

## A new high-pressure phase of FeSi

DAVID P. DOBSON,<sup>1,\*</sup> LIDUNKA VOČADLO,<sup>2</sup> AND IAN G. WOOD<sup>2</sup>

<sup>1</sup>Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth D95440, Germany

<sup>2</sup>Geological Sciences, University College London, Gower Street, London WC1E 6BT, U.K.

### ABSTRACT

A new high-pressure phase of FeSi with the CsCl structure has been synthesized by high-temperature reaction of Fe and Si mixtures at 24 GPa. Powder X-ray diffraction measurements yield a cubic unit cell of  $a = 2.7917(1)$  Å for the CsCl-FeSi phase which has composition  $\text{Fe}_{0.52}\text{Si}_{0.48}$  by electron microprobe. The transition from  $\epsilon$ -FeSi to the high-pressure phase occurs at  $1950 \pm 50$  K at 24 GPa and has a negative Clapeyron slope.

### INTRODUCTION

The Earth's core is believed to consist of iron-nickel alloy with several percent of light alloying elements. Silicon has been suggested, from geochemical arguments, as a possible light element in the core. As such, iron silicide has been the focus of several recent experimental and theoretical studies. Equation of state measurements have been performed on  $\epsilon$ -FeSi to 50 GPa and 1100 K (e.g., Knittle and Williams 1995; Wood et al. 1995; Guyot et al. 1997; Vočadlo et al. 2001). Williams and Knittle (1996) suggested that measured values of  $K'$ , the pressure derivative of the bulk modulus, in  $\epsilon$ -FeSi are sufficiently low to preclude Si as the major light element component of Earth's outer core. Recent computer simulation studies suggest, however, that  $\epsilon$ -FeSi is not the stable high-pressure structure, with a CsCl-type phase being thermodynamically stable above 13–15 GPa (Vočadlo et al. 1999; Moroni et al. 1999). Knittle and Williams (1995) failed to produce CsCl-type FeSi after treatment of  $\epsilon$ -FeSi at 50 GPa and 1500 K. Thin films of CsCl-structured FeSi have, however, been grown on silicon substrates, with a compressive strain in FeSi equivalent to about 25 GPa (von Känel et al. 1992; Girlanda et al. 1994). Vočadlo et al. (1999) suggested that direct transformation of  $\epsilon$ -FeSi to the CsCl structure will be kinetically inhibited by the large predicted activation barrier (1.5 eV) and  $\epsilon$ -FeSi may, therefore, have persisted metastably in previous high-pressure experimental studies. While this is possible, dislocation migration helps to overcome activation barriers in metals and may well also do so in FeSi.

Comparison with the RuSi system may provide an alternative explanation for the stability of  $\epsilon$ -FeSi to high pressures. At ambient conditions, RuSi takes the FeSi structure, transforming to CsCl structured phase above 1578 K (Buschinger et al. 1997). Ruthenium silicide accommodates several percent solid solution and in Si-rich bulk compositions a mixture of FeSi- and CsCl-structured phases are recovered. It is only on the metal

excess side of the solid solution that pure CsCl-RuSi can be synthesized. Previous experimental studies may, therefore, have failed to detect CsCl-FeSi at high pressure because their starting sample compositions were slightly enriched in silicon.

To evaluate the stability of  $\epsilon$ -FeSi in  $P$ - $T$ - $X_{\text{Fe}}$  space we have synthesized FeSi directly from powder mixtures of Fe and Si starting materials at high pressures and temperatures with iron-deficient and iron-excess bulk compositions. We find that CsCl-type FeSi is stable at 24 GPa and temperatures above  $1950 \pm 50$  K.

### EXPERIMENTAL METHODS

Experiments were performed in 1000 ton split-cylinder and Walker-type multi-anvil-presses at the Bayerisches Geoinstitut and University College London, respectively. An octahedral assembly of 10 mm edge length (Fig. 1) was compressed by WC cubic anvils with 4 mm truncation lengths. Starting materials consisted of powders of Fe and Si mixed to  $\text{Fe}_x\text{Si}_{1-x}$  stoichiometry where  $0.475 < x < 0.525$ . These mixtures were packed in 200  $\mu\text{m}$  wall thickness  $\text{Al}_2\text{O}_3$  (99.7% density) capsules, which were then placed in the inner MgO sleeve of the octahedral assembly. Tungsten-rhenium thermocouples terminated directly on one end of the capsule: no correction was applied for the effect of pressure on thermocouple EMF. Ther-

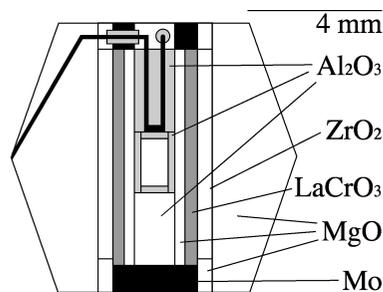


FIGURE 1. High-pressure cell for 24 GPa synthesis experiments. The  $\text{Al}_2\text{O}_3$  components colored pale grey are polycrystalline corundum and the white  $\text{Al}_2\text{O}_3$  component consists of crushable alumina.

\* E-mail: David.Dobson@uni-bayreuth.de

mal gradients are estimated to be 150 K/mm in the sample region; quoted experimental temperatures are not corrected for the temperature difference between sample and thermocouple. Experiments were performed by compressing to the desired load at room pressure, followed by heating to experimental temperature. Temperature was maintained for 30 to 60 minutes before quenching by cutting power to the furnace.

Samples were recovered and analyzed by powder X-ray diffraction and electron microprobe. Recovered phases were identified using a Rigaku microdiffractometer in reflection geometry with a position sensitive detector (PDS) covering an angular range from 20–130°  $\theta$  and  $\text{CrK}\alpha$  radiation. The incident beam was collimated to 100  $\mu\text{m}$  diameter. Unit-cell measurements were performed at the European Synchrotron Radiation Facility on a white-beam line with X-rays monochromated to 0.3738(1) Å. Diffraction patterns were collected on a Mar345 image plate detector, the distance to which was calibrated using an Si standard placed at the sample position. The integrated 2 $\theta$ -I patterns were obtained after correction for detector distortion and tilt using the Fit2D package, Hammersley et al. (1995). The patterns were subsequently fit to obtain unit-cell volumes by the LeBail technique using GSAS, Larson and Von Dreele (1994).

Sample compositions were measured using a Cameca SX50 electron microprobe in wavelength dispersive mode. Analytical conditions were as follows: a 20 mA beam with 15 kV accelerating voltage was focused to 1  $\mu\text{m}$  spot size. Elemental

standards were used for Fe, Si, and W;  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  were used as oxygen and aluminum standards, respectively. Elemental  $K\alpha$  X-ray emissions were measured for 20 s on peak with 5 s background measurements either side of the peak. Ten to twenty measurements were performed on each phase. X-ray element maps were collected using a Leo 1530 scanning electron microscope with Inca software. Instrumental drift during the long collection times resulted in a spatial resolution of about 1  $\mu\text{m}$ .

## RESULTS AND DISCUSSION

Experimental conditions and compositions of recovered phases are presented in Table 1. Figure 2 shows a secondary electron image and element maps of a polished surface of CsCl-

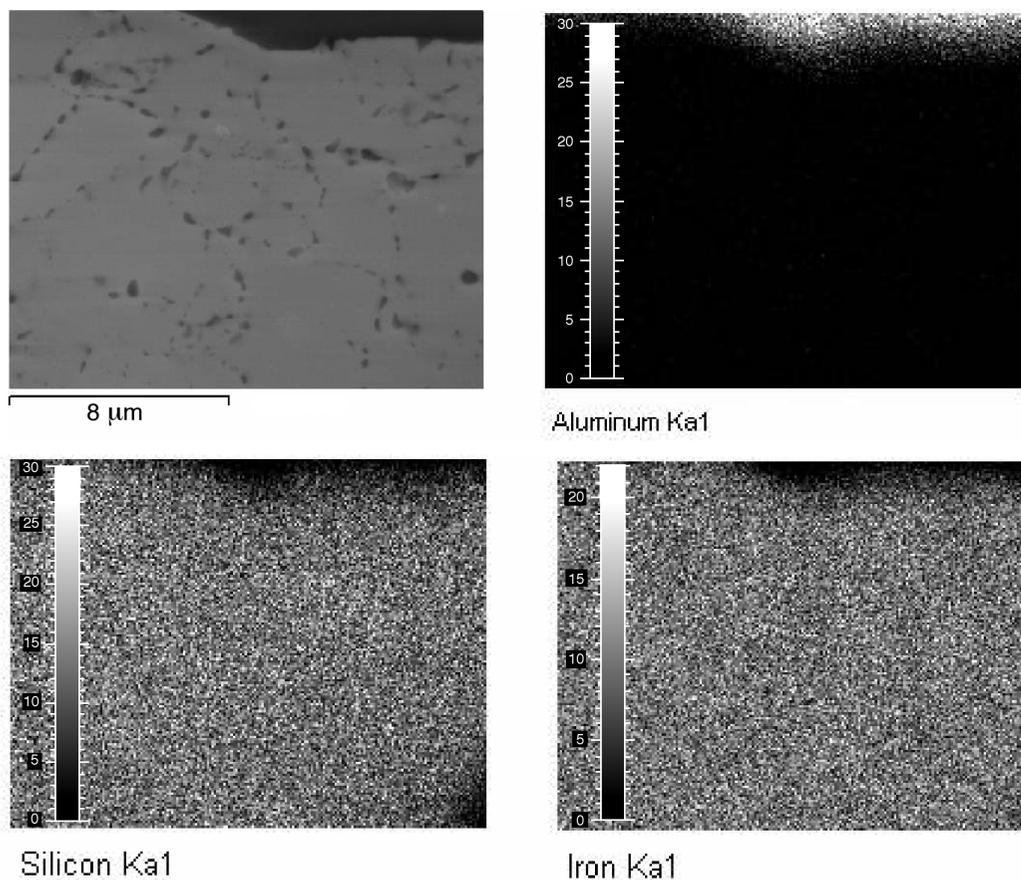
**TABLE 1.** Experimental conditions and recovered phases

Run number	Starting $X(\text{Fe})$	$P(\text{GPa})$	$T(\text{K})$	Recovered phases	$X(\text{Fe})\dagger$
H1533	0.52	24	2023	CsCl-FeSi $\epsilon$ -FeSi§ $\alpha$ -Fe§ $\epsilon$ -FeSi	–
H1537	0.52	24	1903	CsCl-FeSi* $\text{Fe}_3\text{Si}_2$ $\gamma$ -Fe§	0.496(6) 0.508(2) 0.588(4)
H1526	0.48	24	2023	$\epsilon$ -FeSi $\text{FeSi}_2$ $\epsilon$ -FeSi	0.491(4) 0.328(9)
FSI1	0.505	15	1873	$\epsilon$ -FeSi	

\* Volumetrically minor phase.

† Samples only contained Fe and Si.

§ Identified from Rigaku diffraction patterns.

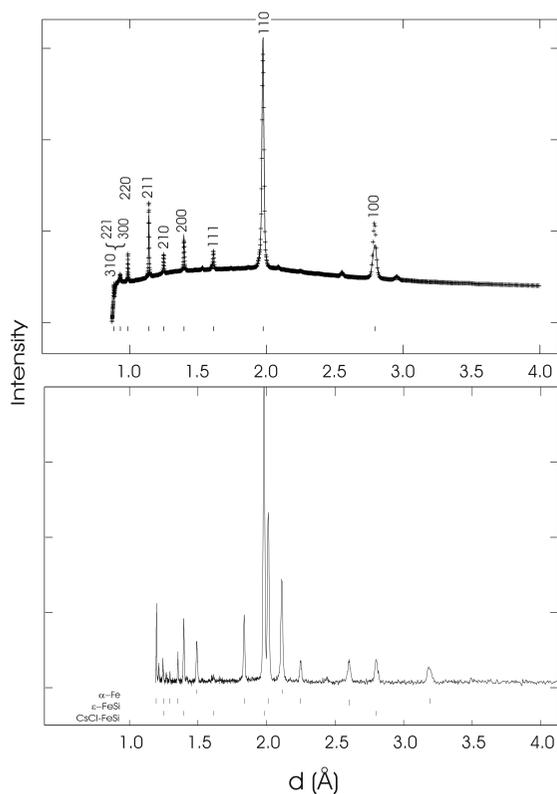


**FIGURE 2.** Secondary electron and X-ray element map images of sample recovered from H1533. The equilibrium texture is clear, with small Fe-rich silicides on the FeSi grain boundaries. There is no evidence of reaction between the sample and  $\text{Al}_2\text{O}_3$  capsule material.

FeSi recovered from experiment H1533. Al<sub>2</sub>O<sub>3</sub> capsule material is seen in the top right. The sample displays an equilibrium texture with a mean grain size of around 5  $\mu\text{m}$ . The small dark grains on grain boundaries have been preferentially polished away and consist of Fe-rich silicides. X-ray element maps show no indication of reaction between the sample and Al<sub>2</sub>O<sub>3</sub> capsule.

At 15 GPa and 1873 K only  $\epsilon$ -FeSi was recovered, with a small excess of Fe in the starting material. Synchrotron X-ray diffraction of the sample recovered from 24 GPa, 2023 K (H1533) showed it to consist of nearly pure CsCl-structured phase of FeSi (Fig. 3a). By contrast, X-ray diffraction experiments in reflection mode using a laboratory X-ray source invariably showed extra reflections, which could be indexed as  $\alpha$ -Fe and  $\epsilon$ -FeSi (Fig. 3b). We interpret these to be breakdown products on the surface of bulk CsCl-FeSi due to shear stresses induced during breaking the capsule open. The low energy laboratory X-rays only penetrates the top few microns, whereas the synchrotron X-rays sample the bulk sample. Crushing the sample under liquid N<sub>2</sub> resulted in decomposition to  $\epsilon$ -FeSi.

CsCl-FeSi was found to have a cell parameter of  $a = 2.7917$  (1)  $\text{\AA}$ ;  $V = 21.76 \text{\AA}^3$ , which is in reasonable agreement with ab initio simulations results ( $a = 2.768 \text{\AA}$ , Vočadlo et al. 1999),



**FIGURE 3.** X-ray diffraction patterns of sample recovered from H1533;  $d$  spacing vs. intensity. Top = synchrotron transmission diffraction pattern; CsCl-FeSi is the dominant phase. Bottom = laboratory reflection geometry spectrum. The extra Fe and  $\epsilon$ -FeSi peaks in this pattern are surface features, probably due to decomposition of the CsCl-FeSi surface during sample preparation.

having a 2.5% larger volume than the predicted 0 K value.

For synthesis conditions of 24 GPa and 1903 K the dominant phase was  $\epsilon$ -FeSi, with a small region at the center of the capsule, corresponding to the furnace hot-spot, which contained CsCl-FeSi. The transition temperature is bracketed to  $1950 \pm 50$  K at 24 GPa. The fact that CsCl-FeSi was found as the high-temperature phase in experiments where both CsCl and  $\epsilon$ -FeSi were recovered implies that the reaction has a negative Clapeyron slope. The observed transition pressure is considerably higher than the value predicted from ab initio simulations, but in good agreement with estimated stabilization pressure for thin films of CsCl-FeSi deposited on Si substrates.

As with the RuSi analogue,  $\epsilon$ -FeSi was found to be stabilized by a small excess of Si; a second experiment (H1526) at 2023 K and 24 GPa with a small Si excess yielded  $\epsilon$ -FeSi. This is consistent with CsCl-FeSi compositions in epitaxially stabilized thin films (Fanciulli et al. 1999). Knittle and Williams (1995) found no evidence of a pressure-induced phase change in FeSi to 50 GPa. Vočadlo et al. (1999) suggested that this was due to the strong metastability of  $\epsilon$ -FeSi, however the present results suggest that any activation barrier to the direct transformation route can be easily overcome by shear stresses. We suggest the persistence of  $\epsilon$ -FeSi in the experiments of Knittle and Williams (1995) may be due to excess Si in their starting composition. A high-pressure synthesis route from powder mixtures of the elements circumvents problems of metastability in FeSi since the stable phases are synthesized directly from the Fe and Si elements. In addition, we were able to easily vary the composition of the starting material and recover CsCl-FeSi and  $\epsilon$ -FeSi from their respective stability fields.

Williams and Knittle (1996) rejected Si as a major light element in the outer core based on the equation of state of  $\epsilon$ -FeSi. We have synthesized a new high-pressure phase of FeSi with the CsCl structure. If  $\epsilon$ -FeSi is not the stable high-pressure phase, Si cannot be ruled out as the main light element. CsCl-FeSi is predicted to have a sufficiently large  $K'$  (Vočadlo et al. 1999) to satisfy Williams and Knittles' criteria for Si to be the light element in the outer core. Further experimental work is required to delineate the stability field and equation of state of CsCl-FeSi.

## ACKNOWLEDGMENTS

We thank W. Crichton for collecting synchrotron diffraction patterns and D. Andrault and one anonymous referee for helpful reviews. High-pressure experiments were performed at the Bayerisches Geoinstitut under the EU "IHP-Access to Research Infrastructures" Programme (Contract No. HPRI-1999-CT-004 to D.C. Rubie). D.P.D. is grateful for his Alexander von Humboldt Fellowship.

## REFERENCES CITED

- Buschinger, B., Geibel, C., Diehl, J., Guth, W., Weiden, M., Wildbrett, A., Horn, S., and Steglich, F. (1997) Preparation and low temperature properties of FeSi-type RuSi. *Journal of Alloys and Compounds*, 256, 57–60.
- Fanciulli, M., Weyer, G., Svane, A., Christensen, N.E., von Känel, H., Müller, E., Onda, N., Miglio, L., Tavazza, F., and Celino, M. (1999) Microscopic environment of Fe in epitaxially stabilized c-FeSi. *Physical Review B*, 59, 3675–3687.
- Girlanda, R., Piparo, E., and Balzarotti, A. (1994) Band-structure and electronic properties of FeSi and  $\alpha$ -FeSi<sub>2</sub>. *Journal of Applied Physics*, 76, 2837–2840.
- Guyot, F., Zhang, J., Martinez, I., Matas, J., Ricard, Y., and Javoy, M. (1997) P-V-T measurements of iron silicide ( $\epsilon$ -FeSi) Implications for silicate-metal interactions in the early Earth. *European Journal of Mineralogy*, 9, 277–285.
- Hammersley, A.P., Svensson, S.O., Thompson, A., Graafsma, H., Kvick, A., and Moy, J.P. (1995) Calibration and correction of distortion in two dimensional

- detector systems. *Review of Scientific Instruments*, 66, 2729–2733
- Känel, H. von, Mader, K.A., Muller, E., Onda, N., and Siringhaus, H. (1992) Structural and electronic-properties of metastable epitaxial FeSi<sub>1-x</sub> films on Si(111). *Physical Review B*, 45, 13807–13810.
- Knittle, E. and Williams, Q. (1995) Static compression of  $\epsilon$ -FeSi and an evaluation of reduced silicon as a deep Earth constituent. *Geophysical Research Letters*, 22, 445–448.
- Larson, A.C. and Von Dreele, R.B. (1994) General Structure Analysis System (GSAS). Los Alamos National Laboratory Report LAUR, 86–748.
- Moroni, E.G., Wolf, W., Hafner, J., and Podloucky, R. (1999) Cohesive, structural, and properties of Fe-Si compounds. *Physical Review B*, 59, 12860–12871.
- Williams, Q. and Knittle, E. (1996) Constraints on core chemistry from the pressure dependence of the bulk modulus. *Physics of the Earth and Planetary Interiors*, 100, 49–59.
- Wood, I.G., Chaplin, T.D., David, I.W.F., Hull, S., Price, G.D., and Street, J.N. (1995) Compressibility of FeSi between 0 and 9 GPa, determined by high-pressure time-of-flight neutron powder diffraction. *Journal of physics: Condensed matter*, 7, L475–L479.
- Vočadlo, L., Price, G.G., and Wood, I. (1999) Crystal structure, compressibility and possible phase transitions in  $\epsilon$ -FeSi studied by first-principles pseudopotential calculations. *Acta Crystallographica*, B55, 484–493.
- Vočadlo, L., Knight, K.S., Price, G.D., and Wood, I.G. (2001) Thermal expansion and crystal structures of FeSi between 4K and 1173K determined by time-of-flight neutron powder diffraction. *Physics and Chemistry of Minerals*, in press.

MANUSCRIPT RECEIVED AUGUST 23, 2001

MANUSCRIPT ACCEPTED DECEMBER 13, 2001

MANUSCRIPT HANDLED BY LEE A. GROAT