Structure Analysis of Tetrahedral-Molecular Crystal and Amorphous at High Pressure

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Molecular crystal SnI_4 exhibits structure sequence, crystalline phase(CP) I – metallic CP II – amorphous – CP III with increasing pressure at room temperature. CP III becomes stable at 60 GPa and is a non-molecular phase.

We previously proposed three structure models that could account for the observed diffraction pattern from CP III. The first is a partially disordered structure, in which four iodine atoms form a regular fcc unit cell, while a tin atom randomly occupies one of interstitial sites. The second model is a fully disordered structure; both tin and iodine atoms are randomly placed at the fcc lattice sites. The third is a phase separation into the fcc I_2 and amorphous tin or SnI_2. One may notice that those three models exhibit different x-ray energy dependence of the intensity of diffraction peak near the absorption edge of Sn. Thus, we conducted high-pressure powder x-ray diffraction measurement utilizing anomalous x-ray dispersion.

A diamond anvil cell (DAC) was used to apply a pressure of 63 GPa to a sample. Diffraction measurements were carried out at BL10XU using a monochromatic x-ray tuned at an energy between 28.796 and 29.186 keV below the Sn-K-absorption edge E_A=29.1936 keV. An imaging plate was used as a detector. The intensity of an incident x-ray and an x-ray passed through DAC was measured with pin photodiodes. A beam size was 40 x 40 μm^2.

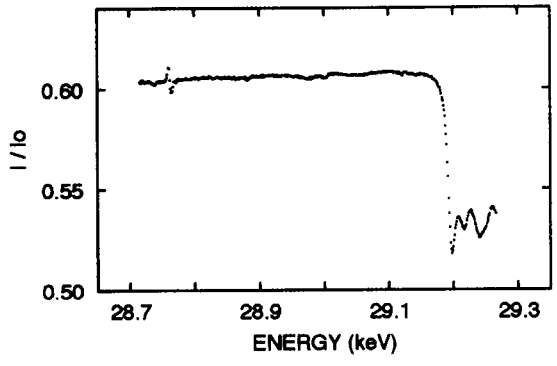

Figure 1. Transmission spectrum of SnI_4 at 63 GPa

Figure 1 illustrates the transmission spectrum of SnI_4 measured at 63 GPa near E_A. XANES modulation is clearly seen and the spectrum is quite smooth below E_A except for a spike at 28.8 keV from unknown origin. This spectrum was used to estimate the absorption due to the sample.

Measured diffraction patterns were corrected for the incident flux, absorption due to diamonds and the sample, and the Lorentz factor. A typical example of the variation of the intensity of reflection with x-ray energy is shown in Figure 2. The 111 reflection becomes weak with increasing photon energy near E_A, indicating the contribution of the scattering from Sn atoms to this reflection. All other reflections 200, 220, 311, 222, 400, 331, 420, were observed to exhibit similar behavior. Such a variation is that expected for the crystal structure of the second model.

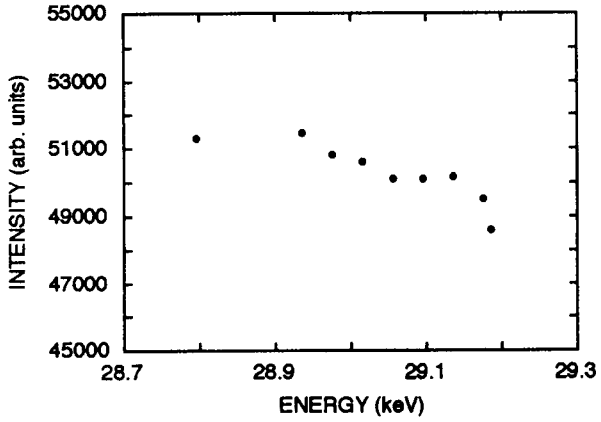

Figure 2. Variation of the intensity of the 111 reflection with x-ray energy