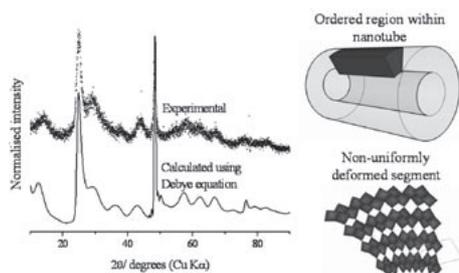


continuous increase in the interatomic distances extending radially outwards across the tube wall. The distances in the outer half of the tube are greater than those in the ideal structure, resulting in wider bottlenecks for Li^+ ion transport, consistent with a higher rate of Li^+ intercalation, and with the greater accessibility of Li^+ sites, consistent with a higher maximum Li composition



Keywords: powder diffraction techniques, nanotubes, structure-properties relationships

MS.32.4

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The application of a molecular replacement approach to the refinement of a copper nanoball complex

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The reaction of equimolar amounts of $\text{Cu}(\text{NO}_3)$ and bdc-5-OH (benzene-1,3-dicarboxylate-5-hydroxy) is an example of a one-step synthetic method which may be used to generate nanoscale molecules via self-assembly. In this case, the discrete structures, termed 'nanoballs' are molecular versions of faceted polyhedra, namely small rhombihexahedra. The structural characterization of specific nanoball complexes, $[\text{Cu}_2(\text{bdc-5-OH})_2\text{L}_2]_{12}$ (where L is a dimethyl sulfoxide, methanol or water ligand), via single crystal x-ray diffraction is very difficult. In many respects, the diffraction patterns obtained from these large metal-organic molecules resemble those obtained from protein crystals, largely due to disordered solvent molecules inside the nanoballs and between the nanoballs. We have utilized an approach similar to isomorphous replacement to refine the structure of $[\text{Cu}_2(\text{bdc-5-OH})_2(\text{H}_2\text{O})_2]_{12}$ (1) from 1.4 Å data. An idealized small rhombihexahedron structure based upon the previously-determined $[\text{Cu}_2(\text{bdc-5-OH})_2(\text{DMSO})(\text{MeOH})]_{12}$ (2) structure, was used to generate a 432-atom rigid body unit (with axially coordinated solvent ligands removed). The orthogonal Angstrom coordinates for this idealized unit were then imported into SHELXTL, using the FRAG instruction. This fragment was fit to the 48 Cu atoms for two independent molecules in structure 1, resulting in the generation of fractional coordinates for all of the nanoball atoms. Complex 1 crystallizes in the space group $P2_1/n$ with $a = 47.993(2)$ Å, $b = 27.763(1)$ Å, $c = 48.131(2)$ Å, $\beta = 110.341(2)^\circ$, volume = $25095(1)$ Å³, with $Z = 2$. The Cu atoms were refined anisotropically and all other non-hydrogen atoms were refined isotropically to yield $RI = 13.77\%$ for 13551 observed reflections and 1577 parameters.

Keywords: refinement problematic structures, SHELX, isomorphous replacement

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Coherent diffractive imaging of nanostructures at synchrotron and FEL sources

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Coherent X-ray Diffractive Imaging (CXDI) is a new microscopy technique that has potentiality to produce images up to diffraction limited resolution at x-ray wavelengths. The basic principles of the technique will be presented in this talk. A number of applications for imaging the shape and strain fields of the nanometer size crystals will be presented as well. It will be demonstrated how a few nanometer resolution can be achieved if a large number of identical samples are illuminated coherently. In the end recent results of CXDI at FLASH Facility at Hamburg will be given.

Keywords: coherent diffractive imaging, phase retrieval, nanosamples

MS.33.1

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New liquid structures of alkali metals under pressure predicted from first principles theory

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We present results from *ab initio* calculations that predict a series of electronic and structural transitions in alkali liquids under pressure. The transitions are initially driven Peierls distortions in the local order of the liquids, followed at higher pressure by electron core overlap effects. In the case of Li, weakly bound tetrahedral clusters are found at pressures above 150 GPa. Similarities and differences between the phase diagrams of Li, Na and K are studied. We establish correlations between the solid and liquid phases of these elements, on the basis of which we predict their melting properties and provide evidence for the low-temperature crystalline phases likely to be found at extreme pressures.

Keywords: high-pressure physics, *ab initio* calculations, liquid structure

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Total scattering studies of pressure induced amorphization

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Solid state amorphization is a widely studied effect, recently highlighted in the interpretation of the structural process underlying rewritable digital versatile discs [1]. Pressure-induced amorphization (PIA) falls within this field and is typified by the behaviour of ZrW_2O_8 . Indeed, the mechanism for amorphization in this system

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.

[1] F. Hensel and W. W. Warren, Jr., Fluid Metals; Liquid-Vapor Transition of Metals, (Princeton University Press, Princeton, NJ, 1999).

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