



<b>Experiment title:</b> Magnetic collapse in levitated liquid FeO		<b>Experiment number:</b> HD-295
<b>Beamline:</b> ID16	<b>Date of experiment:</b> from: 05/02/2009 to: 09/02/2009	<b>Date of report:</b> 28/02/2010  <i>Received at ESRF:</i>
<b>Shifts:</b> 12	<b>Local contact(s):</b> Giulio MONACO	

**Names and affiliations of applicants (\* indicates experimentalists):**

S  verine BRASSAMIN - CEMHTI Orl  ans\*

Louis HENNET - CEMHTI Orl  ans\*

Jad KOZAILY – ILL Grenoble\*

Marl  ne LEYDIER - CEMHTI Orl  ans\*

Irina POZDNYAKOVA - CEMHTI Orl  ans

David PRICE - CEMHTI Orl  ans

Didier ZANGHI - CEMHTI Orl  ans\*

**Report:**

**Introduction**

W  stite (FeO) is an interesting material because a possible magnetic collapse has been predicted by first-principles calculations at pressures accessible by using existing diamond anvil cell techniques. In the past, this has motivated the experimental search for the high spin to low-spin (HS to LS) transitions in this compound. One of these works, using XES, shows that the high-spin state in FeO is preserved at least to 140 GPa [1] while a Mossbauer spectroscopy study has shown a HS to LS transition in FeO at about 90 GPa [2].

Usually, a material can undergo a magnetic transition because of band widening or because of changes in the crystal field. In the liquid state at normal pressure, such magnetic collapse has never been observed or computed. However some structural observations in the molten state of FeO open the question of the existence of such HS to LS transition on melting.

The stable solid phase FeO presents a NaCl structure which contains iron vacancies corresponding to a wide range of composition  $\text{Fe}_{1-x}\text{O}$  with  $x$  varying between 0.05 and 0.15. These vacancies introduce some  $\text{Fe}^{3+}$  ions in the structure. In all cases,  $\text{Fe}^{2+}$  ions are found in octahedral sites surrounded by six oxygen neighbors at a mean distance varying from 2.19   for  $x=0.05$  ( $\text{Fe}_{0.95}\text{O}$ ) to 2.12   for  $x=0.15$  ( $\text{Fe}_{0.85}\text{O}$ ).

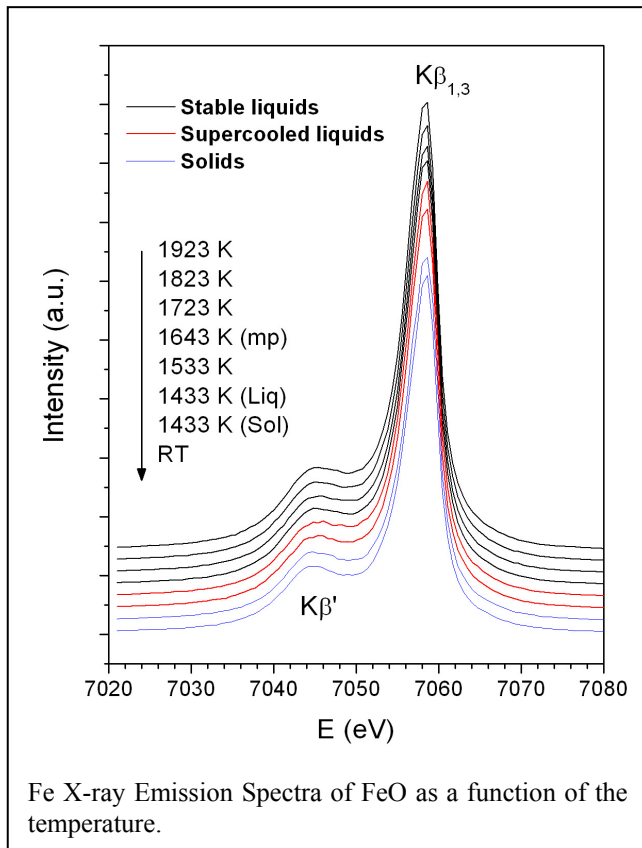
We previously determined the structure factor of levitated liquid FeO above the melting point (1643 K) at 1800 K by using X-Ray Diffraction (XRD). From the pair distribution functions  $g(r)$  we found an averaged Fe-O bond length of 1.96   . This value is much lower than the value of about 2.15    found in the solid phase. In addition, from X-ray Absorption Spectroscopy (XAS), we found that Fe is octahedrally coordinated in the liquid state [3]. It was difficult to confirm this coordination number by XRD due to fluorescence problems. Finally, the study of the following peaks in  $g(r)$  seemed to show that FeO maintains its NaCl structure above the melting point but with a 10% linear contraction.

If we consider the ionic radii for all oxidation and spin states of 6-coordinated Fe ions, a reasonable explanation of this behavior was to suppose the existence of a HS to LS transition of the  $\text{Fe}^{2+}$  ions on melting.

## Experiment

The purpose of this experiment was to confirm or rule out experimentally the existence of such a transition. It has been carried out at the ID16 beamline by using X-Ray Emission Spectroscopy (XES) which is a powerful local probe of  $3d$  magnetism. In the past it has been used successfully to probe the transition-metal magnetism [1]. In particular the  $K\beta$  ( $3p \rightarrow 1s$ ) emission line from transition metal atoms (and to a less extent the  $K\alpha$  ( $2p \rightarrow 1s$ ) line) turns out to be extremely sensitive to the metal spin state.

For this experiment we used a levitation system specially designed to be used at the ID16 beamline. The 2.5mm spherical samples ( $\text{Fe}_{0.95}\text{O}$ ) were aerodynamically levitated using an argon gas flow arriving below the sample and melted with two  $\text{CO}_2$  lasers directed to the sample from the top and from the bottom in order to have a homogeneous temperature. The temperature was measured using an optical pyrometer.



Fe X-ray Emission Spectra of FeO as a function of the temperature.

The experiment was conducted on the Rowland circle spectrometer equipped with a Si(531) spherically bent analyzer and an APD (avalanche photodiode) detector. We used a monochromatic radiation at an energy of 7800 eV (above the Fe K absorption edge).

The figure shows the measured XES spectra of FeO between 7020 and 7080 eV at 8 temperatures in the solid, liquid and supercooled liquid state. We started in the stable liquid 280 K above the melting point and we decreased the temperature down to the solidification.

The emission spectrum of HS Fe is characterized by a main peak  $K\beta_{1,3}$  positioned at an energy of 7058 eV, and a satellite peak  $K\beta'$  located at lower energy (7045 eV) appearing as a result of the  $3p$  core-hole  $3d$  exchange interaction in the final state of the emission process. Since the LS state of  $\text{Fe}^{2+}$  ( $d^6$  configuration) is characterized by a total magnetic moment equal to zero, the collapse of the  $3d$  magnetic moment should lead to the disappearance of the low energy satellite.

At all temperatures, the  $K\beta'$  satellite at 7045 eV indicates that spin exchange still occurs and that Fe is in the HS state. The small changes in the spectral region

between the two peaks is due to a broadening of the  $K\beta_{1,3}$  and  $K\beta'$  line with increasing the temperature.

## Conclusion

This experiment shows that FeO does not exhibit any HS-LS transition on melting and that the value of the coordination number found by EXAFS is not correct. New high-energy XRD and neutron diffraction experiments on levitated liquid FeO [4] confirmed that Fe is principally 4-fold coordinated as observed with liquid alumina [5]. This result is consistent with the observed decrease by about 20% of the FeO density on melting [6]

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