

Strain Evolution Imaging during Hydrogen Reduction of Magnetite

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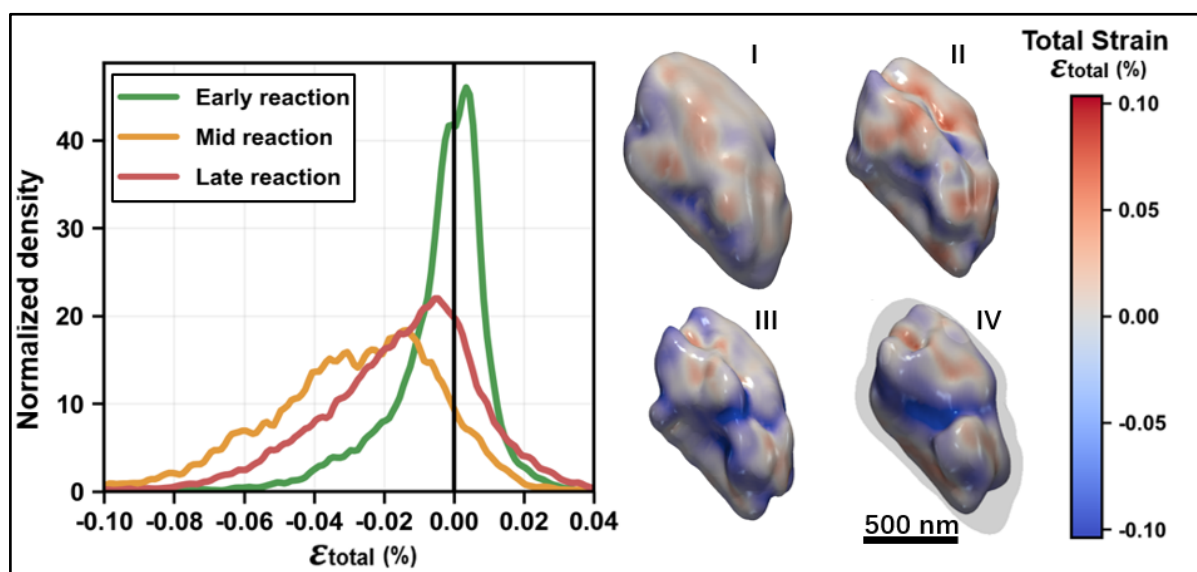
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Abstract

In situ Bragg Coherent Diffraction Imaging (BCDI) measurements were used to visualize the three-dimensional distribution of strain in a micron-sized crystal of magnetite, Fe_3O_4 , during reduction under H_2 at 475 °C. BCDI images only crystalline parts of the sample. The BCDI-reconstructed crystalline volume was initially observed to increase steadily with time upon temperature ramping, indicating an annealing effect of the damage caused by focused ion beam sample preparation. Under H_2 reduction conditions at 475 °C, the volume decreased substantially, and the crystalline surface adopted an undulating pattern of ridges and valleys. Meanwhile, the amplitude gradient beneath the surface first sharpened and then markedly broadened inward. The local heterogeneous strain projected along the 111 crystallographic direction was found to localize near edges and corners, with prominent hot spots around valleys. A negative shift in strain suggests overall lattice contraction. Together, these describe a surface-to-interior etching-like progression within the visible Fe_3O_4 crystal, accompanied by a net contractive lattice response to which lattice-oxygen removal may contribute. Local strain evolves in spatial correspondence with the undulating morphology. These observations help clarify the nanoscale changes in crystalline morphology and lattice strain during hydrogen reduction of magnetite, relevant to the steam-iron reaction proposed as a hydrogen storage method.

KEYWORDS: *Bragg coherent diffraction imaging; hydrogen economy; hydrogen reduction; lattice strain; nanocrystals; steam-iron reaction*

Green hydrogen has emerged as a central energy carrier in the transition toward clean energy storage and carbon-free industrial processes, owing to its high gravimetric energy density [1] and compatibility with renewable electricity, for example through electrolytic water splitting [2,3]. Unfortunately from a safety perspective, hydrogen is extremely flammable, making its storage a challenge, especially for large-scale, long-duration deployment. In the so-called steam-iron reaction, iron and iron oxides are reversibly interconverted through reactions with H_2 and steam, offering an attractive approach for hydrogen storage and release [4]. The same system may also contribute to carbon-free iron and steel production [5–7], whose conventional production is energy-intensive and produces large CO_2 emissions [8]. While such iron-oxide cycling has been actively pursued [4,9,10], there are material science questions that must be addressed to understand its known rate-limiting mechanism and to optimize it for more store/release cycles.

The hydrogen-driven reduction of iron oxides is a hierarchical, multi-scale process [11,12], where different mechanisms operate on scales spanning from the macroscale, e.g., strain within an oxide particle due to phase volume mismatch [13], to the microscale, e.g., cracks and pore networks affecting both the reduction rate and final extent of conversion through facilitated gas diffusion, beyond the predictions of homogeneous kinetic models [11–13], and the atomic scale, e.g., defects and interfacial structure influencing solid-state diffusion, local phase transformation pathways, and the evolution of phase boundaries [11,12,14]. An example fluidized-bed study reported a

transition around 570 °C for magnetite reduction, below which magnetite was observed to reduce directly to porous metallic iron, preserving good gas permeability [15,16]. Above this temperature, reduction proceeded through wüstite and produced dense iron layers that restricted gas access [16]. Solid-state oxygen diffusion through this blocking layer was found to limit further reduction [16,17]. Another three-dimensional (3D) study above 570 °C identified two modes of reduction. These included topochemical reduction resulting in an iron layer that covered the remaining $Fe_{1-x}O/Fe_3O_4$ parts and hence limited subsequent reduction, whereas topotaxial growth along crystallographic directions allowed reduction to go deeper [18]. In situ atomic-scale studies further reveal that hydrogen-driven reduction can proceed through coexisting interfacial pathways involving wüstite and transient amorphous metallic Fe, with the formation of amorphous Fe attributed to interfacial strain arising from lattice mismatch at metal-oxide boundaries [14]. These findings indicate that temperature is a crucial parameter controlling the internal reduction mechanism of iron oxides, while other factors—including the initial oxidation state of the material [19] and the heating rate [20]—also affect the process, resulting in a multi-scale reduction process involving multiple reaction pathways and complex intermediate states [12].

Understanding how such internal structures evolve during redox reaction is essential for further elucidating the origins of kinetic blockage and irreversibility in steam-iron systems. One technique capable of imaging crystalline material in 3D and probing its lattice variations with excellent sensitivity is Bragg coherent diffraction imaging (BCDI) [21,22].

It is a non-destructive technique that reconstructs 3D nanoscale images of finite crystalline objects from coherent X-ray diffraction measured around a selected Bragg reflection. Phase retrieval—a key algorithm in the reconstruction [23] converts these measurements into a complex-valued crystallographic electronic density in real space, $\rho(\mathbf{r}) = A(\mathbf{r})e^{i\phi(\mathbf{r})}$. The amplitude A represents the crystalline contribution to the measured reflection, therefore reveals the morphology and internal structure of the diffracting volume. The phase ϕ corresponds to the projection of the lattice displacement field onto the scattering vector Q associated with the same Bragg reflection. The spatial derivative of this displacement component along Q gives the corresponding strain component, which directly maps regions of local lattice expansion and contraction. Tracking these quantities throughout a reaction sequence therefore provides direct access to the evolution of crystal morphology, defects, and lattice displacement. The high spatial resolution (≈ 40 nm) [21] and fine strain sensitivity ($\approx 0.01\%$) [24,25] of the 3D BCDI method make it well suited for tracking reaction effects on a single crystal at micron to sub-micron length scales. And indeed, there have been 3D studies of magnetite crystals using BCDI under conditions such as temperature variation [26] and oxidative environments [27], demonstrating its capability of tracking internal lattice variation caused by temperature and redox changes. Operando BCDI has also been applied to Bi_2WO_6 nanoflakes to resolve the morphology and strain evolution during defect-associated phase nucleation and structural transformation under an H_2/N_2 atmosphere [28].

Here, we used 3D BCDI to study the reduction of a single micron-sized magnetite crystal subjected to H_2 exposure at elevated temperature. The sample was prepared using focused ion beam (FIB) cutting. We tracked the evolution of reconstructed quantities such as amplitude, volume, lattice parameter, and strain fields throughout the reaction. Pronounced changes in the BCDI-visible Fe_3O_4 morphology were observed, with a global enhancement of negative strain corresponding to lattice contraction and the formation of local strain domains associated with etching-like

features. Results are compared with previous studies to examine the structural mechanisms involved in the iron-oxide reduction process.

Results and Discussion

Amplitude:

For the present analysis, the reconstructed amplitude, A , was normalized to the range $0 \leq A \leq 1$ by default. BCDI reconstructions reveal continuous changes in the reconstructed amplitude field throughout the experiment, as shown in Figs. 1 and 2. The amplitude distributions in Fig. 2 contain a common low-amplitude spike and a medium- to high-amplitude component whose shape varies with the reconstructed crystal's feature. Comparison with the corresponding 3D reconstructions shows that the $A = 0.2$ threshold safely removes low-amplitude signal external to the main crystal boundary; whereas the $A > 0.4$ region selects the compact interior part of the reconstructed object (Supplementary I), reproducing the morphology observed in the Scanning Electron Microscope (SEM) image (Fig. 3). We therefore take the reconstructed crystal's effective amplitude range to be $0.2 < A < 1$, ensuring that subsequent analysis is robust against low-amplitude noise. Additional $0.4 < A < 1$ range is treated as an operational measure of the higher-amplitude crystalline component.

For each measurement scan, the reconstructed crystalline volume was defined as the number of voxels within the amplitude range multiplied by the voxel volume. The voxel volume ranged between 2.27×10^{-5} and $4.81 \times 10^{-5} \mu\text{m}^3$ across the reconstructed datasets, depending on the preprocessing and cropping parameters. The spatial resolution was then estimated from the Gaussian standard deviation, fitted to the derivative of the local amplitude transition across the crystal boundary (Supplementary II). For stable reconstructions, the spatial resolution ranged from 30-45 nm, depending on the direction.

As an overview of the full in situ experiment, the reconstructed crystalline volume was tracked using the two amplitude-based definitions introduced above (Fig. 1). Progressive heating ramps and isothermal

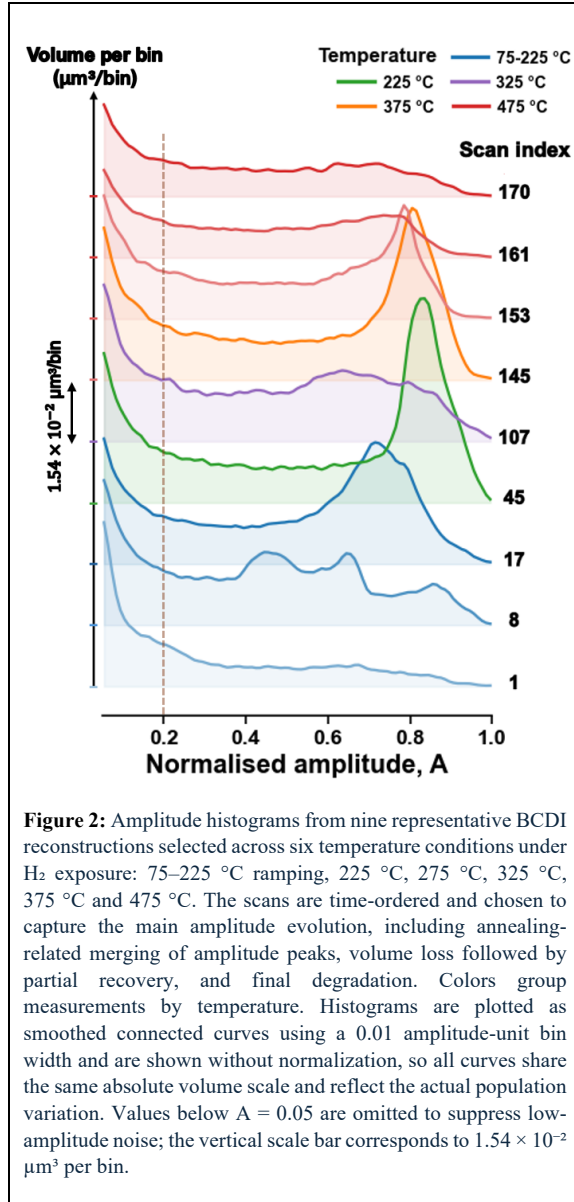
steps were applied between periods of H₂ exposure, as shown. Transient volume fluctuations were observed, including the “selective fluctuations” inherent to the pipeline reconstruction procedure [29,30].



The $A > 0.2$ volume represents the BCDI-visible crystalline volume after removal of the low-amplitude external signal and is shown as the solid blue line. During the initial temperature increase from 75 to 225 °C, the reconstructed crystalline volume increased from approximately 0.35 to 1.15 μm^3 , approaching the nominal volume of the as-prepared crystal, estimated as 1.01 μm^3 from the SEM image. We consider this to be caused by recrystallisation of the lattice due to defect annealing in the crystal [31], including defects introduced by FIB sample preparation [32] and possibly those of mineral origin. From 275 °C (scan 48), the reconstructed volume decreased, more steeply during the 325 °C stage. The volume began to recover on ramping to 375 °C and continued to increase under the following H₂ exposure. The V-shaped trajectory over 275–375 °C shows a partially reversible volume response. A further decrease in volume occurred upon heating to 475 °C after the temperature had stabilized. The rapid volume reduction persisted through the first half of the 475 °C stage, followed by minor fluctuations toward the end

of this final hydrogen treatment. The overall decreasing trend in this stage is consistent with the reduction in total scattered photon counts in detector space (Supplementary III).

The $A > 0.4$ volume follows the $A > 0.2$ volume with an offset of 0.146–0.284 μm^3 (central 90% interval) across the experiment. No clear monotonic trend in this offset is observed overall, except for an apparent widening during the 475 °C stage. The lattice parameter was also averaged within the same BCDI-visible volume for each reconstruction and followed across the full experiment (Supplementary IV). The initial value at 75 °C is approximately 8.399 Å, close to the reported expectation for magnetite at this temperature [33]. The lattice parameter then rises together with temperature, following the reported thermal-expansion behavior [33,34]. We found that a decline begins to appear under constant temperature (from 375 °C), suggesting possible H₂-induced structural responses.



The amplitude distribution series in Fig. 2 provides a statistical view of the evolution. It starts with a relatively flat distribution, then rapidly develops multiple medium- to high-amplitude peaks and subsequently evolves toward a more dominant single peak during the ramp from 75 to 225 °C and the subsequent H₂ exposure at 225 °C. We attribute this to homogenization of the initially weak diffracting volume, likely affected by residual defects, around the targeted Bragg peak. This occurs in the same annealing context as the earlier volume recovery. At 325 °C, partial degradation appears in the amplitude distributions. This trend recovered again during the following 375 °C stage, corresponding closely to the V-shaped volume trend in Fig. 1. From 475 °C onwards, the peak gradually shifts toward lower amplitudes and diminishes simultaneously, increasing the fraction of low-amplitude voxels. This is largely a

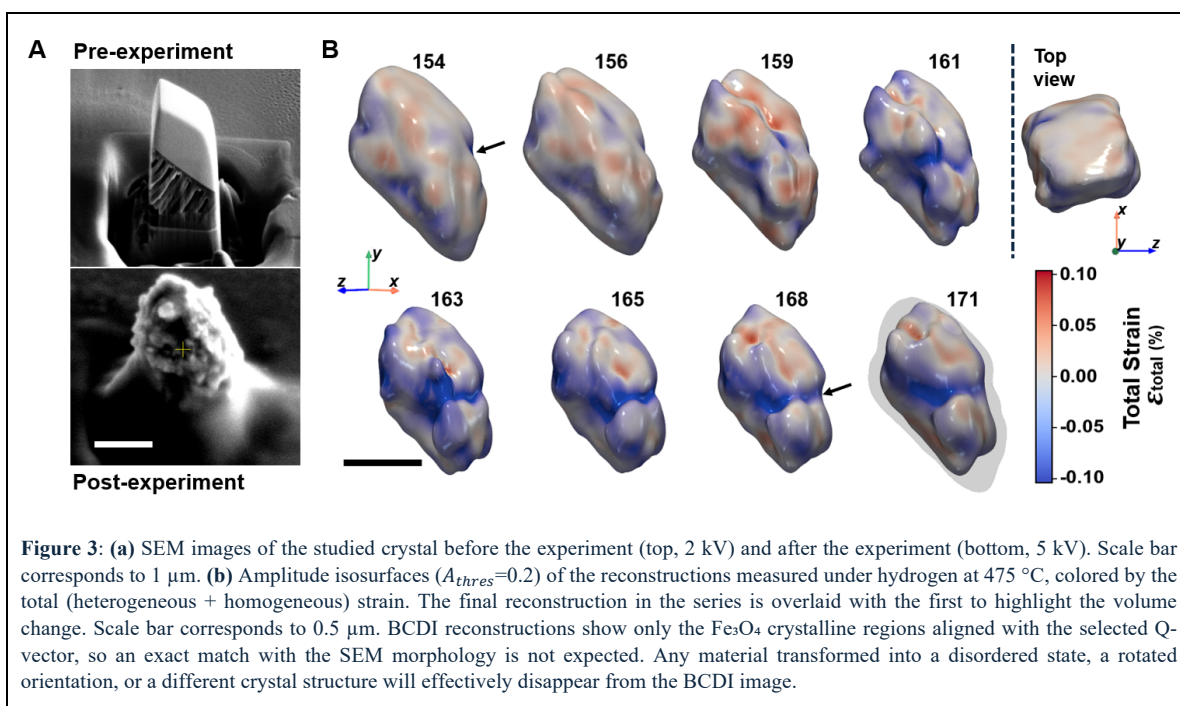
monotonic evolution. The volume and amplitude-distribution analyses agree, and both show the clearest H₂ reaction response at 475 °C. The response here is largely irreversible and represents the most distinct permanent change observed in the experiment, in broad agreement with previous reports on H₂-driven reduction of magnetite [12,15,16]. This dataset was therefore given analytical priority.

The 3D morphological evolution during the final 475 °C H₂ exposure is further studied using the BCDI reconstructions in Fig. 3b, shown as isosurfaces at $A = 0.2$. The reduction in size is accompanied by surface roughening, expressed as local peaks and valleys on the reconstructed isosurface. Reactive/unreactive regions remain at similar spots from scan to scan, arguing for a continuous and spatially localized reaction process. For instance, the crack-like depression (arrowed) on the surface clearly develops across the series. And the bottom facet, which is attached to the supporting Pt pillar shown in the SEM image (Fig. 3a), appears resistant to the reaction, likely because of its limited H₂ exposure. Persistent features like these help us distinguish the reconstructed morphology from possible twin-solution artefacts. The undulating surface pattern contrasts with what was observed at lower temperatures, where the surface remained comparatively smooth during volume variation. We also remind the reader that only the ordered crystal regions contributing to the selected 111 reflection are imaged: the part of the Fe₃O₄ sample that appears to disappear is merely losing its crystalline order. Such an “etching-like” effect is consistent with porous and cracked microstructures reported during magnetite reduction [11,15,16].

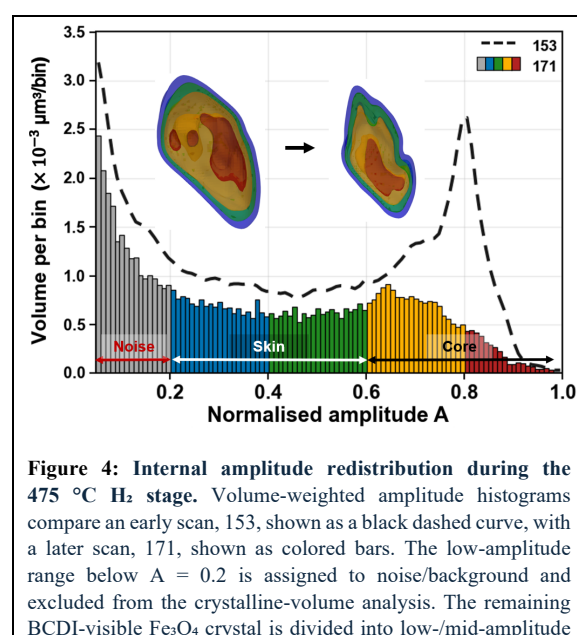
The pre-experiment SEM image (Fig. 3a) defines the initial crystal morphology and is broadly consistent with the earliest 475 °C BCDI reconstruction. The alignment is illustrated in detail in Supplementary Section V. By contrast, the post-experiment SEM image exhibits additional rough features. They do not correspond to the etched surface observed in the BCDI reconstruction, since the two are located on different radial levels. Post-experiment SEM Energy Dispersive X-ray (EDX) spectroscopy analysis

(Supplementary VI) shows that the central region forms a compact Fe-rich structure, while Fe signal is also detected in the outer regions corresponding to the rough morphology observed in SEM, with a comparatively weaker oxygen signal. A gap between these regions coincides with a Si signal. The oxygen distribution is more spatially diffused and not confined to the Fe-rich regions. The oxidation states and phase identities of the Fe-containing regions

cannot be determined from the present EDX measurement. In the postmortem electron energy-loss spectroscopy (EELS) analysis, the fitted Fe $L_{3\alpha}$ peak position showed no resolvable spatial shift across the studied regions (Supplementary VII). Any reduction-induced Fe-valence heterogeneity may have been transient or remained below the spatial or spectral sensitivity of the EELS measurement. Reoxidation may also have been involved after the experiment [35].



Scans 153 and 171 effectively mark the beginning and end of the reliable 475 $^{\circ}\text{C}$ H_2 sequence, over which the amplitude evolution is largely monotonic. Figure 4 compares the two scan's amplitude distributions with successive iso-volumes rendered. In scan 153, the lower-amplitude regions show approximately parallel offsets from the isosurface ($A = 0.2$). This radial ordering breaks down toward the crystal interior, as seen from the irregular $A = 0.8$ isosurface. The unstable internal high-amplitude extrema are commonly associated with instability near intensity maxima in the diffraction pattern. Such surface-parallel layering is blurred in scan 171, while the amplitude gradient

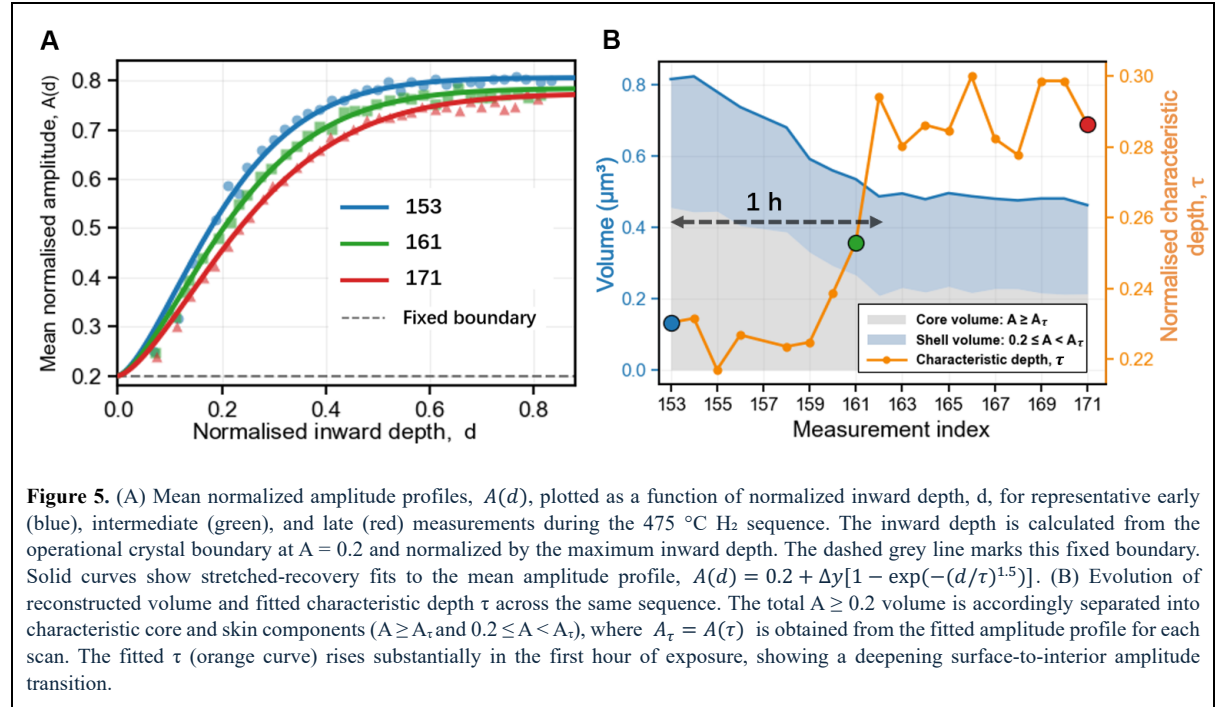


skin region and a high-amplitude core region, as indicated by the colored amplitude intervals. The displayed amplitude range, $A = 0.05\text{--}1.0$, is divided into 100 bins. The clipped iso-volume views show the corresponding 3D spatial arrangement of these amplitude bands, using the same color scheme as the histogram.

remains near the surface. Noticing the positive correlation between amplitude level and inward depth into the crystal, we considered amplitude level a spatial proxy for radial position. This provides the basis for later labelling of the different volume components.

The amplitude distributions below the 3D clipping images in Fig. 4 shown on a shared volume scale and rendered using the same color groups as the iso-

volumes. Beyond the overall decrease in bin height due to global shrinkage, we also see the initial high-amplitude volume peak shift toward lower amplitudes and broaden. For comparison between different radial regions, we partition the crystal volume into skin ($0.2 < A < 0.6$) and core ($0.6 < A < 1.0$) components. A common threshold is chosen near the transition between the medium-amplitude plateau and the high-amplitude peak across the series; the two shrink by $0.105\text{ }\mu\text{m}^3$ (27.5%) and $0.252\text{ }\mu\text{m}^3$ (57.2%), respectively. The stronger loss of the high-amplitude component raised the low-/medium-amplitude fraction relative to the remaining volume, resulting in the apparent skin thickening relative to the crystal size.



We further characterize the radial amplitude variation beneath the crystalline boundary at $A = 0.2$. Each voxel was assigned a normalized 3D Euclidean distance (d) from the boundary, obtained by dividing its physical depth by the maximum depth from the surface. Voxels were then aggregated layer by layer into depth shells (Supplementary VIII) The mean amplitude vs depth profile $A(d)$ was found to fit a

stretched-exponential form shown in Fig. 5A. We define $\tilde{A}(d) = A(d) - 0.2$, offsetting the amplitude by the $A = 0.2$ mask threshold for simplicity,

$$\tilde{A}(d) = \Delta y \left[1 - e^{-(d/\tau)^\beta} \right],$$

The stretching exponent was fixed stably at $\beta = 1.5$. Here, Δy and τ constitute the two free parameters,

corresponding to the amplitude recovery above surface threshold and the characteristic depth of the amplitude transition, respectively. Fits for three representative scans are shown in Fig. 5A.

The surface-to-interior amplitude transition becomes shallower and moves deeper into the crystal over scans, seen from the fitted curves (Fig. 5A). A surface-initiated progression has also been reported during topochemical reduction of hematite [18]. The full evolution of the depth τ is plotted in Fig. 5B together with the reconstructed volume evolution. There is a slight decrease at the start, followed by a sharp rise between scans 159 and 162, before levelling off at a higher value. This takes about one hour from the start of the 475 °C H₂ sequence, coinciding with the previously identified stabilization of the crystal volume. Same overall sequence observed for the denormalized depth τ_{nm} , with a more pronounced initial decrease from approximately 97 nm to 83 nm, followed by a rise to around 95 nm and subsequent fluctuations around this level.

The characteristic amplitude $A(d = \tau)$ on the fitted amplitude profile, was further used to define a characteristic skin/core partition for each scan. As shown in Fig. 5B, the reconstructed volume, particularly the core component, decreases substantially during the first hour. This period can be further divided into two windows: up to scan 158, the core volume decreases more mildly; from scan 159 to 162, the core volume decreases faster. And a similar transition was observed during the first hour in the τ analysis. Such concurrent transitions support two degradation stages: an initial stage dominated by preferential loss of the skin, with this “peeling” behavior giving a thinner characteristic depth, followed by a stage in which the reaction extends beyond the thinned skin and the depth increases. The core and total volumes subsequently level off at a lower value at approximately the same time that τ reaches a higher level. This subsequent levelling off may indicate the onset of kinetic retardation after a certain extent of reduction.

The skin volume declining more mildly than the core

does not necessarily mean that the core is more reactive. As the high-amplitude peak shifted toward lower amplitudes, some core voxels may have entered the skin amplitude range, partly offsetting the skin loss. The core has no comparable source of replacement. This feature is embedded in the amplitude redistribution seen in Fig. 4.

Strain:

A second level of detail concerns strain evolution. Following the method of Atlan et al. [36], the homogeneous strain, derived from the Bragg-angle shift, and the heterogeneous strain, obtained from the derivative of the local lattice displacement, were combined to give the total strain field of the particle. Fig. 6 plots a sequence of total-strain histograms. Each histogram collects the strain values of voxels within the reconstructed crystal boundary ($A > 0.2$). During

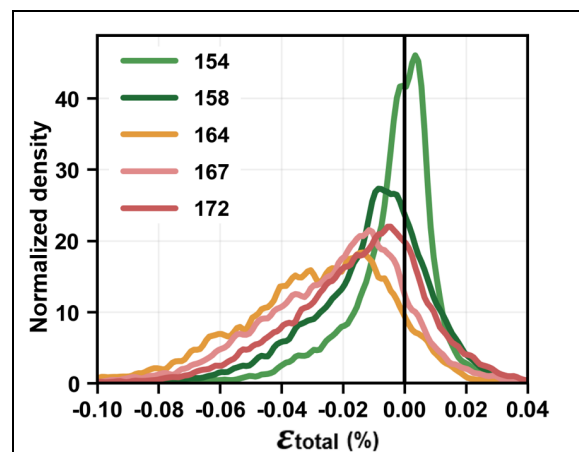
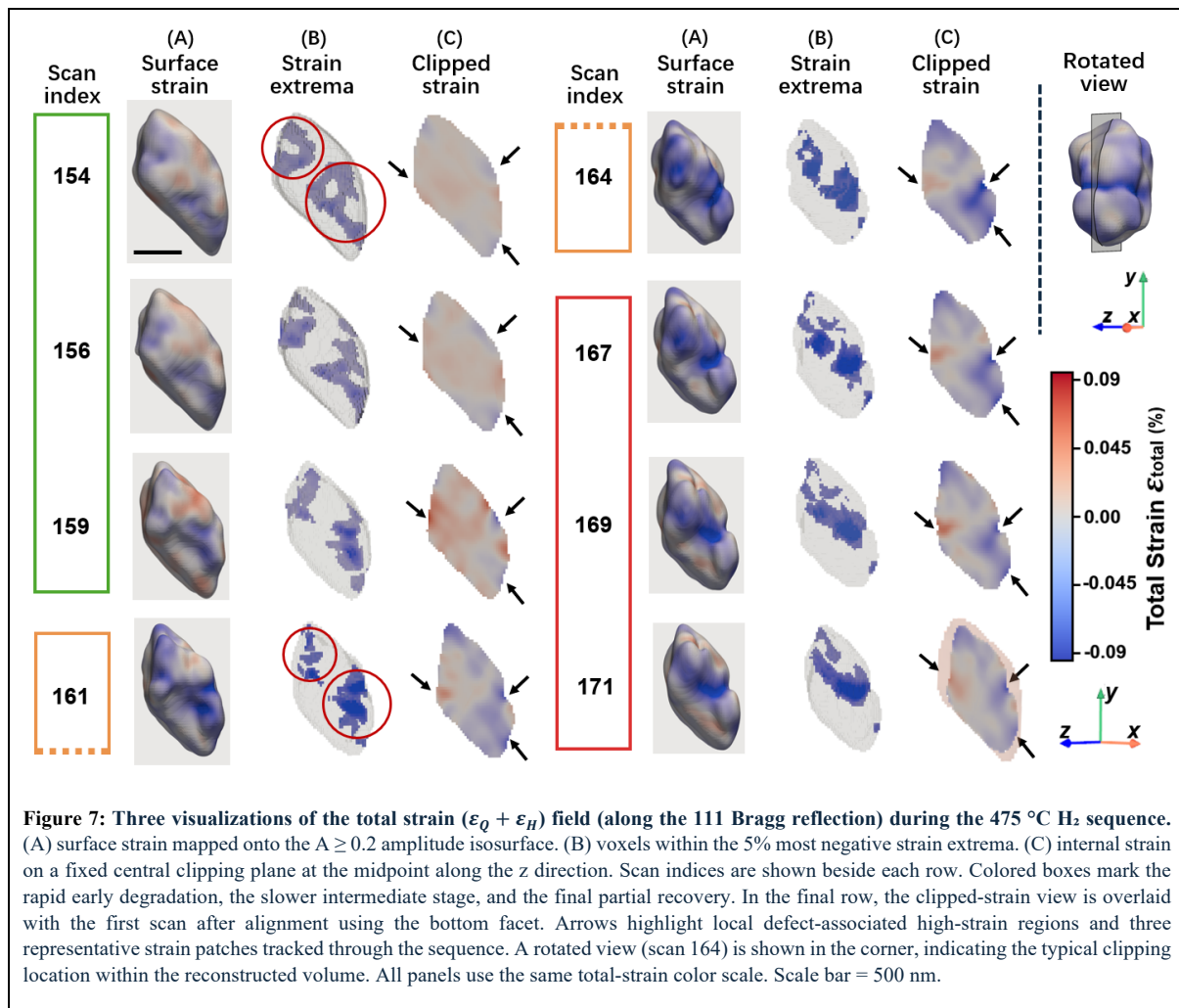


Figure 6: Total-strain distributions for five representative measurements during the 475 °C H₂ stage. Curves correspond to global measurement indices 154, 158, 164, 167 and 172, calculated from voxels within the crystalline amplitude range $0.20 < A < 1.00$. Each histogram is independently normalized to highlight changes in strain-distribution shape. The strain ranges from -0.10% to 0.04% is divided into 140 bins of 0.001% . Histograms are displayed as smoothed curves by Gaussian filtering.

the first half of the sequence (scans 154 to 164), the distribution underwent substantial broadening and a negative shift. From scan 164, where it reached its most negative peak position and maximum width, to the final scan 172, this trend partially reversed. By the end of the sequence, this leaves a net peak-center shift

of -0.008 strain percentage relative to scan 154, with a net full width at half maximum (FWHM) broadening of 149%. This is a recovery from the shift of -0.018 strain percentage and a 221% broadening at scan 164. The strain minimum at scan 164 occurs close to the levelling-off transition around scan 162 identified from the amplitude analysis. This common transition may correspond to the onset of kinetic retardation suggested by the amplitude analysis, while the continued strain evolution shows that lattice changes remain detectable afterwards. Meanwhile, the strain distribution also shows an apparent negative tail

throughout. Such asymmetry indicates a preference for strain development on the negative side. The homogeneous component of the total strain distribution exhibits a net negative drift with time, matching the trajectory of the total-strain histograms, while the heterogeneous part governs the asymmetric, broadening feature of the distribution (Supplementary IX). This left shift in strain indicates lattice compression along the probed 111 scattering vector. This would further imply a contraction of the average lattice spacing, assuming cubic symmetry remains throughout this sequence.



3D strain reconstructions during H_2 exposure at 475 °C are shown in Fig. 7. Column A presents the surface strain distribution, which overall agrees with the histogram trends. During the early stage up to scan 159, both positive and negative strain regions

gradually intensify, accompanied by substantial etching of the reconstructed morphology. From scan 159 to 164, the surface strain field becomes increasingly dominated by negative strain. This interval overlaps with the sharp rise in τ . The most

negative point at scan 164 is illustrated by the predominantly blue surface. In the later scans, this negative dominance partially relaxes, and the strain range narrows slightly.

The most heavily compressed voxels (the most negative 5% of the total-strain distribution) are shown in Fig. 7, column B. These strongly negative-strain voxels consistently appear close to the crystal surface, and their distribution becomes more concentrated and intense following the initial pattern. This is most clearly seen between scans 154 and 161, during which the two highlighted extrema populations become progressively more concentrated. From scans 164 to 171, the extrema distribution instead appears to form more bridging features between the dominant negative-strain populations. In a different reaction

Unlike the amplitude field, which shows a radial-like organization, the internal strain field (Fig. 7, column C) can vary strongly at similar inward depths. How these strain features are arranged seems to be inherited from the initial strain and morphology patterns. The persistence of strain at similar locations across the sequence reduces the likelihood that these features are dominated by reconstruction artefacts [21,38]. From the initial state to scan 164, the internal strain field shifts globally toward negative values and becomes more heterogeneous. The visible crystalline volume also shrinks up to this point. We then see the strain field shift partly back toward positive values from scans 167 to 169 and become further neutralized at scan 171, during the volume plateau. We note that the internal strain pattern develops inward and remains connected to strain hot spots at the crystal boundary, which are preferentially located near the corners of the morphology. This localization may reflect geometry-dependent surface strain, for example near edges [36,39]. These strained regions are also found to correspond to areas of active volume loss shown by the final comparison. One such strain feature, arrowed near the upper-right, develops continuously together with the local crack.

Both the 3D strain field and the statistical distribution

system, BCDI similarly revealed preferential calcite dissolution near tensile-strained macrosteps [37], further supporting this interpretation. There is a notable absence of strong negative strain near the bottom facet attached to the supporting Pt pillar, which was likely shielded from the gas atmosphere. We interpret those strained regions, which follow local variations in facet morphology, as regions of enhanced chemical reaction. Several factors may contribute to this localization. Residual strain heterogeneity associated with pre-existing defects may remain after annealing also continue to evolve with reaction. Local gas exposure also varies with the crystal geometry, as suggested by the smooth supported facet. This is in line with the reported influence of interfacial strain on local transformation pathways during H₂ reduction [14].

show active strain variation during H₂ exposure. The global enhancement of negative strain indicates overall lattice compression, which may be associated with oxygen removal from the Fe₃O₄ lattice during H₂ reduction. There could also be other factors involved, such as changes in the Fe²⁺/Fe³⁺ population and associated ionic radii. An earlier hydrogen-reduction study, however, reported lattice expansion in an intermediate magnetite state, linked to unequal rates of oxygen removal and Fe-valence/cation redistribution [40]. Although not directly visualized in the present experiment, a shell-like transformed region outside the probing reflection may also introduce interfacial strain to the remaining crystalline surface [14]. Their relative contribution may vary with the reaction conditions. The strain evolution during reduction is shaped jointly by anisotropic exposure to the reactive environment, pre-existing strain heterogeneity, and the evolution of local morphological features. During the morphology-stabilized period, the strain still evolves at a measurable level, suggesting that strain may provide key information for understanding the subtle structural mechanism underlying the apparent kinetic

blockage [12,16,17,41]. This is also consistent with the high sensitivity of BCDI to strain.

Conclusions and Outlook

By collecting diffraction from a single Bragg peak, BCDI selectively images only the regions of the sample that remain crystalline and aligned with the selected magnetite reflection. The reconstructed crystal volume therefore reports only the BCDI-visible crystalline fraction of the sample with the magnetite structure. For the sample studied, this crystal volume was observed to increase steadily during the initial temperature ramping, consistent with an annealing process. The crystal ordering recovers toward the size observed by SEM after focused ion-beam preparation, reflecting the removal of ion-beam-induced damage [31] and possibly pre-existing mineral-origin defects. The lattice parameter initially followed the expected thermal expansion, before beginning to decline under constant-temperature H₂ exposure from 375 °C onward.

The crystal volume starts to fall again at 475 °C under H₂. The skin and core components show two sub-stages with different rates of degradation during the first hour, followed by stabilization. This is also reflected in the τ and τ_{nm} evolution. These observations converge on an active-reaction-to-stagnation timeline across the 475 °C H₂ stage. During the initial active period, the characteristic depth first decreases and then rises, suggesting an inward-progressing reaction mode with further penetration after a certain extent of surface recession. The subsequent stagnation may correspond to kinetic retardation, which has also been reported in conventional hydrogen reduction of iron oxides [4], including late-stage kinetic slowing shown in TTT analyses [41] and retardation after partial reduction of magnetite [17]. Morphologically, the reconstructed volume shrinkage is overall inward but locally anisotropic, with an undulating pattern of ridges and valleys, as shown in Fig. 3. A related combination of inward progression and increasingly irregular surface morphology has been observed during topotaxial

hydrogen reduction of hematite [18]. Such etching-like behavior also matches observations that magnetite reduction progresses under the continual influence of the evolving microstructure [15]. The etching progression slows down in the later stage. During this period, strain variation remains detectable, pointing to a possible role of strain in explaining the apparent reaction blockage.

The heterogeneous strain is overall stronger near the reconstructed boundary and appears preferentially near edges and corners. Local hot spots are found also around valleys and active regions, developing strain clouds fading gradually inward. This spatial distribution may reflect a mixture of interfacial strain near the reacting interface [14], shape-induced factors [39]. Spatially heterogeneous strain accompanying oxidation-driven structural change has also been reported in magnetite [27]. Meanwhile, the strong negative total strain indicates an overall contraction of the lattice constant, assuming cubic symmetry. This contraction may be associated with oxygen depletion from the Fe₃O₄ lattice [12], but other competing factors may also be involved in the variation, such as interfacial strain [14] and Fe-valence changes/cation redistribution [40]. Combined, the total strain becomes more negative throughout this sequence. In future work, a full 3D strain tensor could be obtained from measurements of additional Bragg reflections. This would show how the strain varies with crystallographic direction and local morphology, and could also provide an additional validation of our current cubic-symmetry assumption.

No sign of new structures or localized barrier states was detected. BCDI is highly sensitive to lattice-parameter changes and local crystal strains corresponding to picometre-scale displacements, and hence to planar defects and dislocation structures in crystals [21,22]; however, neither of these defect structures was observed in the example presented. A following BCDI experiment on a second sample (not shown) showed the appearance of a paired dislocation structure during the annealing stages, but this promptly disappeared.

The progressive loss of signal from the outer regions of the BCDI images may reflect transformation into reduced Fe-containing phases, potentially including wüstite or metallic Fe, which are widely reported along hydrogen-reduction pathways of iron oxides but are not detected at the selected Fe_3O_4 reflection [12,14–16]. The SEM image of the final state (Fig. 3) suggests that the material remains present but has undergone significant morphological rearrangement. Cross-sectional EDX analysis further probes the elemental distribution of the post-experiment sample, revealing a relatively compact Fe-rich core, while the oxygen signal appears more spatially extended.

We traced the amplitude and reconstructed-volume evolution, showing how the BCDI-visible Fe_3O_4 crystal morphology responds as H_2 reduction proceeds. The strain analysis at 475 °C complements these results by revealing the lattice response within the reconstructed volume. Two levels of structural change are visible. Crystal shrinkage and negative homogeneous strain occur on the overall scale, while local etching and strain accumulation develop on top. Here we report a layerwise inward, etching-like progression during magnetite reduction, with lattice contraction potentially related to oxygen loss. How such contraction accumulates across many crystallites in a practical oxide, and how it may contribute to kinetic blockage, could be relevant to optimizing steam–iron system.

Methods:

Sample Preparation

The Fe_3O_4 BCDI sample was manufactured using a FIB lift-out [42] from a bulk single crystal commercially sourced natural magnetite mineral from Pakistan. The bulk crystal was preoriented using X-ray diffraction such that a (111) facet was out-of-plane. Using a Field Electron and Ion Helios 600 dual-beam FIB (Ga^+ source), a protective carbon patch, approximately $\approx 2 \mu\text{m} \times 2 \mu\text{m} \times 2 \mu\text{m}$, was deposited

on the surface of the bulk crystal. A Fe_3O_4 lift-out was extracted (30 kV, 2.6 nA) beneath this carbon using an Omniprobe manipulation system. The bottom of the lift-out was polished (5 kV, 63 pA) prior to welding it using platinum onto a platinum post on a single-crystal silicon wafer. The exposed sides and top of the sample were milled (16 kV, 61 pA) to a size of $\approx 1.2 \mu\text{m} \times 1.2 \mu\text{m} \times 1.2 \mu\text{m}$ before polishing (5 kV, 63 pA) it to a size of $\approx 1 \mu\text{m} \times 1 \mu\text{m} \times 1 \mu\text{m}$.

The mounted crystal was installed on the European Synchrotron Radiation Facility (ESRF) beamline ID01 heating stage and enclosed within a sealed gas-flow dome equipped with independent inlet and outlet lines. The crystal was fixed on the furnace plate using Resbond 940 thermal adhesive to ensure stable thermal and mechanical contact.

In-situ Bragg coherent diffraction imaging experiment

Bragg coherent diffraction imaging experiments were carried out at the ID01 beamline [43] of the ESRF. A coherent hard X-ray beam was used for the measurements. We used 8.333 keV X-rays ($\lambda = 1.488 \text{ \AA}$). The beam was focused using a set of seven Be compound refractive lenses (radius of curvature 50 μm , lens spacing 200 μm), with a focal distance of 72.9 cm. The coherence-defining slit was set to $0.08 \times 0.08 \text{ mm}^2$, resulting in a beam size at the sample position of 1.16 μm .

A two-dimensional Maxipix detector [43] recorded the diffracted intensity. It has 516×516 pixels of size $p = 55 \times 55 \mu\text{m}^2$ and was positioned 1.32 m downstream of the sample. This experimental geometry, in principle, allows diffraction from crystals with characteristic sizes smaller than $\lambda D / (2p) = 1.78 \mu\text{m}$ to be oversampled by at least a factor of two [21,44], satisfying the oversampling requirement for the $\sim 1.01 \mu\text{m}$ -sized crystals studied here.

BCDI measurements were performed by recording 3D

coherent diffraction patterns in the vicinity of the magnetite 111 Bragg reflection ($2\theta = 17.7^\circ$). The sample was rocked through $\pm 0.50^\circ$ around the Bragg condition in 0.005° increments (201 frames), producing the 3D reciprocal-space intensity dataset. An exposure time of 1 s per frame was used, resulting in a total acquisition time of approximately 8.5 min per rocking scan with 201 frames, including detector realignment and sample recentering in the focused beam.

Temperature and gas environments were controlled throughout the experiment using a dedicated furnace and gas-handling system [45,46]. Two gas compositions were employed: pure argon (Ar) as an inert atmosphere during temperature ramping and stabilization, and 5% H₂ in Ar as the reducing atmosphere for tracking the reduction after each temperature stabilization. This enabled the isothermal reduction under H₂ to be measured separately from the Ar thermal control. Following each H₂ exposure, the system was flushed with Ar before subsequent temperature changes or measurement. The chamber atmosphere was maintained at 100 mbar and monitored in situ using a mass spectrometer. BCDI data were acquired throughout temperature ramps, stabilization periods, and H₂-exposure stages. H₂ was introduced at 75, 225, 275, 325, 375, and 475 °C, following the schedule in Fig. 1.

Algorithms:

The measured coherent diffraction intensities were cropped around the main Bragg peak and then converted into real-space images of the crystal through iterative phase-retrieval reconstruction using the PyNX library [47,48], under the cdiutils analysis framework [29,30]. Reconstructions were performed using 300 cycles of the hybrid input–output (HIO) algorithm, followed by 500 cycles of the relaxed averaged alternating reflections (RAAR) algorithm and 200 cycles of error reduction (ER) [23,49].

A real-space support constraining the spatial extent of the diffracting crystal is crucial for the convergence of the phase-retrieval algorithms. The initial support threshold was allowed to vary in the range 0.19–0.50, with shrink-wrap [50]

support updates applied during phase retrieval. The reconstruction was then performed using a two-pass workflow. The first pass identified stable support behavior and provided the initial support and support-threshold range for the following run. The second pass used a support-guided reconstruction based on the first-pass results. This improved consistency across the scan series and reduced the influence of local-minimum solutions.

For each scan, and in each pass, the procedure was repeated from 200 random initializations, and 100 independent reconstructions were retained for further analysis. These reconstructions were first screened using the conventional mean-to-max criterion [29,30]. The top candidates were further screened using amplitude- and morphology-based metrics. These covered reconstructed volume across several amplitude thresholds, internal continuity and connectivity, high-amplitude peak quality, and boundary fragmentation. These metrics were combined into a composite score, which was used as the final ranking criterion for the candidate reconstructions.

To avoid mixing distinct reconstruction solutions, the retained candidates were also grouped using a twin-aware geometry comparison. Candidate amplitudes were compared at several amplitude thresholds, considering both the normal and fully inverted twin-related orientations. The dominant geometry family was then used for final candidate selection. Within this family, five mutually consistent reconstructions were selected and merged using modal decomposition [30,48] to generate a final, single 3D reconstruction. The weight of the first modal component, $W > 0.9$, was used as an additional convergence criterion, and reconstructions that did not satisfy this requirement were rejected from following analysis. The failed reconstructions with $W < 0.9$ are shown as hollow points in Fig. 1.

The resulting complex-valued reconstruction contains both amplitude and phase information of the crystal in real space, following coordinate transformation from the measurement coordinates [47,48]. The amplitude, A , represents the part of the crystallographic electronic density distribution contributing to the measured Bragg vector $\mathbf{Q}$ [21,22], thus reflecting the morphology of the effective crystalline portions and thus the shape of the diffracting volume. In cdiutils the amplitude is normalized to $0 < A < 1$

by default. The phase corresponds to the projection of the lattice displacement field $\mathbf{u}(\mathbf{r})$ onto the same $\mathbf{Q}$ -vector, according to $\phi(\mathbf{r}) = \mathbf{Q} \cdot \mathbf{u}(\mathbf{r})$ [21,22]. Therefore, the phase variations encode the atomic displacements relative to the ideal lattice, providing direct access to the strain field.

From the reconstructed phase, the displacement component projected along the scattering vector is obtained as $u_{\mathbf{Q}}(\mathbf{r}) = \phi(\mathbf{r})/|\mathbf{Q}|$. In the small-strain limit, the heterogeneous strain can be written as the spatial derivative of this displacement field along the $\mathbf{Q}$ direction [21,42,51].

$$\varepsilon_{\mathbf{Q}}(\mathbf{r}) = \frac{\partial u_{\mathbf{Q}}(\mathbf{r})}{\partial r_{\mathbf{Q}}},$$

Here, $r_{\mathbf{Q}}$ is the spatial coordinate along the $\mathbf{Q}$ direction. This quantity describes local lattice distortion within the crystal. The homogeneous strain, ε_{H} [36], represents the uniform expansion or contraction of the lattice, derived from the shift of the recorded Bragg peak center position $|\mathbf{Q}|$. Unless stated otherwise, strain here refers to the total strain,

$$\varepsilon_{\text{tot}}(\mathbf{r}) = \varepsilon_{\mathbf{Q}}(\mathbf{r}) + \varepsilon_{\text{H}},$$

which contains the global lattice contribution and local strain heterogeneity.

Associated content

Supporting Information: Additional information on amplitude-range selection, spatial-resolution evaluation, peak intensity, lattice parameters, SEM–reconstruction alignment, EDX and EELS analyses, inward-depth profiles, and decomposition of total strain (PDF).

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