Electronic Structure of Ca 3d Levels of Superconducting CaC_6 using Soft X-rays Absorption and Emission Spectroscopy

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Introduction

Graphite intercalation compound (GIC) is a candidate for a conventional BCS type superconductor because of the strong covalent bonding and light mass of constituent element, carbon. A large number of alkali-metal GIC has been synthesized and studied, but the superconducting transition temperature T_c of these compounds has not been high. Recently the highest T_c value was reported in alkali-earth metal GIC, i.e., CaC_6 shows superconductivity below 11.5 K [1]. This value is the highest value among GICs at present. The theoretical calculation of the electronic structure of GIC predicts a strong correlation between the occupation factor of interlayer (IL) band and the value of T_c: Ca 3d electrons forms an IL band and will play an important role on CaC_6 superconductivity. It is consistent with Ca isotope effect and photoelectron experiment results[2-5], but there are few studies on unoccupied states of GICs. X-ray absorption and emission spectroscopy (XAS and XES) near Ca-L edge give unoccupied and occupied partial electron density of states of Ca 3d levels, respectively. The purpose of the present study is to elucidate the electronic structures of Ca 3d in CaC_6 using XAS and XES methods.

Experiment

Sample was synthesized by a conventional liquid-solid reaction between molten Li-Ca alloy and graphite. As the graphite material, HOPG plates and/or Grafoil sheets were used. X-ray diffraction (XRD) patterns show that the samples are almost single phase of the first stage CaC_6 with a small amount of intermediate products, Li-GIC. XRD pattern also suggests that the normal axis of the sample plate is highly oriented to the *c*-axis, however the sample is not the single crystal. It is noted that there is no trace of Ca metal and Ca compounds without CaC_6 in XRD pattern. A magnetization measurement clearly shows the Meissner effect below 11.5 K (Fig. 1).

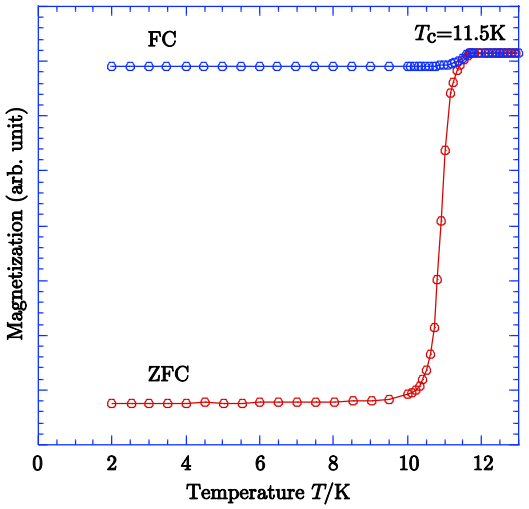

Figure 1 Magnetization measurement of CaC_6. The value of T_c represents previous report.[1]

XAS and XES experiments were performed at BL-19B and 2C in KEK-PF. The total photon yield using the photodiode detector was used as the intensity of absorption in XAS spectra. Both the angles of incident and reflection are kept at 45 degrees, during XAS and XES measurements.

Results and Discussion

Figure 2 shows Ca-L XAS spectrum of CaC_6. It shows the clear two peaks correspond to the L_2 and L_3 edges. A small satellite peak is observed on the low energy side. In comparison with the spectrum of Ca metal and $CaCO_3$, observed energy difference between main peak and satellite peak suggests that Ca in CaC_6 is metallic rather than ionic. Figure 3 shows XES spectra with the excitation energies of E_{3m} in XAS spectra. Large elastic peak

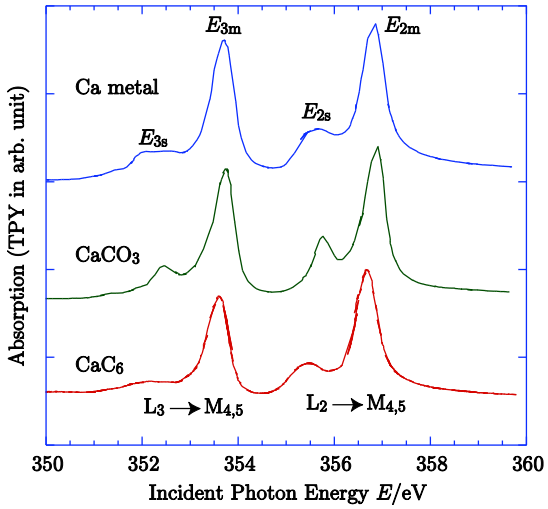

Figure 2 Ca-L XAS spectra of Ca metal, $CaCO_3$ and CaC_6. The separation energy between main peak and satellite peak suggests that the electronic structure of Ca-3d of CaC_6 is close to that of Ca metal rather than ionic $CaCO_3$.

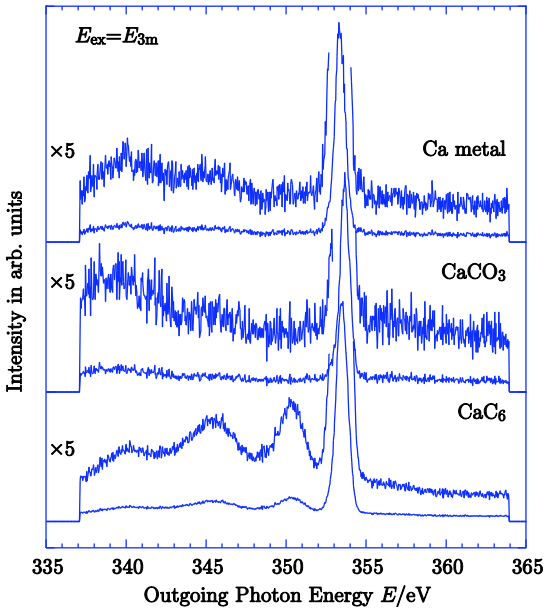

Figure 3 Ca-L XES spectra of Ca metal, $CaCO_3$ and CaC_6. Incident photon energy was set to E_{3m} in Fig. 2.

and some inelastic peaks are observed in CaC_6 spectra. These inelastic spectra consist of both the fluorescence and Raman peaks. The fluorescence near Ca-L edge resulted from the radiative relaxation of Ca-3d electron to Ca 2p levels. One can see that XES spectrum of Ca metal shows small amount of inelastic peaks, and XES of $CaCO_3$ shows almost no inelastic peaks. The valence of Ca in $CaCO_3$ is divalent so there is no electron in Ca 3d and Ca 4s levels in the compound. In this context, the observed fluorescence spectra of CaC_6 indicate that considerable amount of Ca 3d electrons are in occupied states of CaC_6. It suggests that Ca 3d electrons would form an interlayer band with Ca 4s electrons. The present result strongly supports the important role of Ca 3d in the superconductivity of the compound, as previous theoretical and experimental studies.

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