



## The NiSi melting curve to 70 GPa



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### ABSTRACT

The melting curve of NiSi has been determined to 70 GPa on the basis of laser-heated diamond anvil cell (LH-DAC) experiments in which changes in the gradient of temperature vs. laser power functions were used as the melting criterion. The melting curve was corroborated with *in situ* X-ray diffraction experiments in both the LH-DAC and multi-anvil press in which the appearance of liquid diffuse scattering in the diffraction patterns was used as the melting criterion. At all pressures, the NiSi melting curve is lower than that of FeSi, with the difference in melting temperature reaching a maximum of 900 K at 14 GPa. The location of the B31 + B20 + L triple point has been constrained to  $12 \pm 2$  GPa and  $1550 \pm 100$  K and the B20 + B2 + L triple point to  $28.5 \pm 1.5$  GPa and  $2165 \pm 60$  K. On the basis of the *in situ* LH-DAC experiments the Clapeyron slope of the B20 → B2 transition is estimated at  $-67 \text{ MPa K}^{-1}$ . Extrapolation of the B2-NiSi liquidus to core-mantle boundary (CMB) conditions (135 GPa) suggests the melting point of NiSi ( $3700 \pm 400$  K) will be only marginally lower than that of isostructural FeSi ( $4000 \pm 200$  K). Thus any (Fe,Ni)Si solid solution present within the D' layer is expected to remain solid, with the possible exception of the very hottest region adjacent to the CMB.

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## 1. Introduction

Historically, the primary interest in nickel monosilicide (NiSi), an intermediate compound along the Ni–Si binary (Massalski et al., 1990), owed to its usefulness as a contact material in micro-electronic devices (see e.g. Lavoie et al., 2006). Consequently, NiSi was studied extensively at the conditions at which these devices are manufactured and operated, i.e. at ambient conditions (e.g. Connétable and Thomas, 2009) and at high temperatures (e.g. Detavernier et al., 2003), where NiSi has the MnP (B31) structure. In contrast, we are interested in NiSi because of its position as an end-member in the Fe–Ni–Si system, of relevance to the cores of the terrestrial planets, not least that of Earth. Geochemical models based on cosmochemical arguments suggest that Earth's core could contain at least 5 wt.% nickel (e.g. Allègre et al., 1995) and up to

20 wt.% silicon (e.g. Allègre et al., 1995; Fischer et al., 2012; Balchan and Cowan, 1966). Attempts to reconcile experimental measurements of sound velocities with 1-D seismic profiles (Badro et al., 2007) suggest that silicon is an effective candidate for the light element required to explain Earth's core density deficit. More recent *ab initio* determinations of sound velocities in FeSi exclude silicon as an inner core component (Ono, 2013). However, this conclusion depends on the temperature at the inner core boundary (ICB) being less than 6500 K, which is within error of current estimates and thus may be in doubt (Anzellini et al., 2013; Sola and Alfè, 2009) and on the absence of any strong pre-melting effects (Martorell et al., 2013). Recent measurements indicating that the silicon of the bulk silicate Earth is isotopically heavy relative to the chondritic meteorites from which Earth is postulated to have formed, lends further credence to the argument for a significant silicon reservoir within the core (Armytage et al., 2011). As a result, several studies have been published concerning the sub-solidus phase relations (e.g. Sakai et al., 2011) and melting behavior (e.g. Morard et al., 2011) of a range of ternary alloys within the Fe–Ni–Si system. The phase diagram of the FeSi end-member has also been extensively studied (Lord et al., 2010;

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Santamaría-Pérez and Boehler, 2008; Dobson et al., 2002; Vočadlo et al., 1999; Guyot et al., 1997), as have the physical properties of its constituent phases (e.g. Sata et al., 2010; Dobson et al., 2003; Vočadlo et al., 1999). Recently, we began an ongoing effort to study the NiSi end-member, the behavior of which was entirely unknown at the high-pressure, high-temperature conditions relevant to the interior of the Earth. These efforts include static *ab initio* simulations that predicted a multitude of new high-pressure phases at 0 K (Vočadlo et al., 2012) and complementary laser-heated diamond anvil cell (LH-DAC) experiments (Lord et al., 2012) in which at least two of these were detected: the  $\epsilon$ -FeSi (B20) structure and the CsCl (B2) structure. Both studies also reported equations of state (EoS) for these structures as well as for the room pressure phase, at 0 K (for the *ab initio* study), and 300 K (for the LH-DAC study). A third installment (Wood et al., 2013) reported the discovery of another high-pressure phase, with space group *Pmmn*, in multi-anvil press (MAP) experiments together with *ab initio* simulations of this new structure, including a 0 K EoS. The present study, in which the melting curve of NiSi is reported, forms a further part of this ongoing effort; it is accompanied by Dobson et al. (Submitted for publication) in which the sub-solidus phase relations of NiSi are described using off-line and *in situ* MAP experiments, in combination with the *in situ* LH-DAC experiments described here.

Our primary motivation for studying the NiSi melting curve is to provide vital data for those involved in continuing efforts to produce accurate thermodynamic descriptions of core liquids. The composition of these liquids falls within a multi-component system, and their physical properties can be determined by interpolation from the system end-members if the relevant physical properties of those end-members are known. For example, by using the melting curves and room temperature EoS of the end-members in the Fe–O–S system, Helffrich (2011) and Helffrich & Kaneshima (2010; 2004) constructed a thermodynamic model and calculated sound velocities for a range of possible core liquids, and then constrained the composition of the liquid outer core by comparison with seismically determined wave speeds. To make these models more realistic, additional components must be added to the compositional space, with nickel and silicon being the most important. This requires a more extensive database of end-member physical properties, with FeSi and NiSi being of primary importance. For both FeSi and NiSi it is the B2 (CsCl) structured phase that is likely to be relevant at the conditions of the deep Earth (Lord et al., 2012, 2010). The room temperature EoS and melting curve of B2-FeSi (Sata et al., 2010; Lord et al., 2010) and the EoS of B2-NiSi (Lord et al., 2012; Vočadlo et al., 2012) are already known; the melting curve of NiSi is the subject of this study.

Additionally, we wanted to determine the effects of nickel on FeSi at the conditions of Earth's core mantle boundary (CMB) region. Solid B2 structured FeSi may well be present within Earth's lowermost mantle (the  $D''$  layer; Lord et al., 2010). All pathways for the formation of FeSi involve the iron-rich alloy of the underlying core, and so, given the expected solid solution between the isostructural NiSi and FeSi phases, we would expect any silicide present to be iron-rich (Fe,Ni)Si in the B2 structure (Lord et al., 2012). Knowing the melting curve for NiSi will give an additional constraint on the stability of this material within  $D''$ , which depends on its melting curve being above the geotherm.

Finally, this study is a further test of the accuracy of our primary method for determining melting in the LH-DAC, namely the observation of changes in the gradient (i.e. plateaux) of temperature vs. laser power curves. This method has been successfully adopted on a number of occasions (Asanuma et al., 2010; Lord et al., 2010, 2009) but the underlying cause behind the observed plateaux is still poorly understood (Geballe and Jeanloz, 2012) leading to inevitable

questions about its reliability. To address this issue, we present here not just off-line LH-DAC melting data using this method, but also *in situ* experiments, in both the LH-DAC and the MAP in which melting can be observed directly from the appearance of liquid diffuse scattering (LDS) in X-ray diffraction (XRD) patterns acquired at simultaneous high-pressure, high-temperature conditions, and even from visual identification of convective motion during *in situ* X-radiography.

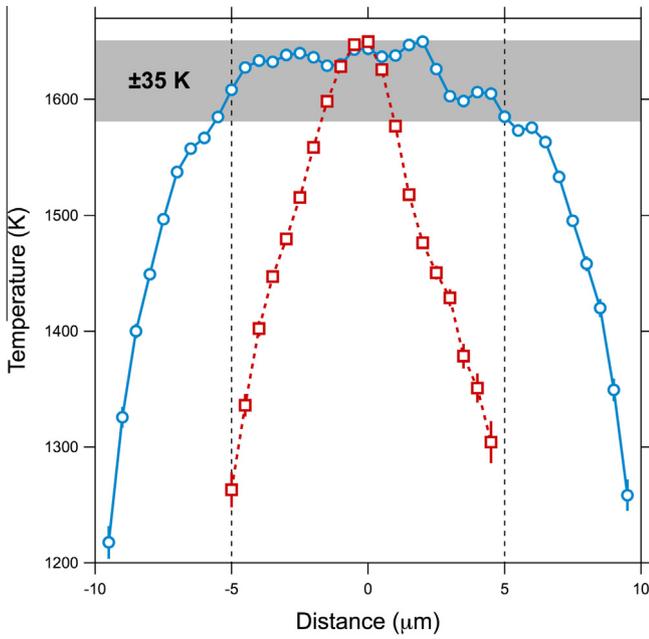
## 2. Methods

This study consists of three sets of NiSi melting experiments. The first (see Section 2.1) was performed off-line in the LH-DAC at the School of Earth Sciences, University of Bristol. The second (see Section 2.2) consists of a pair of LH-DAC experiments coupled with *in situ* XRD measurements at beam line ID-27 of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The final set (see Section 2.3) consists of a single MAP experiment, again coupled with *in situ* XRD and X-radiography measurements, at beam line X17B2 of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, New York, USA. The NiSi starting material was from the batch used in Lord et al. (2012). Additionally, two off-line experiments at Bristol were performed on an Fe<sub>85</sub>–Ni<sub>5</sub>–Si<sub>10</sub> alloy (subscripts are in wt.%), from the batch used in Morard et al. (2011).

### 2.1. Off-line LH-DAC melting experiments, University of Bristol

These experiments were performed in Princeton-type symmetric DACs using anvils with 200–250  $\mu\text{m}$  diameter culets. Rhenium gaskets were used, pre-indented to 25 GPa and drilled centrally to create a sample chamber  $\frac{1}{3}$  the diameter of the culet. Between 1 and 5 densified foils (Lord et al., 2012) of the starting material, 10–40  $\mu\text{m}$  in diameter and 5–10  $\mu\text{m}$  thick, were loaded into the sample chamber between discs of NaCl the same diameter as the sample chamber and  $\sim 15$   $\mu\text{m}$  thick. These form-fitting discs, which act as both pressure medium and thermal insulation, were cut using an automated UV (266 nm) laser ablation unit (New Wave Research, LUV series) from sheets produced by compressing powder, either between a pair of diamond anvils or between steel plates in a hydraulic press. Form-fitting pressure media eliminate void space in the sample chamber, helping to maintain the sample geometry during compression. In addition, this ensures a near identical thickness of insulation on either side of the sample, which makes equalizing the temperatures on the two sides by varying the laser power significantly easier. Several sub-micron Cr:Al<sub>2</sub>O<sub>3</sub> (ruby) grains were placed between the sample and NaCl on one side, to allow the pressure to be monitored by ruby fluorescence spectroscopy before and after heating. Each cell was held for 1 h under a N<sub>2</sub> atmosphere at 120 °C before being sealed under the same conditions to remove any adsorbed water.

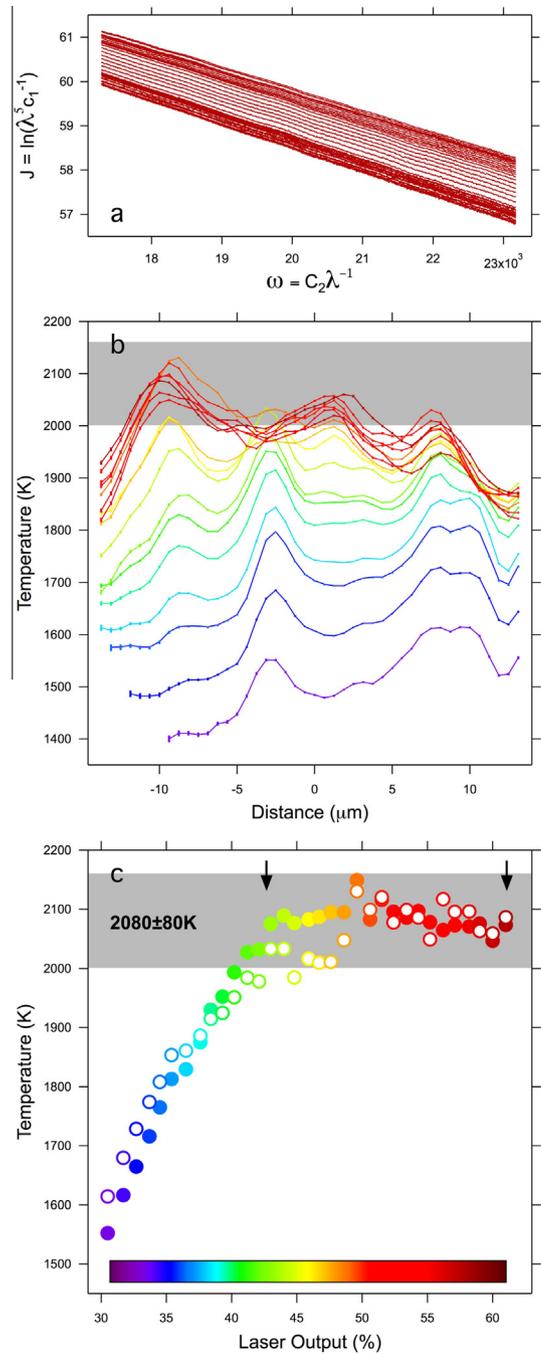
Once at pressure, samples were heated in a double-sided geometry using two 100 W diode pumped TEM<sub>00</sub> (Gaussian mode) fiber lasers (model R4, SPI lasers Ltd., Southampton, UK) operating at 1070 nm. If used in their raw state, the Gaussian energy distribution of the lasers inevitably results in strong Gaussian temperature gradients on the sample surface (Fig. 1) that can lead to overestimates of temperature when measured using spectroradiometry due to chromatic aberration imparted by the refractive optics (Walter and Koga, 2004). Furthermore, strong temperature gradients increase the sensitivity of the measured temperature to misalignment of the emitted light with the aperture of the spectrometer and so can result in underestimates of temperature. Finally, they can promote thermally induced (Soret) diffusion in the sample (Sinmyo & Hirose et al., 2010). To minimize these problems, we



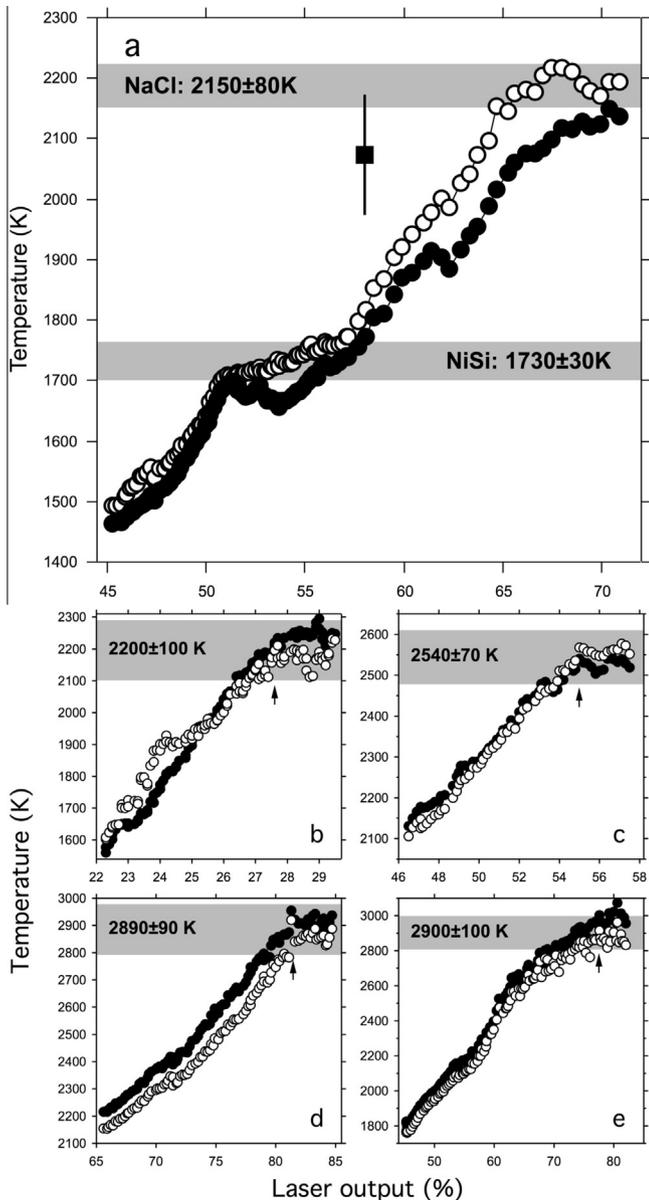
**Fig. 1.** (a) Temperature cross-sections measured by spectroradiometry across an NiSi sample at 25 GPa. The beam shaping optics used in the present study produce relatively isothermal conditions over wide areas ( $\pm 35$  K over 10  $\mu\text{m}$ ; blue circles); without them, much larger gradients are created by the Gaussian energy profile of the laser (red squares). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

have employed beam-shaping optics (focal- $\pi$ Shaper, AdlOptica, Berlin, Germany), which convert the Gaussian energy distribution into a distribution with a flat-topped profile (Fig. 1; Prakapenka et al., 2008). Subsequent variable beam expansion optics (model 56-30-2-8X, Special Optics Inc., New Jersey, USA) allow the diameter of the spot to be varied up to  $\sim 30$   $\mu\text{m}$ .

Long working distance infinity-corrected apochromatic near infra-red objective lenses (M Plan Apo NIR 10 $\times$ , Mitutoyo) were employed to focus the laser light onto and collect the incandescent light from the sample. These lenses absorb a small proportion of the IR radiation causing them to heat up, flex, and change their focal length. Consequently we have found it necessary to water cool the lenses as well as the LH-DAC. These lenses significantly reduce chromatic aberration compared to the optics used in previous studies (Fig. 2a; Lord et al., 2010, 2009). As a result, it is no longer necessary to eliminate the most aberrant non-paraxial rays using f-stops, thus making temperature measurement feasible at lower temperatures (down to 1400 K). While the shorter focal length of these objectives increases the magnification (50 $\times$  vs. 20 $\times$  previously) and ideal system resolution (0.5  $\mu\text{m}$  vs. 1.25  $\mu\text{m}$  previously), the system is diffraction limited to 1.0–1.5  $\mu\text{m}$  across the spectral range available for temperature fitting (570–840 nm). This is confirmed by measurement of the width of a sharp interface focused onto the CCD, which indicates an actual resolution of  $\sim 1$   $\mu\text{m}$ . Optical aberrations, especially of the chromatic variety, reduce the effective spectroradiometric resolution further (Walter and Koga, 2004). On the basis of the measured focal deviations of our system (a maximum of  $\sim 10$   $\mu\text{m}$  at the image plane over the 200 nm spectral window used for temperature fitting), we calculate an actual system temperature measurement resolution of  $\sim 3$   $\mu\text{m}$  at the sample surface (object plane). Thus, a temperature calculated from the spectrum recorded by a single row of the CCD (e.g. every 0.5  $\mu\text{m}$  at the object plane), must be



**Fig. 2.** Results from experiment 25D at 27 GPa. (a) Thermal emission spectra collected from the left hand side, plotted as normalized intensity ( $J$ ) versus normalized wavelength ( $\omega$ ) where  $c_1 = 2hc^2$  and  $c_2 = hc/k$  ( $c$ , speed of light;  $h$ , Planck's constant;  $k$ , Boltzmann's constant). Each line represents the spectrum from a point along a transect across the laser heated spot. The straightness of the data leads to very low fitting errors (1.6 K in this case) and indicates the successful minimization of the effects of chromatic aberration, which would be manifested as curvature in the data. (b) Selected temperature cross-sections collected from the left hand side of the sample during the melting experiment (in this case, the sample is larger than the heated spot) and (c) the resulting temperature vs. laser power function showing a clear melting plateau on the left side (open circles) and right side (closed circles). Temperatures in (c) represent the maxima of the cross-sections in (b). The gray bars represent  $\pm$  one standard deviation of the data in the plateau, which is defined by the arrows in (c). The uncertainty reported in Table 1 is larger than that reported here because it includes additional terms (see text). All figures are color coded as a function of laser power. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Further examples of melting induced plateaux in temperature vs. laser power functions in NiSi. (a) Experiment 25B at 21 GPa, (b) experiment 40B at 30 GPa, (c) experiment 28C at 42 GPa, (d) experiment 28E at 54 GPa and (e) experiment 29A at 69 GPa. The small kink in (a) at 62% laser output is due to a slight adjustment made to the positioning of the laser on the right hand side. Open circles: left hand side; filled circles: right hand side; filled square: melting point of NaCl from the melting curve of [Boehler et al. \(1997\)](#).

viewed as a temperature representing an integration of light from a  $\sim 9 \mu\text{m}^2$  region. This integration will lead to errors in the measured temperature that are a function of the temperature gradient at the sample surface ([Walter and Koga, 2004](#)), minimized in this study by the use of beam-shaping optics. The degree of chromatic aberration is reflected in the precision of the spectral fits to the ideal greybody Wien function ([Fig. 2a](#); [Walter and Koga, 2004](#)), which in the case of this study was typically 2–5 K ([Figs. 1 and 2b](#)), a significant improvement over the 3–13 K reported previously ([Lord et al., 2010](#)). All things considered, we conservatively estimate the error associated with optical aberrations at less than 50 K. As in our previous publications, we do not attempt to assign uncertainties due to the unknown emissivity of the sample. Ambient pressure calibration experiments on a range of metals indicate that this uncertainty does not exceed 200 K ([Lord et al., 2010, 2009](#)).

To minimize uncertainties due to radial pressure gradients, pressures were measured after heating as close as possible to the location of melting. No correction for the effects of thermal pressure can be made to the off-line melting data (cf. [Section 2.2](#)) because we have insufficient *in situ* data to accurately determine the empirical relationship between the thermal pressure and the factors that control its magnitude. These include the specific geometry of each assembly, the physical properties of the sample and pressure medium (both of which undergo phase transitions within the range of our data), the degree of compression and the melting temperature (e.g. [Errandonea et al., 2003](#)). The *in situ* experiments ([Section 2.2](#)) indicate maximum thermal pressures of 6 GPa. The resulting overestimate in the melting temperature never exceeds  $\sim 200$  K, is  $< 100$  K by  $\sim 60$  GPa and becomes insignificant at the pressures relevant to the deep Earth.

We use the ruby pressure scale of [Dewaele et al. \(2008\)](#), which falls approximately in the middle of several recent calibrations, with a range of  $\sim 4$  GPa at 100 GPa (see their [Fig. 4a](#)); we add an uncertainty to our pressure measurements encompassing this range. Additional uncertainty terms of  $\pm 0.5$ – $1.0$  GPa (to take account of radial pressure gradients) and  $\pm 0.2$  GPa (the analytical error on the position of the  $R_1$  ruby fluorescence line) are also included.

## 2.2. *In situ* LH-DAC melting experiments, ESRF

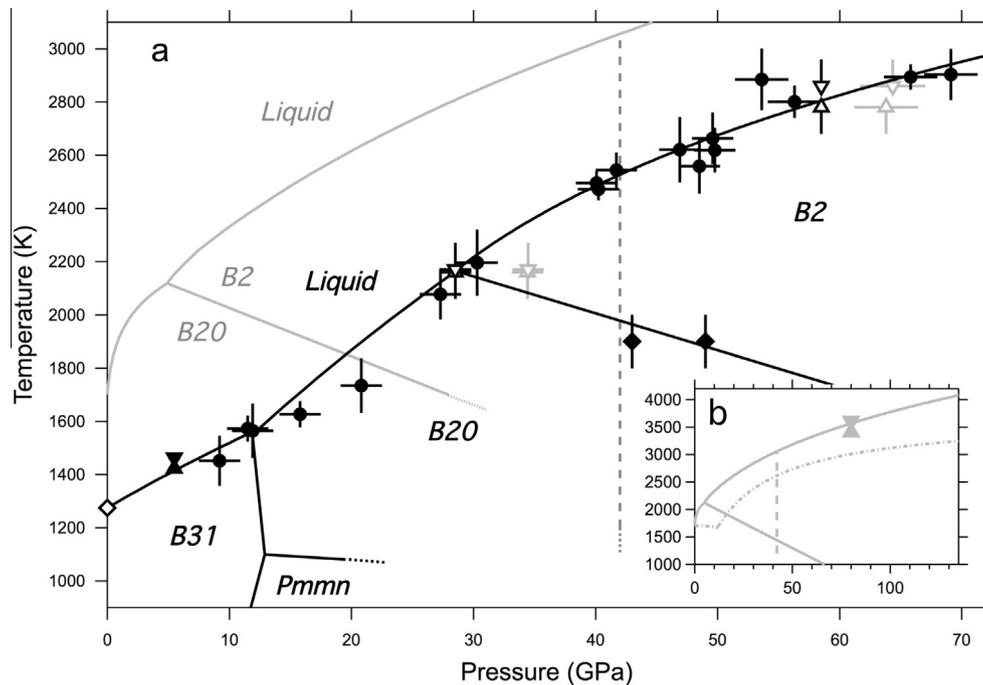
Sample assemblies were identical to those used off-line ([Section 2.1](#)), except that no ruby grains were placed in the sample chamber, to simplify XRD analysis. Instead, pressure was monitored using the measured unit cell volumes of NaCl, in either the B1 or B2 structures, and their known thermal EoS ([Dorogokupets and Dewaele, 2007](#)). The total pressure at high temperature was determined using the method of [Campbell et al. \(2009\)](#). However, to ensure comparability between all datasets, the melting pressures reported in [Table 1](#) for the *in situ* data are also post-heating pressures determined at room temperature.

Laser heating was performed using a double-sided, off-axis geometry with heated spots 20–30  $\mu\text{m}$  in diameter. The incandescent light from the sample was collected using reflective optics while a  $2 \times 2 \mu\text{m}$  area centered on the heated spot was selected using a pinhole and analysed spectroradiometrically to determine the sample temperature. Temperatures were measured on both sides of the sample before the start of the experiment to allow the temperatures to be equalized by varying the laser power, but on the upstream side only during the melting run due to the necessity of removing the light collecting optics from the path of the diffracted X-rays. For further details see [Schultz et al. \(2005\)](#).

The  $3 \times 3 \mu\text{m}$  X-ray beam ( $\lambda = 0.3738 \text{ \AA}$ ) was co-aligned with the laser-heated spot using the X-ray induced fluorescence of the NaCl pressure medium. Diffracted X-rays were collected on a MAR345 CCD with exposure times of 2–10 s. The distance between the sample and detector was calibrated using a  $\text{LaB}_6$  standard. For further details of the beam-line see [Mezouar et al. \(2005\)](#). The resulting 2-D diffraction patterns were carefully masked to remove any saturated spots and then integrated into 1-D diffraction patterns using the Fit2D program ([Hammersley, 1997](#)). The 1-D patterns 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, 1994; Toby, 2001](#)).

## 2.3. *In situ* MAP melting experiment, NSLS

This experiment was performed in a cubic DIA type apparatus. The cylindrical sample chamber contained three compartments, separated with Re foil, the first containing NiSi, the second an NaCl + BN pressure standard with a 10:1 ratio by weight and the



**Fig. 4.** (a) The NiSi phase diagram above 900 K (black lines). Filled circles: off-line LH-DAC melting points (Bristol); open black (gray) triangles: *in situ* LH-DAC melting brackets determined at the ESRF without (with) thermal pressure included; filled triangles: *in situ* MAP melting bracket determined at the NSLS; filled diamonds: B20 → B2 transition bracket from Lord et al. (2012); open diamond: ambient pressure melting point (Massalski et al., 1990). For the *in situ* experiments, the appearance of LDS was the melting criterion, with the downward pointing arrow representing its first appearance and the upward pointing arrow representing the preceding measurement. The solid gray lines and text relate to the FeSi phase diagram of Lord et al. (2010) while the dashed gray line represents the B20 + B2 → B2 transition determined by Fischer et al. (2013). The sub-solidus parts of the NiSi phase diagram reported here are from Dobson et al. (Submitted for publication). (b) The FeSi phase diagram. Lines are as in (a) except for the dot-dash line, which indicates the melting curve of Santamaría-Pérez and Boehler (2008). The solid triangles represent the *in situ* melting bracket from Fischer et al. (2013).

**Table 1**  
NiSi melting data.

| Code   | Pressure (GPa) | Temperature (K) |
|--|----------------|-----------------|
| <i>Off-line LH-DAC experiments (NiSi)</i>                                      |                |                 |
| 24A  | 9.2 ± 1.7      | 1452 ± 94       |
| 26B  | 11.5 ± 1.7     | 1573 ± 49       |
| 26C  | 11.9 ± 1.7     | 1565 ± 103      |
| 25A  | 15.8 ± 1.7     | 1627 ± 50       |
| 25B  | 20.8 ± 1.7     | 1734 ± 102      |
| 25D  | 27.3 ± 1.7     | 2077 ± 94       |
| 40B  | 30.3 ± 1.7     | 2196 ± 124      |
| 57A  | 40.1 ± 1.7     | 2495 ± 45       |
| 57B  | 40.2 ± 1.7     | 2473 ± 42       |
| 28C  | 41.7 ± 1.7     | 2544 ± 66       |
| 25E  | 46.9 ± 1.7     | 2621 ± 123      |
| 28D  | 48.5 ± 1.7     | 2559 ± 103      |
| 57D  | 49.6 ± 1.7     | 2663 ± 97       |
| 57E  | 49.8 ± 1.7     | 2619 ± 84       |
| 28E  | 53.6 ± 2.2     | 2885 ± 116      |
| 57F  | 56.3 ± 2.2     | 2801 ± 61       |
| 57I  | 65.8 ± 2.2     | 2894 ± 48       |
| 29A  | 69.1 ± 2.2     | 2903 ± 96       |
| <i>In situ LH-DAC experiments (NiSi)</i>                                       |                |                 |
| 31A  | 28.5 ± 1.3     | 2165 ± 61       |
| 31B  | 58.5 ± 0.3     | 2780 ± 92       |
| <i>In situ MAP experiments (NiSi)</i>  |                |                 |
| NiSi-04  | 5.5 ± 1.7      | 1443 ± 50       |
| <i>Off-line DAC experiments (Fe<sub>85</sub>Ni<sub>5</sub>Si<sub>10</sub>)</i> |                |                 |
| 41B  | 47 ± 1.7       | 2705 ± 118      |
| 41C  | 49 ± 1.7       | 2810 ± 136      |

third containing a mixture of elemental nickel and silicon in a 1:1 atomic ratio. The sample was surrounded by a BN sleeve, followed by a cylindrical graphite heater separated from the 6 mm pyrophyllite cube with an Al<sub>2</sub>O<sub>3</sub> sleeve. A D-type thermocouple

(W/3% Re-W/25% Re) was inserted through the furnace and BN sleeve, with the contact just inside the pressure standard.

The sample was compressed at room temperature to an end load of 70 tons (a sample pressure of 7 GPa) and then heated in increments of 50–100 K up to 1523 K. At each step, all three samples were analysed using an incident white X-ray beam with a diameter of 50 μm. The diffracted X-rays were collected using a 10 element energy-dispersive detector (Weidner et al., 2010) with a 2θ angle of ~6.6° calibrated using the diffraction pattern of Al<sub>2</sub>O<sub>3</sub> recorded at 1 atmosphere. By widening the slits collimating the incident X-ray beam, radiographic images were recorded regularly to monitor sample geometry. Once melting was determined from the appearance of LDS, this imaging mode was used to produce X-ray videography of the sample at 10 frames per second to monitor the sample for evidence of convection.

#### 2.4. Melt detection

In the *in situ* MAP and LH-DAC melting experiments, the appearance of LDS during XRD was the primary melting criterion. In the off-line LH-DAC experiments however, melting was detected by the appearance of plateaux in the laser power vs. temperature function (Figs. 2c, 3, and 9) generated during automated linear incremental ramping of the power to the lasers, coupled with regular temperature measurements (also automated). Lord et al. (2009) suggested that plateaux would be expected at any invariant melting point as the laser power provides the latent heat of melting. However, it has since been suggested that this explanation of the observed plateaux is unlikely because the magnitude of the latent heat involved in the melting of such small samples is dwarfed by the heat provided by the laser (Geballe and Jeanloz, 2012; Lord et al., 2010). It is likely that several factors contribute to the observed thermal perturbations, including differences in the optical and thermal properties of the liquid and solid phases. For

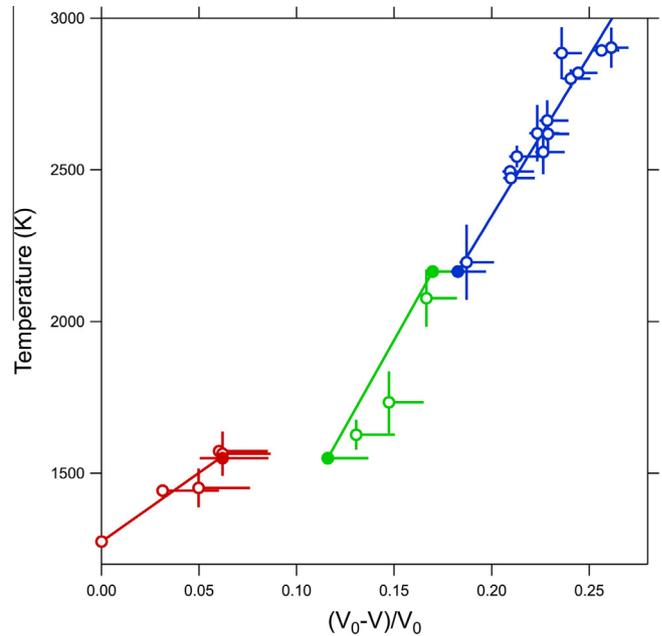
example, convection in the liquid rapidly moves excess heat from the melt pool (upon which the laser is incident) to the solid/liquid boundary, where it promotes further melting, thus moving the boundary further away from the center of the heated spot without significantly increasing the temperature. This process continues until the whole sample is molten or, more likely, until the boundary is sufficiently far from the incident laser beam that any additional power is lost by conduction to the surroundings rather than promoting further melting. At this point, the molten part of the sample often becomes super-liquidus, its temperature rising linearly with increasing laser power, until a second plateau is reached, often within error of the known melting curve of the surrounding NaCl pressure medium (Fig. 3a; Boehler et al., 1997). Alternatively, the melt may become mechanically unstable and flow, leading to sudden variations in temperature. Whatever the underlying process, the key point is that this melting criterion has been used to successfully detect melting in a broad range of metallic and intermetallic compounds, including Fe, Pt, Pb, FeS, Fe<sub>3</sub>C, Fe<sub>7</sub>C<sub>3</sub>, the Fe–Fe<sub>3</sub>C eutectic (Lord et al., 2009) and FeSi (Lord et al., 2010). All of these data either match closely with LH-DAC melting data, published by other research groups and produced using a range of different melting criteria (Fe, Pt, Pb, FeS, FeSi) including *in situ* XRD (Fe, Pb, FeSi) or have been corroborated at low pressures using large volume press (LVP) apparatus based on *ex situ* textural analysis (Fe<sub>3</sub>C, Fe<sub>7</sub>C<sub>3</sub>, the Fe–Fe<sub>3</sub>C eutectic and FeSi; see Lord et al. (2010 and 2009) and references therein). The present study provides two additions to this list: firstly, the melting curve of NiSi corroborated using *in situ* XRD in both the LH-DAC and the MAP and secondly, two offline melting experiments on an Fe<sub>85</sub>–Ni<sub>5</sub>–Si<sub>10</sub> alloy, for which *in situ* melting data already exist (Morard et al., 2011).

In the case of the off-line experiments, the uncertainties in the melting temperatures reported here are a sum of: (1) the analytical precision in the blackbody spectral fitting (typically  $\pm 2$ –5 K; see Section 2.2); (2) the standard deviation of the temperatures within the melting plateau (typically  $\pm 50$ –150 K); and (3) an additional estimate of the temperature variations within the central part of the hotspot from which the temperature is determined (typically  $\pm 25$ –50 K; see Fig. 1a) leading to total uncertainties of  $\pm 80$ –200 K. In the case of the *in situ* experiments, the reported uncertainties are simply chosen to encompass the temperatures of the two XRD analyses that bracket the appearance of LDS plus the maximum estimated uncertainty in the temperature measurements ( $\pm 150$  K; e.g. Morard et al., 2011).

### 3. Results

The NiSi data are listed in Table 1, and plotted as a function of pressure in Fig. 4a, and as a function of isothermal compression, relative to the ambient pressure volume of B31–NiSi in Fig. 5.

At ambient pressure, NiSi melts congruently from the MnP (B31) structure but undergoes a series of solid-state phase transitions with increasing pressure. The next liquidus phase on increase in pressure has the  $\epsilon$ -FeSi (B20) structure, with the transition initially bracketed at  $12.5 \pm 4.5$  GPa and  $1550 \pm 150$  K on the basis of the XRD analysis of LH-DAC experiments (Lord et al., 2012). The Clapeyron slope of this transition has since been refined from the XRD analysis of off-line MAP experiments (Fig. 4a; Dobson et al., Submitted for publication). All melting data below this transition have been fitted separately, using two methods. Firstly, the  $P$ – $T$  data (Fig. 4a) are fitted using the Simon–Glatzel equation  $T_m = [(P_m/A + 1)]^{1/C} \times T_0$ , where  $T_m$  is the melting temperature at pressure  $P_m$ ,  $T_0$  is the ambient pressure melting point and  $A$  and  $C$  are fitting parameters (Simon and Glatzel, 1929; see Table 2). Secondly, the melting temperatures are plotted as a function of iso-



**Fig. 5.** The same melting data shown in Fig. 4, plotted as a function of isothermal compression  $(V_0 - V)/V_0$  where  $V$  is the volume of the liquidus phase at the pressure of melting and  $V_0$  is the ambient pressure volume of B31–NiSi (open circles). The horizontal error bars are asymmetric because they include a contribution equivalent to the maximum measured thermal pressure of +6 GPa. Solid lines represent fits to the Kraut–Kennedy equation for, from left to right, B31–NiSi (red), B20–NiSi (green) and B2–NiSi (blue). The solid circles represent the two triple points, each of which appears twice because of differences in the EoS parameters of the two solid phases which define each triple point, while the size of the gaps between them are proportional to the magnitude of the volume decrease across the two transitions. Note: the fit to the B20 liquidus is constrained to pass through both triple points. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 2**  
Fitting parameters.

| Phase     | Simon–Glatzel       |                |               | Kraut–Kennedy       |               |
|-----------|---------------------|----------------|---------------|---------------------|---------------|
|           | $T_0$ (K)           | $A$ (GPa)      | $C$           | $T_0$ (K)           | $C$           |
| MnP (B31) | 1275 <sup>a,b</sup> | $10 \pm 5$     | $4 \pm 1$     | 1275 <sup>a,b</sup> | $3.5 \pm 0.2$ |
| CsCl (B2) | 2165 <sup>a,c</sup> | $12.8 \pm 6.1$ | $4.7 \pm 1.4$ | 2165 <sup>a,c</sup> | $4.9 \pm 0.2$ |

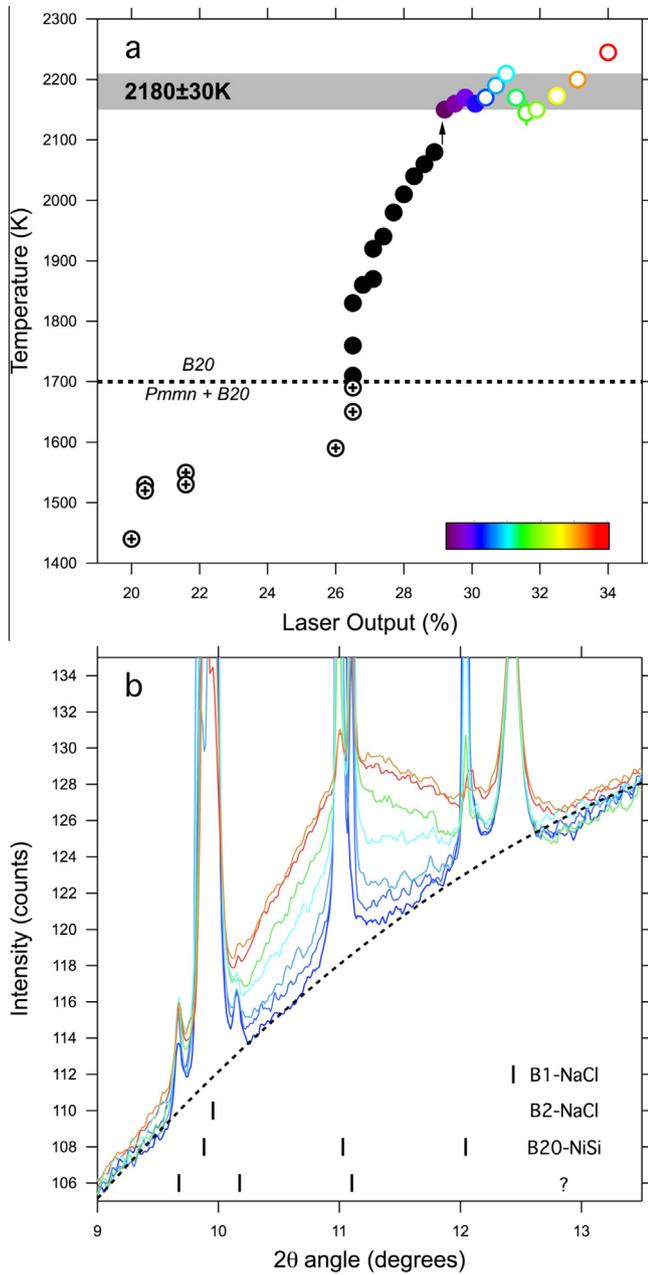
<sup>a</sup> Parameters kept constant during fitting.

<sup>b</sup> (Massalski et al., 1990).

<sup>c</sup> Value of  $T_0$  taken from the B20 + B2 + L triple point (TP2) defined by *in situ* experiment 31A (Section 3).

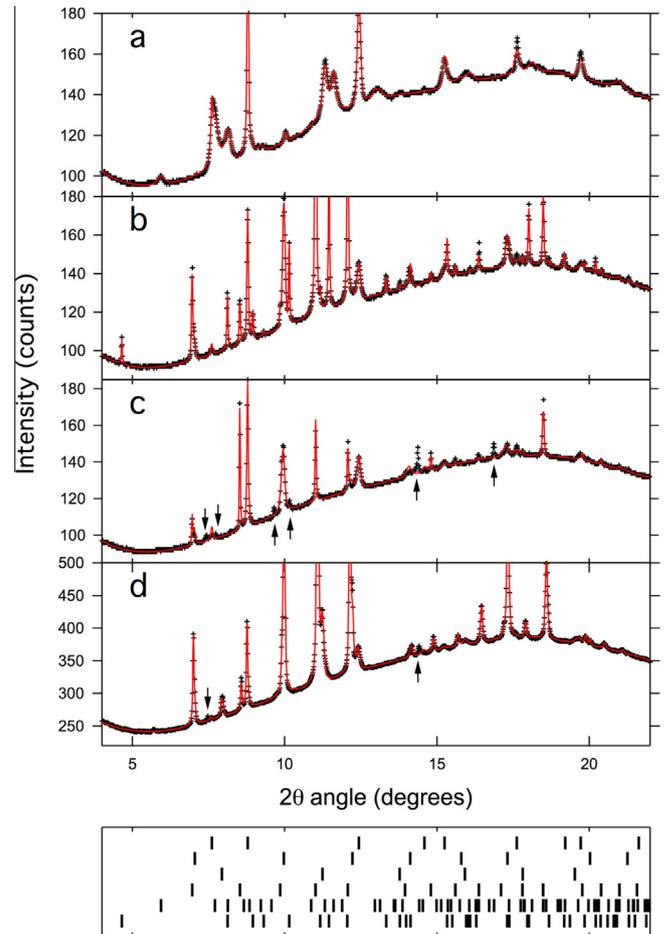
thermal compression,  $(V_0 - V)/V_0$ , using the EoS for B31–NiSi (Lord et al., 2012) and fitted using the Kraut–Kennedy equation  $T_m = T_0(1 + C(V_0 - V)/V_0)$  where  $V_0$  is the ambient pressure volume of B31–NiSi, and  $V$  is the volume of the liquidus phase at the pressure of melting (Fig. 5; Kraut and Kennedy, 1966). This approach is justified because the data are linear in  $T$  vs.  $(V_0 - V)/V_0$  space. Both fits pass within error of the off-line LH-DAC data and the single *in situ* MAP melting point at 5.5 GPa. In the latter experiment melting was not only detected by the onset of LDS in the XRD patterns, but is also clearly demonstrated by the appearance of convective motion in an X-radiographic video acquired after the onset of LDS (see Supplementary video). The invariant point at which our newly determined B31–NiSi liquidus intersects the B31  $\rightarrow$  B20 transition line (Dobson et al., Submitted for publication) defines the B31 + B20 + L triple point (TP1;  $12 \pm 2$  GPa,  $1550 \pm 100$  K).

Fig. 6 shows the first of the *in situ* LH-DAC experiments at the ESRF (experiment 31A) while Fig. 7 shows selected diffraction



**Fig. 6.** *In situ* LH-DAC experiment 31A at 29 GPa. (a) Temperature vs. laser power plot. Open circles with plus sign: *Pmmn* + B20-NiSi; Solid black circles: B20-NiSi + unknown trace phase (see text). The dashed line represents the temperature above which the *Pmmn* phase was no longer observed and the gray bar represents the melting temperature determined from the points within the melting plateau, which are color coded as a function of laser output. The open circles represent XRD patterns in which LDS was observed. (b) XRD patterns color coded to match (a). The black dashed line represents the background fit to the pattern collected immediately before LDS was observed. Tick marks from top to bottom represent B1-NaCl, B2-NaCl, B20-NiSi and the unidentified trace phase (see text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

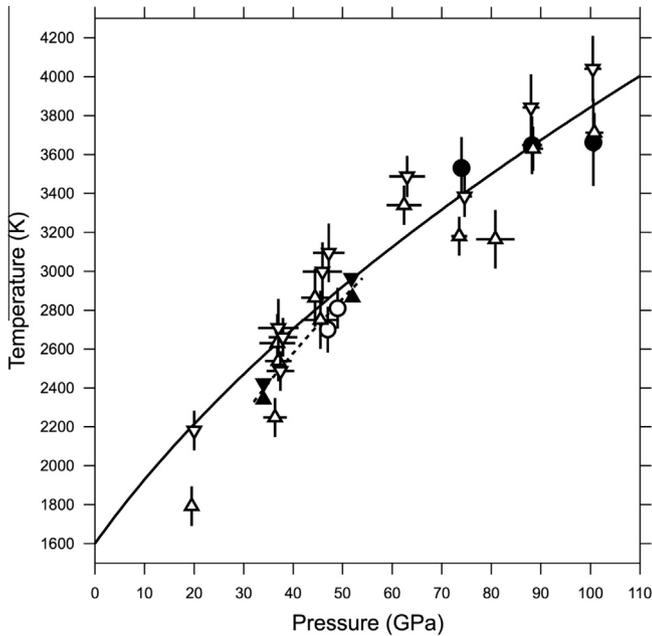
patterns. Before heating the sample consists of pure B31-NiSi (Fig. 7a). Up to 1700 K the assemblage consists of B20-NiSi plus the orthorhombic *Pmmn* phase (Figs. 6a and 7b; Wood et al., 2013) which are known to share a broad two-phase region. The *Pmmn* phase has been found to be stable above a pressure of ~13 GPa and below a temperature of ~1100 K (Dobson et al., Submitted for publication). At a constant laser output of 26.5% the temperature of the sample rose from 1650 K to 1850 K, during



**Fig. 7.** XRD patterns (black crosses) from experiment 31A (29 GPa) fitted with the LeBail method using GSAS (red lines). (a) Before heating, (b) at 1650 K, (c) at 1710 K and (d) after heating. Tick marks from top to bottom represent B1-NaCl, B2-NaCl, B20-NiSi, B31-NiSi and the *Pmmn* phase. The arrows denote the peaks associated with the unidentified trace phase (see text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

which time the *Pmmn* phase disappeared, leaving B20-NiSi plus several, small, unidentified peaks (Fig. 7c). From this point up to 29% laser power these unidentified peaks diminish in both number and intensity, while temperature increases linearly, followed by a sudden jump and then a plateau that yields a melting temperature of  $2180 \pm 30$  K. At 30% laser power, while on the plateau, LDS was observed during XRD (Fig. 6b), with the magnitude of the LDS signal increasing as laser power is increased while the temperature remains approximately constant. In this experiment, the B2-NiSi phase appeared simultaneously with the onset of melting, suggesting that this run fortuitously intersected the B20 + B2 + L triple point (TP2). After heating (Fig. 7d), the quenched assemblage consists of B20-NiSi + B2-NiSi while two of the unidentified peaks, both very small, persist. Given that the integrated area under these peaks is only 0.8% that of the peaks from the indexed NiSi phases, we are confident that the molten system is close to the NiSi stoichiometry. Nevertheless, a detailed discussion of the nature of these peaks can be found in the Supplementary material. Using the post-heating pressure for this run, the triple point is thus defined as  $28.5 \pm 1.3$  GPa and  $2165 \pm 61$  K.

The melting data that fall within the narrow pressure range where B20-NiSi is the liquidus phase, between TP1 and TP2, were too few to fit. Instead, we have opted to connect the two triple points with a slightly convex upward curve in *P*-*T* space to prevent



**Fig. 8.** Melting data for selected Fe-Ni-Si alloys. The solid line is a fit to the *in situ* LH-DAC melting data for  $\text{Fe}_{91}\text{Si}_9$  of Fischer et al. (2013) that includes melting brackets, in which the appearance of LDS was the melting criterion (open triangles), and melting points in which plateaux in temperature vs. laser power curves were used (solid circles). The dashed line is a fit to the *in situ* LH-DAC melting brackets (solid triangles) for  $\text{Fe}_{85}\text{Ni}_5\text{Si}_{10}$  of Morard et al. (2011). Open circles are the melting data for  $\text{Fe}_{85}\text{Ni}_5\text{Si}_{10}$  from this study in which plateaux in temperature vs. laser power curves were used to define melting.

Schreinemaker's rules being contravened (Fig. 4a; Zen, 1966) and by a straight line in  $V$ - $T$  space (Fig. 5).

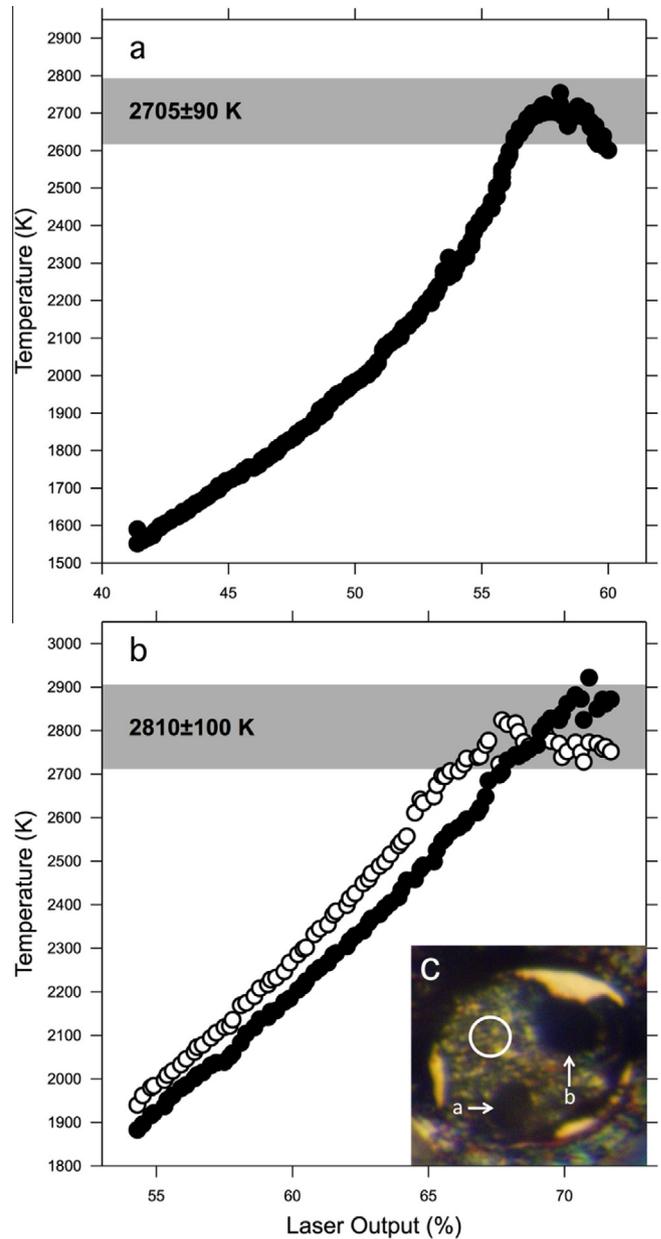
The melting data above TP2 have also been fitted separately using the Simon-Glatzel and Kraut-Kennedy equations (Table 2). In this case the Simon-Glatzel equation has been modified such that  $T_m = [((P_m - 28.5)/A + 1)]^{1/c} \times T_0$  in order to force the melting curve through the triple point. The Kraut-Kennedy equation is also modified, such that  $T_m = T_0[1 + (C(V_0 - V)/V_0) - 0.104557]$ .

The pair of off-line melting experiments performed on  $\text{Fe}_{85}\text{-Ni}_5\text{-Si}_{10}$  are presented as a function of pressure in Fig. 8 with the raw data in Fig. 9. Both points fall within error of the melting curve of Morard et al. (2011), which is defined by two brackets determined from the appearance of LDS in *in situ* LH-DAC experiments. Our data also agree with those of Fischer et al. (2013) on a similar composition ( $\text{Fe}_{91}\text{Si}_9$ ) in which both LDS and plateaux in temperature vs. laser power functions were used as melting criteria.

## 4. Discussion and conclusions

### 4.1. The NiSi phase diagram

The data reported here and in Dobson et al. (Submitted for publication) provide additional constraints on the NiSi phase diagram, including the melting curves of all three liquidus phases (B31, B20, B2) and the positions of both triple points. It is clear from Figs. 4a and 5 that the inflection associated with TP1 is much larger than that associated with TP2. This is probably related to the fact that the volume change across the B31  $\rightarrow$  B20 transition ( $-6\%$ ) is significantly larger than that across the B20  $\rightarrow$  B2 transition ( $-0.8\%$ ) as is clear from Fig. 5. Although there are insufficient data to determine the liquidus for B20-NiSi by fitting, the constraints on the two triple points are independent and thus the slope is tightly



**Fig. 9.** Melting plateaux from off-line LH-DAC experiment 41 ( $\text{Fe}_{85}\text{Ni}_5\text{Si}_{10}$ ) with symbols as in Fig. 3. (a) Run 41A at 47 GPa. Only the right side is plotted due to a fault on the left side. (b) Run 41B at 49 GPa. The small ( $\sim 80$  K) difference in the plateaux temperature between the left and right sides is most likely due to small misalignments between the heated spot and the spectrometer. (c) Photomicrograph of the left side of the sample taken after laser heating. The dark spots resulting from runs A and B are marked by the arrows. The white circle represents the location of a third heating run, halted at 2000 K. Note the lack in the latter position of any change in the nature of the sample surface.

constrained, and clearly significantly steeper than that of B31-NiSi, but similar to that of B2-NiSi (Fig. 5).

The *in situ* LH-DAC experiments allow us to refine our estimate of the Clapeyron slope of the B20  $\rightarrow$  B2 transition. Our initial estimate of  $\sim -105$  MPa  $\text{K}^{-1}$  was based on an experimental bracket at  $46 \pm 3$  GPa and  $1900 \pm 150$  K (Lord et al., 2012) and a prior *ab initio* study (Vočadlo et al., 2012) which determined that B2-NiSi would become stable relative to the preceding Pnma-II structure at 247 GPa and 0 K. Wood et al. (2013) have since shown that at 0 K the B2 structure becomes stable at 264 GPa, from the newly discovered Pmmn structure. However, if we use the more relevant

B20 → B2 transition pressure of 170.5 GPa at 0 K from Vočadlo et al. (2012), the Clapeyron slope decreases to  $\sim -67$  MPa K<sup>-1</sup>. The new *in situ* data (TP2 plus an additional bracket at  $1715 \pm 35$  K and  $58.5 \pm 1$  GPa from the second of the two experiments) yields an identical value (Dobson et al., Submitted for publication). This new slope passes within the bracket reported by Lord et al. (2012) and extrapolates to 173 GPa at 0 K, in excellent agreement with the 0 K B20 → B2 transition pressure of 170.5 GPa from Vočadlo et al. (2012). This new estimate is preferred because the previous estimate was constructed assuming a linear boundary between the pressure at which the B2 phase becomes stable at 0 K and the experimental value from Lord et al. (2012); in fact there are likely to be additional phase boundaries in between, leading to inflections in the transition to the B2 phase (Dobson et al., Submitted for publication). This explains the difference between the 0 K stabilization pressure of B2–NiSi predicted by the *ab initio* simulations (264 GPa; Wood et al., 2013) and the pressure that would be expected from a linear extrapolation of the experimentally determined Clapeyron slope (173 GPa). This new value confirms that the B2 structure is the relevant one for NiSi at Earth's core conditions given that no further phase transitions are expected at higher pressures (Wood et al., 2013; Vočadlo et al., 2012).

#### 4.2. Comparison with FeSi

The NiSi phase diagram has two significant differences from the phase diagram of FeSi (Lord et al., 2010). Firstly, it exhibits a greater degree of polymorphism at pressures and temperatures below the B20 → B2 transition, with at least two additional stable phases (B31 and *Pmmn*) and perhaps several more (Wood et al., 2013; Lord et al., 2012; Vočadlo et al., 2012). Secondly, its liquidus is considerably lower in temperature, by 425 K at 1 atmosphere and by a maximum of  $\sim 900$  K at 12 GPa (TP1). On the other hand, the B20 → B2 transition, shared by both compositions, involves a very similar reduction in volume (0.8% for NiSi vs. 1.1% for FeSi, at 300 K; Lord et al., 2012) and has a very similar Clapeyron slope ( $-67$  MPa K<sup>-1</sup> for NiSi compared to  $-56$  MPa K<sup>-1</sup> for FeSi; Lord et al., 2010). In fact if the FeSi phase diagram were shifted in pressure such that the B20 + B2 + L triple points for both compositions coincided, the B2 liquidus and B20 → B2 transitions would be almost indistinguishable (Fig. 4a). However, the more recent *in situ* FeSi phase diagram (Fischer et al., 2013) contradicts this conclusion (see their Fig. 1d). In that study, a two-phase loop was observed in which the assemblage B20 + B2 is stable (the compositions of which must be non-stoichiometric but complementary), followed by a near vertical transition at 40 GPa to single phase, B2–FeSi. Presumably this two-phase region is bounded at lower pressures by a transition to single-phase B20–FeSi at a pressure below the lower limit of their experiments. Looking at the phase diagram presented in Fig. 2 of Lord et al. (2010), this interpretation could explain the majority of the data. Although the results of *ex situ* MAP synthesis experiments published by Dobson et al. (2002), in which pure B2–FeSi was observed at 24 GPa and 2023 K, appear to contradict this new interpretation, those experiments purposefully used non-stoichiometric starting material (Fe<sub>52</sub>Si<sub>48</sub>). This slight metal excess is known to stabilize the B2 structure in both FeSi and RuSi (Dobson et al., 2002) and might explain its appearance at lower pressures in the MAP experiments. However, it seems unlikely that an iron excess of 2% could reduce the pressure at which B2–FeSi becomes the sole polymorph by such a large extent (18 GPa). Furthermore, Dobson et al. (2002) found that at 24 GPa the width of the two-phase loop is less than 4 wt.% (i.e. pure B20 at Fe<sub>48</sub>Si<sub>52</sub> and pure B2 at Fe<sub>52</sub>Si<sub>48</sub>), which is hard to reconcile with the width of 28 GPa in pressure space reported by Fischer et al. (2013). In light of this contradiction, we have chosen to present both of the proposed boundaries in Fig. 4.

It has been predicted that FeSi could be present within the D'' region, either as a reaction product between the (Mg,Fe)SiO<sub>3</sub> perovskite or post-perovskite of the lower mantle and the Fe–Ni alloy of the outer core (Knittle and Jeanloz, 1991) or as a result of exsolution from the core during secular cooling (Buffett et al., 2000). Based on its melting curve and estimates of the geotherm within the D'' region (Lord et al., 2010), it is expected that any FeSi present would be solid at the top of the D'' region, but almost certainly molten toward the bottom (with the depth of the transition dependent on the geotherm), making it a potential candidate for a component of the partial melts postulated to explain the seismic ultra-low velocity zones (ULVZs) observed at the CMB (e.g. Idehara, 2011; Buffett et al., 2000). A recent *in situ* XRD study on FeSi confirms that the B2 structure is stable to at least 150 GPa and 2200 K (Fischer et al., 2013) while no further phase transitions are expected in NiSi on the basis of extensive *ab initio* simulations on a range of possible polymorphs (Wood et al., 2013; Vočadlo et al., 2012). FeSi and NiSi are therefore likely to be isostructural at CMB conditions probably forming the end-members of a simple binary solid solution. Given this assumption and that the core contains at least 5 wt.% Ni (e.g. Allègre et al., 1995), any silicide produced would be expected to be B2 structured (Fe,Ni)Si, with a liquidus temperature falling somewhere between the two end-members. If we extrapolate our Simon–Glatzel fit of the B2–NiSi melting data to the CMB pressure of 135 GPa we find an NiSi melting temperature of  $3700 \pm 400$  K, well within error of the value for FeSi of  $4000 \pm 200$  K (Lord et al., 2012). Employing our Kraut–Kennedy fit yields essentially the same result. Combined with the fact that any (Fe,Ni)Si phase is likely to be iron-rich, largely reflecting the composition of the core, the present results strongly indicate that the incorporation of Ni has little effect on the conclusions discussed in Lord et al. (2010).

The present data do not cover a sufficient pressure range to allow a reliable extrapolation of the NiSi melting curve to ICB conditions (330 GPa). The likelihood that FeSi and NiSi will be isostructural at inner core conditions means that the melting temperature of any iron-rich B2 structured (Fe,Ni)Si phase at the ICB pressure of 330 GPa is likely to be only slightly lower than the value of 6200 K determined for FeSi (Lord et al., 2010). Consequently, such a phase could be a stable solid at inner-core conditions, given favorable sub-solidus phase relations in the Fe–Ni–Si system, which are largely unknown at these conditions. However, most recent experimental data (Fischer et al., 2013; Brosh et al., 2009) and *ab initio* simulations (Zhang and Oganov, 2010) in the Fe–Si system suggest that if the inner core contains more than 4 wt.% Si, as predicted by most experimental and modeling studies (e.g. Allègre et al., 1995; Fischer et al., 2012; Balchan and Cowan, 1966) an assemblage of hcp + B2 structures will be stabilized. These results contradict earlier experimental studies (e.g. Asanuma et al., 2008; Kuwayama et al., 2009) which suggested that such bulk compositions would stabilize a single, hcp-structured alloy phase. An alternative inner core model containing 1–2 wt.% Si and 4–5 wt.% Ni, based on sound velocity measurements, has been proposed by Antonangeli et al. (2010). In this case, the phase diagram proposed by Fischer et al. (2013) would also predict a single phase, hcp-structured inner core.

#### 4.3. Melting criteria

The data described here provide additional evidence that plateaux in temperature vs. laser power curves are a reliable proxy for melting in those materials that we have tested to date. The close correspondence between the MAP experiment and LH-DAC experiments suggests that our spectroradiometric temperature measurements are accurate and that the temperature gradients within our LH-DAC experiments, minimized by beam shaping,

are not an issue. This is because, in the MAP experiment, temperature was measured directly using a thermocouple while the temperature gradient is expected to be small due to the external heating geometry.

The *in situ* LH-DAC experiments are particularly informative, because they afford us the opportunity to measure the temperature vs. laser power function simultaneously with an independent and direct determination of the melting temperature from the appearance of LDS. In run 31A (Fig. 6a) LDS does not appear until some way into the plateau, either because there is too little liquid within the diffracted volume to produce a visible signal, or because of slight misalignments between the laser heated spot and the X-ray beam. Once the LDS signal appears, however, its magnitude increases with increasing laser power while the temperature remains constant, which strongly suggests that the additional power is causing an increase in the volume of melt rather than increasing the temperature. This behavior is to be expected given the axial temperature gradients within the sample (likely less than 100 K; see Campbell et al., 2009). The melt volume appears to reach a maximum by 33% laser output and in the next measurement, at 34%, the temperature has risen above the plateau, suggesting that the sample was fully molten within the laser-heated volume and that the additional laser power was forcing the melt into the super-liquidus region, but the experiment was halted before this relationship had become convincing. The observation that LDS is coincidental with a plateau in the temperature vs. laser power function confirms that the observed plateaux are the result of progressively increasing melt volumes rather than of sub-solidus transitions.

The jump in temperature at the onset of the melting plateau (indicated by the arrow in Fig. 6a), sometimes observed (cf. Fig. 2c), may be the result of the difference in emissivity or laser absorption between the solid and liquid phase. Similar behavior has been observed in an Fe<sub>82</sub>Si<sub>18</sub> alloy (see Fig. 1 of Asanuma et al., 2010), but not in FeSi (see Fig. 1 of Lord et al., 2010). Given these inconsistencies, no definitive explanation of this behavior can yet be made.

The good agreement between the published *in situ* melting curves of Fe<sub>85</sub>Ni<sub>5</sub>Si<sub>10</sub> (Morard et al., 2011) and Fe<sub>91</sub>Si<sub>9</sub> (Fischer et al., 2013) and the two off-line melting points on Fe<sub>85</sub>Ni<sub>5</sub>Si<sub>10</sub> reported here indicates that the correspondence between the *in situ* and off-line measurements on NiSi is not a material-specific coincidence. Visual inspection of samples after laser heating provides an additional, secondary, melting criterion. Fig. 9c shows a photomicrograph of experiment 41 (sample Fe<sub>85</sub>Ni<sub>5</sub>Si<sub>10</sub>) after laser heating. The two dark spots at the bottom and top right of the sample foil were observed to have formed at the locations of melting runs 41A and 41B respectively. A third heating cycle in which a temperature of 2000 K was maintained for 10 min (the white circle in Fig. 9c) produced no change in the sample surface compared to adjacent unheated regions. The exact cause of this discoloration is not known, but it is unlikely to be the result of reaction between the sample and its environment, given the lack of evidence of carbides or other extraneous compounds in diffraction patterns collected on quenched samples of various compositions (Fig. 7d; Lord et al., 2010).

Further examples of the reliability of discontinuities in temperature vs. laser power curves as a melting criterion are provided by two recent studies performed by independent groups. Firstly, Fischer et al. (2013) report melting data for Fe<sub>91</sub>Si<sub>9</sub> based on the appearance of LDS during *in situ* XRD. At 88 GPa (3648 ± 149 K) and 101 GPa (3662 ± 224 K), the appearance of LDS coincides with clear plateaux in temperature vs. laser power curves (see their Fig. 4). Fischer et al. (2013) also report a single *in situ* melting bracket for FeSi that closely matches our previously published off-line melting curve (Fig. 4b; Lord et al., 2010) but is ~600 K

above the melting curve of Santamaría-Pérez and Boehler (2008) in which melting was determined from visual observations of changes in laser speckle patterns. The second example comes from the new melting curve for iron reported by Anzellini et al. (2013). In Fig. 1c of their paper the authors report a clear example of a discontinuity in the rate of change in temperature as a function of time (equivalent to power given the linear ramp rate) at 4100 K. This matches exactly their LDS based melting curve. Anzellini et al. (2013) note that discontinuities in their temperature vs. power curves are not always apparent (as in their Fig. 1d), but that this non-appearance is associated with thicker samples. These two examples indicate that although it is preferable to determine melting curves from the appearance of LDS during *in situ* XRD, in lieu of such data, discontinuities in temperature vs. laser power curves are a useful and accurate alternative approach. In contrast, Anzellini et al. (2013) make clear that earlier measurements of the iron melting curve based on visual observations of motion in laser speckle patterns presumed to represent convection in the liquid considerably underestimated the iron melting curve, as was also the case for FeSi (described above). Anzellini et al. (2013) suggest that these visual methods can potentially misidentify dynamic recrystallization in the solid as melt convection. Therefore it appears that plateaux in temperature vs. laser power curves provide the more accurate criterion in off-line melting experiments.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.pepi.2014.05.005>.

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