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

Daiki Terashima¹, Kohei Sakamoto¹, Toshiharu Kadono¹, Koji Nakanishi², Toshiaki Ohta², Haruhiko Morito³, and Shin Imada¹

1) Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan
2) SR center, Ritsumeikan University, 1-1-1 Noji-higashi, Kusatsu, Shiga, 525-8577, Japan
3) Institute of Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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 Na₈Si₄₆ 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 Na₈Si₄₆.

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 Na₈Si₄₆ 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 Na₈Si₄₆.

In order to discuss the unoccupied electronic states in more detail, theoretical band structure calculation of Na₈Si₄₆ has to be performed.

Reference