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LETTER TO THE EDITOR

Compressibility of FeSi between 0 and 9 GPa, determined by high-pressure time-of-flight neutron powder diffraction

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Abstract. The cell parameter of cubic iron monosilicide, ϵ -FeSi, has been determined at 25 pressures between 0 and 9 GPa by time-of-flight neutron powder diffraction, using the POLARIS diffractometer at the ISIS spallation neutron source. NaCl was used as an internal pressure standard. Fitting of the data to a third-order Birch–Murnaghan equation of state with K'_0 fixed at a value of 4.0 gave an isothermal bulk modulus, K_0 , of 160(1) GPa.

Direct observation of the Earth's core is not possible and so its composition, structure and properties must be inferred from geophysical and geochemical data. The physical properties of iron–silicon compounds are, therefore, of considerable interest to geophysicists, since silicon (together with oxygen, carbon, hydrogen and sulphur) has been proposed as a major alloying element in the outer core. Very recently, two determinations of the compressibility of the cubic iron monosilicide, ϵ -FeSi, by x-ray diffraction have been reported, with unfortunately rather contradictory results. In the first [1], a diamond-anvil cell and angle-dispersive x-ray powder diffraction were used to determine the lattice parameter of FeSi to pressures of 50 GPa; the bulk modulus derived from these data was 209(6) GPa. This value is much higher than that which has been reported for iron [2], 165(4) GPa, leading the authors to the conclusion that, like oxygen but unlike sulphur [3, 4], silicon produces a stiffening of iron-rich alloys by an amount sufficiently large to prompt their suggestion that silicon might, therefore, be excludable as a major outer core alloying element on geophysical grounds alone. In the second very recent study of FeSi [5], energy-dispersive x-ray powder diffraction was used, together with a multi-anvil press, to pressures of 10 GPa. A bulk modulus of 172(3) GPa was obtained at ambient temperature, a value which differs from that given in [1] by far more than would be expected on the basis of the quoted experimental errors. Single-crystal ultrasonic measurements of the ϵ -FeSi phase have also been reported [6, 7], leading to values of the bulk modulus of 115 GPa and 173 GPa respectively; the former is much lower than that of iron and agrees with neither of the diffraction experiments, whilst the latter agrees extremely well with [5]. No other compressibility measurements for the monosilicide have been made but a number of experiments (reviewed in [1]) have been carried out for materials of composition $\text{Fe}_{1-x}\text{Si}_x$, with $0.05 < x < 0.4$, leading to bulk moduli in the range 115–250 GPa. It is clear that more experimental work is required to resolve these contradictions. In this letter we report the results of a time-of-flight powder neutron study carried out at the ISIS spallation neutron source, using the Paris–Edinburgh high-pressure cell on the POLARIS diffractometer.

ϵ -FeSi has space group $P2_13$, with four formula units per cell; the Fe and Si atoms both occupy sites of type 4a (x, x, x), with coordinates $x_{Fe} = 0.137(2)$ and $x_{Si} = 0.842(4)$ [8]. The compound is unusual in that each atom is in sevenfold coordination. The material used in the present study (obtained from the Technical Glass Company, Cambridge) had been prepared by reaction of a stoichiometric mixture of iron (99.998% purity) and silicon (99.9999% purity) under argon gas. The powder sample was prepared by breaking the boule supplied in a percussion mortar, sieving the resulting material through a 30 mesh (0.5 mm) sieve, and grinding this fraction for five minutes with distilled water in a McCrone micronizing mill using agate grinding elements. An x-ray powder diffraction pattern of this material, collected using a Philips PW1050 vertical goniometer with Fe-filtered $\text{CoK}\alpha$ radiation, showed little evidence of any impurity phases, though there was possibly a very small peak (less than 0.4% in height relative to the strongest peak in FeSi) at about 1.15 Å, a d -spacing corresponding to the strongest reflections from Fe_2Si and Fe_3Si . Rietveld refinement of the x-ray data gave a cell parameter at ambient temperature of 4.486 88(6) Å and fractional coordinates $x_{Fe} = 0.1363(5)$ and $x_{Si} = 0.8441(5)$, which were in excellent agreement with those previously reported by single-crystal x-ray diffraction [8].

The neutron diffraction sample was prepared by mixing FeSi and NaCl in the ratio 1:2 FeSi:NaCl by weight. A pellet containing 252 mg of this mixture was then formed and placed in the pressure cell. In essence, the cell [9] consists of two opposed, hydraulically driven, toroidal, tungsten carbide anvils giving quasi-spherical compression of the sample, which is contained within a Ti-Zr alloy 'null scattering' gasket. The pressure cell was mounted on the POLARIS powder diffractometer at ISIS [10], a high-flux, medium-resolution instrument. The diffracted neutrons were measured using a detector bank at 90° to the incident beam, with the cell aligned such that the incident beam passed along the axis of one of the anvils and the diffracted beam exited through the gasket. Data with flight times between 2.5 and 14 ms were used in the refinement, corresponding to a d -spacing range of 0.56–3.12 Å. This range of spacings allows the use (at ambient pressure) of reflections with Miller indices in the range 111 to 810 for FeSi and 200 to 1000 for NaCl. Data were collected at 25 points between 0 and 9 GPa; each data set took approximately 90 minutes to collect.

The analysis of the diffraction patterns was carried out using the in-house software available at ISIS, based on the Cambridge Crystallography Subroutine Library (CCSL) [11, 12, 13]. Multi-phase Rietveld refinement was used to obtain the cell parameters shown in table 1. A total of 16 parameters were included in the refinements, the cell parameter and two halfwidth parameters for both FeSi and NaCl, an overall temperature factor, the two positional parameters for FeSi, an overall scale factor, a factor related to the amount of each phase present in the mixture and five background parameters. The weighted profile R -factors for the refinements increased steadily from about 7% at low pressures to 10% close to 9 GPa, reflecting the poorer counting statistics of the patterns. As might be expected for such simple structures, it was found that the cell parameters were very insensitive to changes in the other variables and, therefore, these are not reported here (for example, refinements made with the positions of the Fe and Si atoms fixed gave cell parameters which differed always by less than one standard deviation from those shown in table 1). Similarly any magnetic contribution to the diffracted intensity could be safely neglected. Some weak peaks from the WC anvils of the pressure cell were present in the diffraction pattern and the regions containing the two strongest of these were omitted during the refinements; again, however, this was found to make a negligible difference to the cell parameters. The value of the cell parameter measured with the sample in the cell at nominally atmospheric pressure agrees fairly well with that determined by x-ray diffraction, with the difference, which is a

Table 1. Cell parameters of FeSi and NaCl as a function of pressure. Figures in parenthesis are estimated standard deviations, referring to the least significant figures (the data are generally reported here to one more significant figure than is merited by the precision of the results, so as to ensure that any values derived from them will not be affected by rounding errors). The precisions of the pressures quoted were derived on the assumption that the Dekker equation of state for NaCl [13] is exact, i.e. they reflect only the inaccuracy of the present experiment.

| a (Å) (FeSi) | a (Å) (NaCl) | P (GPa) |
|----------------|----------------|-----------|
| 4.485 52(30) | 5.638 22(24) | 0 |
| 4.483 38(37) | 5.620 46(29) | 0.230(5) |
| 4.479 18(33) | 5.589 01(26) | 0.666(5) |
| 4.472 15(40) | 5.548 00(32) | 1.292(7) |
| 4.468 10(41) | 5.525 06(33) | 1.674(7) |
| 4.467 44(43) | 5.512 98(32) | 1.883(7) |
| 4.463 30(41) | 5.486 78(33) | 2.365(8) |
| 4.460 39(42) | 5.472 82(34) | 2.637(8) |
| 4.456 73(46) | 5.454 43(38) | 3.006(9) |
| 4.453 01(49) | 5.430 79(39) | 3.511(10) |
| 4.448 63(51) | 5.409 84(38) | 3.983(10) |
| 4.445 29(57) | 5.388 68(40) | 4.489(12) |
| 4.441 74(55) | 5.371 85(40) | 4.912(12) |
| 4.438 29(62) | 5.353 17(43) | 5.402(13) |
| 4.432 55(58) | 5.333 62(41) | 5.937(13) |
| 4.430 73(67) | 5.321 39(43) | 6.285(14) |
| 4.426 51(65) | 5.306 14(44) | 6.741(15) |
| 4.424 72(64) | 5.294 80(43) | 7.088(15) |
| 4.424 50(62) | 5.296 12(44) | 7.047(15) |
| 4.425 19(59) | 5.293 01(44) | 7.144(15) |
| 4.421 52(64) | 5.283 44(47) | 7.445(17) |
| 4.418 21(73) | 5.272 89(57) | 7.787(20) |
| 4.415 37(76) | 5.259 41(52) | 8.240(20) |
| 4.413 26(84) | 5.250 48(53) | 8.548(20) |
| 4.411 91(87) | 5.240 85(52) | 8.884(20) |

little greater than that expected on the basis of the errors quoted, possibly being due in part to the material in the cell being slightly compressed. Although, in the neutron experiment, the Bragg reflections from both phases remained sharp up to the highest pressure observed, there was an increase in their halfwidths of about 30%, possibly indicative of some inhomogeneity in pressure. The pressure values shown in table 1 were obtained by linear interpolation of the equation of state for NaCl [14], assuming a temperature of 25 °C throughout.

Figure 1 shows the observed and calculated unit-cell volume of FeSi. The calculated values were obtained by fitting the data, using non-linear least squares, to a third-order Birch–Murnaghan equation of state [15, 16], of the form

$$P = (3K_0/2)[(V_0/V)^{7/3} - (V_0/V)^{5/3}][1 + 0.75(K'_0 - 4)[(V_0/V)^{2/3} - 1]] \quad (1)$$

where K_0 is the isothermal bulk modulus and K'_0 its first derivative with respect to pressure. The values of the parameters obtained are listed in table 2. Since these values are to some extent sensitive to the weighting scheme used in the least-squares fitting, we have also applied the same procedure to the data given in [1], obtaining results which are very similar to those published (see table 2), thus indicating that our value of the bulk modulus should be directly comparable with those reported previously. Because of the relatively restricted pressure range of the present experiment it was found that the refinement of our data in which K'_0 was allowed to vary led to a rather high value, 7.7(9), for this variable, which

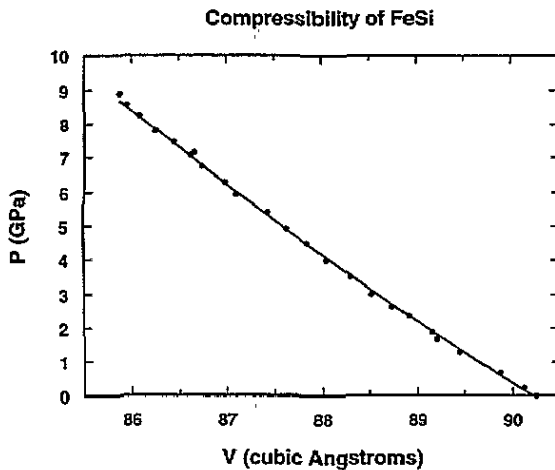


Figure 1. Unit-cell volume (\AA^3) of FeSi as a function of pressure (GPa). Experimental values are shown as dots; error bars on both P and V axes are smaller than the symbol (see table 1). The line shows a Birch-Murnaghan equation with $V_0 = 90.21 \text{ \AA}^3$, $K_0 = 160 \text{ GPa}$ and $K'_0 = 4.0$ (see table 2).

was also only poorly determined, having a correlation coefficient of 96% with respect to K_0 ; typically K'_0 lies in the range $3.5 < K'_0 < 5.5$ [16]. We prefer, therefore, to adopt the procedure used in [5] and fix K'_0 at a value of 4.0, equivalent to using a second-order Birch-Murnaghan equation.

Table 2. Values of isothermal bulk modulus for FeSi.

| | V_0 (\AA^3) | K_0 (GPa) | K'_0 | GOF ^a |
|---------------------------|--------------------------|-------------|------------------|------------------|
| Present work | 90.25(1) | 147(3) | 7.7(9) | 0.0062 |
| Present work | 90.21(2) | 160(1) | 4.0 ^b | 0.0087 |
| Data taken from [1] | | 212(5) | 3.6(5) | 0.937 |
| fitted to equation (1) | | 209(2) | 4.0 ^b | 0.686 |
| Values as reported in [1] | | 209(6) | 3.5(4) | |
| Values as reported in [5] | | 172(3) | 4.0 ^b | |

^a Equation (1) was fitted in the form $P = f(V)$, with the goodness of fit $= \sum_i (P_{i,obs} - P_{i,calc})^2 / (N - M)$, where N is the number of observations and M the number of variable parameters.

^b Parameter fixed at value shown.

The value we obtain for K_0 , 160(1) GPa, is in reasonable agreement with one of the previous determinations by x-ray diffraction (172(3), [5]), although the difference between the two is a little larger than that which would be expected solely on the basis of random experimental error. It also agrees well with the most recent ultrasonic measurements [7]. If correct, these results imply that, at ambient conditions, the compressibility of ϵ -FeSi is very similar to that of pure iron. The agreement with the other x-ray determination (209(6), [1]) is very poor. These discrepancies may be due to significant systematic errors in some or all of the experiments, to real differences in the behaviour of the three different samples, or to failure of the material to obey the Birch-Murnaghan equation, thereby giving a value of K_0 which is dependent on the pressure range covered. This latter possibility seems unlikely, however, to explain the much larger value of K_0 reported in [1], since

if analysis of their results is limited to data at pressures less than 1.5 GPa a value of K_0 of 215 GPa is obtained. We believe that the present experiment represents the most precisely determined cell parameters of FeSi so far reported. Ideally, it would be desirable to extend our neutron diffraction measurements to pressures above 10 GPa but facilities for this are not yet available. It is interesting to note that powder neutron diffraction, for many years considered to be much slower and less precise than x-ray measurements, can now offer significant advantages for the study of equations of state. In particular, time-of-flight neutron diffraction uses fixed scattering geometry (fixed 2θ) and the powder pattern is measured (and subsequently analysed) over a wide range of d -spacings, with minimal contamination by Bragg peaks from the components of the pressure cell. Furthermore, the resolution $\Delta d/d$ is essentially independent of d -spacing, allowing low-index reflections to be used in the determination of the cell parameters. This contrasts very favourably with the situation which obtains in angle-dispersive x-ray diffraction, where to obtain good precision requires the use of high-angle reflections which are often weak. Similarly, with modern neutron sources and diffractometers the amounts of sample and time required are now greatly reduced. The present experiment, for example, required only about 80 mg of FeSi and a time of 90 minutes per data point. Again, this compares favourably with x-ray photographic powder diffraction using diamond cells in which exposures of 24 h or more may be needed [1].

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