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ABSTRACT

Laser heating in a diamond anvil cell (DAC) is a common method for studying material behavior at high-pressure and high-temperature conditions. It has been previously proven that during continuous wave (CW) laser heating of a sample, carbon of the diamond anvils is mobilized, and its diffusion into the sample can lead to undesirable chemical reactions, which, if not detected, may cause misinterpretations of the results of the experiment. Minimizing the heating time with the use of a pulsed laser (PL) is thought to reduce the risk of possible carbon contamination of the sample; however, this has not been proven experimentally. Here, we report the results of our comparative study of the effect of pulsed and continuous wave (CW) laser heating on the mobilization of carbon and its chemical interaction with iron in a diamond anvil cell. Using X-ray absorption near edge structure spectroscopy, Synchrotron Mössbauer Source spectroscopy, and Synchrotron X-ray diffraction, we examined iron samples that were laser heated in DACs in various pressure transmitting media (neon, argon, and potassium chloride). According to our results, the use of the PL heating does not prevent the sample from carbon contamination. A reaction between carbon and iron happens within a few seconds even at moderate temperatures. We found that one analytical technique was generally insufficient to fully characterize the phase composition of the laser-heated samples.

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I. INTRODUCTION

Laser heating of materials inside a diamond anvil cell (DAC) allows one to study various chemical and physical phenomena which happen at non-ambient conditions. Knowledge of the melting of metals is of fundamental importance, but the high-pressure melting curve of iron is of particular interest for geosciences,

as it provides crucial constraints for modelling thermal conditions in the Earth's core and at the core-mantle boundary. Despite extensive research, it still remains uncertain, and available data are contradictory.^{1–4}

The results of studies of melting depend on many factors, including the heating method, melting criterion, and the

temperature measurement technique. Undesirable chemical reactions are among the major experimental obstacles. It is well known that laser heating of iron in a DAC may lead to the formation of iron carbides or a solution of carbon in iron^{5–8} as a result of a chemical reaction between the sample and carbon diffusing from a diamond anvil into the sample chamber. This is highly unwanted in melting experiments, since the presence of carbides or Fe-C solid solutions can significantly affect the melting temperature.^{9–11} The carbon contamination problem is not limited to iron¹² but due to the important geological implications of its melting curve, iron is a highly investigated material.

Detection of products of undesirable chemical reactions often presents a separate complex task. Indeed, laser heating affects the surface of the sample and the volume of the laser-heated material may be very small. Thus, the amount of products of undesirable chemical reactions can appear to be below the detection limit of the applied analytical methods. The question of whether a chemical reaction indeed took place becomes crucial for establishing correct melting curves of metals (or, more generally, for any experiments in laser-heated DACs).

Solid state chemical reactions are driven by mutual diffusion of the components, which is promoted by high temperature and prolonged heating. As the pulsed laser (PL) heating minimizes the heating duration in individual pulses down to microseconds or even shorter, it is considered to be a technique that suppresses diffusion and thus improves the chemical stability of the system under investigation. However, there have not been studies to date, which could allow a direct comparison of the effects of pulsed laser (PL) and continuous wave (CW) laser heating on the mobilization of carbon in a DAC and its chemical reaction with the sample. Such experiments require a sample in a particular chemical environment to be heated using both a PL and a CW laser.

In this study, we examine the chemical interaction between iron and carbon of the diamond anvils during continuous wave and pulsed laser heating. Iron samples were loaded into DACs along with different materials, Ne, Ar, and KCl, which served as pressure media and provided different chemical environments. The chosen pressure media are often used in laser-heated diamond anvil cell (LHDAC) experiments, as they are chemically inert, serve as good thermal insulators, and have been suggested as good choices for diminishing the diffusion of carbon from the diamond anvils.¹² In the course of a series of experiments, in which different spots of iron samples were heated by either a PL or a CW laser and by varying the duration of heating, we kept track of the iron-carbon interaction using energy dispersive X-ray absorption spectroscopy (XAS), as implemented at the ID24 beamline at the European Synchrotron Radiation Facility (ESRF). The compositions of the heated samples were examined afterwards using Mössbauer spectroscopy at the Synchrotron Mössbauer Source (SMS) at the ID18 beamline at the ESRF, and X-ray diffraction (XRD) at the P02.2 beamline at PETRA III, DESY. Our results suggest that upon laser heating, Fe and carbon chemically react independently of the heating mode applied (CW or PL). Products of the Fe-C chemical reaction could be detected if an appropriate, sufficiently sensitive analytical technique is applied.

We report our experimental results in detail in the following three sections. Section II provides information about the sample preparation and DAC design (Sec. II A) and the laser heating procedure and the methodology of the data collection (Sec. II B). The X-ray absorption near edge structure (XANES) data analysis is described in Sec. II C, which aims at explaining our approach to the X-ray absorption data processing that allows quantifying the changes in the chemical composition of the samples. Section II D presents the Mössbauer spectroscopy and X-ray diffraction methods used for sample characterization. Section III includes a detailed description of our results and their analysis in the context of previous observations. It is divided into three subsections dedicated to examining different iron samples in Ne (Sec. III A), in Ar (Sec. III B), and in KCl (Sec. III C) pressure media. Section IV briefly summarizes the results and provides their discussion in respect of the available literature. In Sec. V, we give some suggestions regarding future experiments.

II. EXPERIMENTAL METHODS

A. Sample preparation

BX90-type¹³ and membrane-type¹⁴ DACs equipped with Boehler-Almax anvils¹⁵ (culet size 250 μm) were prepared. Rhenium gaskets were pre-indented from an initial thickness of 200 μm down to 25–35 μm and laser-drilled to create circular pressure chambers of 100–120 μm in diameter. A strip of an iron foil (Goodfellow Inc., 99.99%) with a thickness of 5–10 μm was used as a sample. To improve the SMS data quality, a ⁵⁷Fe-enriched iron foil (thickness of 5 μm or thinner) was used. Ar, Ne, and KCl were used as pressure media.

Prior to loading into a DAC, a powder of KCl was dried in an oven at 250 °C for at least 48 h. The iron foil was placed between two KCl disks to assure a distance of at least a couple of micrometers between the sample and the diamond anvils. In the case of Ne and Ar, the cells were gas loaded using the gas loading system in Bayerisches Geoinstitut¹⁶ at 140(5) MPa. A small portion of the iron foil strip was clamped between the rhenium gasket and the diamond anvil to secure its position during gas loading (Fig. 1). The rest of the iron strip was slightly folded inside the pressure chamber to suspend it in the pressure medium so that neither of the sides of the foil would be lying on diamond anvils (Fig. 1). The spots for heating were chosen to be relatively in the middle of the strip, avoiding the ends, where the sample is closer to the diamond anvils. In different experiments, the DACs were compressed to 41–53 GPa.

FIG. 1. Configuration of the pressure chamber in experiments with gaseous pressure media (argon or neon). The schematic is drawn to scale.

B. Laser heating procedure and X-ray absorption spectroscopy

Laser heating experiments were conducted at the ESRF in Grenoble with the energy dispersive X-ray absorption setup of ID24.¹⁷ The X-ray beam was focused horizontally using a curved polychromator Si 111 crystal in Bragg geometry and vertically with a bent Si mirror. The obtained focus at the sample position was approximately $3\text{ }\mu\text{m}$ (horizontal) $\times$ $4\text{ }\mu\text{m}$ (vertical) full width at half maximum (FWHM). The second-order polynomial for the pixel to energy conversion parameters was calibrated using a reference α -Fe foil spectrum.

The iron samples were PL or CW laser heated at temperatures ranging from 1600 K to 3450 K, i.e., both below and above the melting point of iron for the selected pressure range. Two IR ytterbium-doped fiber lasers (YLR-100-AC of IPG Photonics) operating at 1070 nm with a maximum power of 100 W were used each time to heat the sample from both sides with a focal spot of approximately 10–15 μm in diameter, which is larger than the X-ray beam size.^{18,19}

Each laser heating (LH) sequence, numbered LH1–LH6, was realized through a number of cycles characterized by the number of pulses of a certain duration (in μs) for PL or by duration (in seconds) for CW laser heating. In the case of pulsed heating, the pulse duration ranged between 2 and 12 μs at a 25 kHz laser frequency, except of one case, when pulses of 100 μs at 10 kHz were used. The number of cycles (repetitions) varied from 1 to 15, with the total heating time being in the range of 2 s to 3 min. X-ray absorption spectroscopy (XAS) spectra at the Fe K-edge ($E_0 = 7112\text{ eV}$) with an energy resolution of approximately 0.24 eV were collected from the quenched sample spot during the time between two heating cycles.

The temperatures were measured during heating from both sides of the sample using spectroradiometry,¹⁹ and an effort was made to keep the temperature similar on both sides of the sample and the same for each heating cycle during one LH sequence. In

PL, heating temperatures were tracked along the pulse duration using time-resolved spectroradiometry, as described in Ref. 20, with a PI-MAX 4 detector. Reported temperature values refer to the highest temperature achieved, with an uncertainty of $\pm 150\text{ K}$ arising from possible temperature gradients, heating instability, and inaccuracy of the gray body approximation. At the end of each heating sequence, a full mapping of the sample was made in a grid with a step size of $2 \times 2\text{ }\mu\text{m}^2$. An X-ray absorption spectrum was collected at each position²¹ in the grid to detect all possible chemical changes in the sample, even if the heated area slightly moved from the focus of the X-ray beam upon heating.

The data maps were treated using the Region of Interest (ROI) Imaging Tool of the PyMCA software,²² which allowed the batch normalization of the XAS spectra for consistency within every mapping and the visualization of maps with a pixel representing each spectrum. Before or after normalization, using appropriate color-coding, the value of every pixel could be chosen to represent the edge-jump on Fe (i.e., the difference in X-ray absorption between energies below and above the K-edge) or a feature in a specific energy range on the XAS spectrum.

C. XANES data analysis

Changes in the X-ray absorption near edge structure (XANES) region of XAS spectra give evidence of changes in the iron chemical environment. Figure 2 shows, as an example, the X-ray absorption spectra of Fe in Ne taken from a sample quenched at 41 GPa after the heating sequence LH3 (the XANES region outlined by the dashed rectangle is enlarged in the inset). The shoulder of the rising K-edge in the XAS spectra at approximately 7119 eV (pointed out by the blue arrow in Fig. 2) is a characteristic feature of ϵ -Fe.^{23,24} It was recently recognized that vanishing of this shoulder after heating indicates a chemical reaction between iron and

FIG. 2. X-ray absorption spectra of Fe in Ne taken from a sample quenched at 41 GPa after heating at a maximum temperature of 2500 K (heating sequence LH3). The inset shows the enlarged XANES region of the spectra (dashed grey rectangle). The spectra were collected at room temperature from three locations at different distances (0–2, 4–6, and 8 μm) from the center of the heated spot (red, magenta, and blue curves, respectively). The rising edge feature is pointed out by the blue arrow. The blue spectrum resembles the one taken from the non-heated areas of the sample and is characterised by the most pronounced shoulder, which is specific for ϵ -Fe. ROI 1 and ROI 2 designate the two energy regions (Regions of Interest 1 and 2, highlighted in pink and blue colors), which were used to define the ratio r (see text).

carbon, which arises from the diamond anvils, resulting in the synthesis of iron carbide Fe_3C .¹¹

As seen in Fig. 2, vanishing of the shoulder directly correlates with the distance from the center of the heated spot. The closer to the center of the heated spot, the less pronounced is the shoulder. This was interpreted as a change in the chemistry of the sample, as it will be shown below. To quantify the difference in the spectra, we introduced the value r , which is the ratio of the normalized absorption within the two energy regions ROI 1 and ROI 2 (regions of interest 1 and 2), which represent the peak and the valley of the shoulder. The regions are chosen to be equally wide, with a range of 1 eV (highlighted by different colors in Fig. 2). The energy range of 7118.3–7119.3 eV (pink in the inset in Fig. 2) corresponds to ROI 1, and the range of 7119.6–7120.6 eV (light blue in the inset in Fig. 2) corresponds to ROI 2. Then, r is defined as follows:

$$r = \frac{\int_{\text{ROI2}} \mu(E)}{\int_{\text{ROI1}} \mu(E)},$$

where $\int_{\text{ROI2}} \mu(E)$ and $\int_{\text{ROI1}} \mu(E)$ are the integrals of the normalized X-ray absorption μ , over the respective energy ranges.

For ϵ -Fe iron at room temperature before heating, r is equal to about 0.97. The ratio increases up to 1.06 for the points close to the centers of the heated spots. Thus, the transition from $r < 1$ to $r > 1$ indicates a significant change in the rising edge of the spectrum and marks the disappearance of the local maximum in the shoulder. Such a change is observed in the absorption spectra of both ϵ -Fe and γ -Fe under high temperatures,^{3,24,25} but a value of $r > 1$ at room temperature is a sign of iron contamination.¹¹

D. Sample characterization: SMS and XRD

The phase composition of the samples was investigated using different experimental techniques. Mössbauer spectra were collected using the **Synchrotron Mössbauer Source (SMS)** of ID18²⁶ at the ESRF, where a $^{57}\text{FeBO}_3$ single-crystal monochromator was used to obtain pure nuclear reflection (approximately 6 neV FWHM) at the Mössbauer energy of 14.4 keV from a wide spectrum of synchrotron radiation. Kirkpatrick-Baez mirrors were used to focus the beam to a cross-section size of 14×13 [horizontal $\times$ vertical] μm^2 . The velocity scales of all Mössbauer spectra were calibrated relative to a 25 μm thick α -Fe foil. Each SMS spectrum took approximately 30 min to collect, and all spectra were fit using the MossA software package.²⁷

X-ray diffraction experiments were conducted at the High-Pressure Diffraction Beamline ID15B (ESRF, Grenoble)²⁸ and the Extreme Conditions Beamline (ECB) P02.2 of PETRA III (DESY, Hamburg).²⁹ At the ECB, data were collected with a Perkin Elmer XRD1621 flat panel detector using X-rays with a wavelength of 0.29 Å and a size of $2.5 \times 2.5 \mu\text{m}^2$ at the focal position. At ID15B, a large area MAR555 flat panel detector was used and X-rays ($\lambda = 0.41$ Å) were focused at approximately $10 \times 10 \mu\text{m}^2$. At each position of interest, 90- or 180-s wide-scans of continuous exposure were collected during ω rotations of $\pm 15^\circ$ of the DAC (it

took 3 or 6 s per degree of rotation, respectively). The resulting diffraction images from both experiments were analyzed using Dioptas software.³⁰

III. RESULTS AND ANALYSIS

Iron samples in Ne and Ar pressure media were pressurized to 41 and 42 GPa, respectively. Two samples of iron investigated in KCl pressure medium were made of ^{57}Fe -enriched iron to improve the SMS data quality. They were pressurized to 41 and 47 GPa, respectively. In this section, we present the results of our experiments in detail.

A. Fe in Ne pressure medium

A strip of Fe foil was loaded into a DAC with Ne as the pressure transmitting medium and pressurized to 41(1) GPa. The pressure was determined from the change in the position of the high-frequency edge of the diamond Raman line in Raman spectra taken from the culet of one of the diamond anvils.³¹ The sample was heated at different points, and XAS spectra were collected as described in Sec. II. After heating, X-ray diffraction patterns were collected from the quenched sample *in situ* in the DAC. The patterns were taken from the center of each heated spot and from two different non-heated spots as references. The pressure after heating was 41(1) GPa, as determined from the X-ray diffraction of iron using the equation of state of ϵ -Fe.³²

Figure 3(a) shows a microscope image of the quenched iron sample after heating. The sample was heated six times (heating sequences), to which the numbers from LH1 through LH6 were assigned (Table I), at 4 different locations. After LH2, and after the mapping of the area, the alignment of the lasers was realized prior to pulsed heating at the same location as LH2 and was named LH3. Heating sequences LH5 and LH6 had similar laser pulse settings for different laser powers. After the laser power (LH6) was increased, the sample was heated at the same position to track the progress of the changes. The locations of all LH spots are marked in Fig. 3(a).

The mapping of the whole sample after each heating revealed a difference in the edge jump (i.e., the difference in X-ray absorption between energies below and above the K-edge) around each LH area [Fig. 3(c)], which is directly correlated with the amount of Fe at that location. However, the analysis of the edge jump variation is insufficient to judge whether it is due to a change in the thickness of the iron foil or because of a change in the sample composition. To resolve this question, a detailed analysis of jump normalized XAS spectra was performed, as described in Sec. II B. The map of the sample with the calculated r value at each sample position is presented in Fig. 3(d).

Table I summarizes the experimental details for all heating cycles in the experiment with Fe in Ne as the pressure medium at 41 GPa. In most of the cases, the change in the shoulder of the rising edge was observed immediately after the first heating cycle, i.e., after a few seconds of total heating time. This was the case for both CW and PL heating with relatively long pulses. It is important to note that even in the case of heating at peak temperatures of approximately 1600 K, i.e., well below the melting point of iron and below the ϵ -to- γ -Fe transition, the alteration was almost immediate,

FIG. 3. Upper panel—Microscope image of Fe in Ne quenched at 41 GPa: (a) positions of the laser heated spots on the sample; (b) positions of the spots for the X-ray diffraction data collection—dots 1 through 4 mark the heated spots and the dots labeled “ref1” and “ref2” mark the positions on the unheated reference points. Lower panel—A XAS map of Fe in Ne color-coded for (c) the edge jump and (d) the ratio r of the XANES spectra (for details, see Secs. II B and II C). Each black pixel marks a position without iron or relates to an unusable spectrum.

happening after a few seconds. In three different heating attempts (LH4, LH5, and LH6) with very short pulses of approximately 2 μ s, there was no visible change in any of the spectra taken from the center of the heating spot between the heating cycles. However, mapping of the whole sample area at the end of the heating cycles revealed sample positions, at which the rising edge shoulder in the spectrum was visibly reduced. One possible explanation is that the short-pulse heating produces high temperatures in smaller sample areas,³³ which are difficult to focus on. The mapping of the quenched sample after LH5 is shown as an example in Fig. 4.

In order to address the question of the phase composition of the sample in laser-heated spots, *in situ* X-ray diffraction was performed at the Extreme Conditions Beamline (P02.2) at PETRA III. The positions of the X-ray beam on the sample are designated in Fig. 3(b). Diffraction patterns collected from the heated areas revealed reflections that do not belong to ϵ -Fe,³² Re,³⁴ or Ne,³⁵ which was not the case for the reference unheated points. Particularly, at least three peaks with d-spacings 1.665(1), 1.715(1), and 1.754(1) Å were observed in all heated spots (Fig. 5). Although these data are insufficient to determine the phase unambiguously,

TABLE I. Characteristics of all heating cycles for Fe in Ne at 41 GPa.

Heating sequence	Heating cycle	Repetitions (cycles)	Total heating time	Max. T (K)	Remarks ^a
LH1	50 000 $\times$ 100 μ s (PL)	4	20 s	1600	$r > 1$ after two heating cycles (no spectra collected at first cycle)
LH2	10 s (CW)	6	60 s	2500	$r > 1$ after one heating cycle
LH3	Alignment heating	...	...	...	Same spot position as LH2 (after mapping)
LH4	100 000 $\times$ 2 μ s (PL)	10	20 s	2800	No changes ($r < 1$) in single collections between 10 cycles, but mapping ^b reveals $r > 1$ on the heated area
LH5	100 000 $\times$ 2 μ s (PL)	2	4 s	1700	No changes ($r < 1$) in single XAS collections between 2 cycles, but mapping ^b reveals $r > 1$ on the heated area
LH6	100 000 $\times$ 2 μ s (PL)	1	2 s	2700	No changes ($r < 1$) in the single collection after 1 cycle, but mapping ^b reveals $r > 1$ on the heated area

^aThe ratio r of the normalized absorption values for two energy regions in the X-ray absorption spectra of Fe (Fig. 2) was introduced to quantify the difference in the spectra collected at different points within and around a heated spot (see Sec. II B and Fig. 2). $r > 1$ indicates that chemical reaction(s) occurred.

^bUpon heating, the heated spot can slightly shift because of thermal expansion and optical effects in the laser optics, and the mapping on the quenched sample reveals chemical reaction(s), which could not be detected *in situ*.

FIG. 4. A XAS map of Fe in Ne color-coded for the ratio r of the XANES spectra (for details, see Secs. II B and II C) around the quenched spot after LH5 (2 μ s pulses), visible at approximately the center of the image. Each black pixel marks a position without iron or relates to an unusable spectrum. The heated area after LH1 (100 μ s pulses) is visible in the upper right corner.

all these peaks may be assigned to iron carbide(s) (Fe_3C^{10} or $\text{Fe}_7\text{C}_3^{36}$).

B. Fe in Ar pressure medium

An iron foil (thickness 10 μm) along with a ruby sphere was pressurized to 42(1) GPa with Ar as the pressure transmitting medium (see Fig. 1 for the experimental design). The sample was heated at different spots with a CW laser (LH1 and LH2) and a PL (LH3). XAS spectra were collected as described in Sec. II.

FIG. 5. (a) Diffraction patterns collected from the sample of iron in Ne at 41 GPa at positions 1 through 4 (red curves, heated spots) and reference positions ref1 and ref2 (green curves, non-heated areas) [see Fig. 3(b)]; reflections from diamond anvils are masked. The dashed rectangle highlights the region with three new peaks. (b) The same three peaks highlighted in the image of the integrated pattern collected at position 3 [see Fig. 3(b)].

The pressure increased to 49(1) GPa after heating, as determined using the ruby pressure scale.³⁷ SMS spectra were collected from the heated spots of the quenched sample and from the two unheated (reference) locations.

Table II presents details for all heating cycles. Heating sequences LH1 and LH2 consisted of CW heating cycles with single exposures for 5 s on the same sample spot. The temperature was gradually increased after every heating cycle starting from 1700 K (the first temperature recorded) and achieved 2700 K in LH2. Figure 6 shows the XANES spectra collected on the quenched sample between the heating cycles of LH1. The only observed change is the transition from ϵ -Fe to γ -Fe, which is in agreement with the spectral changes observed in Ref. 3, although in the present study, spectra are from the quenched sample at room temperature and not at high temperatures. The transition occurred only when the temperature reached 2050 K, which is in general agreement with the study of Anzellini *et al.*² It is known from the Fe-C diagram at ambient conditions that even a small amount of carbon can stabilize γ -Fe at lower temperatures.³⁸ It was shown by Narygina *et al.*³⁹ that quenching of γ -Fe at room temperature may be the result of stabilization of this iron phase by a small amount of carbon, which prevents its transformation to ϵ -Fe upon temperature decrease. Thus, it is still possible that in this experiment carbon might have been mobilized, but we have only indirect evidence of this.

Heating sequence LH2 also consisted of CW heating cycles. After a few cycles, due to the surface deformation of the iron foil, the absorption spectra were strongly affected, i.e., the relevant intensity of the absorption oscillations was modified, making the background level indistinguishable. This effect is known for inhomogeneous samples or samples with an irregular surface and is

TABLE II. Characteristics of all heating cycles for Fe in Ar at 49 GPa.

Heating sequence	Heating cycle	Repetitions (cycles)	Total heating time	Max. T (K)	Remarks
LH1	5 s (CW)	15	75 s	2600	Transition hcp $\rightarrow$ fcc between 1900 K and 2050 K
LH2	5 s (CW)	6	30 s	2700	Flashes during heating (>2700 K), no qualitative changes, distortion of absorption spectra due to inhomogeneous sample surface
LH3	1 000 000 $\times$ (5.5–12) μ s (PL)	7	39–84 s	3450	Strong distortion of absorption spectra, no evident qualitative changes

normally observed at the edges of the sample, making the spectra unusable. No other qualitative change was observed. The edge jump maps [Figs. 7(a) and 7(b)] directly reflect variations in the sample thickness and show locations of cavities produced on the

FIG. 6. (a) Normalized X-ray absorption spectra of quenched Fe in Ar taken from the center of the heated area in the course of LH1 (15 exposures of CW heating for 5 s each). The legend in the inset shows the maximum temperature recorded during each step of heating, and the total heating duration before the spectrum was collected. (b) Enlarged region of the same spectra (outlined by the dashed grey rectangle in (a); first, only ϵ -Fe is observed (green curves), the appearance of γ -Fe is indicated in spectra shown in blue. The red spectrum evidences the coexistence of both phases. (Successive spectra are vertically shifted for clarity. Increase in temperature during heating follows the positive direction.)

sample by laser heating at high temperatures. There is no surface deformation after LH1, but two cavities appear after LH2 and LH3.

Pulsed heating (LH3) consisted of relatively short pulses of 5.5 to 12 ms (Table II). The duration of the pulses varied due to minor adjustments of the laser power after every heating cycle. The sample was heated initially at 3050 K (pulse peak temperature), and its deformation was immediate. The next cycles resulted in increasing peak temperatures up to 3450 K. As in LH2, no other qualitative changes were observed.

The calculation of the ratio r that tracks changes in the Fe rising edge shoulder did not reveal any differences between the non-heated and the heated areas of the sample [Fig. 7(c)] after all three heating sequences.

Mössbauer absorption spectra were collected at room temperature on four different locations on the sample (Fig. 8). Position A corresponds to the area of LH1 and LH2, and position B is in the area of LH3. The spectra could be fit using a singlet with a center shift (CS) of $-0.399(5)$ mm/s and $-0.403(3)$ mm/s for positions A and B, respectively, using the full transmission integral with a normalized Lorentzian-squared source line. The spectra for the reference positions C and D (not heated) could be similarly fit with center shifts $-0.399(6)$ mm/s for C and $-0.405(5)$ mm/s for D, which are expected values for pure iron at this pressure.⁴⁰ Before fitting, a correction was applied by subtracting a known small contribution due to iron impurities in the Be refractive lenses used to decrease the divergence of the beam incident to the SMS.

No contamination is observed by Mössbauer spectroscopy, since all probed areas of the sample reveal only the presence of elemental Fe, which is also confirmed by XAS. However, since γ -Fe was observed in the quenched sample, the possibility of carbon diffusion in iron cannot be ruled out.

C. Fe in KCl pressure medium

Two samples of ^{57}Fe -enriched iron in DACs with KCl as a pressure transmitting medium were investigated. They were pressurized to 41(1) GPa [increased to 42(1) GPa after heating] and 47(1) GPa [increased to 53(1) GPa after heating], as determined using Raman spectra of diamond taken from the culets of the anvils.³¹

The first sample was heated at different positions during four heating cycles (Table III). XAS spectra were collected as described in Sec. II.

Continuous heating at temperatures up to 3000 K (LH1 and LH2) resulted in a significant deformation of the surface of the sample. Figure 9 shows the maps of the ratio r for the first sample before heating (a) and after LH3 (b) and LH4 (c). All spectra with

FIG. 7. A XAS map of quenched Fe in Ar representing (a) the edge jump after LH1, (b) the edge jump after LH3, and (c) the ratio r (after LH3) of the XANES spectra (see text). Each black pixel marks a position without iron or unusable spectrum. (d) Annotated microscope image showing the heated areas.

$r > 1$ were checked individually. It was found that the quality of these spectra was insufficient to conclude whether chemical changes took place, as $r > 1$ could be attributed to the effect of the heavily deformed sample surface and/or to the increased noise in the collected data. A transition from ϵ -Fe to γ -Fe was observed in the course of LH3.

Pulsed heating (LH4a, LH4b) deformed the sample even more than CW heating LH1 and LH2, which, along with the sample thinning, caused reduction of the area from which valid absorption spectra could be collected [Fig. 9(c)].

After heating, SMS spectra were collected from the quenched sample at the heated spots and at one other unheated position (Fig. 10). Position A corresponds to the area of heating sequences LH2, LH3, and LH4a, and positions B and D are in the area of LH4b. Position C was selected to be as far as possible from the heated spots. The SMS spectra were fit using the full transmission integral with a normalized Lorentzian-squared source line after having corrected the contribution from iron impurities in Be lenses.

SMS spectroscopy revealed changes in the quenched sample, both in the heated areas and around them. In all spectra, the singlet, characteristic for metallic iron at this pressure,⁴⁰ featured a shoulder, which suggested the appearance of an additional

chemical component in the sample after heating. The singlet had a center shift (CS) of approximately $-0.34(4)$ mm/s in all spectra, as expected. To take into account the additional component, a paramagnetic doublet was added to achieve the best fit of the experimental data. The CS of the doublet ranges from $-0.18(11)$ mm/s to $-0.12(44)$ mm/s and quadrupole splitting (QS) from $0.64(4)$ mm/s to $0.77(6)$ mm/s. The hyperfine parameters of the doublet are in close agreement with the hyperfine parameters of Fe_3C at similar pressure.⁴¹ It should be noted that the observed new component cannot be interpreted as γ -Fe, since such a component is not observed in the SMS spectra of Fe with Ar, while the presence of γ -iron is identified in both cases by XANES.

The second ^{57}Fe -enriched iron sample was heated for several minutes in total, at temperatures up to 3800 K (peak temperature of the pulse), using the double-sided pulsed laser heating system of the Nuclear Resonance beamline at the ESRF,⁴² with laser modulation frequency at 1 kHz and pulses of 700 μs duration. Apart from the pure iron singlet of the non-heated sample [Fig. 11(a), the blue singlet indicates the non-heated iron], the second absorption component appeared after less than a minute of alignment heating [Fig. 11(b), the green doublet; the red singlet indicates the heated iron]. Alignment heating was done at a low laser power (the

FIG. 8. SMS spectra of Fe pressurized in Ar at 49 GPa (black dots). The spectra were collected at different locations (A, B, C, and D) designated in the microscope image on the right. Positions A and B correspond to the laser heated areas; the sample was not directly heated at spots C and D. The red solid lines show the theoretical fit, and the residuals are indicated above the spectra (red dots). Singlets marked blue correspond to the unheated Fe; singlets marked red correspond to the heated Fe. The size of the crosshair in the microscope image matches approximately the size of the focused X-ray beam on the sample.

sample temperature was less than 1500 K) to align and synchronize the lasers for the pulsed operation. After heating, the second component became more prominent, as seen in Fig. 11(c). The spectra were fit using the full transmission integral with a normalized Lorentzian-squared source line. The single line has a central shift

(CS) of $-0.410(6)$ mm/s. The best fit was obtained with the addition of a paramagnetic doublet with a CS of $-0.15(22)$ mm/s and a quadrupole splitting (QS) of $0.65(32)$ mm/s after alignment and with a CS of $-0.17(12)$ mm/s and a QS of $0.81(19)$ mm/s at the end of the heating experiment. The uncertainties are high, but

TABLE III. Characteristics of all heating cycles for Fe in KCl at 42 GPa.

Heating sequence	Heating cycle	Repetitions (cycles)	Total heating time	Max. T (K)	Remarks
LH1	15 s (CW)	7	105 s	2300	No evident qualitative changes apart from sample deformation at the heated area
LH2	15 s (CW)	4	60 s	3000	Flashes during heating ($\gg 2700$ K). Evidence of hcp $\rightarrow$ fcc transition after heating at 2500 K
LH3	Long (CW)	1	3 min	2700	Significant deformation of the sample, hole formation, no evident qualitative changes in the spectra from the heated areas.
LH4a	$500\,000 \times 2$ μ s (PL)	1	1 s	3400	Each burst of pulses on different sample positions (LH4a and LH4b)
LH4b	$500\,000 \times 2$ μ s (PL)	1	1 s	3300

FIG. 9. XAS map of quenched Fe in KCl based on the ratio r of the XANES spectra (a) before heating, (b) after heating cycle LH3, and (c) after heating cycle LH4. Each black pixel marks a position without iron or unusable spectrum. (d) Annotated microscope image showing the positions of the heated spots.

expected, considering the small contribution of the new component and the high degree of overlap. Nevertheless, the Fe_3C interpretation is plausible and in close agreement with the literature.⁴¹

X-ray diffraction at the ID15 beamline at the ESRF revealed both ϵ -Fe and γ -Fe in the sample at room temperature, but iron carbide could not be detected. The sample was mapped at several locations covering the whole heated area. The pressure of 53.0(5) GPa was determined using the KCl equation of state.⁴³

IV. DISCUSSION

In most of the cases examined here, laser heating of iron resulted in the formation of iron carbides, which were detected by XRD, XANES, or SMS in agreement with the literature. Each time, two different techniques were used to investigate the heated samples in order to cross-validate the results, which are summarized in Table IV. Mössbauer spectroscopy was very sensitive for detection of carbides in two experiments with ^{57}Fe -enriched iron in KCl as a pressure medium, whereas XANES gave an uncertain result and XRD appeared to be insufficiently sensitive as the amount of the carbide was negligibly small in comparison with the amount of Fe and KCl, which dominated the XRD pattern.

In all experiments reported here, no significant difference was observed in the effect of CW and PL heating on iron-carbon reactivity. Thus, we could conclude that pulsed laser heating (microseconds

pulses duration, up to a 100 kHz repetition rate) does not provide an obvious advantage in the prevention of chemical reactions between the heated iron sample and the carbon from the diamond anvils. There are examples when more reacted material was observed in the CW laser heated areas [Figs. 3(d) and 10]. However, no definitive conclusions can be drawn regarding the advantages of PL for minimizing reactions, because other factors, such as heating temperature, sample thickness, heating duration, etc., could not be quantified in our experiments. Thus, our principal conclusion is that laser heating in DACs can lead to chemical reactions, and this effect must be taken into account, particularly, for interpretation of experiments on melting of iron and other metals.

Our observations suggest that in cases where a chemical reaction with carbon occurs, it happens almost immediately, after only a very few seconds of heating at moderate temperatures (independently of the heating method, CW or pulsed). It means that chemical contamination by carbon may be an important factor even if efforts are applied to minimize the heating time, because, as a rule, tens of seconds are usually necessary to characterize the temperature and the state of the hot sample.

In all experiments in this study, at sufficiently high temperatures, we observed the formation of γ -Fe, and this phase was quenchable. Preservation of γ -Fe at ambient temperature in both the multi-anvil apparatus and the laser heated DAC experiments^{44,45} has been previously reported as an effect of slow

FIG. 10. SMS spectra at different areas of the ^{57}Fe -enriched iron sample pressurized in KCl at 42 GPa (microscope photo on the right). Positions A, B, and D correspond to the laser heated areas of the sample, while C was not directly heated. The red solid line shows the theoretical fit, and the residuals are indicated above the spectrum (red dots). Singlets marked red correspond to iron, and doublets marked green correspond to the new compound that appeared after heating (see text for details). The crosshair size marked on the photograph matches approximately the size of the focused X-ray beam on the sample.

FIG. 11. SMS spectra at different positions of the ^{57}Fe -enriched iron sample pressurized in KCl at 53 GPa. The red solid line shows the theoretical fit, and the residuals are indicated above the spectrum: (a) before heating (the singlet marked by the blue surface corresponds to the unheated iron), (b) after less than one minute of low-power pulsed heating for laser alignment (the singlet marked by the red surface corresponds to the heated iron; the doublet marked by the green surface corresponds to the new compound that appeared after heating and was interpreted as iron carbide; see text), and (c) after several minutes of pulsed heating ($f = 1$ kHz, pulse duration $700\ \mu\text{s}$) at temperatures up to 3800 K (red singlet—heated iron; green doublet—the new compound).

TABLE IV. Summarized results.

Sample	Pressure medium	Pressure (GPa)		Analysis	Evidence of reaction
		Before heating	After heating		
Fe	Ne	41	41	XANES	Yes
Fe	Ar	42	49	XRD	Yes
				SMS	No
⁵⁷ Fe enriched	KCl	41	42	XANES	Uncertain
⁵⁷ Fe enriched	KCl	47	53	SMS	Yes
				XRD	No

transformation kinetics to ϵ -Fe, or due to the high cooling rate. However, Narygina *et al.*³⁹ demonstrated that γ -Fe can be also stabilized by a small amount of carbon that hinders martensitic transformation during quenching. Thus, in experiments in which carbides are not detected (like in our experiments with the Ar pressure medium) but γ -Fe is quenched at ambient temperature, carbon contamination cannot be ruled out.

V. CONCLUSIONS

For the purposes of this study, a series of DACs were heated using continuous wave (CW) and pulsed laser (PL) heating and the quenched samples were analyzed *in situ* using energy dispersive X-ray absorption spectroscopy, X-ray diffraction, and synchrotron Mössbauer source spectroscopy. Iron carbide formation was detected in most experiments regardless of the laser heating method. While pulsed laser heating is generally considered advantageous in preventing the mobilization of carbon from the diamond anvils and its chemical interaction with the sample, this is refuted by our results. Generally, one experimental technique was not enough to fully characterize the chemistry of the sample, and a cross-validation of techniques was necessary. For this reason, extra precautions should be taken in experiments with iron in a laser-heated diamond anvil cell and the application of more than one analytical technique is strongly suggested, as well as *ex situ* analysis of the recovered sample if possible.

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