Na and Si K-edge XANES of type I Na-Si clathrate

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Clathrates with host cage made of Si or Ge have attracted much attention because of interesting features like superconductivity and thermoelectric effect. Recently single crystals of Na-Si clathrate, not only of type I (Na_8Si_{46}) but also of type II ($Na_{24}Si_{136}$) have been grown [1, 2]. We have reported X-ray absorption near-edge structure (XANES) of type-I Na-Si clathrate [3].

In this report, we present a study about the Si unoccupied states of type-I and II Na-Si clathrates by Si K-edge XANES. Measurements have been performed in both total electron yield (TEY) and fluorescence yield methods. Results of the former are presented in this article and those of the latter will be published elsewhere. Fractured sample exposed to air was measured. Since the size of the fractured area was smaller than the spot size of X-ray, the epoxy adhesive around the sample was also irradiated.

Figure 1 shows the XANES spectra at the Si K edge. Since the epoxy adhesive's strongest peak was at 0 eV, the 0-eV peak in Fig. 1 is expected to be due to the epoxy adhesive around the Na_8Si_{46} sample and/or the oxidized surface region of the samples. It is known that the Si K-edge XANES of oxidized Si such as SiO_2 has no structures below –3 eV. Therefore, spectra below –3 eV can safely be attributed to the samples. Here, Si 1s electrons are excited to Si 3p unoccupied band. The onset of absorption around –8.8 eV is at lower energy than that of semiconductor Si, which is consistent with the metallic nature of the samples. Leading edge is at the same energy in type I and in type II. The first peak of type II at around –6.7 eV is sharper and is found at slightly lower energy than that of type I. The second structure for type II is found at around –4.2 eV, where the spectrum of type I is nearly flat. The second structure for type I is found at –3 eV. These differences between type I and II are expected to reflect the difference in the unoccupied band structure.

In order to discuss the unoccupied electronic states in more detail, theoretical band structure calculation of type-I and II clathrates has to be performed.

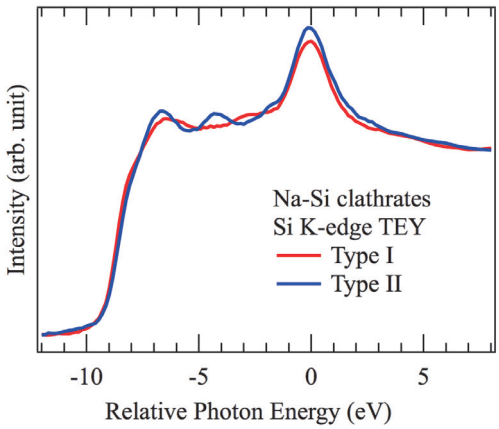

Fig. 1. XANES at Si K edge in TEY mode. The origin of the relative photon energy was taken at the main peak of Si K XANES of SiO_2, the photon energy of which is around 1845 eV. The 0-eV peak presumably comes from the oxidized surface region and/or the epoxy adhesive around the sample.

References

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