

is particularly interesting since crystalline  $ZrW_2O_8$  shows isotropic negative thermal expansion (NTE) [2] and NTE and PIA are believed to be theoretically linked [3]. Total scattering, an extension of the powder diffraction method is an extremely powerful tool for studying this type of phenomena. The unique combination of Bragg and diffuse scattering can be used to determine both the average structure and the short-range fluctuations from this average within a single experiment. In this way a single experimental technique can bridge the gap between amorphous and crystalline structures. However, obtaining high quality total scattering data from a sample contained within a pressure cell is a considerable challenge. Here I will present an RMCProfile [4] study of the pressure induced amorphisation in  $ZrW_2O_8$  [5,6] using neutron and x-ray total scattering. I will also discuss the current and future developments on the high pressure beamline at ISIS (PEARL/HiPr) to improve the quality of neutron total scattering data at high pressures.

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Keywords: amorphization, pair distribution function, high-pressure neutron diffraction

### MS.33.3

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#### Polyamorphism in tin tetraiodide

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The occurrence of different noncrystalline forms of the same chemical composition, with different atomic or molecular arrangements, is much less common. Only in liquid phosphorus a thermodynamically stable polyamorphic transition has been reported thus far (Katayama et al., 2000). Here, using in situ synchrotron x-ray diffraction measurements, firm evidence is given for the existence of thermodynamically stable polyamorphs in liquid tin tetraiodide. To the best of our knowledge, this is the first example of thermodynamically stable polyamorphic transitions found in general compounds. A series of the investigation was initiated to unravel the physical origin of pressure-induced solid-state amorphization of tin tetraiodide (Fujii et al., 1985). It was revealed that there exist two types of amorphous state (Hamaya et al, 1997). The lower-pressure amorphous state consists of randomly oriented molecules, whereas the higher-pressure amorphous state initially found is attained by molecular dissociation. Later, investigation on melting transition could serve to elucidate a peculiarity in the melting curve of the low-pressure crystalline phase; it is not a monotonically increasing curve of pressure but breaks near 1.5 GPa and then becomes almost flat with increasing pressure (Fuchizaki et al., 2004). This finding suggested the existence of two liquid states below and above the break pressure. This was indeed true as mentioned at the beginning. A phase diagram, which includes the two solid amorphous states, is constructed on the basis of pseudo-binary regular solution model. A possible scenario for the liquid-to-liquid phase transition can be sketched with the aid of molecular dynamics simulations, which will be presented separately in the poster session.

Keywords: liquid state, high pressure, synchrotron X-ray diffraction

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#### Structural studies of expanded fluid alkali metals

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Liquid alkali metals in the vicinity of the triple point behave as a simple monatomic metallic liquid, whereas alkali metal vapors are insulating and consist of monomers, dimers in equilibrium. These facts tell us that fluid alkali metals finally experience a metal-insulator (M-I) transition with volume expansion. The M-I transitions of fluid alkali metals occur around the critical density [1]. In order to investigate how this electronic transition is correlated with the structural properties, we have performed x-ray diffraction and small angle x-ray scattering measurements for fluid rubidium and cesium up to the supercritical regions using synchrotron radiation at SPring-8. The experimental results show that the nearest neighbor distance starts to decrease and the density fluctuation increases below the density of 1.1 g/cc for rubidium and 1.3 g/cc for cesium, respectively. These structural features are clearly different from those of classical fluids such as inert gas and indicate spatial atomic-density fluctuations appear in the fluid. The density range where such inhomogeneity of the atomic arrangement appears corresponds to the region where the compressibility of the interacting electron gas has been predicted to become negative, which suggests that the observed structural changes are those induced by the instability of the electron gas.

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Keywords: alkali metals, structure, electron gas

### MS.33.5

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#### Structural transition in amorphous sulfur compressed up to 100 GPa

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Pressure-induced amorphization and polyamorphic transitions retain a growing interest in both fundamental and applied physics in the search for new families of useful materials. We report in situ synchrotron x-ray diffraction data on amorphous sulfur (a-S) between 50 to 100 GPa and 40 to 175 K, and an implemented method to extract the density of non-crystalline materials at such extreme conditions. Measurements of the structure factor yielded the radial distribution function and the densities of two amorphous forms. Synthesized from pressurizing Sulfur I (S-I), a-S undergoes an abrupt structural transition above 65 GPa, accompanied by a density discontinuity of 7 %. These results show that this is a polyamorphic transition, from a low density (LDA) to a high density (HDA) form. Densities and structures of LDA and HDA forms are similar to those of S-III and S-IV phases respectively, arguing in favor of their

nanocrystalline nature. The results cast light on the nature of pressure amorphization, and provide a potential route for the synthesis of new nano-materials.

Keywords: amorphization under pressure, X-ray diffuse scattering, diamond anvil high-pressure apparatus

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### HR-TEM imaging of the carbon networks

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Identification of individual C-C bonds is an ultimate goal of the carbon nanostructure characterization. We have been developing a high sensitivity transmission electron microscopy (TEM) which enables us to visualize a single C-C bond. A TEM equipped with an aberration corrector allows a higher spatial resolution without increasing its tension (the accelerating voltage). Then we have achieved the resolution of 0.14 nm, which corresponds to a typical C-C distance, at a moderate accelerating voltage (120kV). This merits a lot to realize the visualization of carbon atomic chain such as the alkyl chain without electron irradiation damage (1). Here we show some examples for atomic-level characterization of carbon nanostructures. The C<sub>60</sub> fullerene molecule has been successfully identified its structure and orientation at a single-molecular basis (2). Also the active topological defects have been eventually caught red-handed (3). The technique can be widely applicable to visualize a biological activity, at an atomic level, for which any conformation change of the C-C bonds is responsible. The cis-/trans-isomerization of retinal molecules have been successfully visualized (4).

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- (2) Z. Liu et al., *J. Am. Chem. Soc.*, 129 (2007) pp.6666-6667
- (3) K. Suenaga et al., *Nature Nanotech.* 2 (2007) pp.358-360
- (4) Z. Liu et al., *Nature Nanotech.* 2 (2007) pp.422-425

Keywords: electron microscopy, carbon nanotube, defects

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### Image contrast in atomic resolution high-angle annular dark-field images

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High-angle annular dark-field scanning transmission electron microscopy (HAADF or Z-contrast) is remarkably sensitive to the atomic number (Z). Quantitative HAADF imaging holds enormous potential for extracting chemical information in parallel with information on the atomic structure. To date, comparisons between experimental and theoretical HAADF images have been based on image contrast or scaling by an arbitrary amount. Such comparisons are only semi-quantitative and place severe limitations on identifying the origins of any contrast mismatch between experiments and simulations. In this presentation, we demonstrate

that the HAADF detector can measure the incident beam intensity to normalize Z-contrast images onto an absolute intensity scale. We report on a practical approach that ensures that the detector is sufficiently linear over the intensity range of interest. Limitations of the current generation of HAADF detectors, such as scintillator heating and intensity saturation, will be discussed in the context of the probe intensity measurements. By normalizing the atomically resolved signal to the incident probe, we demonstrate quantified HAADF imaging of a SrTiO<sub>3</sub> single crystal as a function of sample thickness. Experimental images are compared with Bloch wave image simulations that incorporate thermal diffuse scattering. Provided that spatial incoherence in the probe is taken into account in the simulations, excellent agreement is found between simulation and experiment. The electron energy-loss spectroscopy (EELS) log-ratio method was used for determination of the local thickness. We will discuss how thickness determination by EELS can be combined with information from the HAADF background to provide improved estimates of the thickness.

Keywords: STEM, electron microscopy techniques, analytical electron microscopy

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### In aberration corrected STEM, shrinking some dimensions expands others

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Crystallography is usually associated with coherent elastic scattering. Having atomically localised inelastic information, however, can allow the solving of crystal structures particularly when crystals are nanometres in size. A particular advantage of the STEM geometry is that inelastic signals, in particular electron energy loss spectroscopy (EELS), are localised and the high angle annular dark field image can be collected simultaneously with the spatially resolved spectroscopic information. Aberration correctors have improved the spatial resolution of EELS as well as significantly improving the signal-to-noise in both imaging and spectroscopy. Results on atomically resolved EELS data will be presented where light has been shed on a periodic structure. Necessarily the sample is only a few tens of nanometres thick in the beam direction but many structures are spatially of similar or smaller scale in one of the other dimensions as well. Systems that will be discussed include silicon/metal disilicide interfaces and silicon nanowires. In addition to using these two dimensional projections of nanostructures, the three dimensional shape of nano-crystals is of crucial importance for heterogeneous catalysis. Conventional tomographic techniques are not expected to get down to the atomic scale. An alternative approach will be presented with data on the shape of gold nano-particles.

Keywords: aberration correction, HAADF, EELS

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### Development of new electron diffraction microscope for diffractive imaging

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