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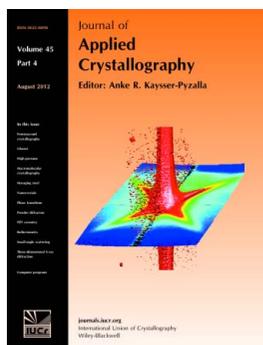
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High-pressure phase transitions and equations of state in NiSi. II. Experimental results

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The high-pressure structures of nickel monosilicide (NiSi) have been investigated to 124 GPa by synchrotron-based X-ray powder diffraction studies of quenched samples from laser-heated diamond anvil cell experiments, and the equations of state of three of these phases have been determined at room temperature. NiSi transforms from the MnP (B31) structure (space group *Pnma*) to the ϵ -FeSi (B20) structure (space group *P2₁3*) at 12.5 ± 4.5 GPa and 1550 ± 150 K. Upon further compression, the CsCl (B2) structure (space group *Pm3m*) becomes stable at 46 ± 3 GPa and 1900 ± 150 K. Thus, NiSi will be in the B2 structure throughout the majority of the Earth's mantle and its entire core, and will likely form a solid solution with FeSi, which is already known to undergo a B20 \rightarrow B2 transition at high pressure. Data from the quenched (room-temperature) samples of all three phases have been fitted to the third-order Birch–Murnaghan equation of state. For the MnP (B31) structure this yields $K_0 = 165 \pm 3$ GPa with K'_0 fixed at 4 and V_0 fixed at $12.1499 \text{ \AA}^3 \text{ atom}^{-1}$ [V_0 from unpublished neutron diffraction measurements on the same batch of starting material; Wood (2011), personal communication]. For the ϵ -FeSi (B20) structure, $K_0 = 161 \pm 3$ GPa and $K'_0 = 5.6 \pm 0.2$ with V_0 fixed at $11.4289 \text{ \AA}^3 \text{ atom}^{-1}$. For the CsCl (B2) structure, $K_0 = 200 \pm 9$ GPa, $K'_0 = 4.6 \pm 0.1$ and $V_0 = 11.09 \pm 0.05 \text{ \AA}^3 \text{ atom}^{-1}$. The ambient volume of NiSi, therefore, decreases by 6% at the first phase transition and then by a further 3% at the transition to the CsCl structure. Traces of additional NiSi structures predicted by Vočadlo, Wood & Dobson [*J. Appl. Cryst.* (2012), **45**, 186–196; part I], and labelled therein as *Pbma*-I, *Pnma*-II, and possibly also *Pnma*-III and *P4/nmm*, have been detected.

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1. Introduction

Nickel silicide (NiSi) is an intermetallic compound which crystallizes in the MnP (B31) structure (space group *Pnma*) under ambient conditions, with $a \simeq 5.18$, $b \simeq 3.33$, $c \simeq 5.61 \text{ \AA}$, $Z = 8$ and $V_0 \simeq 12.10 \text{ \AA}^3 \text{ atom}^{-1}$ (Toman, 1951). Owing to its utility as a contact material in electronic devices and its possible presence as an impurity in silicon-based electronics, this material has been studied extensively under ambient conditions with respect to its structural, electronic, vibrational, elastic and thermal properties (e.g. Connétable & Thomas, 2009; Acker *et al.*, 1999). NiSi has also been studied at high temperatures, where it exhibits the unusual property of highly anisotropic thermal expansion, whereby the b axis contracts as the temperature is raised (Wilson & Cavin, 1992; Rabadanov & Ataev, 2002*a,b*; Detavernier *et al.*, 2003). As yet, though,

this material has not been studied experimentally at high pressures, probably because such studies have no obvious utility to the electronics industry. The high-pressure behaviour of NiSi is, however, of interest to geophysicists because both elements within the compound are expected to be present within the Earth's core. Geochemical models based on cosmochemical arguments (e.g. Allègre *et al.*, 1995) suggest that the bulk core (i.e. the solid inner core and liquid outer core combined) could contain at least 5 wt% nickel and 7 wt% silicon (in combination with other light elements such as C, S, O and H). As a result, many studies have been published which focus on various aspects of binary and ternary alloys within the Fe–Ni–Si system, including their phase relations (Lin *et al.*, 2002; Mao *et al.*, 2006; Asanuma *et al.*, 2008; Kuwayama *et al.*, 2008, 2009; Sakai *et al.*, 2011), melting behaviour (e.g. Morard *et al.*, 2011), equations of state (e.g. Lin, Campbell *et al.*, 2003; Asanuma *et al.*, 2011) and sound velocities (e.g. Badro *et al.*, 2007; Lin, Struzhkin *et al.*, 2003).

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While the majority of these studies focus on alloy compositions towards the iron-rich corner of the Fe–Ni–Si ternary, studying the high-pressure behaviour of end-member compounds, such as NiSi, is also of great utility, in spite of the fact that they are unlikely to be present as pure phases within the Earth.

Here, the primary motivation for studying NiSi is to better understand both the solid inner and liquid outer regions of the Earth's core. Candidate inner and outer core alloys can be described within a multi-component system of which NiSi forms one of many end-member components. Thermodynamic models of core liquids within this system can then be derived from the known physical properties of the solid end-member compounds. Using this method, models of liquids in the Fe–O–S system have successfully been used to constrain the chemical and physical state of the core (*e.g.* Helffrich, 2012; Helffrich & Kaneshima, 2004, 2010). To extend these models to include additional elements, such as nickel and silicon, knowledge of the physical properties (specifically the crystal structure, equation of state and melting curve) of the end-member compounds within the extended Fe–Ni–Si–O–S system is needed.

As described in detail in a preceding paper (Vočadlo *et al.*, 2012), an additional motivation for the study of NiSi is to allow comparison of the phase diagram and physical properties of this material with those of FeSi, which, unlike NiSi, has been the subject of several recent high-pressure studies, both experimental (Lord *et al.*, 2010; Dobson *et al.*, 2002, 2003) and theoretical (Caracas & Wentzcovitch, 2004; Vočadlo *et al.*, 1999; Moroni *et al.*, 1999). Comparing these two phases should provide insights into the likely effects of the alloying of nickel with iron in the Earth's core. Specifically, it is necessary to determine whether NiSi is stable in the B2 (CsCl) structure under conditions relevant to the deep Earth, as is known to be the case for FeSi (Vočadlo *et al.*, 1999; Dobson *et al.*, 2002, 2003; Lord *et al.*, 2010) and as is predicted to be the case for NiSi by recent *ab initio* calculations (Vočadlo *et al.*, 2012). If these two end members are isostructural it is reasonable to assume that they will form a solid solution. Consequently, the B2-structured FeSi phase postulated to be present within the Earth's core–mantle boundary region (*e.g.* Lord *et al.*, 2010) could contain significant amounts of nickel, leading to an (Fe,Ni)Si phase. Thus, the question of the structure of NiSi at high pressure pertains directly to the phase relations of the deep Earth.

In a preceding paper on NiSi, Vočadlo *et al.* (2012) used static *ab initio* calculations to determine the stable structures and their equations of state at high pressure. These authors detailed a sequence of predicted structural transitions. First, the MnP (B31) structure, which is the known stable phase under ambient conditions, transforms to the tetragonal γ -CuTi (B11) structure (space group $P4/nmm$) at ~ 23 GPa, and then to an orthorhombic structure (space group $Pbma$) at ~ 61 GPa. As the pressure is raised further to ~ 168 GPa, the orthorhombic FeB (B27) structure (space group $Pnma$) becomes stable, followed by a final transition to the CsCl (B2) structure (space group $Pm3m$) at ~ 247 GPa. Further to this, the authors calculated equations of state for each of these phases, as well as for several others that are not stable at 0 K

but may become stable at high temperatures. In particular, it was found that the difference in enthalpy between the ε -FeSi (B20) structure and the lowest-enthalpy (most stable) structure is very small, dropping to as little as 8 meV atom^{-1} at ~ 60 GPa. However, as these calculations do not include temperature, they cannot tell us about the Clapeyron slopes of the phase boundaries between the predicted phases. Because these boundaries are likely to be sensitive to temperature we cannot use the calculations to say definitively which phases will be stable under the combined high-temperature and high-pressure conditions relevant to the deep Earth.

To address this issue, we have performed a set of synchrotron-based X-ray powder diffraction experiments at high pressure in a diamond anvil cell (DAC) on quenched laser-annealed samples up to 124 GPa. The primary aim of these experiments was to test whether the B2 (CsCl) structure is the stable form of NiSi under conditions relevant to Earth's core, as predicted by the *ab initio* calculations of Vočadlo *et al.* (2012), and, if so, to measure its room-temperature equation of state (EoS). As will be described below, our successful pursuit of this aim has led to the detection of a minimum of two, and possibly all four, of the non-ambient pressure structures predicted to be stable at 0 K by Vočadlo *et al.* (2012) and listed above. Additionally, we have also detected one (and possibly two) of the structures that were considered by Vočadlo *et al.* (2012) but found not to be stable at any pressure at 0 K, including the ε -FeSi (B20) structure previously mentioned, for which we have also obtained a room-temperature EoS. None of these high-pressure polymorphs of NiSi has previously been reported from experiment. Finally, we have measured the EoS of the known B31 (MnP) structure, which is stable under ambient conditions.

Combining these observations with the results of the *ab initio* calculations has allowed us to make some preliminary inferences about the topology of the NiSi phase diagram. However, because of its apparent complexity and the fact that the experiments presented here were not optimized for the determination of phase relations (especially at the lower end of the relevant pressure and temperature range), further experimental work will be required to map the phase diagram accurately. This will require (i) the acquisition of *in situ* structural information, to distinguish those phases which are thermodynamically stable from those that form during quench; and (ii) much longer annealing times to reduce phase co-existence. To access the full P – T space of interest, such a campaign may well require the use of laser-heated DACs (for the very high temperature region) and a combination of externally heated DACs and multi-anvil presses (for the moderate-temperature region). Such experiments are beyond the scope of the present study.

2. Methods

2.1. Starting material

The starting material for these experiments was prepared at the ISIS facility, Rutherford Appleton Laboratory, England, by arc-melting a stoichiometric mixture of nickel (99.99%

purity) and silicon (99.999% purity) under ~ 500 mbar pressure of argon gas (1 bar = 100 000 Pa). The resulting boule was then broken up using a percussion mortar, and several of the resulting pieces were imaged using a scanning electron microscope and analysed using an electron microprobe. This revealed that the sample consisted of two phases. The first, majority, phase with the composition $\text{Ni}_{49.84(6)}\text{Si}_{50.16(6)}$, corresponding to near stoichiometric NiSi, forms $>99\%$ by volume of the sample. The second phase appears as thin veins (probably representing quench needles) and has the composition $\text{Ni}_{60.99(38)}\text{Si}_{39.01(38)}$, which corresponds closely to Ni_3Si_2 stoichiometry. An X-ray powder diffraction pattern of this material collected using a PANalytical X'pert PRO diffractometer with $\text{Co } K\alpha_1$ radiation also shows that NiSi is the dominant phase but that some very weak broad Bragg reflections are also present, corresponding to $\delta\text{-Ni}_2\text{Si}$ (Toman, 1952). This strongly suggests that the minor phase seen in the scanning electron microscope images is in fact an intergrowth of NiSi + $\delta\text{-Ni}_2\text{Si}$ which is too fine to be resolved by the microprobe, thus yielding an average composition of Ni_3Si_2 . The composition of this phase, coupled with its texture, suggests it represents a quenched residual eutectic melt and that the bulk starting material is slightly nickel rich. This is not unexpected in silicides produced using the arc-melting process, in which silicon is preferentially lost because of its greater volatility. Given the tiny volumetric contribution of this contaminant phase, it is very unlikely to have significant effects on the results presented below.

2.2. Diamond anvil cell experiments

Two separate compression experiments were performed in this study, both using Princeton-type symmetric DACs. The first (from 0 to 62 GPa) used anvils with a culet diameter of 250 μm , while the second (from 55 to 124 GPa) used bevelled anvils with a 120 μm culet surrounded by an annulus with an 8° slope out to a diameter of 300 μm . In both cases rhenium was used as the gasket material, pre-indented to an initial thickness of ~ 40 μm and drilled out to form a central cylindrical sample chamber approximately one-third of the diameter of the culet. On compression, the gasket thickness and sample chamber diameter both decrease, to ~ 20 μm and approximately one-quarter of the diameter of the culet, respectively, at the highest pressures reached.

For both compression experiments, the sample consisted of an ~ 10 μm -thick flake of NiSi taken from a foil produced by compressing the powdered sample (ground under ethanol in an agate mortar to a grain size of the order of 1 μm) between a pair of diamond anvils. This flake was sandwiched between two ~ 15 μm -thick flakes of NaCl (99.99% purity) produced in the same fashion, which act as pressure medium, thermal insulator and pressure marker. Several grains of ruby (a few micrometres in size) were also added to the sample chamber so that the pressure could be monitored by ruby fluorescence spectroscopy during off-line compression before the start of each X-ray diffraction measurement. To minimize moisture within the assembly, the NiSi and NaCl samples were stored in

an oven at 393 K and, after loading, each cell was heated at 393 K for 1 h under an argon atmosphere before being sealed under the same conditions.

X-ray diffraction measurements were performed on beamline 12.2.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory, California, USA, using a Gaussian monochromatic X-ray beam of $\lambda = 0.6199$ \AA with a nominal diameter (full width at half-maximum) of 10 μm (Caldwell *et al.*, 2007). Before each X-ray diffraction pattern was acquired, the sample was annealed by laser heating to help reduce deviatoric stresses within the sample chamber in an effort to minimize broadening of the diffraction peaks. Laser heating was performed in a double-sided geometry using two ytterbium fibre lasers of $\lambda = 1.09$ μm and a spot size of 20–30 μm . Temperatures were measured at the surface of the sample on both sides using standard radiometric techniques (Walter & Koga, 2004). The annealing temperature was increased with increasing pressure from 1400 to 2700 K, with the uncertainty in the measured temperature, estimated at ± 150 K, incorporating both the reproducibility of the calibration experiments (Yan *et al.*, 2010) and variations in temperature during the annealing process. The sample was first ramped up to the target temperature by increasing the power to the lasers over a period of a few minutes, and once there, the laser was scanned around the entire sample for 10 min, to minimize the chance that any part of the sample might remain unreacted. After the annealing was complete, the samples were quenched rapidly to room temperature by cutting the power to the laser. Annealed samples were exposed to the X-ray beam for 60–180 s and the diffracted X-rays were collected on a Marresearch mar345 imaging plate. The sample-to-detector distance was calibrated using an LaB_6 standard. The two-dimensional diffraction patterns were integrated into one-dimensional spectra using the *Fit2D* program (Hammersley, 1997), and these were in turn fitted and analysed using the Le Bail method (Le Bail *et al.*, 1988), as implemented in the *GSAS* suite of programs (Larson & Von Dreele, 2000; Toby, 2001). Sample pressure was determined using the EoS of NaCl in the B1 structure below 30 GPa (Dorogokupets & Dewaele, 2007) and in the B2 structure above 30 GPa (Fei *et al.*, 2007). The reported uncertainties in the pressure are the sum of the analytical uncertainty in the EoS of NaCl and an additional uncertainty of 2% designed to take account of pressure gradients within the sample chamber. This is based on the maximum measured pressure gradients of 2 GPa up to 150 GPa (*i.e.* 1.3%) from a previous study in which an NaCl pressure medium, laser annealing and a similar sample geometry were employed (Lord *et al.*, 2010).

It should be noted that the phase transitions reported below did not occur at room temperature. As described above, the samples were ramped rapidly to the target temperature, allowed to anneal, then rapidly quenched in the DAC (*i.e.* from high temperature to room temperature within 1 s). This yields a temperature–time path along which the sample spends the majority of the total heating time at the target annealing temperature. Given that the reaction rate has an Arrhenius relationship with temperature (*e.g.* Moore, 1963), the majority

of the reaction is likely to have occurred at high temperature and, as a result, the annealing temperature is likely to give a much more realistic idea of the conditions at which the phase transitions occurred. Therefore, the annealing temperature is appended in parentheses to the reported pressures at which diffraction patterns were acquired. For estimates of the pressures of the phase transitions, the appended temperature represents the mid-point between the annealing temperatures at which the diffraction patterns that bracket the transition were acquired, with the uncertainty calculated to encompass those temperatures.

3. Results¹

In the diffraction patterns collected in this study, the diffracted intensity can be attributed to NiSi, rhenium from the gasket and the NaCl pressure medium (in the B1 structure below 30 GPa and the B2 structure above 30 GPa). However, very occasionally weak peaks are observed, most likely from other Ni_xSi_y phases (see §3.1). The presence of rhenium in all the diffraction patterns is caused by a combination of the significant tails of the Gaussian X-ray beam (Caldwell *et al.*, 2007), the very high X-ray scattering cross section of rhenium and the reduction of the diameter of the sample chamber at high pressure. The greater intensity of the rhenium reflections in experiment 2 compared with experiment 1 is due to the necessarily smaller sample chamber required for this experiment (~30 μm *versus* ~60 μm at high pressure) in which much higher pressures were achieved (124 GPa *versus* 62 GPa).

In the majority of diffraction patterns more than one NiSi phase is present, but in all cases one of the NiSi structures dominates the others. The dominant phases, in order of increasing pressure, are those with the MnP (B31), ε-FeSi (B20) and CsCl (B2) structures. Given the Arrhenius relationship between reaction rate and temperature (*e.g.* Moore, 1963), these phases most likely represent those that were stable at the temperature at which the sample was annealed before it was quenched. These phases define a transition sequence at high temperature of B31 → B20 → B2 as the pressure is increased. Six subordinate phases were also detected with certainty and include the three described above. The fourth is orthorhombic and related to the FeB (B27) structure (hereinafter called *Pnma-II*; Vočadlo *et al.*, 2012), and the fifth, also orthorhombic, has the space group *Pbma* (hereinafter called *Pbma-I*). The peaks of the sixth subordinate phase are not inconsistent with yet another orthorhombic structure related to *Pnma-II* (hereinafter called *Pnma-III*). Finally, several patterns contain peaks that may represent a seventh subordinate phase. This phase can be explained in terms of several related structures, namely the tetragonal γ-CuTi (B11) structure (hereinafter called *P4/nmm*), a distortion of this structure in space group *Pmnm* that has been detected in unpublished multi-anvil quench experiments (Ahmed, 2011), or *Pbma-I*. However, it is not possible to

discriminate between these three related structures with the present data.

Barring *Pnma-II*, ε-FeSi (B20) and *Pmnm*, all of these phases were predicted to be stable for some pressures at 0 K in the *ab initio* calculations of Vočadlo *et al.* (2012). In some diffraction patterns as many as three of these subordinate phases can be identified, in addition to the dominant phase. Assuming that no decomposition of the sample into phases with different stoichiometries occurs (*i.e.* that the phase diagram remains unary), the presence of four phases within a nominally single-component system clearly violates the phase rule and indicates that one or more of the phases is metastable. Indeed, the presence of the subordinate phases can be explained by a combination of the following: (i) metastable phase persistence, most likely due to certain regions of the sample (perhaps at the edges, or caught between the insulator and diamond anvil) having been heated for an insufficient time and/or to an insufficient temperature to overcome kinetic barriers; and (ii) formation during quench as the cooling sample passes through the stability field of the phase in question. For the sake of clarity, given this dichotomy between the dominant and subordinate phases, we first discuss the transition sequence of the dominant phases in two sections (§§3.1 and 3.2), one for each of the two experiments performed, followed by a description of the associated *P–V* data and the fitting of the EoSs (§3.3). We then treat the subordinate phases together in a separate section (§3.4).

3.1. Experiment 1, 0–62 GPa

In the four diffraction patterns collected at pressures up to 7 GPa (1400 K), NiSi was found to crystallize in the known B31 structure that is stable at ambient pressure (Fig. 1*a*). One weak peak at $2\theta = 8.6^\circ$ ($d = 4.13 \text{ \AA}$), which appears in a single pattern at 5 GPa, may index to θ -Ni₂Si (note that a trace of δ -Ni₂Si was detected in the starting material, see §2.1). However, as this peak does not persist beyond this single pattern and has an intensity below 3% relative to the strongest peak from the dominant B31-NiSi phase, and no EoS is available for θ -Ni₂Si, this assignment must be considered tentative. Nevertheless, it is the most likely explanation, because this peak does not match the expected positions of any reflections from any of the NiSi polymorphs studied by Vočadlo *et al.* (2012), from the other known compounds in the Ni–Si system (NiSi₂, Ni₃Si or Ni₃Si₂) or from Cr:Al₂O₃ (ruby), which is the only other material expected to be present within the sample chamber.

In the next pattern, at 18 GPa (1700 K), new peaks appear, which index to the FeSi (B20) structure (Fig. 1*b*). Owing to the lack of diffraction data between 7 GPa (1400 K) and 18 GPa (1700 K), the location of this B31 → B20 transition cannot be determined beyond the precision defined by this bracket and it is thus estimated at $12.5 \pm 4.5 \text{ GPa}$ and $1550 \pm 150 \text{ K}$. The presence of this phase transition is corroborated by the results of as yet unpublished multi-anvil press quench experiments, which were also analysed by X-ray diffraction (Ahmed, 2011).

Up to 43 GPa (1900 K) B20-NiSi remains the dominant phase (Fig. 2*a*), but in the next two patterns, taken at 49 GPa

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: KS5299). Services for accessing these data are described at the back of the journal.

(1900 K) and 52 GPa (2000 K), three new weak peaks appear which can be indexed to the B2 structure (Fig. 2*b*). The P – T conditions of this B2 \rightarrow B2 transition are estimated as 46 ± 3 GPa and 1900 ± 150 K. By 62 GPa (2100 K), the highest pressure attained in the first experiment, these new peaks have grown in intensity to rival those of B20-NiSi.

3.2. Experiment 2, 55–124 GPa

In the second experiment, weak reflections from B2-NiSi are present in the first two diffraction patterns, acquired at 54 GPa (1900 ± 150 K) and 57 GPa (2000 ± 150 K), increasing rapidly in intensity by 62 GPa (2100 ± 150 K), in line with the results of the first experiment. In both experiments it was found that a small tetragonal distortion to the cubic B2 structure, of between 0.8% and -1.4% , was required to fit the peak positions accurately; a similar effect but with a smaller magnitude (up to -0.7%) was observed in the NaCl pressure medium, which shares the same structure. This is the result of

increasing deviatoric stresses caused by the hardening of the pressure medium at high pressures. As was the case in experiment 1, the B2-NiSi reverted entirely to B20-NiSi on decompression to ambient conditions.

3.3. Equations of state

We have not attempted to fit EoSs to those structures which only ever appear as subordinate phases (see §3), because either their diffraction peaks are too few and too weak to allow accurate volumes to be determined and/or they appear in too few diffraction patterns for an EoS to be accurately fitted to the data. The P – V data for the dominant B31, B20 and B2 structures acquired from the compression experiments are presented in Fig. 3 and Table 1. The data were fitted using the third-order Birch–Murnaghan EoS with the data all equally weighted, since the errors in volume and pressure were similar for all measurements. The resulting fitted parameters are

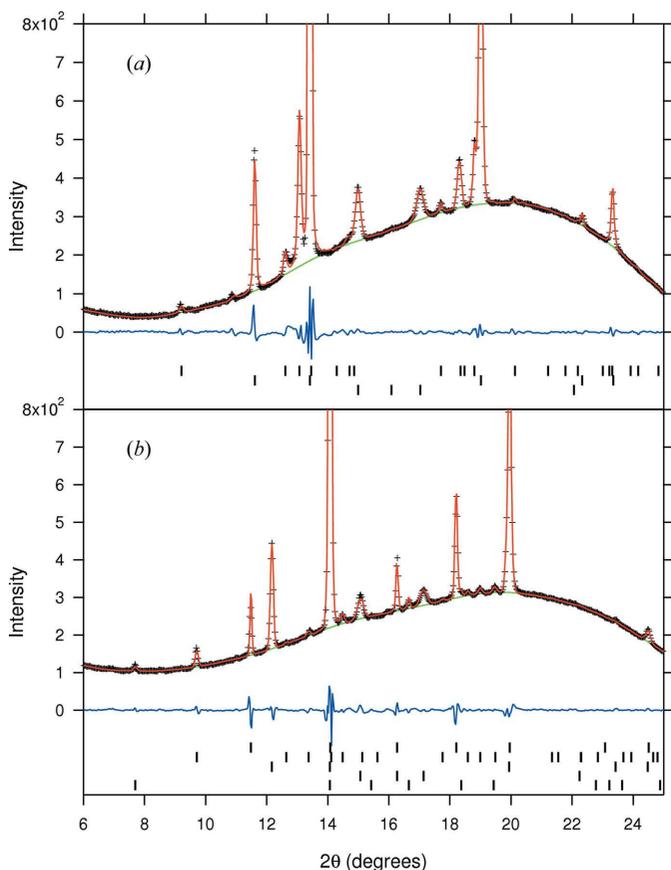


Figure 1 Diffraction data (black crosses) bracketing the B31 \rightarrow B20 transition, modelled using the Le Bail method (red line). The background (green line) and residual (blue line) are also shown. (a) At 7 GPa (1400 K) NiSi is in the B31 structure. The single unindexed peak at $2\theta = 10.9^\circ$ ($d = 3.26$ Å) possibly represents a trace of the orthorhombic *Pbma*-I phase (see §3.4 for details). Tick marks indicate the positions of the peaks from (top down) B31-NiSi, B1-NaCl and Re. (b) At 18 GPa (1700 K) NiSi is in the B20 structure. Unreacted B31-NiSi is still present, as is a trace of an orthorhombic or tetragonal phase, either *Pbma*-I, *Pmnm* or *P4/nmm* (see §3.4 for details). Tick marks indicate the positions of the peaks from (top down) B20-NiSi, B31-NiSi, B2-NaCl, Re and *P4/nmm* NiSi.

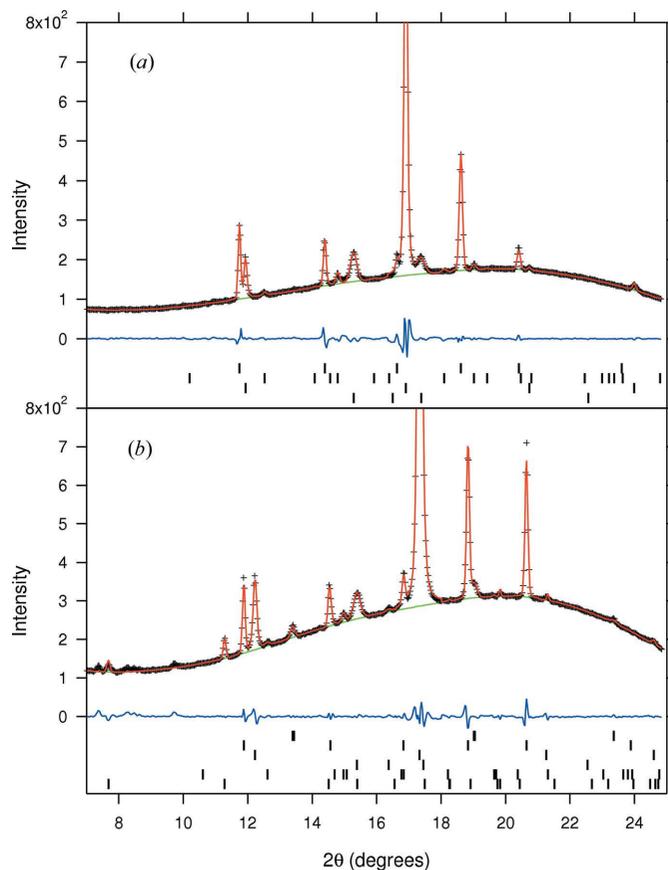


Figure 2 Diffraction data (black crosses) bracketing the B20 \rightarrow B2 transition, modelled using the Le Bail method (red line). The background (green line) and residual (blue line) are also shown. (a) At 43 GPa (1900 K) NiSi is in the B20 structure. A trace of unreacted B31-NiSi is also present. Tick marks indicate the positions of the peaks from (top down) B20-NiSi, B31-NiSi, B1-NaCl and Re. (b) At 49 GPa (1900 K) peaks from the B2-structured NiSi polymorph appear but are still weak compared with the dominant peaks from B20-NiSi. Traces of both *Pnma*-II and an additional orthorhombic or tetragonal phase (either *Pbma*-I, *Pmnm* or *P4/nmm*) are also present (see §3.4 for details). Tick marks indicate the positions of the peaks from (top down) B2-NiSi, B20-NiSi, B2-NaCl, Re, *Pnma*-II NiSi and *P4/nmm* NiSi.

Table 1

Unit-cell parameters of the B31 (MnP)-, B20 (ϵ -FeSi)- and B2 (CsCl)-structured phases of NiSi as a function of pressure.

Values in parentheses represent the uncertainty in the final digit.

P (GPa)	a (Å)	b (Å)	c (Å)	V (Å ³ atom ⁻¹)
B31 (MnP)-structured NiSi†				
0.02 (2)	5.182 (1)	3.3558 (6)	5.611 (1)	12.196 (3)
2.5 (1)	5.244 (1)	3.211 (1)	5.669 (1)	11.931 (2)
5.0 (2)	5.329 (1)	3.1410 (3)	5.6663 (5)	11.864 (2)
6.9 (3)	5.282 (1)	3.1039 (5)	5.674 (3)	11.628 (4)
17.0 (4)	5.046 (1)	3.316 (2)	5.324 (3)	11.134 (8)
22.6 (5)	5.107 (4)	3.234 (2)	5.294 (2)	10.930 (7)
28 (1)	4.85 (1)	3.469 (1)	5.063 (3)	10.65 (2)
B20 (ϵ-FeSi)-structured NiSi				
0.0001	4.5050 (5)	–	–	11.4289 (1)
17.0 (4)	4.38115 (5)	–	–	10.5118 (4)
22.6 (5)	4.3541 (4)	–	–	10.318 (3)
28 (1)	4.3246 (2)	–	–	10.110 (1)
36 (1)	4.2862 (1)	–	–	9.843 (1)
42 (1)	4.2652 (1)	–	–	9.699 (1)
49 (1)	4.2366 (1)	–	–	9.505 (1)
52 (1)	4.2269 (4)	–	–	9.440 (3)
54 (1)	4.2213 (2)	–	–	9.403 (1)
57 (2)	4.2140 (2)	–	–	9.354 (3)
61 (1)	4.1959 (2)	–	–	9.234 (2)
62 (1)	4.1918 (1)	–	–	9.207 (1)
68 (1)	4.1794 (4)	–	–	9.125 (4)
73 (2)	4.1678 (4)	–	–	9.049 (3)
77 (2)	4.1552 (5)	–	–	8.968 (3)
85 (2)	4.134 (1)	–	–	8.832 (6)
B2 (CsCl)-structured NiSi‡				
61 (1)	2.6394 (3)	–	2.612 (1)	9.098 (4)
62 (1)	2.6361 (4)	–	2.6151 (4)	9.086 (2)
68 (1)	2.6288 (3)	–	2.6033 (3)	8.995 (1)
73 (2)	2.6201 (2)	–	2.5834 (3)	8.868 (1)
77 (2)	2.6101 (2)	–	2.5879 (3)	8.815 (1)
85 (2)	2.5805 (2)	–	2.5986 (2)	8.652 (1)
101 (2)	2.5788 (2)	–	2.5503 (3)	8.481 (1)
104 (2)	2.5751 (2)	–	2.5388 (3)	8.418 (1)
116 (3)	2.5543 (3)	–	2.5273 (5)	8.245 (2)
124 (3)	2.5275 (3)	–	2.5473 (6)	8.137 (1)

† It is interesting to note that the b axis of the B31 (MnP) phase appears to show negative linear compressibility at high pressure, as predicted by the computer simulations of Vočadlo *et al.* (2012), but more precise measurements are required to confirm this. ‡ The B2 phase includes a small tetragonal distortion.

presented in Table 2, together with the corresponding values from the *ab initio* calculations of Vočadlo *et al.* (2012).

For B31-NiSi, V_0 was fixed at the value determined by time-of-flight neutron powder diffraction for the same batch of starting material as was used in this study (Wood, 2011). This value is 1% lower than the *ab initio* result (Table 2; Vočadlo *et al.*, 2012), which is in keeping with the well known over-estimation of volume of around 1% common in simulations that rely on the generalized gradient approximation. The limited number of P - V data for the B31-NiSi phase requires that K'_0 also be fixed during fitting. We performed two fits. In the first, B31-1, $K'_0 = 4$ (*i.e.* the Birch–Murnaghan EoS is truncated to second order), and in the second, B31-2, $K'_0 = 4.47$ [the value determined from the 0 K *ab initio* simulations of Vočadlo *et al.* (2012)]. Both fits yield values of K_0 that are very similar to the *ab initio* values, with fit B31-2 having a marginally better residual of 3.33 *versus* 3.39 for fit B31-1

Table 2

Third-order Birch–Murnaghan EoS parameters for the B31 (MnP)-, B20 (ϵ -FeSi)- and B2 (CsCl)-structured phases of NiSi (see text for details).

Structure	This study			Vočadlo <i>et al.</i> (2012)		
	V_0 (Å ³ atom ⁻¹)	K_0 (GPa)	K'_0	V_0 (Å ³ atom ⁻¹)	K_0 (GPa)	K'_0
B31-1	12.1499 (1)†	165 (3)	4‡	12.277 (3)	160.572 (2)	4.47 (6)
B31-2	12.1499 (1)†	161 (3)	4.47‡	–	–	–
B20	11.4289‡	161 (3)	5.6 (2)	11.593 (3)	180.143 (4)	4.48 (1)
B2-1	11.4 (1)§	148 (7)	5.5 (3)	11.5020 (5)	173.1770 (6)	4.488 (2)
B2-2	11.0 (1)	210 (10)	4.488‡	–	–	–
B2-3	10.87 (7)	240 (10)	4‡	–	–	–
B2-4	11.09 (5)	200 (9)	4.6 (1)	–	–	–

† From unpublished neutron diffraction data on the same batch of starting material (Wood, 2011). ‡ Values fixed during fitting. § Value derived by subtracting 1.2% from the value reported by Vočadlo *et al.* (2012); see text. The uncertainty includes the magnitude of the correction.

(throughout this paper, the term ‘residual’ is taken to mean the sum of the squares of the differences between the observed pressure at each data point and that calculated from the EoS). The scatter observed in the data for B31-NiSi is likely due to nonsystematic errors that arise when trying to perform Le Bail refinements on phases with numerous closely spaced and overlapping peaks. This situation arises because of the relatively low symmetry of this orthorhombic phase and the short wavelength of the X-rays used for diffraction. Compounding the situation, the low pressures at which the

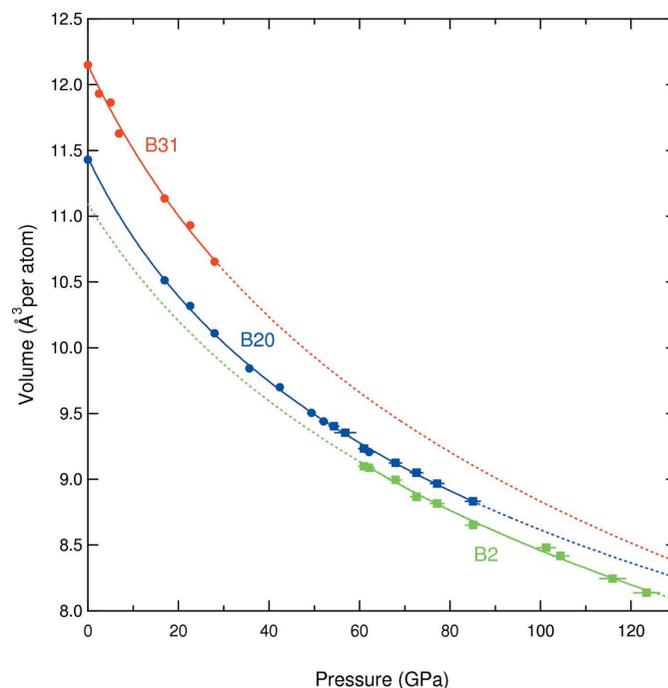


Figure 3
 P - V plot for (in order of decreasing volume) B31-NiSi (red), B20-NiSi (blue) and B2-NiSi (green). The curves represent equally weighted fits to the data using the Birch–Murnaghan EoS truncated to the third order. Dashed lines are extrapolations beyond the region of data coverage. Circles represent data from experiment 1 and squares represent data from experiment 2 (see text). The corresponding P - V data are presented in Table 1 and the EoS parameters in Table 2. Volume error bars are smaller than the symbol size.

B31-NiSi phase is stable require that laser annealing be performed at low temperatures (~ 1400 K) to ensure that the sample does not melt, leading to a less effective release of deviatoric stress and broader peaks as a result of the relative hardness of the NaCl pressure medium. To improve this situation, more precise EoS measurements on this phase using a softer pressure medium such as He or Ne are planned for a future study.

In the case of the B20-NiSi phase, the data are much less scattered and cover a considerable degree of compression. Consequently, both K_0 and K'_0 were left as free parameters in the fit, while V_0 was fixed at the measured value upon release of pressure in the DAC. As with the B31 structure, the measured V_0 is smaller than the value derived from the 0 K *ab initio* calculations of Vočadlo *et al.* (2012), in this case by 1.4%, while K_0 is 11% smaller and K'_0 is 20% larger. However, because these two parameters are so highly correlated, the experimental and *ab initio* P - V curves for B20-NiSi do not stray from one another by more than $\pm 2.4\%$ in volume up to 360 GPa. There is no evidence that the B1 \rightarrow B2 transition in NaCl (which occurs around 30 GPa, *i.e.* within the B20-NiSi stability field) has any effect on its compressibility, whether owing to the greater hardness of the B2 structure, or to the significant volume collapse across the transition, or to any inconsistency between the EoSs of the two NaCl polymorphs used as the internal pressure standard.

Unlike the B31 and B20 structures, the B2-NiSi polymorph could not be recovered to ambient pressure and so no measured value for V_0 is available. Coupled with the relatively small range of compression over which P - V data for B2-NiSi were collected, this leads to substantial uncertainties in the fitted EoS parameters when all three are allowed to vary freely. It is clear, therefore, that either K'_0 or V_0 must be fixed. To this end we have explored three options for choosing reasonable values for one or other of these parameters. First of all, we fixed V_0 at $11.4 \pm 0.1 \text{ \AA}^3 \text{ atom}^{-1}$, a value obtained by subtracting 1.2% from the *ab initio* result (fit B2-1 in Table 2). This correction was estimated by taking the average of the differences between the experimental and *ab initio* values of V_0 for the B31 and B20 structures (1.0 and 1.4%, respectively; see Table 2); the uncertainty was chosen to be of a similar magnitude relative to the correction. This method yields a fit with a residual of 16.76 and a P - V curve that differs in volume from the *ab initio* curve by a maximum of 1.8% between 0 and 360 GPa. The second option consists of fixing K'_0 at 4.488 (fit B2-2 in Table 2), the value determined from the *ab initio* simulations of Vočadlo *et al.* (2012). This fit leads to a marginally better residual (15.23) than the previous attempt. While the resulting P - V curve underestimates the volume by 4.2% at ambient pressure compared with the *ab initio* curve, this mismatch diminishes with increasing pressure such that the two curves are identical above 330 GPa, which is unsurprising given that they share the same value of K'_0 . The third and final option considered here involves fixing K'_0 at 4 (*i.e.* truncating the Birch-Murnaghan equation to second order; fit B2-3 in Table 2). This fit yields the lowest residual (14.51) of all our attempts. The mismatch between the resulting P - V curve

and the *ab initio* curve is 5.8% at ambient pressure but drops to 1.1% at 360 GPa.

Looking at Table 2, it is clear that none of the free parameters from the three fits described above matches the corresponding *ab initio* values within their combined uncertainties. However, the differences are such that they lead to P - V curves which differ from the *ab initio* curve to only a small degree. For example, in fit B2-1, while K_0 is 14% smaller than the *ab initio* value, K'_0 is 27% larger, leading to only marginal differences in volume at any given pressure. This trade-off between the pair of free parameters in each fit is apparent in their correlation coefficient, which is 99.35% for fit B2-1; this is the smallest correlation coefficient of any of the three fits described here. There is no clear reason why any of the three different fits described above should be considered the most accurate. Therefore, our preferred fit is calculated by taking the centre point of the range of volumes defined by the three fits between 0 and 360 GPa and fitting those points in turn to a third-order Birch-Murnaghan EoS (fit B2-4 in Table 2). Compared with the *ab initio* P - V curve, our preferred fit underestimates the volume by 2.7% at ambient pressure, but the two curves are nearly identical above ~ 300 GPa. The uncertainty in the fitting parameters was chosen so that the uncertainty in the resulting P - V curve encompasses the P - V curves of the three individual fits from which the preferred fit was derived. This is the curve plotted in Fig. 3 and the one used in all subsequent discussions (see §4).

It should be noted that the small tetragonal distortion present in this phase above 60 GPa (see §3.2) might have a small systematic effect on the P - V data and the EoS parameters derived from it. Future experiments using softer pressure media, such as He or Ne, might therefore improve the accuracy of the EoS, but the close correspondence with the *ab initio* results suggests that any systematic error caused by this effect is small.

3.4. Subordinate phases

After the B31 \rightarrow B20 transition in experiment 1 (12.5 ± 4.5 GPa and 1550 ± 150 K), the B31 structure persists as a subordinate phase (with peak intensities $< 5\%$ of the dominant B20-NiSi) up to 49 GPa (1900 K), at which point it undergoes a distortion to the $Pnma$ -II structure with which it shares the same space group (Figs. 2*a* and 2*b*). This spontaneous transition is predicted by the *ab initio* calculations of Vočadlo *et al.* (2012) and the crystallographic relationship between the two phases is detailed in Figs. 2(*a*) and 6 of their paper. The $Pnma$ -II structure remains present in all subsequent diffraction patterns, up to and including 62 GPa, the highest pressure reached in the first experiment. It is likely that the persistence of the B31 structure beyond the B31 \rightarrow B20 transition is due to some part of the starting material remaining unheated throughout the experiment. Given that the B31 \rightarrow $Pnma$ -II transition is achieved by a small shift in atomic positions without the rearranging of bonds, and that it occurs spontaneously on compression within the *ab initio* simulations, it is unlikely that there is a significant energy barrier associated

with it which would require high-temperature annealing to overcome. Indeed, the high relative enthalpy of the *Pnma*-II phase (see Fig. 3 of Vočadlo *et al.*, 2012) suggests that, if this phase were to be heated significantly, it would almost certainly convert to the B20 structure, which supports the assumption that this phase, and the part of the B31 structure from which it is formed, remained unheated throughout the experiment. The presence of rhenium in our diffraction patterns indicates that the entire sample chamber is sampled by the X-ray beam. Thus the entire sample, including the edges, contributes to the diffracted intensity. It is possible, therefore, that the unheated material described here resides at the sample edge, where proximity to the gasket prevents adequate laser annealing to transform it, owing to the risk of reactions between the sample and gasket. Alternatively, a small piece of the starting sample may have become trapped, during loading, between the NaCl insulator and the diamond anvil, preventing it from being heated because of the large thermal conductivity of diamond.

After the B20 → B2 transition, the B20 structure remains present in every pattern, although the intensity of its peaks, already small after the transition, diminishes further at each subsequent compression and annealing step. The persistence of the B20 structure far beyond the pressure of the B20 → B2 transition is also observed in DAC experiments on FeSi (Lord *et al.*, 2010), where it was interpreted to be the result of kinetic inhibition brought about by a high activation energy (Vočadlo *et al.*, 1999). However, nonstoichiometry may provide a more compelling alternative explanation. If the B2 structure of NiSi is favoured by excess metal, as is the case for both RuSi (Buschinger *et al.*, 1997) and FeSi (Dobson *et al.*, 2003), then as the transformation proceeds the remaining B20-structured material will become increasingly silicon rich. Once the remaining B20-structured material is richer in silicon than the solubility limit of silicon in the new B2 phase the reaction will cease, leaving a remnant of silicon rich B20-structured NiSi stable with respect to the further addition of silicon into the new B2 phase. This sequence requires that the NiSi B20 structure display some propensity for solid solution, as it is known to do in both the RuSi and FeSi systems. Note that the explanation used for the persistence of the B31 structure beyond the B31 → B20 transition cannot be used to explain the persistence of the B20 structure beyond the B20 → B2 transition; if unheated material were present, it would probably have remained in the B31 structure or undergone a series of distortions, first to the *Pnma*-II structure (described above) and then to the *Pnma*-III structure (Vočadlo *et al.*, 2012).

Between 7 GPa (1400 K; Fig. 1*b*) and 49 GPa (1900 K; Fig. 2*b*), an additional subordinate phase is also present in some but not all patterns. The peak positions are not inconsistent with the *Pbma*-I structure, but they can also be explained by the related *P4/nmm* or *Pmnm* phases (see §3); it is not possible to distinguish between these structures with certainty, given the current data. The *P4/nmm* structure was predicted to be stable between 23 and 61 GPa at 0 K (Vočadlo *et al.*, 2012), although there is likely to be considerable

uncertainty in these transition pressures, perhaps as much as ±10 GPa. An orthorhombically distorted variant of the *P4/nmm* structure, in space group *Pmnm*, was detected very recently in as yet unpublished quenched multi-anvil experiments (Ahmed, 2011); this distortion was not considered in the *ab initio* calculations of Vočadlo *et al.* (2012). The diffraction peaks from this phase, whatever its structure may be, result from the integration of a few spots on the two-dimensional Debye–Scherrer ring, suggesting that only a few crystals contribute to the diffracted signal, unlike the dominant phase in each pattern which is usually associated with continuous powder rings. This texture, combined with the close coincidence between the pressure range of this phase and that in which two candidate structures are found (*P4/nmm* in the *ab initio* calculations and *Pmnm* in the multi-anvil quench experiments), suggests that this phase enjoys a field of stability at temperatures below those at which our samples were equilibrated and therefore formed as the sample quenched through it. Additional experiments will clearly be needed to determine the stability fields of these various candidate structures and to make a definitive assignment.

A similar argument can be made for the presence of the *Pbma*-I structure (Vočadlo *et al.*, 2012), which we find, in this case unambiguously, between 54 GPa (1900 K) and 124 GPa (2700 K), the highest pressure reached in this study. Again, this range fits well with the 0 K stability predictions for this structure from the *ab initio* simulations (61–168 GPa); the Debye–Scherrer rings associated with this phase are spotty rather than continuous.

Between 102 GPa (2500 K) and 124 GPa (2700 K), two peaks are present which are not inconsistent with the cell parameters of the *Pnma*-III phase, as predicted by the *ab initio* simulations, although this assignment is not certain. The simulations indicate that this phase should not be stable until beyond 168 GPa. Nevertheless, the fact that the *Pbma*-I phase and probably also the *P4/nmm* phase, or its orthorhombically distorted *Pmnm* variant, appear in our experiments in the same order as they were predicted to occur at 0 K in the *ab initio* simulations is strong, if not conclusive, evidence that these phases formed on quench. If this is the case, these subordinate phases contain information about the topology of the NiSi phase diagram. However, given that we cannot exclude alternative explanations for the existence of these phases, including the very slight nonstoichiometry of our starting material, we refrain from constructing the phase diagram at this stage and prefer to wait for the results of future experiments which are optimized for the detailed mapping of phase relations. It is intriguing to note, however, that it is possible to formulate a self-consistent phase diagram with a feasible topology which broadly agrees with the 0 K simulations by making just two assumptions, both of which we believe to be reasonable: (i) that the *Pnma*-II structure is metastable and formed from unreacted (and thus probably unheated) B31-structured starting material; and (ii) that the *Pbma*-I and *Pnma*-III structures (as well as the *P4/nmm*, or *Pmnm*, phase, if confirmed) formed as the sample cooled through their respective stability fields.

4. Discussion

4.1. NiSi in the CsCl (B2) structure

The experiments reported here bracket the B20 \rightarrow B2 transition at 46 ± 3 GPa and 1900 ± 150 K, while the *ab initio* simulations indicate that the B2 structure becomes stable above 247 GPa at 0 K. By combining these two P - T points we can calculate that the phase boundary between the B2 structure and the lower-pressure structures adjacent to it has a Clapeyron slope of ~ -9.5 K GPa $^{-1}$. Note that, although we cannot be certain of the topology of the NiSi phase diagram between these two points, the fact that the B20 structure is not stable at 0 K requires that at least one additional phase boundary must intersect the low-pressure boundary of the B2 stability field, which must create an inflexion. Schreinemaker's rules (Zen, 1966) require that this inflexion cause the B2 stability field to be widened even further. We can be nearly certain then, excepting the possibility of further phase transitions at conditions beyond the range of the present experimental study to structures not considered in the simulations (Vočadlo *et al.*, 2012), that B2-NiSi is the stable structure throughout most of the Earth's mantle and the entirety of its core. Therefore, under the conditions of the lowermost mantle, where FeSi is potentially present (Lord *et al.*, 2010; Dubrovinsky *et al.*, 2003), NiSi and FeSi will be isostructural and are likely to form a solid solution. Given that the postulated formation mechanisms for FeSi in the lowermost mantle rely on the nickel-bearing core alloy as their source, we would in fact expect a single (Fe,Ni)Si phase to form. In the inner core, however, where plausible alloys in the Fe-Ni-Si ternary system will plot near the iron-rich apex, recent studies of phase relations suggest that a single phase with a hexagonally close-packed structure will form instead (Asanuma *et al.*, 2008, 2011; Sakai *et al.*, 2011). Although additional *in situ* X-ray diffraction experiments will be required to elucidate the detailed topology of the NiSi phase diagram, these broad conclusions seem robust.

Such a transition was not entirely unexpected; a similar B20 \rightarrow B2 transition is observed in FeSi (Dobson *et al.*, 2002; Vočadlo *et al.*, 1999), while RuSi is known to be stable in both structures at ambient pressure (*e.g.* Göransson *et al.*, 1995). There are additional parallels in the B20 \rightarrow B2 transition between NiSi and FeSi: (i) FeSi also has a negative Clapeyron slope (although it is steeper and offset to lower pressures); and (ii) the volume decrease at the transition is similar (0.8% for NiSi compared with 1.1% for FeSi), as determined from the EoSs for B20-FeSi (Ross, 1996) and B2-FeSi (Sata *et al.*, 2010). However, this similarity in volume decrease at the transition should be considered with caution, because it is based on a room-temperature transition pressure (105 GPa) for FeSi extrapolated from a measurement of the slope of the phase boundary at high temperature (Lord *et al.*, 2010).

The experimental and *ab initio* P - V curves for B2-NiSi, calculated using the EoS parameters in Table 2, are nearly identical above 300 GPa (Fig. 4) with a maximum difference (which occurs at ambient pressure) of 2.7% in volume. For B2-FeSi at ambient pressure, the *ab initio* simulations (Vočadlo *et*

al., 1999) yield a volume that is smaller than the experimentally determined value (Sata *et al.*, 2010), which is the opposite behaviour to that usually seen in *ab initio* calculations employing the generalized gradient approximation but is common in iron-bearing systems. This is followed by a volume crossover (~ 30 GPa) and then a significant divergence between the *ab initio* and experimental results at higher pressures (Fig. 4). Essentially identical differences are observed if the *ab initio* EoS for B2-FeSi of Caracas & Wentzcovitch (2004) is used, although in this case the volume at high pressure ($6.654 \text{ \AA}^3 \text{ atom}^{-1}$ at 330 GPa) agrees a little better with that expected from experiment (see Fig. 4). This means that conclusions drawn from a comparison of the physical properties (specifically density) of NiSi and FeSi in the B2 structure are strongly dependent upon whether we use the *ab initio* or experimental EoSs. Given that the B2 structure is the one relevant to the Earth's core, the following values are all calculated at 330 GPa, the pressure at the boundary between the inner and outer core.

The *ab initio* EoSs (Vočadlo *et al.*, 1999, 2012) indicate that, at 330 GPa, B2-NiSi is denser than B2-FeSi by $5.9 \pm 0.6\%$. Not only is the Ni atom heavier, but the volume of B2-NiSi is smaller than B2-FeSi, owing to a volume crossover at ~ 170 GPa. If the EoS for B2-FeSi of Caracas & Wentzcovitch (2004) is used, this density difference reduces to $3.3 \pm 0.7\%$. No comparison can be made with the *ab initio* EoS for B2-FeSi of Moroni *et al.* (1999) because the authors did not report their value of K'_0 . In contrast, according to the experimental EoS,

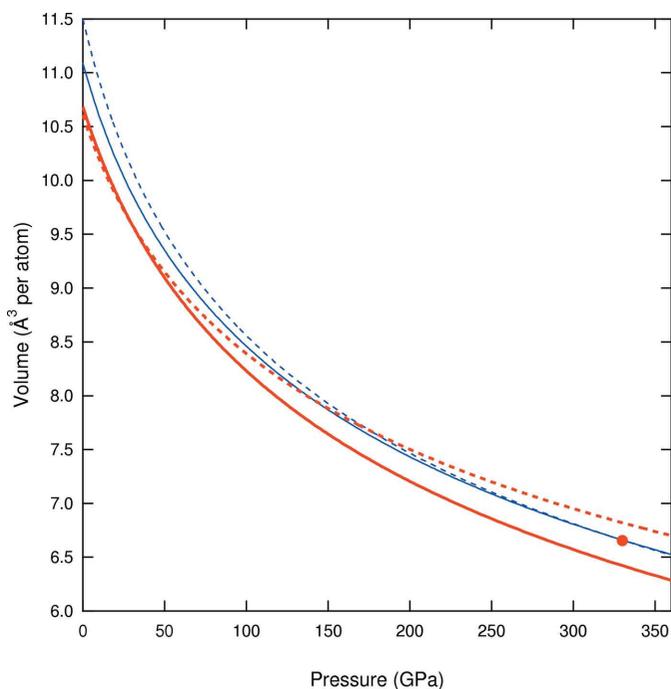


Figure 4
 P - V curves for NiSi (thin blue lines) and FeSi (thick red lines) in the B2 structure. The solid lines represent experimentally determined EoSs from this study for NiSi and from Sata *et al.* (2010) for FeSi. The dashed lines represent EoSs determined from *ab initio* simulations from Vočadlo *et al.* (2012) for NiSi and Vočadlo *et al.* (1999) for FeSi; the red circle indicates the predicted volume of B2-FeSi at 330 GPa from the EoS of Caracas & Wentzcovitch (2004).

the density of B2-NiSi ($10.82 \pm 0.25 \text{ Mg m}^{-3}$) is $1.1 \pm 2.5\%$ lower than that of B2-FeSi ($10.94 \pm 0.10 \text{ Mg m}^{-3}$), although the difference is clearly within the mutual uncertainties. The two published experimental EoSs for B2-FeSi agree very closely (Sata *et al.*, 2010; Dobson *et al.*, 2003), such that this result is almost completely insensitive to which of these is used. It follows that for the B2 structures the discrepancy in the quantity $\rho_{\text{NiSi}} - \rho_{\text{FeSi}}$ between the experimental and *ab initio* techniques at 330 GPa lies somewhere between 4.4 ± 3.2 and $7.0 \pm 3.1\%$. Given the large uncertainty on this density difference it is clear that further work is needed to determine the densities more precisely.

4.2. NiSi in the ϵ -FeSi (B20) structure

The B31 \rightarrow B20 transition occurs at 12.5 ± 4.5 GPa and 1550 ± 150 K. Although the B20 structure is not stable at any pressure at 0 K in the simulations, the lines representing the B31 and B20 structures cross at 33.5 GPa on the ΔH versus P plot (Fig. 3 in Vočadlo *et al.*, 2012), representing a metastable transition point. Given these two P - T points, we can estimate the Clapeyron slope of the transition as -74 K GPa^{-1} . This leads to a transition pressure of 17 GPa at 300 K, with an associated volume decrease of 6%. As mentioned in §1, the difference in enthalpy between B20-NiSi and the structures that are predicted to be stable is only ~ 30 meV at 18 GPa, and decreases to as little as 8 meV at 60 GPa. Such a small enthalpy difference could easily be overcome at the high

temperatures reached during the laser annealing of the sample, and so the appearance of this phase is not surprising.

As was the case with B2-NiSi, a comparison of the experimental and *ab initio* P - V curves for B20-NiSi, calculated using the EoS parameters in Table 2, shows excellent agreement (Fig. 5). Although the *ab initio* P - V curve yields higher volumes at all pressures up to at least 150 GPa, the offset is never more than 1.8%. The closeness of this match is all the more impressive when we consider that simulations that employ the generalized gradient approximation are known to overestimate volume by $\sim 1\%$. In contrast, B20-FeSi behaves in a remarkably similar way to B2-FeSi, showing a systematic difference between the *ab initio* and experimental EoSs (see §4.1). As was the case for B2-FeSi, the *ab initio* simulations of Vočadlo *et al.* (1999) exhibit the unusual behaviour of yielding a volume that is smaller than the experimentally determined value (Wood *et al.*, 1995). This is followed by a volume crossover, in this case at ~ 15 GPa, after which the experimental and *ab initio* P - V curves diverge significantly (Fig. 5). We can employ the same approach as used for the B2 structures (see §4.1) to compare how the two techniques (simulation versus experiment) affect estimates of the relative densities of B20-NiSi and B20-FeSi.

At 150 GPa, the *ab initio* EoSs (Vočadlo *et al.*, 1999, 2012) indicate that B20-NiSi is the denser phase, by $1.5 \pm 0.5\%$. The greater mass of the Ni atom more than compensates for the greater volume of B20-NiSi. If the EoS for B20-FeSi of Caracas & Wentzcovitch (2004) is used, this density difference increases to $3.4 \pm 0.2\%$ [for B20-FeSi, the *ab initio* EoSs of Vočadlo *et al.* (1999) and Caracas & Wentzcovitch (2004) run almost exactly parallel to each other, with the latter having a volume that is greater by $0.016 \text{ \AA}^3 \text{ atom}^{-1}$]. As with B2-FeSi, no comparison can be made with the *ab initio* EoS for B2-NiSi of Moroni *et al.* (1999) because the authors did not report their value of K'_0 . In contrast, the density of B20-NiSi is $1.8 \pm 1.0\%$ lower than B20-FeSi according to the experimental EoS under the same pressure conditions. The majority of published EoSs for B20-FeSi are so similar (Wood *et al.*, 1995; Ross, 1996; Guyot *et al.*, 1997) that this analysis is largely insensitive to which is used. Thus, the difference in the quantity $\rho_{\text{NiSi}} - \rho_{\text{FeSi}}$ between the experimental and *ab initio* techniques at 150 GPa is between 3.3 ± 1.1 and $5.2 \pm 1.1\%$. This difference is clearly statistically significant, unlike the difference for the B2 structures discussed in §4.1, primarily because of the smaller uncertainty in the experimental EoS for B20-NiSi than for B2-NiSi.

4.3. Comparisons with other stoichiometries

Comparing Figs. 4 and 5, it is clear that the P - V systematics of both the B2 and B20 structures are strikingly similar. Further, the difference $\rho_{\text{NiSi}} - \rho_{\text{FeSi}}$ between the *ab initio* and experimental methods is of the same sign in both structures. The question is, from where does this discrepancy arise? Two points are pertinent here: (i) there is close agreement between the *ab initio* and experimental P - V curves for both B2-NiSi and B20-NiSi; and (ii) the P - V curves derived from the

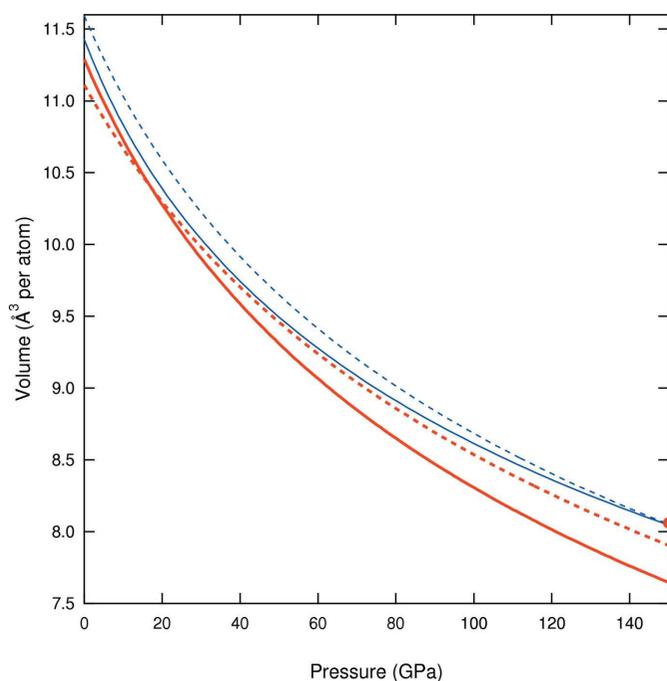


Figure 5
 P - V curves for NiSi (thin blue lines) and FeSi (thick red lines) in the B20 structure. The solid lines represent experimentally determined EoSs from this study for NiSi and Ross (1996) for FeSi [taking the value of V_0 from Wood *et al.* (1995)]. The dashed lines represent EoSs determined from *ab initio* simulations from Vočadlo *et al.* (2012) for NiSi and Vočadlo *et al.* (1999) for FeSi; the red circle indicates the predicted volume of B20-FeSi at 150 GPa from the EoS of Caracas & Wentzcovitch (2004).

majority of published experimental EoSs for B20-FeSi agree very closely with each other, as do both published experimental EoSs for B2-FeSi. This hints that the problem may lie with the *ab initio* simulations performed on FeSi (Vočadlo *et al.*, 1999; Caracas & Wentzcovitch, 2004). The fact that these discrepancies occur in both the B2 and B20 structures suggests that the problem is not related to the structure itself, but perhaps instead to the theoretical description of the Fe atom. One possible manifestation of this potential problem is the difference between the experimentally determined values of V_0 and those determined by the *ab initio* simulations that rely on the generalized gradient approximation. Such calculations would be expected to overestimate V_0 significantly compared with experiment (as indeed they do for B20-NiSi, B2-NiSi and B31-NiSi, by between 1.0 and 3.7%). However, for B20-FeSi the *ab initio* simulations (Vočadlo *et al.*, 1999; Caracas & Wentzcovitch, 2004) underestimate V_0 compared with experiment, by between 0.2 and 1.6%. For B2-FeSi the *ab initio* simulations of Vočadlo *et al.* (1999) also underestimate V_0 compared with experiment, in this case by 0.7%. The only exceptions to this behaviour are the *ab initio* simulations for B2-FeSi of Caracas & Wentzcovitch (2004), which barely overestimate V_0 compared with experiment, but by less than 0.02%. Possible reasons for the discrepancy between the experimental EoS for B20-FeSi and that from *ab initio* simulations were discussed by Vočadlo *et al.* (2000), who concluded that it was unlikely to have arisen either from slight variations in the stoichiometry of the material used in the experiments or from any failure to incorporate magnetism correctly in the simulations. In view of this, it is instructive to look at whether similar behaviour is evident in iron silicides with different stoichiometries. Errandonea *et al.* (2008) saw a similar underestimate in the volume of both α -Fe₂Si and Fe₅Si₃ (xifengite) in their *ab initio* calculations at ambient pressure compared with their experimentally determined values, while calculations by the same authors on δ -Ni₂Si yielded the expected overestimate. All these simulations employed the generalized gradient approximation. However, it is not always the case that *ab initio* simulations on iron silicides overestimate volume: Moroni *et al.* (1999) found that the opposite is true for Fe₃Si (suessite) and both α - and β -FeSi₂, but given this limited data set it is not currently possible to draw any firm conclusions about the reasons for the discrepancy observed in the monosilicides.

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