MS36-O3 **Pressure-induced structural and related electronic transitions in $CaFe_2O_4$ and Fe_2O_3.** Eran Greenberg,[a] Gregory Kh. Rozenberg,[a] Weiming Xu,[a] Moshe P. Pasternak,[a] Leonid S. Dubrovinsky,[b] Catherine McCammon,[b] *[a]School of Physics and Astronomy, Tel Aviv University, Israel*, *[b]Bayerisches Geoinstitut, University of Bayreuth, Germany.*
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The interest in $CaFe_2O_4$ (SG *Pbnm*) stems from observations that at high-pressure and high-temperature conditions many spinels transform into this structure [1,2]. Yamanaka et al. [3] reported a martensitic structural phase transition in $CaFe_2O_4$ at ~50 GPa accompanied by a large volume drop. However, Merlini et al. [4] based on single-crystal XRD claimed no change in symmetry, suggesting, based on the disappearance of the $K_{\hat{a}'}$ satellite peak observed by XES, that the volume drop is a result of a high-spin (HS) to low-spin (LS) transition. A similar claim was previously given for hematite (Fe_2O_3) [5] based on an XES observation of the existence of a residual signature of finite spin of Fe above 60 GPa. Meanwhile, Mössbauer spectroscopy (MS) and resistance $R(P,T)$ studies of Fe_2O_3 [6] have shown at pressures above 50 GPa an onset of the Mott transition: namely, a corroborating insulator to metal (IM) transition and correlation breakdown. To clarify the mechanism of the transition observed in both materials, complementary MS, Raman spectroscopy (RS) and $R(P,T)$ studies of $CaFe_2O_4$ to 70 GPa, and MS, RS and XRD studies of Fe_2O_3 have been performed. Resistance measurements, along with MS and Raman spectroscopy, reveal a significant change of the electronic and magnetic properties of $CaFe_2O_4$ above 50 GPa resulting in the formation of the nonmagnetic metallic high pressure state. Unlike a typical bandwidth-control Mott transition characterized by a gradual pressure-induced closing of the insulating gap, in $CaFe_2O_4$ the electrical transport activation energy remains almost unchanged up to the transition. This suggests for $CaFe_2O_4$ a scenario of the Hubbard gap closure different from the bandwidth-control mechanism. This scenario could be the increasing crystal-field splitting overcoming the increasing bandwidth. Indeed, the large volume drop of $CaFe_2O_4$ at the IM transition confirms the possibility of a correlation collapse driven by a HS-LS transition. At that, since Mössbauer spectra at low temperatures did not reveal any evidence of a preceding LS state, even at pressures in which both the low- and high-pressure phases coexisted, it appears that the HS-LS transition immediately leads to an IM transition. The results are compared with hematite (Fe_2O_3), where the transition mechanism is even more complicated due to the corroborating structural phase transition to the Rh_2O_3-type structure.

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MS36-O4 **High pressure diamond anvil cell studies of carbon monoxide – viscosity, photochemical polymerization and laser heating.** Nadine Rademacher,[a] Lkhamsuren Bayarjargal,[a] Wolfgang Morgenroth,[a] Jennifer Ciezak-Jenkins,[b] Björn Winkler,[a] *[a]Institute of Geosciences, Goethe University, Frankfurt am Main, Germany,* *[b]US Army Research Laboratory, Aberdeen Proving Grounds, USA.*
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The chemical reaction of carbon monoxide at high pressures has been studied extensively since a first report in 1983 and stability / phase diagrams have been proposed.[1,2,3,4] Assumptions were made that polymeric CO (p-CO) consists of lactone rings, conjugated C=C, epoxy groups – but a detailed structure determination is still lacking. The diamond anvil cell (DAC) studies presented here have been performed with mixtures of 10 – 25 vol% CO and helium in order to ensure quasi-hydrostatic conditions. During compression of the gas mixture, CO separated from the helium at around 3.5 – 3.8 GPa with helium bubbles rising within the CO phase. The velocities of the spheres were used to calculate the viscosity according to Stokes' law. The viscosity of CO at 3.8 GPa was determined to be 4(1) mPa s. Polymerization was induced photochemically at 4.8 – 5.2 GPa with a blue laser (473 nm) yielding a yellow to dark red solid. Subsequent laser heating of p-CO with a pulsed CO_2 laser between 6 and 7 GPa induced a phase transformation to a colorless solid referred to as 'white phase'. p-CO and the 'white phase' have been characterized in-situ at the Extreme Conditions Beamline P02.2 at PETRA III using 43 keV radiation.[5] For p-CO diffraction data suitable for pair distribution function (PDF) analyses and for the 'white phase' single crystal data sets were collected. The PDF of p-CO does not show structural correlations beyond 5 – 10 Å which confirms the earlier proposed lack of long-range order. The 'white phase' was indexed with a cubic cell whose volume indicates that this phase consists of CO_2.

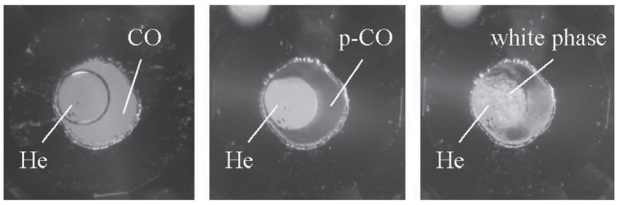

Figure 1: Left: Phase separation of CO and He in the DAC at 3.5 GPa. Middle: p-CO in He in the diamond anvil cell at 5.2 GPa. Right: 'White phase' obtained after heating with a CO_2 laser at around 7 GPa.

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