Experimental report

13/09/2023

Proposal: 5-24-710 **Council:** 4/2023

Title: Heat realease, thermal hysteresis and magnetic ordering evolution with physical and chemical pressure inRbMnFe

Research area: Materials

This proposal is a new proposal

Main proposer: Eric COLLET

Experimental team: Ricardo Guillermo TORRES RAMIREZ
ELZBIETA TRZOP
Eric COLLET

Local contacts: Marie Helene LEMEE

Samples: RbMn[Fe_0.92Co_0.08(CN)_6]·0.3H_2O
Rb_0.73Mn[Fe(CN)6]_0.91.1.4H2O
RbMnFe
Rb0.99Mn0.92Zn0.08[Fe(CN)6]0.99.0.7H2O

Instrument	Requested days	Allocated days	From	To
D20	4	1	30/08/2023	31/08/2023

Abstract:

Heat storage represents an important societal issue. Developing materials able to store, transport and release heat on demand are of great interest and may help lowering energy consumption. RbMnFe materials exhibit phase transition driven by temperature, pressure or light, due to coupled Mn-Fe Charge-Transfer (CT) and symmetry breaking (SB). This large enthalpy transition exhibits 70 K wide thermal hysteresis around room temperature. Our recent model has shown that it results from the coupling between CT and SB, contributing both to the volume strain.
In addition to temperature, pressure is an efficient way to shift from one side of the hysteresis to the other, allowing for heat storing and releasing at room temperature. Chemical substitution also allows shift the thermal hysteresis. Pressure may also affect the ferromagnetic Curie temperature (12 K).
This proposal aims at gaining knowledge on the pressure-induced heat-release and magnetic ordering for both SB, responsible for magnetic anisotropy and Bragg peak splitting, and CT driving volume change. Neutron diffraction, combined to He (P,T) cell allowing for fine pressure tuning, is therefore required.

Heat realease, thermal hysteresis and magnetic ordering evolution with physical and chemical pressure in RbMnFe

Proposal 5-24-710

Experiment performed by:

R. Torres Ramírez (IPR), E. Trzop (IPR), E. Collet (IPR), M. H. Lemée-Cailleau (ILL Grenoble) and T. C. Hansen (ILL Grenoble)

Sample analysed: $Rb_{0.99}Mn_{0.92}Zn_{0.08}[Fe(Cn)_6]_{0.99}\cdot 0.7H_2O$

RbMnFe systems undergo a phase transition driven by temperature, light or pressure. Due to their coupled Mn-Fe charge-transfer (CT) and symmetry-breaking (SB), they exhibit a wide thermal hysteresis (~60 K) around room temperature.[1,2] This property makes them good candidates for heat storage applications. In this context, a detailed analysis of their (P,T) phase diagram is needed to determine behavior of the system through its phase transition points.

Purpose of the experiment

The main objective of this proposal (5-24-710) was the determination of (P,T) phase transition points by neutron diffraction measurements (Figure 1) for a Zn-doped RbMnFe material, which is of great importance for their barocaloric applications.

Experimental details

Given the transition points determined from previous (P,T) analyses, performed by our collaborators in Japan using oil as a pressure transmitter (square markers in Figure 2), for this experiment we decided to use the He-mediated pressure cell with Orange cryostat to perform neutron powder diffraction analyses ($\lambda = 1.54$ Å) within the expected ranges of temperature (200 K – 320 K) and pressure (0.3 MPa -200 MPa, with 1 bar accuracy).

From the first neutron diffraction measurements we performed (pressure scan at 300 K), we noticed that the transition lines measured with He as pressure medium were not matching the ones previously obtained with oil as pressure medium. For this reason, and given the limited and short amount of time allocated for the experiment, in order to find the transition points we decided to perform temperature scans (cooling down and warming up) for different and representative pressures (200 MPa, 175 MPa, 150 MPa, 100 MPa, 50 MPa, 0.3 MPa), while continuously collecting data with the temperature change.

Figure 1 presents a subset of diffraction patterns collected at 100 MPa upon cooling: in full cubic high-temperature (HT) phase, full tetragonal low-temperature (LT) phase, and around phase transition where HT and LT phases coexist. We analysed the different constant pressure sets of diffraction patterns to find signatures of the cubic-tetragonal transition (Bragg peaks splitting and shifting due volume change). After a preliminary inspection of these signatures, the (P,T) transition lines for the system were obtained and represented in a tentative (P,T) phase diagram, shown in Figure 2.

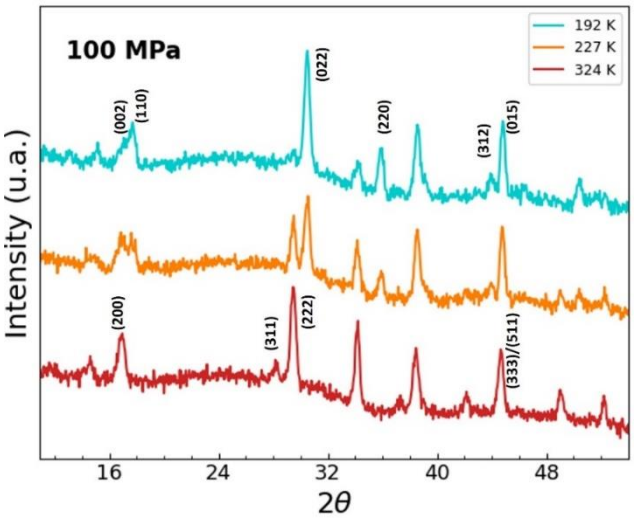

Figure 1. *Diffraction patterns obtained at 100 MPa, representative of full HT phase (red), HT-LT phases coexistence (orange), and full LT phase (blue).*

The results presented in Figure 2 point to an important effect of the pressure medium (oil vs Helium) on the positions and evolution of the transition lines in the (P,T) phase diagram for this system. A first hypothesis is the inclusion of He atoms into the polymeric structure under pressure, which may counterbalance the external pressure and related lattice compression.

In order to solve the crystalline structure from the powder diffraction data collected under He-mediated pressure and to look for the presence of He in the crystalline lattice, a more complete scan has been measured. It will be compared with the data taken at 300 K and ambient pressure on a fresh sample from the same batch that was not exposed to helium atmosphere. A detailed data analysis is ongoing.

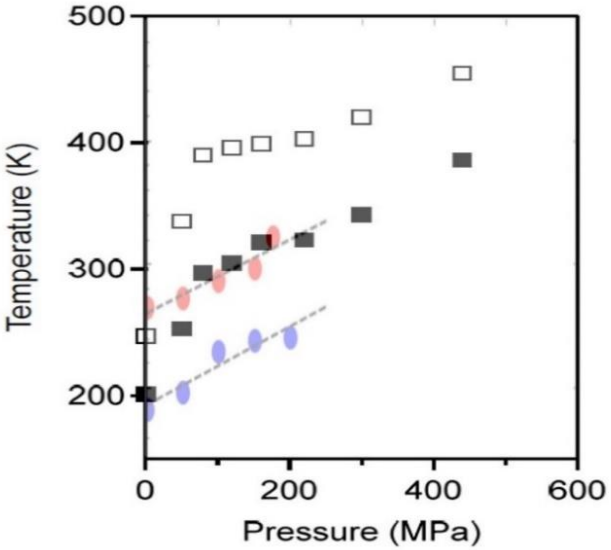

Figure 2. *(P,T) phase diagram obtained from the oil- mediated pressure experiment in Tokyo (square markers) superposed to He-mediated pressure ILL data (circular markers)-proposal 5-24-710.*

The present results open an interesting perspective for performing neutron diffraction experiments under pressure, to understand the observed shift of the phase transition lines while working with either oil or He as pressure transmitters; this appears to be of great importance for barocaloric applications.

Work to be done

An accurate determination of the phase transition lines is needed, as Fig.2 was made with raw data analysis. We will use powder crystallography software to accurately determine the transition at each pressure and temperature point, with phase fractions analysis.

In order to show the pressure and temperature effects on the lattice parameter of the system (contraction and peak splitting due to symmetry change), it is needed to plot the volume, parameters a, c, and (a-c) symmetry-breaking as a function of temperature and/or pressure.

Additionally, in line with transition lines difference between the He- and oil- mediated pressure experiments, we will check for He inclusion in our system by solving the structure.

Data acquisition parameters:

- $\lambda = 1.54$ Å with 2θ range from 0° to 150°
- Temperature range scanned: 150 K to 325 K (Orange cryostat with 50 mm V tail)
- Time needed for each 2θ scan with continuous change of temperature: 5 min + 1 min for detector displacement.
- Time spent in long scans (fixed pressure and fixed temperature): 20 minutes (only three scans of this type were taken).
- Pressure range scanned: 0.3 MPa to 200 MPa.
- Detector: 3He microstrip gas-detector (PSD).

References

[1] Ohkoshi, S. I., & Tokoro, H. (2012). *Accounts of Chemical Research*, 45(10), 1749–1758.

[2] Azzolina, G., Tokoro, H., Imoto, K., Yoshikiyo, M., Ohkoshi, S. ichi, & Collet, E. (2021). *Angewandte Chemie - International Edition*, *60*(43), 23267–23273.