

The equation of state of CsCl-structured FeSi to 40 GPa: Implications for silicon in the Earth's core

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[1] We have measured the compressibility of CsCl-structured FeSi to 40 GPa by X-ray powder diffraction using synchrotron radiation. A third order Birch-Murnaghan equation of state fit to the experimental data yields $V_0 = 21.74 \pm 0.02 \text{ \AA}^3$, with a K_0 of $184 \pm 5 \text{ GPa}$ and $K'_0 = 4.2 \pm 0.3$. The measured density and elastic properties of CsCl-FeSi are consistent with silicon being a major element in the Earth's core. **INDEX TERMS:** 1212 Geodesy and Gravity: Earth's interior—composition and state (8105); 3919 Mineral Physics: Equations of state; 8124 Tectonophysics: Earth's interior—composition and state (old 8105). **Citation:** Dobson, D. P., W. A. Crichton, P. Bouvier, L. Vočadlo, and I. G. Wood, The equation of state of CsCl-structured FeSi to 40 GPa: Implications for silicon in the Earth's core, *Geophys. Res. Lett.*, 30(1), 1014, doi:10.1029/2002GL016228, 2003.

1. Introduction

[2] The Earth's core has long been considered to consist of iron-nickel alloy plus a few percent of light alloying elements [Birch, 1952]. The nature of the light component is still unclear, despite considerable efforts to provide constraints from cosmochemical, equation of state (EOS), phase relations and accretion kinetics considerations. Silicon is a favoured light element in the core on the basis of the depletion of the mantle in Si relative to primitive chondrite compositions [Allegre *et al.*, 1995]. Recent high pressure partitioning studies [Gessmann *et al.*, 2001] suggest that silicon solubility in liquid Fe in equilibrium with silicates reaches a maximum at 24 GPa. This is due to the increase in silicon coordination at the post-spinel transition, which stabilises silicate with respect to metallic Si [e.g. Guyot *et al.*, 1997]. The 24 GPa Si-solubilities are consistent with silicon being a major light element component in the outer core if core segregation occurred at the base of a deep magma ocean as suggested by Li and Agee [1996]. Williams and Knittle [1997], however, suggested a discriminator for candidate light elements in the outer core on the basis of the pressure

derivative of the bulk modulus, K' . They suggested, based on measurements of the EOS of ϵ -FeSi, that silicon is *unlikely* to be the main light element in the outer core and, by extension, the inner core.

[3] We recently reported the high-pressure synthesis of CsCl- (also known as B2) structured FeSi at pressures above 24 GPa and temperatures around 1950 K [Dobson *et al.*, 2002]. Results of *ab initio* simulations predict the CsCl-FeSi phase to have a significantly larger K' than the low-pressure ϵ -phase [Vočadlo *et al.*, 1999]. Clearly, in order to be applicable to the outer core, Williams and Knittle's analysis needs to be applied to the stable high-pressure phase. We have measured the compressibility of CsCl-FeSi to 40 GPa in order to reassess the likelihood of silicon being a major light element in the Earth's core.

2. Experimental

[4] A small, 100 μm diameter by 50 μm thick, polycrystalline sample was taken from run H1533 of [Dobson *et al.*, 2002]. This sample had been synthesised from a powder mixture of the elements with slight excess of Fe at 24 GPa and 2000 K.

[5] Several fractions of the original sample were tested in monochromatic beam ($\lambda = 0.3738(1)\text{\AA}$) to check for impurity content and to assess the quality of powder rings that could be obtained from the unground sample. The selected portion of sample was loaded with a nitrogen pressure medium under cryostatic conditions into an Inconel gasket hole of 125 μm diameter and 30 μm thickness mounted between the two opposed 300 μm diamond culets of the Letoullec-type membrane-driven diamond-anvil cell [Letoullec *et al.*, 1998]. Pressures were measured by the ruby fluorescence method [Piermarini *et al.*, 1975], both before and after collection of each diffraction pattern; exposure to the X-ray beam was typically of 20 seconds duration per pattern.

[6] Diffraction patterns were collected on a Mar345 image plate detector, to which the distance was calibrated using a Si standard placed at the sample position. The integrated 2 θ -I patterns were obtained after correction for detector distortion and tilt using the Fit2D package, Hammersley *et al.* [1995]. The patterns were subsequently fitted to obtain unit-cell volumes by the LeBail technique using

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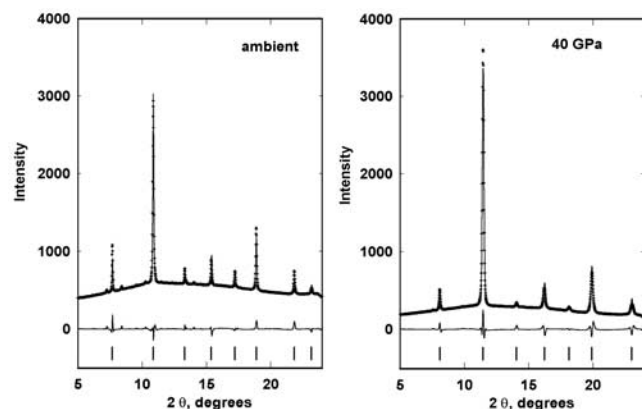


Figure 1. Diffraction patterns collected at 0 and 40 GPa. The data are represented by dots and the solid lines are the fits. Ticks are for CsCl-FeSi reflections. The lower traces are the difference plots.

the GSAS suite of programmes [Larson and Von Dreele, 1994].

3. Results

[7] Diffraction patterns collected between 1 atmosphere and 40 GPa pressure are presented in Figure 1. Reflections of CsCl-FeSi are dominant between all pressures and peak broadening at high pressure is small, indicating that non-hydrostatic stresses on the sample are small. The small reflection around 7.3° is from excess iron-bearing phases from the starting material [Dobson *et al.*, 2002]. The P - V data were fitted to a Birch-Murnaghan (BM) [Birch, 1978] equation of state using the EOS-Fit programme [Angel, 2000]. The second order fit yields $V_0 = 21.76 \pm 0.02 \text{ \AA}^3$, with a K_0 of $187 \pm 2 \text{ GPa}$. A third order fit is indistinguishable to 40 GPa, with $V_0 = 21.74 \pm 0.02 \text{ \AA}^3$, $K_0 = 194 \pm 6 \text{ GPa}$ and $K'_0 = 3.6 \pm 0.4$. Both fits reproduce the observed V_0 to within the experimental error. The P - V data are plotted, with the second and third order BM EOS fits in Figure 2. It can be seen that there is some discrepancy between the data and both fits at around 15 GPa. The f - F plot [e.g.; Angel, 2000] (Figure 2, inset) clearly shows that there is anomalous strain in these measurements. It is possible that this is related to the phase changes in the nitrogen pressure medium which occur in this pressure range [e.g.; Olijnyk, 1990]. Alternatively, the excess compression around 15 GPa may be genuine and related to a magnetic transition similar to that observed in Fe-Ni alloys [Dubrovinsky *et al.*, 2001]. Despite the errant data around 15 GPa, the f - F plot can be fitted within error with a second order BM EOS. In order to assess the effect of these data, we refitted the data excluding the 13, 15 and 17 GPa values. A third order BM fit to the remaining subset yields $V_0 = 21.74 \pm 0.02 \text{ \AA}^3$, $K_0 = 184 \pm 5 \text{ GPa}$ and $K'_0 = 4.2 \pm 0.3$. We conclude, therefore, that the pressure derivative of the bulk modulus, K'_0 , is close to 4 and that a second order BM EOS fits the present data to 40 GPa.

[8] The measured bulk modulus of CsCl-FeSi is some 5–15% larger than most previous measured values for ϵ -FeSi [Sarrazo *et al.*, 1994; Wood *et al.*, 1995; Guyot *et al.*, 1997], although Knittle and Williams [1995] measured a much

higher bulk modulus, $209 \pm 6 \text{ GPa}$. In addition, the pressure derivative of the bulk modulus is larger than measured values for ϵ -FeSi by some 30%. This behaviour of K' is in broad agreement with the zero Kelvin *ab initio* calculations results of Vočadlo *et al.* [1999], although it should be noted that they predict much larger bulk moduli for both the ϵ - and CsCl-structures.

4. Implications for the Earth's Core

4.1. Silicon in the Inner Core

[9] We now address the question of whether silicon can be a major constituent of the Earth's inner core. In order to

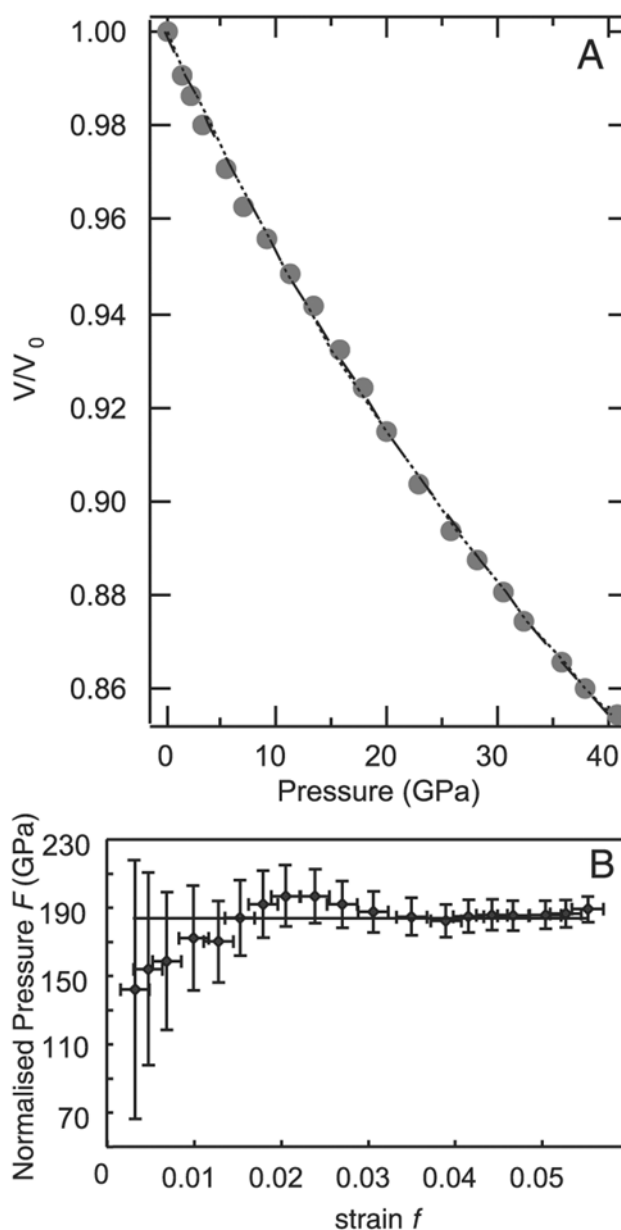


Figure 2. (A) Pressure-volume plot for CsCl-FeSi. Second- and third-order Birch-Murnaghan fits are indistinguishable within the experimental pressure range (dashed and dotted lines, respectively). A K'_0 of 4 is consistent with the f - F plot (B).

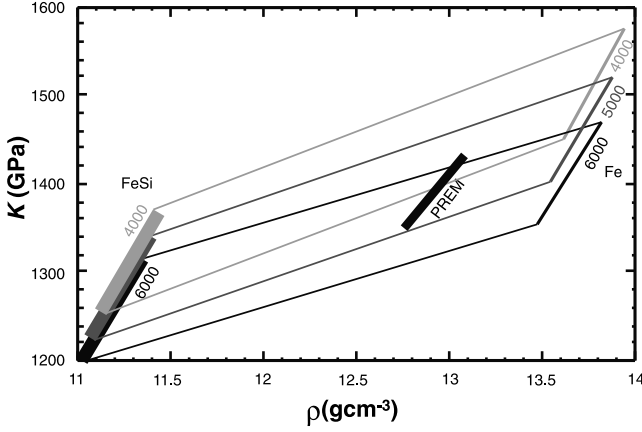


Figure 3. Plot of K_s versus ρ for CsCl-FeSi and Fe at 329–364 GPa and 4000, 5000 and 6000 K. The thickness of the lines for FeSi represents the uncertainty introduced by allowing the Grüneisen parameter, γ , to vary between 1 and 2. The PREM values lie between the values of iron and FeSi for 5000 and 6000 K isotherms and are consistent with an inner core containing 14 at % silicon.

compare our results with the PREM model, we have extrapolated the measured CsCl-FeSi EOS to outer core conditions: the experimental P - V curve was first extrapolated to outer core pressures along a 300 K isotherm. This 300 K P - V curve was then thermally expanded to 4000, 5000 and 6000 K. We assumed a value for the thermal expansivity of CsCl-FeSi of $4.5 \times 10^{-5} \text{ K}^{-1}$ at 1 atmosphere, close to that of iron and ϵ -FeSi [Vočadlo *et al.*, 2002a], and estimated the effect of pressure on α , using the Anderson-Grüneisen parameter for pure Fe [Wood, 1993; Fei, 1995], to be:

$$\left(\frac{d \ln \alpha}{d \ln V}\right)_T \approx 6.5 \quad (1)$$

[10] This yields thermal expansivities of 3 to $6 \times 10^{-6} \text{ K}^{-1}$ under core conditions, close to the values used in previous studies [Williams and Knittle, 1997; Vočadlo *et al.*, 2002b]. Refitting the resultant high-temperature P - V curves to 3rd order BM equations of state we obtain K_T and ρ under inner core P - T conditions. The PREM bulk moduli are adiabatic so we must convert our K_T using:

$$K_s = (1 + \alpha \gamma T) K_T \quad (2)$$

where γ is the Grüneisen parameter (assumed between 1 and 2 for the inner core). Values of K_s and ρ for Fe under inner core conditions were obtained, using a similar procedure, from the 0 K EOS of hcp-Fe of Alfè *et al.* [2000], with $\alpha_0 = 6 \times 10^{-5} \text{ K}^{-1}$ and γ between 1 and 2. These values of α and γ are similar to recent experimental determinations [Anderson *et al.*, 2001; Dubrovinsky *et al.*, 2000a, 2000b]. Figure 3 shows a plot of K_s versus ρ for CsCl-FeSi, hcp-Fe and PREM, under inner core conditions. It is readily seen that CsCl-FeSi has a too low density and bulk modulus to be the main inner core phase. However, the PREM values lie between the values of FeSi and hcp-Fe. Linear interpolation between values for iron and FeSi suggests that a predominantly iron inner core at

5000–6000 K, containing approximately 14 at % Si, would satisfy the PREM constraints on density and bulk modulus.

4.2. Silicon in the Outer Core

[11] Given that Si is a possible major element in the inner core, we now re-examine the method of Williams and Knittle [1997] for assessing the compatibility of different iron/light element mixtures with outer core elastic properties. On the basis of the observation that the outer core according to the PREM model has a nearly identical pressure derivative of its sound velocity, V_p , to that of pure liquid iron, these authors note that the effect of the light element on dV_p/dP for liquid iron must be nearly zero. Expressing dV_p/dP in terms of ρ , K and K' , Williams and Knittle [1997] suggest that K' and $(K\rho)^{1/2}$ of an alloy under outer core conditions must be close to the PREM values in order for the alloying element to be a candidate major light element. Using this test, they suggest that silicon cannot be the main light element in the outer core, because of the low value of K' observed in ϵ -FeSi. The underlying assumptions in this analysis are: 1) that the EOS and physical properties of the solid and liquid Fe-alloys are similar, 2) a linear mixing relationship between Fe and its alloys, and 3) the phase in question is the stable phase under outer core pressures. ϵ -FeSi is, however, not the stable phase at high pressure.

[12] We believe that the grounds for assumption 1, at least, are doubtful, bearing in mind the difference in primary coordination numbers of solid ϵ -FeSi (7), CsCl-FeSi (8) and liquid Fe 13; [Alfè *et al.*, 2002]. We have, nevertheless, performed a similar analysis for CsCl-FeSi in order to compare the results with those obtained previously

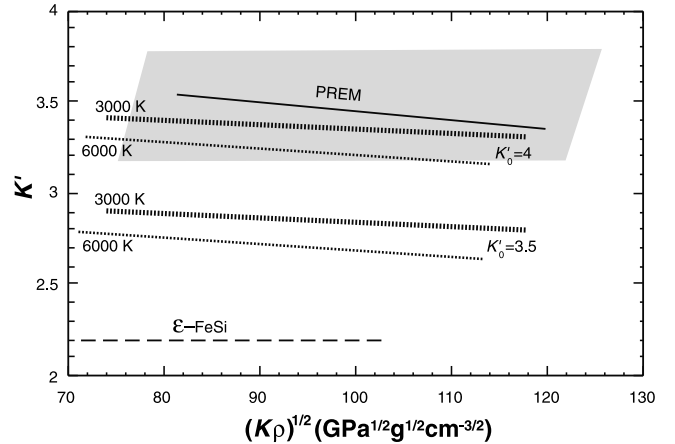


Figure 4. Outer core discriminator plot (K' versus $(K\rho)^{1/2}$), after Williams and Knittle [1997]. Alloys of Fe with O, S and H fall within the shaded region and are compatible with the PREM outer core values (solid line). The Knittle and Williams [1995] values for ϵ -FeSi (thin dashed line) have a significantly too low K' . Values for CsCl-structured FeSi are shown as thick dashed lines. The line thickness encompasses errors introduced from uncertainties in α and γ (see text for details). The CsCl-FeSi curve predicted using our preferred K'_0 of 4 is compatible with the PREM values; the curve for $K'_0 = 3.5$ falls between the allowable PREM K' and that of ϵ -FeSi from Williams and Knittle [1997].

[Williams and Knittle, 1997]. High-pressure EOS at 3000–6000 K were derived using the approach outlined above and the resulting values used to construct Figure 4. The shaded region in Figure 4 represents the range of values obtained for FeO, FeS and FeH, and considered to be consistent with PREM, by Williams and Knittle. In contrast, their estimate based on the EOS of ϵ -FeSi [Knittle and Williams, 1995] falls well outside the acceptable range, with a K' close to 2. Our values for CsCl-FeSi with a K'_0 of 4 fall within the shaded region and are consistent with the PREM model of outer core properties. The effect of uncertainties in thermal parameters, α and γ , is small compared to the effect of the uncertainty in K'_0 . Decreasing K'_0 to 3.5, the value obtained in the third order BM fit to the full dataset, results in high-pressure values of K' outside the acceptable range for candidate outer core major light elements, but still significantly higher than Williams and Knittle's value for ϵ -FeSi.

5. Summary and Conclusion

[13] We have measured the compressibility of CsCl-structured FeSi to 40 GPa and find it to have a near-second order equation of state with $V_0 = 21.74 \pm 0.02 \text{ \AA}^3$, $K_0 = 184 \pm 5 \text{ GPa}$ and $K'_0 = 4.2 \pm 0.3$. Silicon cannot currently be ruled out as a major light element in the Earth's core on the basis of the equation of state of CsCl-FeSi. We note, however, that higher quality data, preferably to higher pressure are needed to better constrain K'_0 .

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