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

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Clathrates are compounds in which guest atoms (or molecules) are trapped within the cage-like structure of the host crystal. 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 type I Na-Si clathrate have been grown [1].

We have studied unoccupied electronic states of metallic Na_8Si_{46} by measuring X-ray absorption near-edge structure (XANES) at Na and Si K edges at BL10 in SR Center, Ritsumeikan University. 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. Therefore XANES of adhesive was also independently measured.

Figure 1 shows the XANES spectrum at the Na K edge. In this energy region, no XANES intensity was found for the epoxy adhesive. TEY intensity is plotted as a function of the photon energy relative to the main peak position of Na K XANES of NaCl. Here, Na 1s electrons are excited to Na 3p unoccupied band. The onset photon energy of absorption was around relative photon energy of –4 eV, which is found to be lower than ionic Na crystals. This is consistent with the metallic nature of Na_8Si_{46}.

Figure 2 shows the XANES spectrum at the Si K edge. Since the epoxy adhesive's strongest peak was at 0 eV, the 0-eV peak in Fig. 2 is expected to be due to the epoxy adhesive around the Na_8Si_{46} sample. Here, Si 1s electrons are excited to Si 3p unoccupied band. The onset of absorption around –8.5 eV is at lower energy than that of semiconductor Si. This is again consistent with the metallic nature of Na_8Si_{46}.

In order to discuss the unoccupied electronic states in more detail, theoretical band structure calculation of Na_8Si_{46} has to be performed.

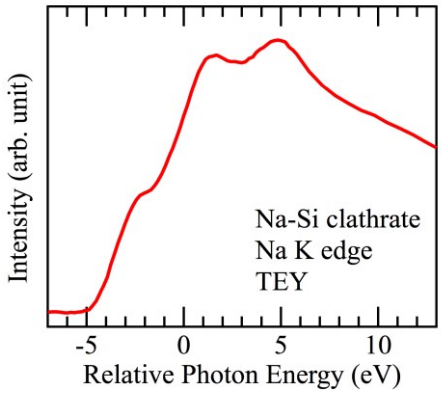

Fig. 1 XANES at Na K edge in TEY mode. The origin of the relative photon energy was taken at the main peak of Na K XANES of NaCl, the photon energy of which is around 1075 eV.

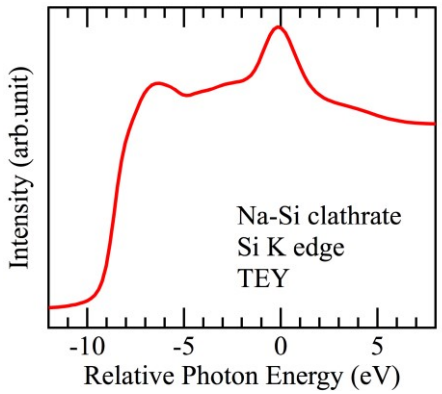

Fig. 2 XANES at Si K edge in TEY mode. The origin of the relative photon energy was taken at the main peak of Si K XANES of SiO_2, the photon energy of which is around 1845 eV. The 0-eV peak presumably comes from the epoxy adhesive around the sample.

Reference

[1] H. Morito, M. Shimoda, and H. Yamane, J. Cryst. Growth **450**, 164 (2016).