Photoemission Study of Ca-Intercalated Graphite Superconductor CaC_6

Hiroyuki Okazaki,[1,2] Rikiya Yoshida,[1] Keisuke Iwai,[1] Kengo Noami,[1] Takayuki Muro,[3] Tetsuya Nakamura,[3] Takanori Wakita,[2,4] Yuji Muraoka,[1,2,4] Masaaki Hirai,[1,4] Fumiaki Tomioka,[5] Yoshihiko Takano,[5] Asami Takenaka,[6] Masahiro Toyoda,[6] Tamio Oguchi,[7] and Takayoshi Yokoya[1,2,4]

[1]*The Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan*

[2] *Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, Okayama 700-8530, Japan*

[3]*Japan Synchrotron Radiation Research Institute (JASRI) /SPring-8, Hyogo 679-5198, Japan*

[4]*Research Laboratory for Surface Science (RLSS), Okayama University, Okayama 700-8530, Japan*

[5]*National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan*

[6]*Faculty of Engineering, Oita University, Oita 870-1192, Japan*

[7]*Department of Quantum Matter, Graduate School of Advanced Sciences of Matter (ADSM), Higashi-Hiroshima, Hiroshima 739-8530, Japan*

Abstract

In this work, we have performed resonant photoemission studies of Ca-intercalated graphite superconductor CaC_6. Using photon energy of the Ca 2*p*-3*d* threshold, the photoemission intensity of the peak at Fermi energy (E_F) is resonantly enhanced. This result provides spectroscopic evidence for the existence of Ca 3*d* states at E_F, and strongly supports that Ca 3*d* state plays a crucial role for the superconductivity of this material with relatively high T_c.

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1. Introduction

The superconducting graphite intercalation compounds (GICs) have been studied, since the discovery of Alkali-metal GIC (AGIC) superconductors of C_8K [1]. However, their superconducting transition temperatures (T_c's) are generally low (< 2 K) [1, 2]. Recently, it was discovered that CaC_6 exhibit T_c of 11.5K [3], which are much higher than those of other GIC superconductors. The observation of high T_c in CaC_6 has provoked much attention. The theoretical studies suggest that Ca 3*d* states in CaC_6 induce relatively high T_c [4]. However, orbital character of CaC_6 did not been experimentally elucidated. Therefore, we have performed resonant photoemission spectroscopy (RPES) of CaC_6 and presented the existence of Ca 3*d* electrons at E_F, which play a crucial role for the superconductivity.

2. Experimental

CaC_6 samples were prepared by reacting highly oriented pyrolytic graphite (HOPG) with a molten Li-Ca alloy at 350°C for several hours [5]. T_c of 11.2 K was confirmed by magnetization measurement. Because of easy deterioration of CaC_6 by exposure to the air, the sample was glued to a sample holder under argon atmosphere and transferred to measurement chamber under the same condition.

Resonant photoemission spectroscopy (RPES) was measured at BL25SU of SPring-8 with a Scienta SES200 electron analyzer. The energy resolution was set to be 70 meV to obtain a reasonable count rate. The sample was cooled by a He-cycled cryostat down to 20 K. Clean surfaces for this measurement were obtained by cleaving the sample under 5×10^{-8} Pa. E_F of the sample was referenced to that of a Au film which was measured frequently during the experiments.

3. Results and discussion

We show the Ca $2p_{3/2}$ (L_3) absorption spectrum of CaC_6, as shown in Fig. 1(a). The Ca $2p_{3/2}$ (L_3)

absorption spectrum consists of a peak at photon energies 348.6 eV and an additional weak structure at the onset. The multiple peaks are similar to the 2*p*-3*d* absorption spectrum of Ca [6]. This result indicates that the absorption spectrum of CaC_6 dominantly comes from the Ca 2*p*-3*d* absorption. Thus, by RPES using the photon energy at the Ca $2p_{3/2}$ threshold, Ca 3*d* states should be enhanced if Ca 3*d* states exist. Figure 1(b) shows valence band spectra of a near E_F measured using photon energies around the Ca $2p_{3/2}$ threshold. The labels on the spectra (A-F) denote photon energies used with RPES. For curve C-F, a new peak, which is denoted an arrow on Fig. 1(b), appears on the high binding energy side of near E_F peak. This is characterized by Auger transition. Going toward Ca $2p_{3/2}$ absorption line (curve A to D), the near E_F peak intensity increases, reaching its maximum at the photon energy of the absorption maximum (curve D), and decreases at higher photon energies (curve E and F). As the result, we observed that the near E_F peak obviously exhibits the resonant behavior. This directly indicates that there are Ca 3*d* states at E_F, as expected on the band calculation [4].

It is important to compare the electronic structure of CaC_6 with superconducting AGICs, in order to clarify why CaC_6 has relatively high T_c. The valence band at E_F of superconducting AGICs (C_8K, C_8Rb, and C_8Cs) consists of C 2*p* and intercalated alkali-metal *s* states [7, 8]. The existence of the states derived from intercalated atom is the same as CaC_6. However, we found a definite difference between CaC_6 and the superconducting AGICs; CaC_6 has Ca 3*d* states at E_F, while the superconducting AGICs have no *d* states. CaC_6 is unique because of the existence of Ca 3*d* states at E_F, suggesting close correlation with its relatively high T_c. This is consistent with the theoretical study [4] suggesting that Ca 3*d* states leads to enhanced T_c. Thus, there is the possibility that transition-metal GICs become GIC superconductor with higher T_c than CaC_6.

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Figure captions

Fig. 1. RPES using incident energy of the Ca $2p_{3/2}$ (L_3) absorption. (a) The Ca $2p_{3/2}$ absorption spectrum of CaC_6. The labels (A-F) correspond to incident energies for RPES. (b) Near E_F photoemission spectra of CaC_6 measured using photon energies near Ca $2p_{3/2}$ absorption. The arrows correspond to the peaks of Auger transition.

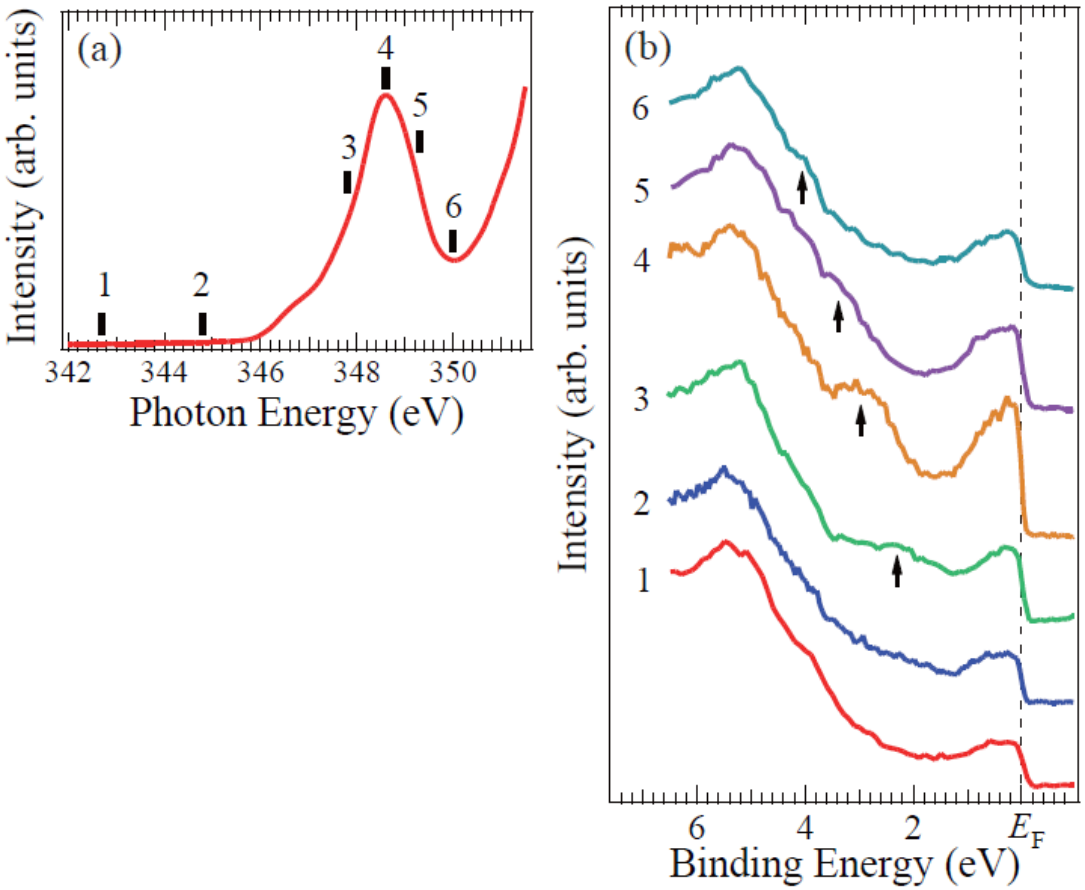

Fig. 1. H. Okazaki