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| Beamline: ID20 | Experiment title: Study of the compositional effect on the pressure-induced spin transition of magnesio-siderite solid solution by x-ray Raman scattering | Experiment number: ES-532 |
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Report:

The purpose of this investigation was to examine the pressure driven magnetic high-spin (HS) to low-spin (LS) transition in magnesio-siderite solid solution using in-situ X-ray Raman scattering (XRS) at the iron $M_{2/3}$ -edge at room temperature with focus on the impact of the material's composition on the transition pressure, the width of the transition and the transition range. Owing to the low solubility of carbon in mantle phases, magnesio-siderite solid solution is a candidate for carbon storage of the inner Earth [1,2]. The spin state in mantle minerals strongly influences its macroscopic properties as conductivity, sound velocity and compressibility. Therefore, it is important to study pressure induced spin state changes at conditions which are present in the interior of the Earth to better understand the dynamic behavior of such a complex system.

A $[(Mg_{0.74}Fe_{0.26})CO_3]$ single crystal of $20 \times 25 \times 10 \mu m^3$ in size was loaded into a diamond anvil cell (DAC) with a gas driven membrane provided by the ESRF with rhenium gasket and argon as pressure medium to guarantee quasi-hydrostatic conditions. The pressure was determined by the ruby fluorescence method. In order to analyze the course of the spin transition we measured the iron $M_{2/3}$ -edge of the sample at selected pressures in between 39 and 57 GPa. Due to partial overlap of the iron $M_{2/3}$ -edge and the Mg $L_{2/3}$ -edge for magnesiosiderite measurements, magnesite powder was measured at similar high pressure conditions. For the XRS measurements we used the multi-analyzer spectrometer at beamline ID20 employing the Si 880 analyzer reflection at 12.9 keV with an overall energy resolution of 2 eV at high momentum transfer. The background subtraction procedure is shown in the report of the previous experiment (ES-357). Various XRS spectra of the iron M-edges are

shown together with the underlying contributions of the Mg L-edge in figure 1 (left) and evidence that the main spectral changes can be attributed to change of the iron's spin state. The total spin moment was extracted using difference spectra (see report ES-182) and is presented in figure 1 (right).

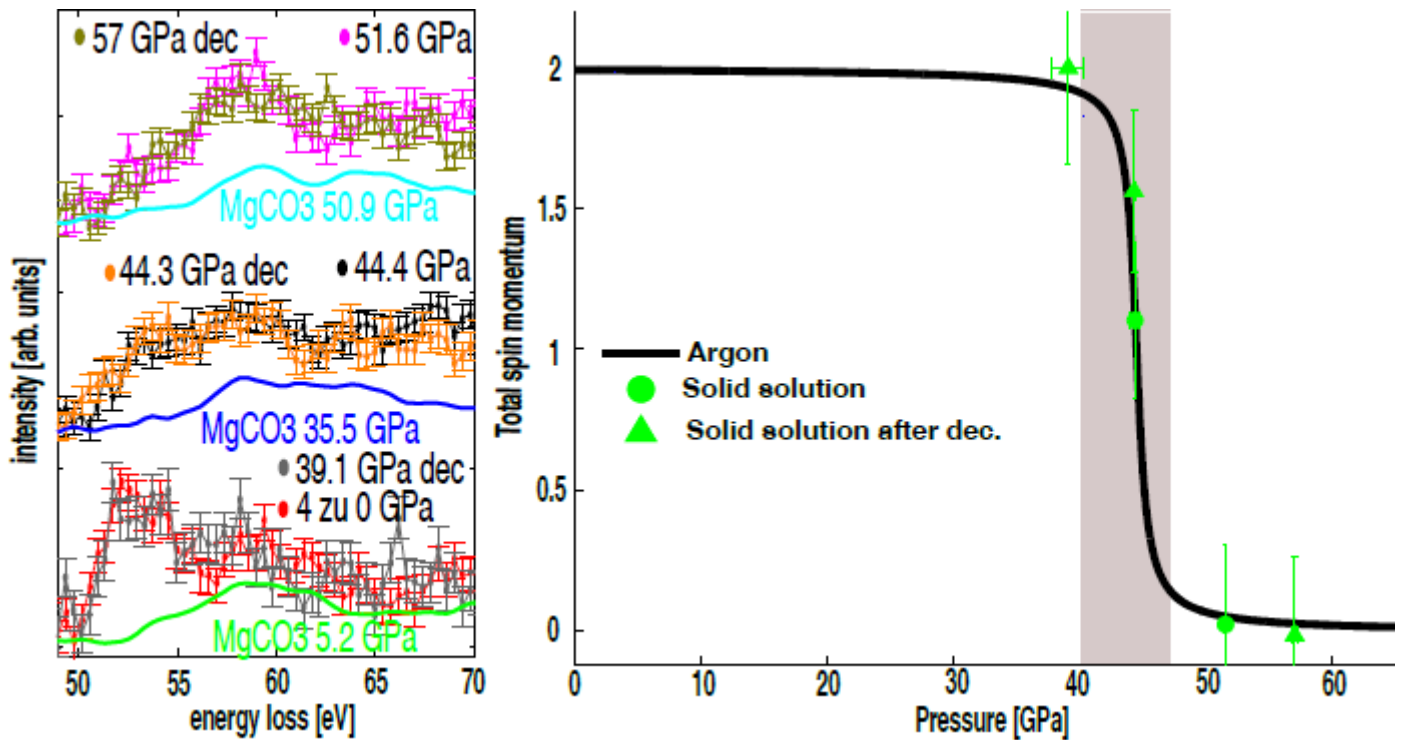


Figure 1: **Left:** XRS M-edges of magnesiosiderite $\text{Mg}_{0.74}\text{Fe}_{0.26}\text{CO}_3$ single crystal with argon as pressure medium and XRS Mg L-edges of magnesite powder shown as solid lines **Right:** Total spin momentum S as a function of pressure for the solid solution using argon as pressure medium (green). The shaded area (40-46 GPa) represents the coexistence regime of HS and LS iron measured by Spivak et al. by means of optical Raman spectroscopy [4].

From this analysis we conclude that there is no compositional effect on the spin transition pressure in contrast to reports by Spivak et al. [3]. Our observations are in accordance with the results of Müller et al. [4, 5] by means of optical Raman spectroscopy. In the next step the experimental findings will be confronted with calculations of the XRS spectra to extract for example the crystal field splitting parameter to get a deeper insight on the spin transition mechanism.

[1] W.R. Panero et al., *Geophys. Res. Lett.* 35, L14307 (2008); [2] M. Isshiki et al., *Nature* 427, 60 (2004); [3] A. Spivak et al., *Physics and Chemistry of Minerals* 41, 633-638 (2014); [4] J. Müller et al., *American Mineralogist* 101, 2638-2644 (2016); [5] J. Müller et al., *European Journal of Mineralogy*, submitted (2017)