

and catalysts. Pressure-induced amorphization (PIA) is commonly observed in such open framework structures. Incorporation of guest species and PIA may confer useful properties in these materials for new potential applications, related to their high porosity, in the field of the absorption of mechanical shocks. PIA, guest insertion and chemical reactions at high pressure were investigated in two prototype systems, the pure SiO<sub>2</sub> siliceous zeolite, silicalite (MFI type) and the aluminum phosphate AlPO<sub>4</sub>-54 (VFI type) by a combination of x-ray scattering techniques and Monte Carlo modelling.

In the case of silicalite, which exhibits a 3-D pore structure with a relatively small diameter of about 5 Å, reverse Monte Carlo refinements of total x-ray scattering data indicate that PIA corresponds to the collapse of the structure of the crystalline phase around the empty pores keeping the same structural topology, but with strong geometrical distortions [1]. This material is a novel topologically ordered, amorphous form of SiO<sub>2</sub>. Whereas amorphization begins in silicalite with empty pores below 2 GPa, the incorporation of CO<sub>2</sub> or argon stabilizes the structure of silicalite up to at least 25 GPa [2]. This is well beyond the stability range of tetrahedrally-coordinated SiO<sub>2</sub>. Both x-ray diffraction and Monte Carlo simulations show that the bulk modulus of silicalite strongly increases due to the incorporation of CO<sub>2</sub> or Ar. The insertion of these species deactivates the normal compression and PIA mechanisms in this material. However, when heated at high-pressure, silicalite is found to react with CO<sub>2</sub> forming a disordered SiO<sub>2</sub>-CO<sub>2</sub> compound [3]. This indicates that a new oxide chemistry exists at high pressure.

AlPO<sub>4</sub>-54 exhibits among the largest pores known for zeolites and aluminum phosphates, with a diameter of 12 Å. The material was found to begin to amorphize near 2 GPa using either a non-penetrating pressure transmitting medium (PTM) or no PTM. When H<sub>2</sub>O is used as a PTM, superhydration effects are observed and no decrease in the unit cell volume is observed up to the beginning of PIA below 1 GPa, due to insertion of the H<sub>2</sub>O molecules in the pores. The opposite effect of guest insertion on PIA in this present case may be due to interactions between the water molecules and the Al<sup>3+</sup> cations providing a possible mechanism for PIA. The present results show that the incorporation and/or reaction with guest species can be used to strongly modify the stability of microporous materials with respect to PIA, the pressure range over which they can be retained and can give rise to new materials.

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### MS.19.3

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#### High-Pressure synthesis of transition metal-hydrides

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The application of extreme conditions, namely high pressures and temperatures, provide an ideal testing ground to study the behaviour of hydrogen and its effect on other materials [1]. The chemical potential of hydrogen rises steeply with pressure and the formation of novel hydrides can be observed in elements that were previously not known to form hydride phases. The process of hydrogenation can induce

drastic changes in the material ranging from structural phase transitions to the emergence of superconductivity.

Here, we present our most recent results from studies on the properties of novel metal-hydride phases at high pressures. Metal samples were loaded into a diamond anvil cell under a hydrogen atmosphere of ~2 kbar. Synchrotron based *in-situ* X-ray diffraction studies enabled the observation of the synthesis and subsequent characterization of a hydride up to pressures of ~50 GPa. In this talk, emphasis will be on the unusual properties of binary platinum hydride (PtH), the synthesis of which was first reported in 2008 at pressures above 26 GPa and room temperature [2]. Platinum is often used in science and industry and is valued for its chemical inertness. Although the observation of a bulk PtH phase came as a surprise and should have encouraged further studies, its structural, electronic and mechanical properties remained unknown.

We confirmed the formation of platinum hydride and observed a coexistence of two PtH-phases (PtH-I and PtH-II) at pressures between 26 and 42 GPa [3]. At higher pressures only the PtH-II phase is visible and can be identified as a NiAs type structure, where hydrogen atoms occupy every octahedral interstitial site of the metal lattice. A detailed analysis of the equation of state of PtH-II revealed an increase of the bulk modulus in comparison to pure Pt. Both, the decreased compressibility and the fcc-to-hcp transition are highly unusual findings for a transition metal hydride. Most interestingly however, ab-initio calculations indicate that PtH is superconducting at pressures above 85 GPa with pressure dependent critical temperatures up to 12K, an enhancement by 4 orders of magnitude compared to pure Pt and an effect otherwise only observed in palladium.

The same technique as described above has been applied to study further d-metal systems. Our latest results of studies on hydrides in the tungsten and rhenium systems will be presented as well.

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### MS.19.4

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#### Xe-H<sub>2</sub>O compound synthesized at extreme conditions

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Water is an important component of terrestrial and giant planets so that any reactivity with Xe at depth would have strong consequences on our knowledge of planetary dynamics as it heavily relies on Xe isotopes geochemistry. The chemistry of ‘noble gas’ has seen fascinating experimental and theoretical advances during the last twenty years as highlighted by review papers [1], [2]. Noble gas chemistry proceeds essentially by photosynthesis of precursors in a low-temperature noble-gas matrix. The pressure variable has seldom been investigated as a mean to enforce Xe to bond other elements [3]. Xe is among the gases that stabilize clathrate hydrates through van der Waals interactions. Xe hydrates are stable up to 2.5 GPa, before dissociating into Xe plus ice VII [4]. However, the chemistry of water with solid Xe has been successfully explored by UV photolysis [5], [6]. Those findings plus our own results on the stability of Xe oxides in the terrestrial crust

[7] let us envisage that the chemistry of Xe with oxygen at extreme conditions could be flourishing.

We have thus explored the reactivity of Xe with water up to 80 GPa by using a laser-heated diamond-anvil cell combined with in situ x-ray diffraction measurements. Formation of a compound is indeed observed at conditions that could occur in the interiors of ice-rich giant planets Uranus and Neptune. To complement the x-ray diffraction data, theoretical calculations have been carried out to determine the molecular structure of the newly found compound. These results hence add another example of noble gas sequestration in giant planets, as recently proposed for Ne [8].

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**Keywords:** noble gases, high pressure, water

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### Structural, magnetic and electrical properties of iron-hydride

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Iron-hydride (FeH<sub>x</sub>) is synthesized at 3.5 GPa in dense hydrogen at room temperature, and is unique in its melting curve, its phase relation, and its magnetism [1]. The hydrogenation of iron leads to dramatic changes in the volume and electronic structure of host metal Fe, resulting in the ferromagnetic double hexagonal-close-packing (dhcp)-FeH<sub>x</sub>, in contrast to the nonmagnetic hcp-Fe. By energy-domain synchrotron radiation <sup>57</sup>Fe-Mössbauer spectroscopy technique [2], we observed the magnetic transition from ferromagnetic to nonmagnetic state on the dhcp-FeH<sub>x</sub> near 27 GPa without structural phase transitions [3]. In order to understand the electronic and magnetic properties of FeH<sub>x</sub>, it is important to know detailed *P-T* phase diagram and physical properties of each phase. Previously we have performed high-*P* and Low-*T* XRD experiments going through various *P-T* paths and reported the emergence of the new structural phase of hcp-FeH<sub>x</sub>, by the hydrogenation of hcp-Fe on pressure unloading process in high-pressure H<sub>2</sub> condition.

In this study, we extended our study to high-temperature region, iron-deuteride (FeD<sub>x</sub>), and electrical properties. The X-ray diffraction experiments were performed at SPring-8/BL10XU in combination with laser heating system and DACs. When dhcp-FeH<sub>x</sub> at 16.6 GPa was heated to 1400 K – 1500 K, the structure transformed to fcc via an unknown intermediate phase. The fcc phase was found to be quenchable to room temperature by rapid cooling. In the study of FeD<sub>x</sub>, it was observed that dhcp- and hcp-FeD<sub>x</sub> could be synthesized at just the same conditions with the case of FeH<sub>x</sub>. FeH was found to be a metal by electrical resistance measurements. We had also observed the changes of *P* and *T*-dependence of electrical resistance that can be thought to reflect the ferro-magnetism collapse reported at corresponding pressures. Currently, we are investigating the possible tuning of hydrogen composition (H/Fe ratio) by the application of

electric current.

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### Disordered and incommensurate crystal structures by transmission electron microscopy - some examples

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Ideal crystals are defined as arrays of atoms that are periodically arranged according to a Bravais lattice; the atomic structures of these edifices are completely characterized by three basis vectors fixing the translational symmetry and the coordinates of the atoms in the unit cell. In this scenario Transmission Electron Microscopy (TEM), apart the possibility of investigating nano-crystals provides information which does not substantially differ from those obtained by X-ray and neutron crystallography.

However, crystalline 'order' can be achieved in different ways than by Bravais translational symmetry, resulting in aperiodic crystals. To investigate aperiodic structures, the stronger interaction of the electrons with matter allows obtaining information about subtle crystallographic details that are usually not available by X-ray diffraction. Using TEM many different types of information can be collected from very small volumes (even down to less than 1 nm) from one single grain. Apart from the structural data obtained via selected area electron diffraction (SAED), bright field (BF) and dark field (DF) imaging and high-resolution transmission electron microscopy (HRTEM), more information can be gathered from this small volume by other innovative techniques. Convergent beam electron diffraction (CBED) discloses information on local symmetry of the structure, and high spatial resolved spectroscopic techniques such as electron energy-loss spectroscopy (EELS) allow studies of local cell composition and light elements determinations, the electronic structure of the crystal and the oxidation state of the transition metals.

As example, an innovative TEM investigation on the co-existence of crystallographically commensurate and incommensurate domains within a (Ba,Sr)<sub>2</sub>TiSi<sub>2</sub>O<sub>8</sub> fresnoite structure is presented, particularly the dependence of modulation on local composition. It is shown that perturbations of the average fresnoite structure, determined from 'single crystals', are in some cases better described as nanometric domain intergrowths where departures from an ideal stoichiometry are cause of incommensuration. Evidences of chemical differentiation are obtained from both SAED patterns and HRTEM images. Simulations and Fourier reconstructions of HRTEM images show that modulation can change within relatively small crystal structure volumes.

**Keywords:** incommensurate structures, electron diffraction, HRTEM