



	Experiment title: Electronic and atomic structures of iron oxalate at extreme conditions	Experiment number: HC-5141
Beamline: ID18 ID15B	Date of experiment: from: 20/09/2022 to: 23/09/2022	Date of report: 27/02/2023
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Report:

Simple inorganic coordination polymers, such as the iron oxalate, have attracted much interest in the past decades because of their fascinating solid state properties such as gas absorption, electrical conduction and catalytic activity. For these reasons, iron oxalate dihydrate has emerged as an important building block for the preparation of new, functional advanced materials, as an important precursor to the synthesis of iron carbonate FeCO_3 and it is also important for planetary science. In HC-5141 experiment, pre-selected single crystals of $\text{FeC}_2\text{O}_4 \times 2 \text{H}_2\text{O}$ (typical dimensions $15 \times 15 \times 10 \mu\text{m}^3$) were characterized by Synchrotron Mössbauer (SMS) and X-ray diffraction (XRD) at ID18 and ID15b respectively. We used SMS to study the nuclear and electronic evolution of the material under compression, while changes in the long-range ordered structure were investigated via XRD. We compressed the samples to 50 GPa and 100 GPa and collected SMS spectra and XRD patterns in situ, during compression, using two different DACs. At the highest pressures both samples were laser heated using the infrared YAG laser installed at ID18. The first DAC, that reached 50 GPa (DAC1), had culetts of 300 μm while the second one, that reached 100 GPa (DAC2), had culetts of 150 μm . The samples were embedded in Neon gas used as pressure-transmitting-medium (PTM) to maintain quasi-hydrostatic conditions during compression.

The Mossbauer spectra were collected at different pressure steps. For the first DAC we only acquired the spectra before and after the laser heating at 50 GPa. For the second DAC we compressed the sample at pressure step of 4/5 GPa from ambient pressure to 100 GPa and we collected 17 spectra. After laser heating $T > 2800 \text{ K}$ and 100 GPa we collected two more spectra in two different positions of the sample.

The XRD spectra were also collected at different pressures. DAC1 was compressed at pressure steps of 3/4 GPa from ambient pressure to 50 GPa and we collected 17 XRD patterns. After laser heating at 50 GPa we performed again a diffraction measurement on the quenched products.

The Mossbauer spectra were fitted using the software package MossA. The analysis of the XRD data with CrysAlis^{PRO} program is still in progress. As a preliminary analysis, the diffraction images taken for each different pressure have been merged to obtain a single wide angle image. In this way we were able to analyze the data as powder diffraction images. A preliminary and qualitative analysis was made using the software Dioptas.

The most relevant Mossbauer fittings are shown in figure 1.

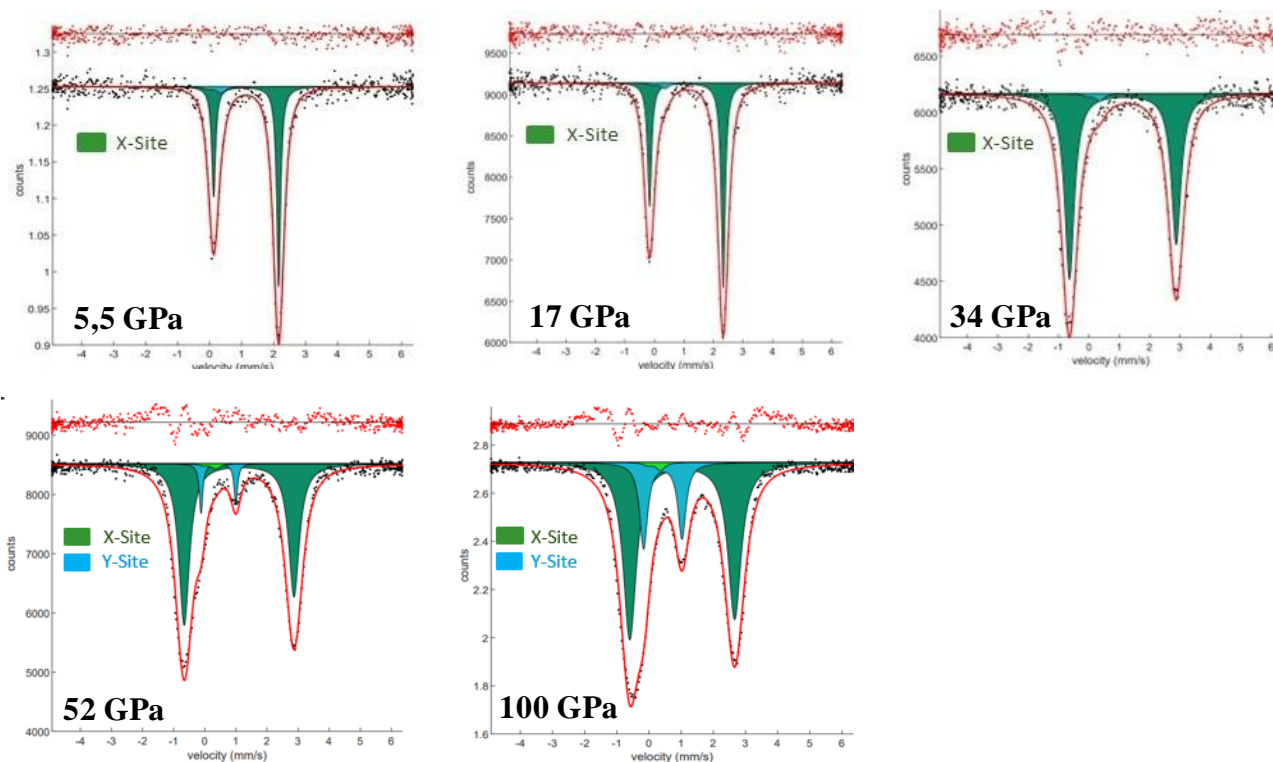


Figure 1 Selected Mossbauer spectra fitted using MossA software package. Fe-oxalate spectrum at lower pressures is characterized by a single and asymmetric doublet component. The asymmetry changes at higher pressures, i.e. $P > 34$ GPa. At $P > 50$ GPa the formation of a second doublet is observed.

Mössbauer spectra were fitted using Lorentzian lines and the lowest number of components, i.e. one component for the initial X-site and one component for the Y-site, which pops-out at around 52 GPa. From Figure 1 we notice that at the beginning there is only one doublet, then between 17 GPa and 34 GPa there is a change in the asymmetry of the doublet due to a phase transition (confirmed by XRD and in accordance with the preliminary studies made by Müller et al. [1]), at 52 GPa another doublet starts to appear and at 100 GPa both doublets are still present. From the hyperfine parameter we can affirm that at the beginning the doublet of X-site is due to the Fe^{2+} in HS configuration and in octahedral coordination (CS = 1,14 mm/s and QS = 2,03 mm/s at 5,5 GPa) then increasing the pressure we increase the distortion of the site and we notice that the Fe^{2+} of the X-site switch possibly to a dodecahedral coordination (CS = 1,11 mm/s and QS = 3,57 mm/s at 44 GPa). At 52 GPa another doublet starts to appear, which we attribute to a spin transition of the Fe^{2+} in octahedral coordination from HS configuration to a LS one.

Center shift (CS) and quadrupole splitting (QS) hyperfine parameters are plot at the increase of pressure for the two sites in Figure 2. We identified four different regions representing changes in the atomic and electronic structures, highlighted in Figure 2 using straight lines of different colors. These regions are identified in accordance with the XRD data.

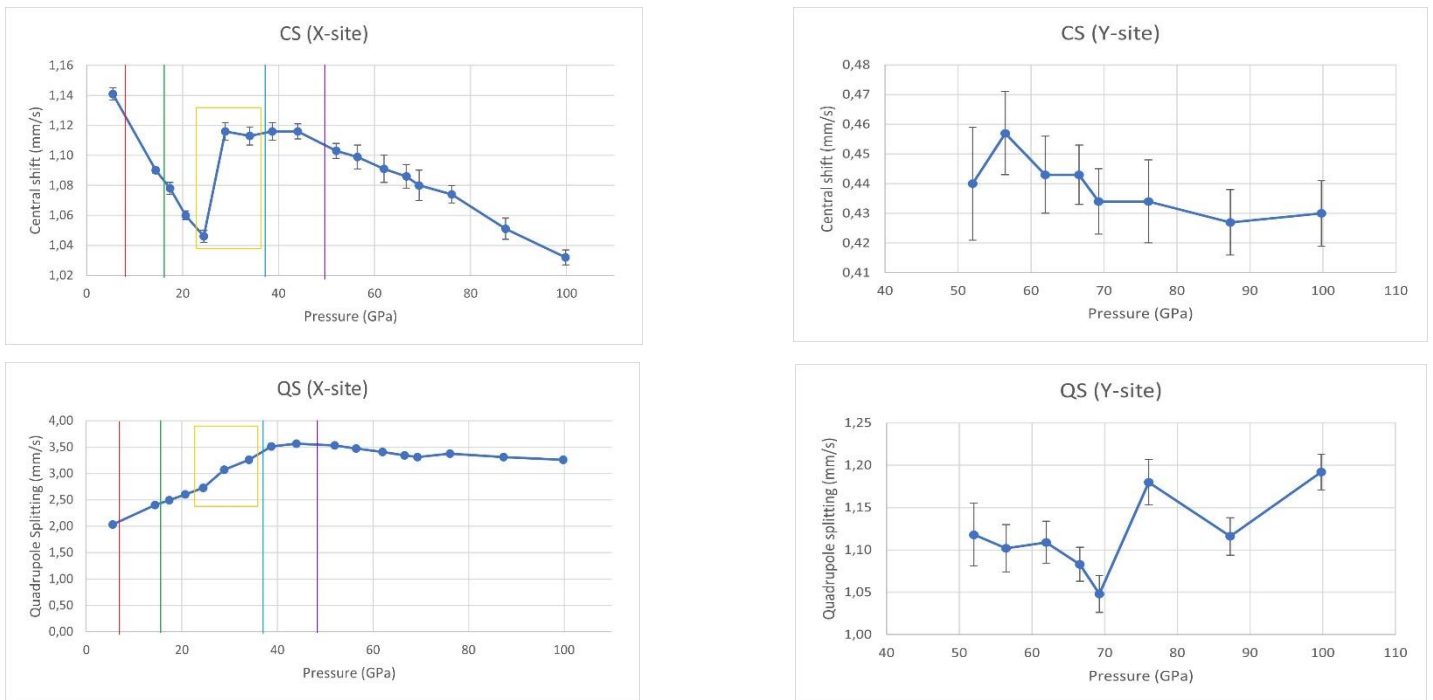


Figure 2. CS and QS of X-site and Y-site

From Figure 2 we notice an initial decrease of the CS for the X-site at the increase of pressure, which we attribute to the rise of the electron density at the nucleus during compression. Between 24 GPa and 29 GPa there is a jump in the CS from 1,046 mm/s to 1,116 mm/s, which then remains more or less constant until 44 GPa. In this pressure interval, around 38 GPa we observed from XRD data the completion of a sluggish structural transition which started at $P > 22$ GPa (Figure 3). At the appearance of the second doublet at 52 GPa, the CS of both sites start to decrease again. From the evolution of the QS values, we notice that the QS for the X-site increases with pressure until ~ 40 GPa, which can be explained by a continuous distortion of the X-site caused by progressive not uniform distribution of the electric field gradient around the Fe nuclei. At the emergence of the second doublet, the value of the QS of X-site is more or less stable while the QS of the Y-site follow a more complicate path, indicating an increasing trend.

The XRD spectra are shown in the figure 3.

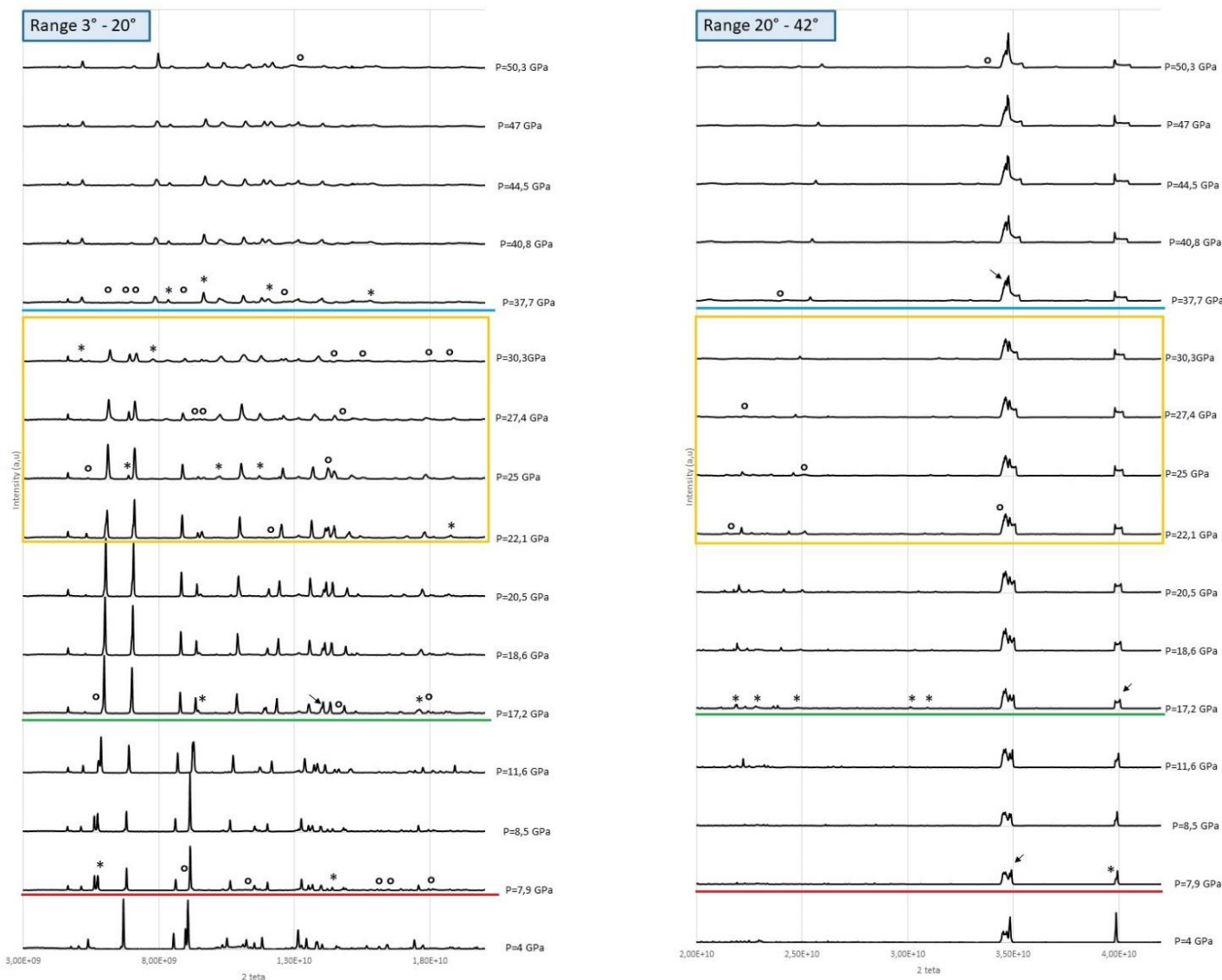


Figure 3. XRD patterns at the increasing of the pressure divided in two range of 2θ (first range from 3° to 20° and second range from 20° to 42°). Lines of different colors highlight the onset of structural transitions.

In the XRD integrated patterns we identified with asterisks the appearance of new peaks, with circles the disappearance of previous peaks and with arrows the evident variations in peaks intensity. Qualitatively, we could locate a first change in the structure at 7,9 GPa, where new peaks emerge and others disappear. We noticed, in accordance with preliminary studies of Müller et al. [1], a second change at 17 GPa due to a phase transition (probably from a monoclinic phase to a triclinic one). Then at 22 GPa, new peaks of a new phase start to appear, while reflections from the previous phase get progressively lower in intensity. We interpret this trend with the coexistence of two structures between 22 GPa and 38 GPa (the one formed at 17 GPa, observed until 38 GPa, and the one that begins to form at 22 GPa and that is completely formed at 38 GPa).

The analyses of both Mossbauer and XRD data are still in progress and in particular we focused, for the moment, only on the fitting of the cold compression spectra.

Reference

[1] Müller et al. Iron(II)oxalate Dihydrate—Humboldtine: Synthesis, Spectroscopic and Structural Properties of a Versatile Precursor for High Pressure Research. *Minerals* 11, 113 (2021).