radius, R_{match}; inside this matching radius the pseudo-wave functions are nodeless and only approximate. This condition poses a serious problem for first-row transition metals as it necessitates a very large basis set to represent the core electrons. A computationally efficient solution to this problem was proposed by Vanderbilt (1990) *via* the use of non-norm-conserving pseudopotentials, in which correction for the difference between the exact and pseudo-charge density is achieved by using localized augmentation functions centred on each atom. This approach results in significantly smoother, 'softer' (*i.e.* requiring smaller basis sets) pseudo-wave functions. The new ultrasoft pseudopotentials give results which are very close to, or even indistinguishable from, those obtained with the best all-electron first-principles methods currently available. Details of the construction of the pseudopotentials used in the present work are given by Kresse & Hafner (1994) and Moroni *et al.* (1997).

A further point requiring some care is the modelling of the exchange-correlation energy, described by the generalized gradient approximation (GGA). It has been shown, for example, that the GGA must be used if an accurate description of the ground-state properties of iron is to be obtained at ambient pressure (Singh *et al.*, 1991) and that neglect of the GGA strongly affects results at high pressure (Söderlind *et al.*, 1996). In the present work, we have used a GGA based on the local density approximation of Ceperley & Alder (1980) (in the parametrization of Perdew & Zunger, 1981) and the gradient corrections according to Perdew *et al.* (1992). All of the pseudopotentials have been constructed with non-linear partial core corrections (Louie *et al.*, 1982). When using *VASP*, the ground state is calculated exactly for each set of ionic positions using an efficient iterative matrix diagonalization scheme and a Pulay mixer (Pulay, 1980). A smearing method was used to avoid problems with level crossing, and the electronic free energy was taken as the quantity to be minimized. Relaxation of atomic coordinates and axial ratios is allowed by the program; when performing such operations these para-meters are changed iteratively so that the sum of the lattice energy and electronic free energy converges to a minimum value. Further details of the computational method are given by Kresse & Furthmüller (1996*a*,*b*).

The calculations discussed below were carried out using the primitive unit cells for the FeSi-, CsCl- and NiAs-type structures and the conventional face-centred-cubic unit cell for the NaCl-type. In the case of the NiAs-type two variants are possible. In the first, the Fe atoms take coordinates within the hexagonal unit cell of $(0, 0, 0)$ and $(0, 0, 1/2)$, with the Si atoms at $(1/3, 2/3, 1/4)$ and $(2/3, 1/3, 3/4)$; in the second, the two sets of coordinates are occupied by the other type of atom. It was found that the first arrangement, which leads to a simple hexagonal substructure of Fe atoms, was the more stable (see below). The number of sampling points in reciprocal space used in the calculations was increased until further increase produced a change of less than 0.001 eV atom^{-1} in the calculated internal energy, equivalent to more than a factor of forty less than the smallest difference in energy between the various structures considered. This convergence condition required, for example, the use of a $5 \times 5 \times 5$ grid of k points for the FeSi-type structure, leading to 11 k points in the symmetry-irreducible volume of the Brillouin zone; sampling points with similar separations in reciprocal space were used for the other structures. Calculation of the electronic density of states (DOS) was performed over intervals of approximately 0.09 eV in energy. We believe, therefore, that the present calculations are sufficiently accurate for our discussion of the different potential FeSi polymorphs, although it might be possible to improve upon them in matters of detail.

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 NaCl and CsCl modifications there are no parameters to relax; the NiAs-type structure requires relaxation of the c/a ratio. In the case of the FeSi-type structure, two sets of calculations were made, the first with the atoms fixed at the ideal sevenfold-coordinate value, $x = \pm 0.15451$, and the second with the fractional coordinates of both

Fe and Si allowed to vary. Although no symmetry constraints were imposed during the relaxation of these coordinates, they retained the form x, x, x to within the expected precision of the calculations (see below). When calculating the electronic density of states for the relaxed FeSi structure, however, the coordinates were returned to their 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 vs V curve may be found using the standard thermodynamic result $P = -(\partial E/\partial V)_{T=0}$ (see e.g. Pippard,

1966), the actual values being determined by fitting the E vs V curve to a sixth-order polynomial in V. 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 vs V curves.

3. Results and discussion

3.1. Behaviour at $P = 0$

Fig. 3(a) shows E vs V curves for all of the potential FeSi polymorphs considered. The values of E and V at the minima of the curves (i.e. at $P = 0$) are given in Table 1, together with the corresponding unit-cell parameters and the fractional coordinates of the relaxed FeSi structure. It can be seen that the $FeSi_{real}$ structure is the most stable, the order of stability of the different structures being $FeSi_{real}$ > CsCl-type > $FeSi_{ideal}$ > NiAs-type (> NiAs-type, second variant) $\gg$ NaCl-type (the subscripts 'real' and 'ideal' refer to the observed FeSi structure and its ideal sevenfold-coordinated variant, respectively). The fractional coordinates predicted by VASP for the $FeSi_{real}$ structure are $x_{Fe} = 0.1367$ and $x_{Si} = -0.1591$; the uncertainty in both, estimated from the spread across values which were expected to be equivalent by symmetry, is ±0.0001. These results are in extremely good agreement with the coordinates determined by Pauling & Soldate [1948; $x_{Fe} = 0.137$ (2), $x_{Si} = -0.158$ (4)] and by Wood et al. [1996; $x_{Fe} = 0.1359$ (3), $x_{Si} = -0.1581$ (4)]. The predicted lattice parameter is 4.463 Å; applying a correction for thermal expansion between 0 and 300 K, based on the low-temperature data of Watanabe et al. (1963), increases this value to 4.473 Å, which is 0.4% smaller than that reported by Pauling & Soldate (1948) and Wood et al. (1996). Again, this agreement is very good and 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.

Table 1 shows that the stability of the $FeSi_{real}$ structure with respect to the NaCl-type structure is about 1.5 eV per formula unit, in good agreement with the value of 1.6 eV/FeSi given by Mattheiss & Hamann (1993); the NaCl structure is, therefore, energetically very unfavourable. The energy differences with respect to the remaining possible structures are much less, being $\simeq0.34$ eV/FeSi for the NiAs-type, $\simeq0.12$ eV/FeSi for $FeSi_{ideal}$ and $\simeq0.08$ eV/FeSi for the CsCl-type. The densest structure is the CsCl-type, our predicted lattice constant of 2.768 Å being in good agreement with the
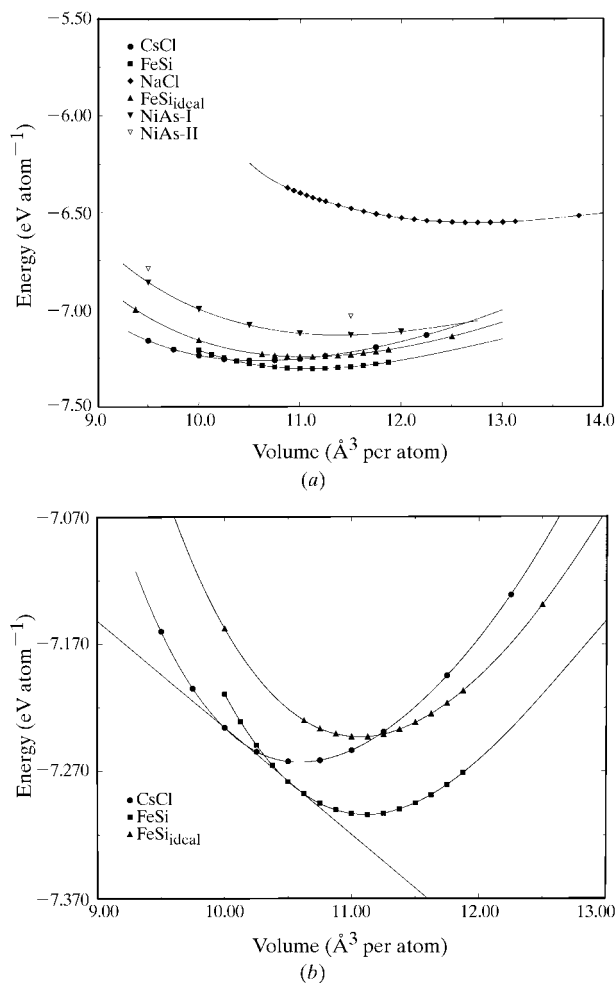

Fig. 3. (a) Internal energy vs volume for all of the different structure types considered. Calculated values are indicated by points, the full lines being polynomial fits to the data (see text). In NiAs-I and NiAs-II the Fe atoms occupy the sites specified for the A atoms in the caption to Fig. 2 (for further details see text); a complete set of calculations was not made for NiAs-II, as it was the less stable of the NiAs structures. (b) Internal energy vs volume for the CsCl-type, $FeSi_{real}$ and $FeSi_{ideal}$ structures. Note that the distortion of FeSi from the ideal sevenfold-coordinated structure is essential for stability with respect to the CsCl-type. The common tangent to the curves for the CsCl-type and $FeSi_{real}$ structures indicates that the former will be stable for pressures greater than 13 GPa (for details see text).

values of 2.717 Å (von Känel *et al.*, 1992) and 2.778 Å (Girlanda *et al.*, 1994) previously obtained by computer simulation and in excellent agreement with the experimental value, 2.77 (1) Å, of von Känel *et al.* (1995). Our results show, therefore, that the distortion of the observed structure from that of $FeSi_{ideal}$ is an essential requirement if it is to be stable with respect to the CsCl-type. The $FeSi_{ideal}$ structure was found to be unstable with respect to $FeSi_{real}$ over the whole of the range of pressure investigated; calculations in which the atoms were allowed to relax from their perfect sevenfold coordinates invariably led to the $FeSi_{real}$ structure.

Some insight into the reasons why FeSi adopts the observed structure can be gained by considering the calculated electronic density of states, shown in Fig. 4. As pointed out by Mattheiss & Hamann (1993) the band

structure of FeSi is such that it is difficult to provide a quantitative representation of the DOS near the Fermi level, E_F, unless an unfeasibly large sampling grid in reciprocal space is used. Nevertheless, our results are qualitatively similar to those of Mattheiss & Hamann (1993) and Grechnev *et al.* (1994); in particular, they predict that the material will be a semiconductor with a band gap of about 0.1 eV. However, although Fermi-surface effects may well be responsible for the unusual electrical and magnetic properties of FeSi (in particular for their similarity to those of the so-called 'Kondo insulators', materials in which there is hybridization between a localized electron state and the conduction band; see *e.g.* Schlesinger *et al.*, 1997) they cannot provide the explanation for the observed crystal structure. As remarked by Mattheiss & Hamann (1993), CrSi,
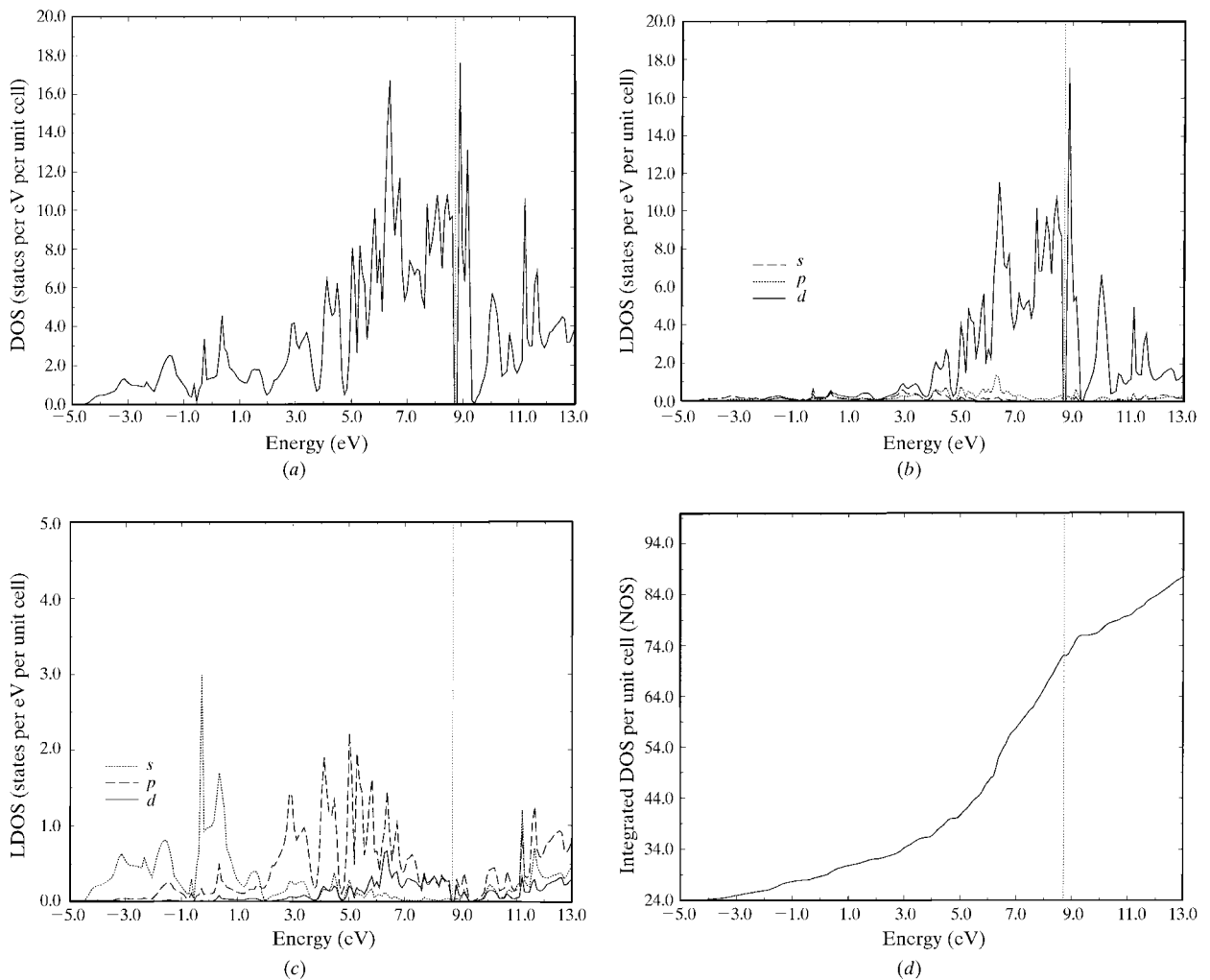

Fig. 4. Electronic density of states calculations for FeSi. (*a*) Total density of states (DOS). (*b*) Local DOS (LDOS) for Fe. (*c*) LDOS for Si. (*d*) Total number of states (NOS). The position of the Fermi level, E_F, is indicated by a vertical line. Note that NOS is horizontal at E_F, indicating that the material is non-metallic. Core electrons are excluded from the calculation, the initial value of NOS = 24.0 being due to the Fe 3*p* electrons which lie in highly localized states over 50 eV below E_F.

MnSi, FeSi and CoSi are isostructural, showing a very similar degree of deviation from the ideal sevenfold-coordinate structure (Borén, 1933). CrSi and MnSi are metallic, FeSi is a narrow-gap semiconductor and CoSi is a semi-metal (Shinoda & Asanabe, 1966). These differences in electrical conductivity are readily interpretable by assuming that the compounds have similar densities of states, with the positions of the Fermi levels determined by the number of available electrons (Evangelou & Edwards, 1983). Thus it is apparent that the exact position of E_F within the DOS is not fundamental to the formation of the FeSi crystal structure.

The common factors leading to the formation of the observed FeSi structure would seem to be the presence of Si and of an element near the centre of the $3d$ or $4d$ blocks in the periodic table (RuSi is also isostructural). We believe that a better understanding of the bonding in this material may be obtained by combining information obtained from the local density of states (LDOS) with a more 'chemical' approach. The LDOS calculated by *VASP* allows projection of the DOS associated with each of the atoms in the structure and, additionally, allows discrimination between electrons with s-, p- and d-like character. Considering firstly the Fe atom (Fig. 4b), it can be seen that, as expected, the DOS near the top of the valence band is dominated by the contributions from the Fe d electrons; the Fe $3p$ electrons lie in highly localized states over 50 eV below E_F (not shown in Fig. 4) and thus make no contribution to the bonding. There is, however, a significant Fe p electron contribution to the DOS in the range from about 2 to 4 eV below E_F, which must, therefore, come from the Fe $4p$ orbitals. Examination of the LDOS for Si (Fig. 4c) reveals several interesting features: firstly, there is a significant contribution to the DOS from Si, as well as from Fe, in the energy range from about 2 to 6 eV below

E_F, thus indicating that there is a strong degree of covalency in the bonding; secondly, the contribution from Si contains a large component of d-like character, as well as s and p. The possibility of a significant degree of hybridization involving the Si d orbitals was not considered by Pauling & Soldate (1948), who restricted their discussion to Si sp^3 hybrids. A detailed calculation of the bonding scheme in the FeSi structure is beyond the scope of the present paper. Nevertheless, we believe that our results are sufficient to show that the stability of the structure arises from the degree of covalency allowed by this atomic arrangement.

3.2. *Behaviour at high pressure*

In discussing the behaviour at elevated pressure, two main questions must be addressed – the predicted change in the observed FeSi crystal structure under compression and the possibility of phase transformations to other polymorphs. Fig. 5 shows the changes in x_{Fe} and x_{Si} as a function of pressure. It can be seen that the magnitudes of the fractional coordinates tend to become equal as P increases and show a clear trend towards the ideal sevenfold-coordinated structure. However, although both coordinates seem to tend asymptotically towards values in the range $0.149 < |x| < 0.154$, neither appears to be approaching exactly the value of $\pm 1/4\tau = \pm 0.15451$, a possible reason for this being the covalent nature of the bonding discussed above. At the highest pressures considered, the fractional coordinates of Fe and Si differ from their ideal sevenfold values by 0.006 and 0.0008, respectively. Examination of the calculated DOS shows that, even for pressures in excess of 500 GPa, the band gap is retained (increasing slightly to ∼0.2 eV) and thus the material does not appear to show a metal–insulator transition. Interestingly, calculations of the DOS for FeSi$_{ideal}$ at ambient pressure suggested that the band gap had narrowed to the point of closure and that, were such a material to exist, it might show metallic behaviour. A calculation for FeSi$_{ideal}$ above 500 GPa, however, indicated a very narrow band gap (∼0.01 eV). This sensitivity of the calculated band structure to small changes (∼0.005) in the atomic fractional coordinates has also been reported by Mattheiss & Hamann (1993).

Fig. 5 also explains the relative insensitivity of the crystal structure to pressure, reported by Wood *et al.* (1996). Over the pressure range accessible in their neutron powder diffraction experiment (0–9 GPa), the expected change in x_{Fe} is of order +0.001 and that in x_{Si} −0.0007. Examination of the experimentally determined coordinates at 0 and 6.3 GPa do, indeed, show an increase in x_{Fe} of 0.0010 (5) and a decrease in x_{Si} of 0.0008 (6) but such changes are not statistically significant. Experimental confirmation of the behaviour shown in Fig. 5 would appear, therefore, to require an increase, by at least a factor of five, in either the accessible
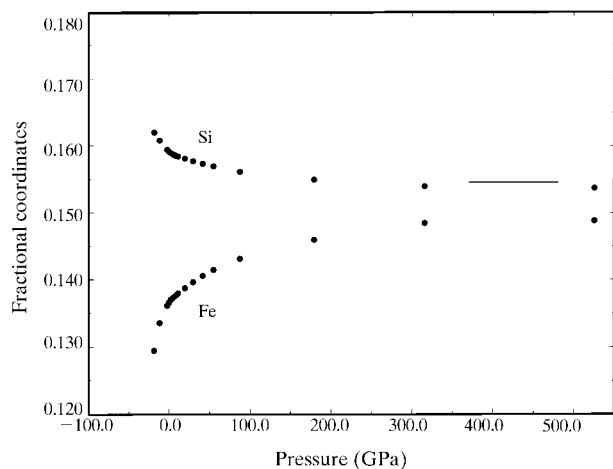

Fig. 5. Fractional coordinates for the Fe and Si atoms as a function of pressure (for convenience $|x_{Si}|$ is plotted). The value of x required for the ideal sevenfold-coordinate structure is shown by the horizontal bar.

pressure range or in the precision to which the fractional coordinates are determined; neither of these requirements can be considered to be easily achievable at present.

Probably the most interesting aspect of the present work is that it indicates that FeSi having the CsCl-type structure will be the thermodynamically most stable phase for pressures greater than about 13 GPa. This point is best illustrated in Fig. 3(b), using the method of common tangents. Since $T = 0$, the Gibbs free energy G is equal to the enthalpy H. In addition, since $P = -\partial E/\partial V$, it may easily be shown that any straight line on a graph of internal energy vs volume is a line of constant H, lines with steeper negative slopes having higher enthalpy values. Thus, if two E vs V curves are joined by a common tangent, the corresponding phases will be in thermodynamic equilibrium. The common tangent, shown in Fig. 3(b), connecting the E vs V curves for the FeSi$_{real}$ and the CsCl-type structures has a slope of -0.081 eV Å^{-3}, equivalent to a transition pressure of 13 GPa. Calculation of the enthalpies for the two phases confirmed this result. Experimental evidence for the stability of a CsCl-type phase is provided by the observation that thin films of FeSi with the CsCl-type structure may be grown on silicon substrates (von Känel et al., 1992; Kafader et al., 1993; von Känel et al., 1994; Dekoster et al., 1997). It has been suggested that formation of this material as an epitaxic layer on Si is associated with a compressive strain, equivalent to an applied pressure of about 25 GPa (von Känel et al., 1992; Girlanda et al., 1994). Bearing in mind the approximations inherent in making this estimate, which required comparison of the lattice parameter of CsCl-type FeSi, derived from band-structure calculations, with the known cell parameter of silicon, we consider this result to be in satisfactory agreement with that found in the present work. The only experimental study to date of bulk samples of FeSi at pressures above 10 GPa is that of Knittle & Williams (1995), who found no evidence of any phase transitions, their study including X-ray examination of a sample that had previously been heated to about 1500 K at 49 GPa. Direct transformation of FeSi to a CsCl-type structure is, however, likely to require a very high activation energy. A continuous path between the two is possible via the NaCl-type but, at ambient pressure, an NaCl-type phase is over 1.5 eV/FeSi higher in energy. It is thus likely that both the FeSi structure and the CsCl-type structure (assuming it exists) will be highly metastable. In this present study we have been unable to address the question of the stability of the different polymorphs with regard to temperature. The only high-temperature structural study reported is that of Watanabe et al. (1963), who found that the fractional coordinates at 573 K were essentially unaltered from their room-temperature values. More recently, Guyot et al. (1997) measured the thermal expansion of the material by X-ray powder diffraction at temperatures up to 1070 K, again finding no evidence for a phase transition. However, both of these studies were carried out at temperatures well below the FeSi melting point (1683 K). In view of the fact that RuSi is known to show a transition from the FeSi to the CsCl structures at 1578 K (Buschinger et al., 1997) it would be of considerable interest to investigate the behaviour of FeSi over a wider temperature range.

3.3. Compressibility

The final aspect of the behaviour of FeSi addressed in the present study is the question of its compressibility. By integration of the standard Birch–Murnaghan third-order equation of state relating P and V (see e.g. Poirier, 1991) the equation

$$E(V) = E_1 + E_2 + E_3$$

is obtained, where

$$E_1 = (9/4)K_0V_0(V_0/V)[0.5(V_0/V)^{1/3} - (V/V_0)^{1/3}],$$

$$E_2 = (9/16)K_0(K_0' - 4)V_0(V_0/V)[(V_0/V) - 3(V_0/V)^{1/3} + 3(V/V_0)^{1/3}]$$

and

$$E_3 = E(V_0) - (9/16)K_0V_0(K_0' - 6).$$

V_0 is the volume of the phase at $P = 0$ and $E(V_0)$ is the corresponding internal energy. K_0 is the (isothermal) bulk modulus (since $T = 0$ K, the adiabatic and isothermal bulk moduli will be equal) and K_0' is its first derivative with respect to pressure. Fitting of the E vs V data for FeSi$_{real}$ to this equation gave values of 227 GPa and 3.9, respectively, for K_0 and K_0'. K_0 was found to be effectively invariant both with respect to the equation of state adopted (showing a range of only ± 1 GPa for nine different equations of state, e.g. Murnaghan, Birch–Murnaghan second-order, Vinet etc.) and with respect to the pressure range used (restriction of the data, for example, to pressures less than 10 GPa gave values of $K_0 = 225$ GPa and $K_0' = 2.5$). In addition, our value for the bulk modulus is in very good agreement with that (220 GPa) obtained by Jarlborg (1995, 1997) using an LMTO method (a result which, however, he considered to be an overestimate). The values of K_0 and K_0' obtained in the present study for FeSi in the CsCl-type structure are 226 GPa and 5.4, which are again in reasonable agreement with the calculated bulk moduli of 263 and 280 GPa reported by von Känel et al. (1992) and Girlanda et al. (1994), respectively. Values of K_0 and K_0' for the other structures considered here are listed in Table 1.

However, although there is adequate agreement between the various calculated values of K_0, the agreement with results obtained experimentally is much less satisfactory. Measurements of the elastic constants of

FeSi at low temperatures have been reported by Zinoveva et al. (1974) and by Sarrao et al. (1994). In both cases the behaviour of the material was found to show a strong temperature dependence, which was attributed to the narrow band gap in the material. Zinoveva et al. (1974) reported a decrease in the bulk modulus of about 12% between 80 and 300 K; inspection of the data published by Sarrao et al. (1994) suggest a somewhat smaller change, of about 7.5%, between room temperature and 0 K. Application of these temperature corrections to our calculated result for K_0 produces a value in the range 200–210 GPa. Although this is in exact agreement with the experimental result of Knittle & Williams (1995), 209 (6) GPa, it is much higher than that obtained by all other workers – values in the range 160–176 GPa having been reported by Sarrao et al. (1994), Guyot & Zhang (1995), Wood et al. (1995), Ross (1996) and Guyot et al. (1997). We are, at present, unable to explain this discrepancy. The experiments performed by Knittle & Williams (1995) covered a much greater pressure range than was accessed in the other studies but our present calculations, in which the derived value of K_0 was found to be effectively independent of the pressure range chosen, suggest that this should not lead to any experimentally observable differences in behaviour. Conversely, it has been shown recently (Vočadlo et al., 1997) that ab initio calculations within the generalized gradient approximation, similar to those reported here, are capable of producing bulk modulus values for the body-centred-cubic phase of iron which are in excellent agreement with experiment; we are, therefore, unable to point to any obvious weakness in the calculation method adopted, such as might have pertained had the local density approximation been used (Sasaki et al., 1995). It seems likely that this problem is now only resolvable by further experimental work. One possible source of variation lies in the stoichiometry of the samples used. The Fe–Si phase diagram (Köster & Gödecke, 1968) indicates that the FeSi structure is stable over a range of compositions, Fe_xSi_{1-x}, for values of x in the range from about 0.494 to 0.506. Relative to the exactly stoichiometric compound, crystals rich in Si will be electron deficient and vice versa. In view of the known strong temperature dependence of many of the physical properties of this material, attributable to thermal excitation across the narrow band gap, it seems possible that variations in composition might give rise to similar effects by changing the electron occupancy levels near E_F.

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