

**Pseudo-Gap at the Fermi Level in  $K_3C_{60}$  Observed by Photoemission and Inverse Photoemission**

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(Received 14 November 1991)

Photoemission and inverse photoemission spectroscopy has been used on  $C_{60}$  and  $K_3C_{60}$  to study the change of the electronic structure upon alkali doping and its relation to the occurrence of superconductivity. The experimental results show that alkali doping does not lead to a rigid filling of the lowest unoccupied molecular-orbital band by the doped electrons but causes a transfer of electronic states from that band to an additional band produced in the band gap. A comparison of the photoemission and inverse photoemission spectra indicates that a pseudo-gap of about 0.5 eV opens at the Fermi level in  $K_3C_{60}$ . Possible origins for the pseudo-gap and its relation to superconductivity are discussed.

PACS numbers: 74.70.Ya, 71.38.+i, 79.20.Kz, 79.60.-i

Since the discovery of superconductivity in alkali-doped solid  $C_{60}$  [1-5], the electronic structure of the host material ( $C_{60}$ ) and the doped compounds ( $A_xC_{60}$ , where  $A$  is an alkali metal) has been actively studied theoretically [6-8] and experimentally [9-13]. It is established that the electronic structure of the host material ( $C_{60}$ ) is well described by band-structure calculations. This presents a striking contrast to the cuprate superconductor where the undoped starting material is not well described by band-structure calculations because of the strong electron correlation, while a band picture seems to recover when the insulator is sufficiently doped with holes or electrons [14,15]. One of the current problems in  $A_xC_{60}$  is whether or not the band-structure approach can be expanded to the doped compound. Another urgent problem for elucidating the mechanism of superconductivity is how the electronic structure is similar to or different from that of the cuprate superconductors since the superconducting transition temperature in alkali-doped  $C_{60}$  [4] is comparable to that of  $La_{2-x}Sr_xCuO_4$ .

We have already reported [16] a comparative photoemission study of  $Rb_xC_{60}$ ,  $Rb_xC_{70}$ , and  $RbC_8$  (graphite intercalation compound) and showed that there are definite differences in the electronic structure among these three compounds which would account for the appearance of the superconductivity only in the  $C_{60}$  compounds. In the previous report, we suggested that there is a pseudo-gap at the Fermi level in the fullerides, from the comparison of the photoemission spectra. In the present study, we have confirmed the existence of the pseudo-gap by the combination of photoemission and inverse photoemission spectroscopies which enables a full and precise determination of the electronic structure in the vicinity of the Fermi level.

$C_{60}$  powders were prepared by arc-heating of graphite

under a 100-Torr He atmosphere and were subsequently separated with high-performance liquid chromatography. The purity is estimated to be better than 99%. The photoemission measurement was done at UVSOR of the Institute for Molecular Science of Japan. The photon energy used was 20 eV and the energy resolution was about 0.15 eV. The inverse photoemission measurement was done with a homemade inverse photoemission spectrometer at Tohoku University; it has a Pierce-type electron gun and a Geiger-Müller-type photon counter with a  $SrF_2$  window and iodine gas in it. The photon counter detects photons of the energy of  $9.5 \pm 0.15$  eV.

In both the measurements, the sample of 100 Å thickness was prepared *in situ* by vapor deposition of  $C_{60}$  powders on a gold-coated molybdenum substrate and by subsequent vapor deposition of potassium atoms on it with an SAES getter. The amount and the rate of evaporation were monitored with a quartz thickness monitor. In order to characterize the film thus prepared, we monitored *in situ* the electrical conductivity of a film deposited on a quartz substrate placed next to the photoemission and inverse-photoemission sample with a two-probe method and a Van der Pauw method. The conductivity of the film gradually increased with potassium doping and showed a maximum around the composition of  $K_3C_{60}$ , estimated on the assumption that the deposited potassium atoms distribute uniformly in the film. The conductivity decreases upon a further doping as reported in the previous study [17]. The maximum conductivity observed in this study (about  $200 \text{ Scm}^{-1}$ ) is in good agreement with that of the previous report where the sample was prepared by a vapor-transportation method [17]. All these results suggest that potassium atoms diffuse rapidly into a  $C_{60}$  film of 100 Å thickness even at room temperature and they also indicate that the present sample show-

ing the maximum conductivity is single phased with the composition of  $K_3C_{60}$  [17,18]. A simultaneous photoemission analysis of the intensity of a shallow core level of K atoms (K  $3p$ ) provided values of  $x$  in  $K_xC_{60}$  similar to those obtained by the resistivity measurement, although there remains a small ambiguity due to a large background in the photoemission spectrum. This indicates that the outer few layers probed by photoemission and inverse photoemission have almost the same composition as in the bulk. An observed good correlation [16] between the conductivity of the film and the magnitude of the density of states at the Fermi level in the photoemission spectrum also supports the above conclusion. No degradation of the sample was observed during the measurement. The Fermi level of the sample is referred to that of a gold film deposited on the sample. We have checked that there was no spurious drift of the Fermi level during the measurement.

Figure 1 shows the photoemission and inverse photoemission spectra of  $C_{60}$  and  $K_3C_{60}$ . As described above, we regarded the film as having a composition of  $K_3C_{60}$  when the monitor film exhibits the maximum conductivity [17]. The photoemission spectrum of pristine  $C_{60}$  has two prominent peaks from  $E_F$  to  $-5$  eV, which are assigned to the  $h_u$  molecular orbital and a combination of the  $h_g$  and  $g_g$  orbitals, respectively. The  $h_u$  orbital is called the HOMO (highest occupied molecular orbital) band. Above the Fermi level, the inverse photoemission spectrum of  $C_{60}$  shows four distinct peaks from  $E_F$  to 6 eV. The first two peaks are assigned to the  $t_u$  and  $t_g$  molecular orbitals, respectively. The latter two peaks are from a combination of some molecular orbitals [19]. The first unoccupied state is called the LUMO (lowest unoccupied molecular orbital) band. The photoemission and the inverse photoemission spectra show good agreement with the previous reports [9–13] as to the number of bands and their energy position. The difference in the relative intensities of the peaks is due to the difference in the photon and electron energies used. It is noticed that

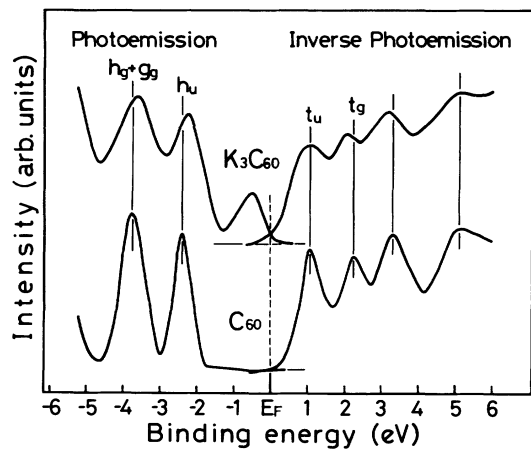


FIG. 1. Photoemission and inverse photoemission spectra of  $C_{60}$  and  $K_3C_{60}$ .

the energy interval between the threshold of the HOMO and the LUMO bands is 2.1–2.2 eV, slightly larger than the optical absorption threshold (1.9–2.0 eV) [20]. This difference may be due to an excitonic effect in the optimal measurement and/or a final-state effect in the photoemission and inverse photoemission processes. The excitonic effect tends to cause an underestimation of the band gap while the final-state effect is likely to overestimate the gap. The discrepancy in the HOMO-LUMO band separation in  $C_{60}$  between the band calculation [6] (about 2 eV) and the present experiment (about 2.5 eV) may also be due to the final-state effect in the experiment, while a possibility that the local-density-approximation calculation underestimates the energy gap is not ruled out. This is because a hole left after photoemission or an electron added in inverse photoemission is not fully screened by conduction electrons in an insulator like  $C_{60}$ . However, the final-state effect is expected to be very small in  $K_3C_{60}$ , since  $K_3C_{60}$  is a metal where the conduction-electron screening severely weakens the effect.

When the  $C_{60}$  film is doped with potassium, the photoemission and the inverse photoemission spectra change remarkably. It is clear from Fig. 1 that a rigid band model does not work in alkali-doped  $C_{60}$ . A rigid band model predicts that the Fermi level should be shifted to the center of the  $t_u$  band since  $K_3C_{60}$  is in the “half-filled” state. The most remarkable change is an appearance of a new band a half electron volt below the Fermi level at the composition of  $K_3C_{60}$ . It is noted that this new band does not have the sharp Fermi edge usually observed in the photoemission spectrum of normal metals, whereas there is certainly a finite density of states at the Fermi level which would give a metallic nature to this compound. The lack of a clear Fermi edge in  $K_3C_{60}$  becomes more evident when compared with alkali-metal graphite intercalation compounds (AGICs) such as  $KC_8$ , which have the same constituents and a similar doping nature. The photoemission spectrum of AGICs exhibits a sharp Fermi edge and its intensity gradually increases with the doping as expected from a simple rigid band filling [21].

The lack of a sharp Fermi edge is also seen in the inverse photoemission spectrum. The  $t_u$  band, which is completely unoccupied in  $C_{60}$ , has a small density of states at the Fermi level in  $K_3C_{60}$ , but it is only a tail of the partially unoccupied  $t_u$  band whose center is still located 1 eV above the Fermi level. The comparison of the photoemission and inverse photoemission spectra leads to the conclusion that  $K_3C_{60}$  has a pseudo-gap of about 0.5 eV at the Fermi level. We are convinced that the additional band appearing below the Fermi level has its origin in the  $t_u$  (LUMO) band, since the intensity of the additional band increases coincidentally with the diminishing of the LUMO band upon the alkali doping, as observed in the present study and also in the core absorption studies [12]. It seems from the spectral change in Fig. 1 that the doping causes a transfer of states from the LUMO band

to an additional band below the Fermi level. A similar behavior is also seen in the doped negative- $U$  semiconductors [22] and the cuprate high-temperature superconductors [23].

The origin of the pseudo-gap at the Fermi level in  $K_3C_{60}$  is not known at present. Benning *et al.* [10] have pointed out that a strong electron correlation in the LUMO band may cause the absence of rigid band filling. It is generally accepted that the electron correlation of a C  $2p$  electron is small compared with that of a Cu  $3d$  electron which is believed to govern the electronic structure of the cuprate superconductor. However, when considering the very narrow feature of the bands in solid  $C_{60}$  due to its strong molecular nature, the electron correlation of the C  $2p$  electron becomes comparable to the bandwidth and may not be negligible. In this case, a pseudo-gap due to the electron correlation may open at the Fermi level. On the other hand, a local lattice distortion caused by the doped electrons may be another explanation for opening of the pseudo-gap. It seems likely that the doped electrons severely distort the structure of  $C_{60}$  molecules and produce polaron (or bipolaron) states deep in the band gap of the host material ( $C_{60}$ ). The observed gradual growth of the additional band with the alkali doping is described in terms of the increase of the density of polaron states. A strong Jahn-Teller effect observed in a negatively charged  $C_{60}$  molecule [24] favors the creation of a polaron state in solid  $C_{60}$ .

It is useful to compare the photoemission spectra reported so far in order to check the peculiar behavior of the electronic structure upon alkali doping in  $C_{60}$ . To our knowledge, there are essentially four different reports on the photoemission of alkali-doped  $C_{60}$  including the present one, while the present report is the first one for inverse photoemission of doped  $C_{60}$ . The photoemission spectra reported by Benning *et al.* [10], by Wertheim *et al.* [11], and by the present authors are essentially the same in the spectral shape and the energy position of the peaks. The difference in the relative intensities of peaks in the spectra is due to the difference in the photon energy used. In all three photoemission spectra for  $K_3C_{60}$ , a sharp Fermi edge is not seen and an additional band produced by the alkali doping is located about 0.5 eV below the Fermi level. On the other hand, Chen *et al.* [12] reported a photoemission spectrum with a sharp Fermi edge for  $K_3C_{60}$  although the intensity at the Fermi level was very small. The difference between the two sets of photoemission spectra might be due to the difference in the photon energies used: Benning *et al.* (65 eV), Wertheim *et al.* (21.2 eV), Chen *et al.* (110 eV), and the present authors (20 eV). The photoionization cross section of a C  $2p$  electron is about  $10^2$  larger than that of a K  $4s$  electron at a photon energy around 20 eV while they are almost comparable at 100 eV [25]. This means that if there is a dominant contribution from the K  $4s$  orbital to the electronic states near the Fermi level, the K- $4s$ -derived portion might be missed in a photoemission spec-

trum at lower photon energy. However, it seems that such a situation does not take place in the present case, because some substantial differences are also observed between the two sets of experiments even in the higher-binding-energy region where the C  $2p$  orbital is dominant.

A difference in the actual composition of the samples may be the cause for the discrepancy. Benning *et al.* [10] estimated the composition from the photoemission spectral change upon K doping, since the incorporation of alkali metals into  $C_{60}$  stops at the composition of  $A_6C_{60}$  [17,18]. Actually we observed that the photoemission spectrum denoted by  $K_3C_{60}$  in Fig. 1 changed further upon additional doping and the change was almost saturated at the composition of  $K_6C_{60}$ . Wertheim *et al.* [11] determined the composition by means of the relative intensity between the HOMO peak and the additional peak near the Fermi level. This procedure may involve a substantial uncertainty because the relative intensity of the peaks changes remarkably with photon energy [9]. Chen *et al.* [12] estimated the composition using the intensity of the additional peak near the Fermi level and the intensity of the K  $2p-3d$  and C  $1s-2p$  absorption spectra. It is noted here that the probing depth is quite different between the two experimental methods. When we use a fluorescence-yield method for the x-ray absorption, the photoemission probing depth at 110 eV (about 5 Å) as used by Chen *et al.* [12] is  $10^2-10^3$  smaller than that of the absorption measurement. So, the two different types of spectra may not be directly compared with each other. In the present study, we used three methods to estimate the composition: a thickness monitor, *in situ* measurement of the conductivity of a monitor film, and the photoemission intensity of the K  $3p$  core level. As described above, the results of these three independent methods coincided very well, showing that the conductivity of the film exhibited a maximum when the composition estimated by the thickness monitor and the core-level photoemission intensity reached about  $K_3C_{60}$ . Thus, the four experimental groups employed different methods to estimate the composition of their samples. It is remarked that three of the four experiments, by Benning *et al.* [10], Wertheim *et al.* [11], and the present authors, obtained almost the same result although the estimation methods were quite different and independent. For example, the energy position of the HOMO band at the composition of  $K_3C_{60}$  is 2.2 eV from the Fermi level in the three experiments, while it is located at 2.6 eV in the spectrum of Chen *et al.* [12]. The total spectral feature at the composition of  $K_{5.8}C_{60}$  in the experiment by Chen *et al.* rather resembles that at the composition of  $K_3C_{60}$  in the other three experiments. It is noted here that in all three experiments the photoemission spectrum at the composition of  $K_3C_{60}$  exhibited a further change upon additional doping and the change was almost saturated when the doping amount reached about a factor of 2. This observation is in excellent agreement with the report that the incorpora-

tion of alkali atoms into  $C_{60}$  stops at the composition of  $A_6C_{60}$  [17,18].

In conclusion, we performed comparative photoemission and inverse photoemission spectroscopy on  $C_{60}$  and  $K_3C_{60}$  and found that the change of the electronic structure by alkali doping is not a rigid band filling but a transfer of the electronic states from the LUMO band to an additional band produced by the doping below the Fermi level. The comparison of the photoemission and inverse photoemission spectra shows that a pseudo-gap of about 0.5 eV opens at the Fermi level in  $K_3C_{60}$ . Further experimental studies, such as optical absorption, to check the photoemission result and also theoretical studies to examine the relationship between the existence of a pseudo-gap at the Fermi level and the superconductivity are required.

The authors thank K. Kamiya, H. Fujimoto, and S. Hino for their help in the photoemission measurement. This work was supported by the grants from the Ministry of Education, Culture and Science of Japan and from the Foundation for Promotion of Material Science and Technology of Japan.

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