ESRF	**Experiment title:** Electronic and magnetic properties of CoO and MnO at high pressure	**Experiment number**: HE-1260
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Report:

We report here on the investigation of the magnetic properties of geophysical relevant systems, MnO, CoO, Fe_2O_3 and MgFeO, at ultra high pressure by x-ray emission spectroscopy (XES) at the Kβ emission line. Transition metal oxides are Mott insulators at ambient condition. Under pressure, band widening eventually leads to the disappearance of the magnetic moment. Ab-initio calculations in these systems [1] predicted the magnetic collapse to occur in the megabar pressure range. The results obtained by XES confirm the magnetic collapse but at pressures surprisingly low compared to the predictions. This has strong implications for the chemistry and composition of the Earth's inner shells (mantle and core).

The experiment was performed on ID16 using the beamline XES spectrometer. The spectrometer consists of a 1 m-radius spherically bent Si-analyzer and a Peltier-cooled Si diode detector laid down in Rowland circle geometry, yielding a total resolution of 1.5 eV at 10 keV. Different analyzers were utilized depending on the transition metal under study in order to work at the highest possible Bragg angle, therefore minimizing the geometrical contribution to the resolution. The samples were prepared as fine powder and loaded in a diamond anvil cell (DAC) using a high-strength Be gasket without pressure medium. Typical sample size was 50 μm diameter. The x-ray beam entered the cell through the diamond axis and emitted photons were detected at 90° scattering angle through the Be gasket.

The pressure dependence of the transition metal Kβ emission line (*3p* → *1s*) is shown on figure 1 for the different samples. The spectra consist of a double structure, a main peak followed by a satellite at lower emitted energy, split by *3p-3d* exchange interaction. Large changes can be observed in the spectra upon pressure change, in particular in the satellite region. Multiplets calculations have shown that the satellite intensity essentially reveals the strength of the *3d* polarization [2]. Thus the Kβ line may serve as a detector of the local transition metal spin magnetic moment. This technique has already been successfully utilized to characterize the Fe spin-state in Fe-based compounds under pressure [3] and in Fe-contained photoswitchable molecules [4]. We show here that it is applicable to other transition metals as well.

Quantitative information may be obtained by estimating the differences between the high-pressure spectra and the one obtained at ambient conditions. The analysis of those differences allows one to extract the spin magnetic moment amplitude on a relative scale. Comparison with emission spectrum of systems where the transition metal spin state is well characterized [4] further leads to a straightforward identification of the high spin (HS) or low spin (LS) character. The final results are illustrated in the insets, figure 1.

In all the samples, a collapse of the magnetic moment at high pressure (and eventually high temperature) is observed. The process shows some hysteresis upon pressure release probably due to the mechanical strain. Although a magnetic collapse in those systems was predicted by theory, the pressures do not correspond. Most importantly, the order in which the MnO—NiO *3d* transition metal oxide series collapses is inverted. Indeed, the highest pressure was predicted for MnO and the lowest for CoO. We observe the opposite. This is probably due to the fact the predicted mechanism for magnetic collapse is not correct. Actually, there are two concurrent processes that drive magnetic collapse, i.e. bandwidth broadening and increase of the ligand field. Form an Earth sciences perspective, we have the first measurement on the bonding chemistry of those siderophile elements.

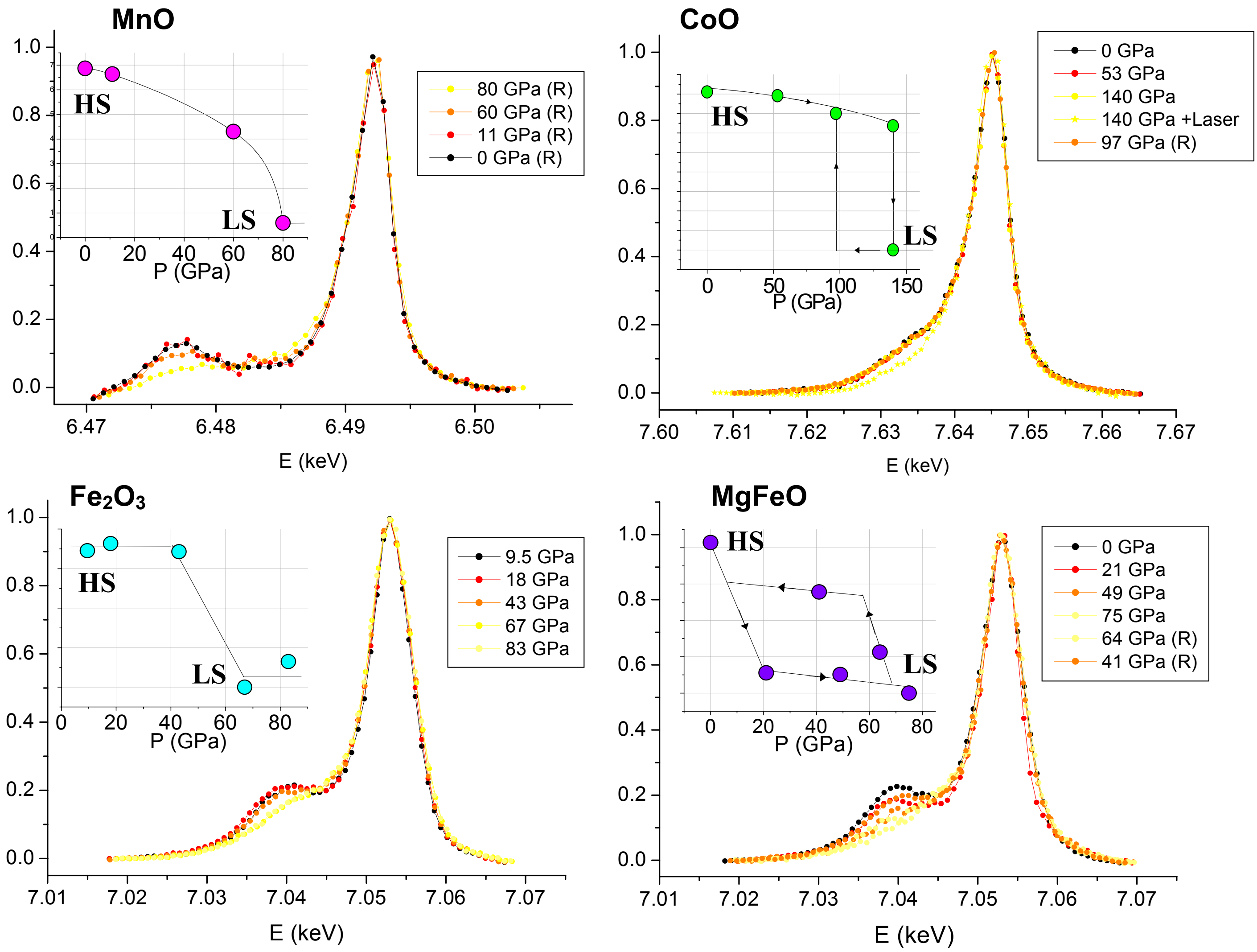

Figure 1 : *Kβ emission lines as function of pressure in MnO, CoO, Fe_2O_3 and MgFeO. (R) indicates measurements done upon pressure released and "Laser" spectra obtained after laser heating at about 2000 K. In inset the pressure dependence of the transition metal magnetic moment deduced from the spectrum analysis (see text).*

[1] R. Cohen , Science **275**, 654 (1997)

[2] G. Peng et al., J. Am. Chem. Soc. **116**, 2914 (1994).

[3] J.P. Rueff et al. , Phys. Rev. Lett. **82**, 3284 (1999) ; J. Badro et al., Phys. Rev. Lett. **83** 4101 (1999)

[4] G. Vanko et al., unpublished