

Fig. 2. Correlation of the first shell peak height h in an FT spectrum with acceptor number A_N of the solvent. HFIP for 1,1,1,3,3,3-hexafluoroisopropanol, AQ for water, TFE for 2,2,2-trifluoroethanol, EG for ethylene glycol, MeOH for methanol, EtOH for ethanol, *i*-PrOH for isopropanol, PrOH for *n*-propanol, BuOH for *n*-butanol, *t*-BuOH for *t*-butanol, NM for nitromethane, AN for acetonitrile, DMSO for dimethyl sulfoxide, PC for propylene carbonate, DMF for *N,N*-dimethylformamide, NB for nitrobenzene, Py for pyridine, DMA for *N,N*-dimethylacetamide, NMP for *N*-methyl-2-pyrrolidone and AC for acetone.

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EXAFS STUDY ON LIQUID SELENIUM UNDER HIGH-PRESSURE

High-pressure XAFS enables structural information difficult to obtain through conventional high-pressure X-ray diffraction studies to be accessed. We have successfully measured XAFS spectra of crystalline and liquid Se at pressure of 2.5 GPa and temperatures up to 1223K at the beamline **BL01B1** [1].

Liquid Se is a typical liquid semiconductor at atmospheric pressure and its main constituents are two-fold coordinated chain molecules. Recently, study on the semiconductor-to-metal transition of liquid Se in the pressure range from 1 GPa to 4 GPa showed that the transition has some features of a first-order transition [2]. We focus on how structural changes of the Se system associate with the changes in its electronic properties.

A large-volume Paris-Edinburgh press was used to generate high-pressure, high-temperature conditions. A mixture of Se powder and BN powder was put in a BN capsule, which was surrounded by a gasket made of Boron and epoxy. The sample was heated using two graphite disk-type heaters inside the gasket. The beam was focused vertically by a mirror. The size of the X-ray beam was reduced to 0.3(H) x 0.2(V) mm² by slits to adjust to the small sample size. The intensities of the incident and transmitted X-rays were measured with ionization chambers.

Figure 1 shows an example of XAFS spectra for liquid Se measured at pressure of 2.5 GPa and temperature of 773 K. Clear EXAFS oscillations were observed in spite of experimental difficulties.

Figure 2 shows the temperature dependence of radial distribution function, $|F(r)|$, obtained by the Fourier transform of EXAFS function $\chi(k)$ multiplied by k , for crystalline and liquid Se at 2.5 GPa. The main peak corresponds to the covalent bonds. The peak height decreases continuously with increasing temperature due to the thermal factor. The radial distribution function changes little upon melting; this indicates that the two-fold chain structure is largely preserved in the liquid. A steep

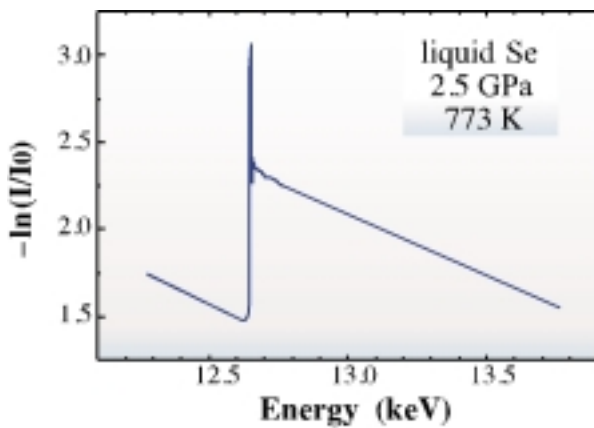


Fig. 1: XAFS spectra for liquid Se measured at pressure of 2.5 GPa and temperature of 773 K.

decrease in the amplitude of the EXAFS oscillation for liquid Se was observed above 1050 K. The decrease was larger than that expected from the normal thermal effect, and it indicates that the two-fold covalent bonds in liquid Se weaken and/or break under high-temperature. The change occurred near the boundary of the reported semiconductor-to-metal transition. This confirms that the transition is accompanied by a structural change.

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XAFS SPECTRA IN THE HIGH ENERGY REGION

There is sufficient photon density even at 100 keV from a bending magnet at the SPRING-8 storage ring. This enables qualitative XAFS spectra to be observed near K absorption edges for almost all heavy elements. Since an EXAFS signal above an L_{III} absorption edge is followed by an L_{II} absorption edge, the energy range is limited for the analysis. Therefore, EXAFS spectra with K absorption edges are anticipated in order to improve the accuracy of local structure parameters for elements, e.g., lanthanoids. However, it has theoretically been pointed out that the finite lifetime of a core hole smears out EXAFS oscillations, and that this effect becomes more serious for K absorption edges of heavier elements [1,2].

Measurements were carried out at the beamline **BL01B1** in the transmission mode with the Si (511) planes of an adjustable inclined double-crystal monochromator, which is the standard monochromator at SPRING-8 and can provide a wide energy range from 4.5 to 110 keV by inclining a pair of crystals. The incident and transmitted X-ray intensities were monitored with flowing Kr gas ionization chambers. It took 5 sec to monitor the X-ray intensities for each data point. The counting of higher-order harmonics was estimated to be less than 1% in comparison with that of the K edge energy, by considering both the photon flux of the source and the efficiency of the detector.

The highly brilliant X-rays of the third generation synchrotron radiation source enable us to measure XAFS spectra with better energy resolution than

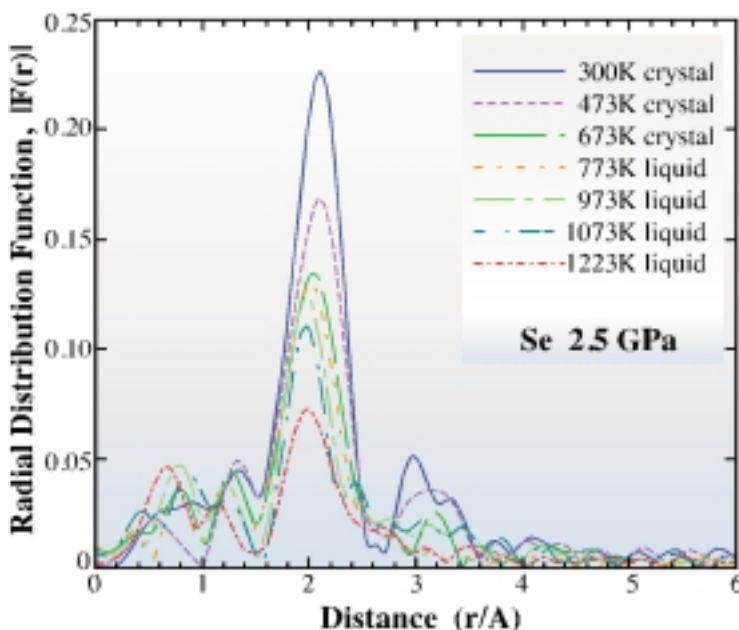


Fig. 2: Temperature dependence of radial distribution function, $|F(r)|$, obtained from EXAFS spectra, for crystalline and liquid Se at 2.5 GPa.