

Comparative High-Energy Resolution Photoemission Study of K_xC_{60} and Cs_xC_{60}

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(Received November 30, 1993)

Comparative high-energy resolution ($\Delta E \sim 30$ meV) photoemission spectroscopy has been performed for Cs_xC_{60} and K_xC_{60} to study the difference and similarity in the electronic structure near the Fermi level (E_F) between the superconducting and the non-superconducting alkali-doped C_{60} . It was found that Cs_xC_{60} ($0 \leq x \leq 6$) is a semiconductor or an insulator in all the composition range except for $0 < x \leq 1$ where the Cs-doped C_{60} appears to be metallic with a finite density of states at E_F . This shows a sharp contrast with the case of K_xC_{60} which exhibits a relatively large density of states at E_F in the composition range of $0 < x < 4$ with the largest intensity around $x=3$.

KEYWORDS: C_{60} , fullerene, superconductor, electronic structure, alkali metal

1. Introduction

The electronic structure of alkali-doped fullerenes has been extensively studied by photoemission spectroscopy¹⁻⁶⁾, which clearly shows a transfer of electronic charge from the s orbital of alkali atom to the LUMO (lowest unoccupied molecular orbital) band of C_{60} upon the doping. The photoemission studies also found a non-rigid filling of the LUMO band by donated electrons, suggesting important contribution from a lattice distortion (Jahn-Teller effect) and/or an electron correlation for understanding the electronic structure as well as the superconducting mechanism in the doped fullerene. Further, a recent remarkable improvement of the energy resolution in photoemission measurement as well as of the quality of *in-situ* prepared alkali-doped fullerene samples has made it possible to study in detail the electronic structure near E_F . A several research groups⁷⁻¹⁰⁾ have already reported their observation of a very sharp Fermi-edge structure in the photoemission spectrum of K_xC_{60} using a high-energy resolution photoemission. In this paper, we report the first high-energy resolution photoemission spectroscopy of Cs_xC_{60} and compare the experimental result with that of K_xC_{60} in order to study the difference and similarity between the superconducting and the non-superconducting alkali-doped C_{60} . In this comparative study, we found remarkable differences in the electronic structure near E_F probably responsible for occurrence or disappearance of the superconductivity in these compounds. The gross feature in the photoemission spectrum of the wide-energy range, on the other hand, appears to be similar between the two compounds as previously reported. Further we observed for the first time a sharp Fermi-edge cutoff indicative of metallic

character of the compound in the photoemission spectrum of Cs_xC_{60} in the composition range of $0 < x \leq 1$.

2. Experimental

A thin pristine C_{60} film ($\sim 100 \text{ \AA}$ thick) was prepared by vapor deposition of C_{60} powders (99.9 % pure) on a gold-coated stainless steel substrate held at ~ 150 °C under ultrahigh vacuum (1×10^{-10} Torr) in the photoemission spectrometer. Doping of alkali atom was achieved by successive deposition of alkali metal onto the C_{60} film with a SAES getter at a very low deposition rate of about 1 \AA/hour with keeping the temperature of substrate at about 150 °C.

Photoemission spectra were measured *in-situ* with the He I and II resonance lines (21.2 eV and 40.8 eV, respectively) as excitation light using an angle-integrated photoemission spectrometer equipped with a VSW 300 mm-in -diameter electron energy analyzer. The sample was kept at 30-40 K during the photoemission measurement to reduce the temperature broadening effect in the spectrum. The total energy resolution including the natural width of the excitation light (He I) and the thermal broadening at this temperature was about 30 meV as estimated from the Fermi-edge cutoff. The Fermi level of the sample was referenced to that of a gold film deposited on the sample and its uncertainty was estimated to be less than 3 meV. No degradation of the sample was observed during the measurement.

Composition of samples was estimated by the intensity ratio between the HOMO and LUMO bands in the photoemission spectrum, as well as with the relative photoemission intensity of a shallow core level of alkali atom (K 3p or Cs 5p). We observed a saturation of the HOMO-LUMO intensity ratio in the spectrum when we gradually

deposited alkali atoms on the C₆₀ film. We assumed that this saturation corresponds to the stage of full occupation of the LUMO band by donated electrons from alkali atoms, meaning that the composition of the sample surface probed by photoemission is A₆C₆₀ (A; alkali atom). We estimated the composition of each stage of doping with the relative intensity of the HOMO and LUMO bands in the measured photoemission spectrum itself. The possible experimental error in determining the x's would be 0.2 - 0.3 and 0.5 in the small and the large x regions, respectively. We also found that the photoemission intensity of the shallow core level shows a good linear relation to the HOMO-LUMO intensity ratio.

3. Results and Discussion

Figure 1 shows high-energy resolution photoemission spectra of Cs_xC₆₀ compared with those of K_xC₆₀. Figure 2 shows the enlargement of spectra in the vicinity of the Fermi level. As found in Fig. 1, the gross feature of change in the photoemission spectrum upon the doping looks similar between the two compounds; for example we find a new band emerging between the E_F and the HOMO band upon the doping, which is ascribed to the occupied LUMO band of C₆₀. However, a remarkable difference is found in the vicinity of the Fermi level as shown in Fig. 2. In the case of K_xC₆₀, a sharp Fermi-edge cutoff indicative of metallic character of the compound is clearly seen in the photoemission spectra of 0 < x < 4, with its largest relative intensity at x ~ 3. As for Cs_xC₆₀, on the other hand, the density of states at E_F is very small in all the composition range in contrast with K_xC₆₀. This clear difference has not been observed in a previous comparative photoemission study on Cs_xC₆₀ and K_xC₆₀ with an ordinary energy resolution¹¹). It is remarked that the photoemission spectra of the sample with composition near Cs₃C₆₀ (x=2.6 and 3.2 in Fig. 2) has negligible intensity at E_F, indicating its insulative or semiconductive nature in sharp contrast with K₃C₆₀, which shows a clear Fermi-edge cutoff in the spectrum. However, since single-phased Cs₃C₆₀ has not yet been separated, it is more likely that the spectrum of Cs_xC₆₀ with x~3 may represent that of Cs₄C₆₀, which has been experimentally separated and is known to have a body-centered-tetragonal (bct) crystal structure as in K₄C₆₀.

At x=4, both K- and Cs-doped C₆₀ appear to be an insulator or semiconductor since no density of states is seen at E_F (see Fig. 2); the energy gap is estimated to be 0.3-0.4 eV when we assume that the Fermi level is located at the center of gap. This obviously contradicts a simple one electron picture since the LUMO band originates in the three-fold degenerate t_{1u} molecular orbital and it is impossible for four electrons per a C₆₀ molecule

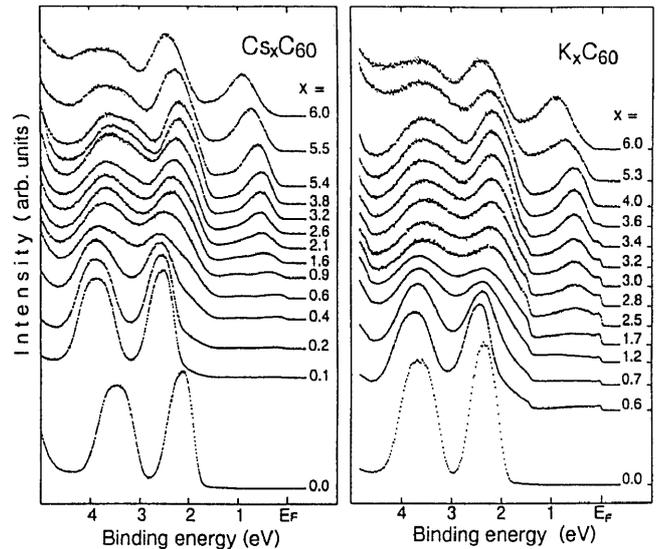


Fig. 1 High-energy resolution photoemission spectra of Cs_xC₆₀ (left) and K_xC₆₀ (right). Composition (x) estimated from the relative intensity of the HOMO and the LUMO band is shown on each spectrum.

donated from alkali atoms to fully occupy the LUMO band. Accordingly it is reasonable that the band structure calculations on A₄C₆₀ (A; alkali atom)^{9,12} have also predicted its metallic nature. However, the insulating or semiconducting behavior of A₄C₆₀ has been also found by a several other experiments such as μ SR¹³, ESR¹⁴ and optical measurements¹⁵). It is noted here that the size of energy gap at E_F observed in the present photoemission experiment (0.3 - 0.4 eV) is in good agreement with the report by the μ SR experiment (0.3 eV). Although the origin to produce the energy gap at E_F in A₄C₆₀ is unclear at present, we should consider at first a lattice distortion (Jahn-Teller effect) and/or an electron correlation in A₄C₆₀ as a possible mechanism. As for the lattice distortion, however, no considerable Jahn-Teller effect which would cause a splitting of the LUMO band by a few tenths eV has not been reported so far for A₄C₆₀. Thus an electron correlation seems to be the most probable origin to create an energy gap at E_F in A₄C₆₀. Since the LUMO band is three-fold degenerate, a Mott-Hubbard gap may open at each stage of doping at x=1 - 5 (x; integer) in A_xC₆₀ if the electron correlation is sufficiently strong. However, it is not clear at present why the energy gap opens only at x=4, but not at x=3 in K_xC₆₀, where a sharp Fermi-edge cutoff indicative of its metallic nature is clearly seen. One may also find in Figs. 1 and 2 that K₃C₆₀ has a very broad distribution of density of states near E_F following the narrow Fermi-edge peak. This may infer that the amplitude of the effective correlation energy may change with the doping; the correlation

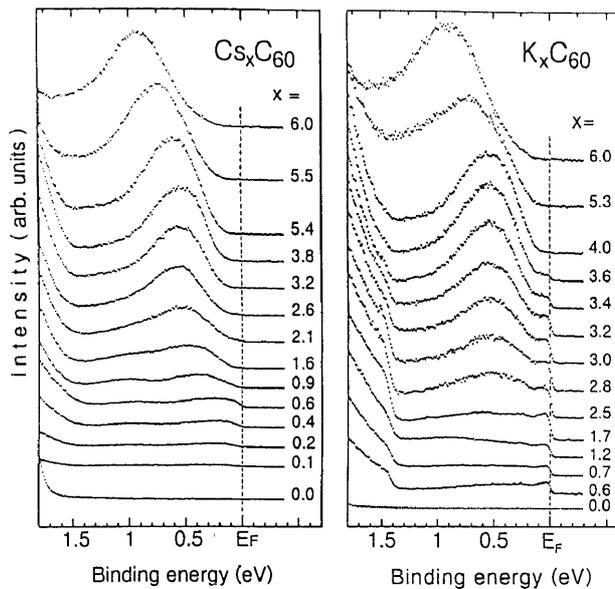


Fig. 2 High-energy resolution photoemission spectra in the vicinity of the Fermi level of Cs_xC_{60} (left) and K_xC_{60} (right). Photoemission intensity is normalized with respect to the total volume of the HOMO band located at 2-3 eV (see Fig. 1).

energy may be comparable to the band width in K_3C_{60} so that a sharp coherent peak at E_F and a broad incoherent band coexist in the photoemission spectrum while in K_4C_{60} (and also Cs_4C_{60}) the correlation energy may overcome the band width and as a result a finite Mott-Hubbard gap may open at E_F . It is noted here that this broad distribution of the density of states following the sharp Fermi-edge peak has been interpreted also as a satellite due to phonons and plasmons¹⁶. In order to check this point, further theoretical studies on the effect of electron correlation in a degenerate band are needed.

Recently the existence of single-phased A_1C_{60} (A; K, Rb, and Cs) has been experimentally confirmed by x-ray diffraction and differential scanning calorimetry studies^{17,18}, which shows that A_1C_{60} has an ordered rocksalt (fcc) structure with only the octahedral sites occupied at relatively high temperature of about 470 K and transforms into a rhombohedral structure at lower temperature. An x-ray photoemission core-level spectroscopy has also suggested the existence of single-phased A_1C_{60} ^{19,20}. In contrast with the precise structural study, the electronic properties of A_1C_{60} is still unclear. Band structure calculations have predicted that the fcc A_1C_{60} (high-temperature phase of A_1C_{60}) is metallic independent of species of alkali atoms (A) because the LUMO band of C_{60} is three-fold degenerate and one electron per a C_{60} molecule donated from the alkali atom would occupy imperfectly the LUMO band. Indeed, the magnetic susceptibility and ESR measurements

on Cs_xC_{60} ¹⁸) as well as an optical measurement on Rb_xC_{60} ²¹) favor the metallic nature of A_1C_{60} . However, an NMR study on Rb_xC_{60} and Cs_xC_{60} ²²) suggests that A_1C_{60} with fcc structure (high-temperature phase) is an insulator contrary to the band structure calculation. Further, a recent ESR study²³) found an unidentified non-superconducting phase in Rb_xC_{60} which shows a metal-insulator transition with temperature. The authors²³) guessed that it is Rb_1C_{60} . Thus, a controversy lies in the metallicity of A_1C_{60} and also this problem closely relates to the observed insulative behavior of A_4C_{60} as described above. However, the present experimental result looks more complicated, because, as shown in Fig. 2, a sharp Fermi-edge cutoff indicative of the metallic nature is obviously seen at $x=0.6$ in both K_xC_{60} and Cs_xC_{60} , but it completely disappears at $x=0.9$ or 1.6 in Cs_xC_{60} while it continues to grow up to $x \sim 3$ in K_xC_{60} . It is noticed that the metallicity of A_1C_{60} is not finally confirmed by the experimental result only of K_xC_{60} , because the sharp Fermi-edge cutoff observed in the spectrum of $x=1.2$ in K_xC_{60} might be due to K_3C_{60} when we take into account of the phase separation. But, as for the composition range of $x \leq 1$, where the contribution from K_3C_{60} would be negligible even when the phase separation occurs, the observed small Fermi-edge cutoff in the photoemission spectrum may be attributed to that of K_1C_{60} since the photoemission spectrum would be a superposition of insulative pristine C_{60} (or α -phase C_{60}) and K_1C_{60} . However, when we further consider a possibility of inhomogeneity at the sample surface as suggested by a previous STM study²⁴), the sharp Fermi-edge cutoff is not necessarily ascribable to that of K_1C_{60} , but might be due to K_3C_{60} . Thus, it becomes clear that only the experimental result of K_xC_{60} is not enough to extract the conclusion that A_1C_{60} is metallic. On the other hand, in the case of Cs_xC_{60} , a sharp Fermi-edge cutoff indicative a metallic nature of the compound is seen in the spectrum of $x=0.6$ but it almost disappears at $x=0.9$. This experimental result would be interpreted in the following two different ways. First, as found in Fig. 2, the photoemission spectrum of $x=0.9$ has negligible intensity at E_F , which would be regarded as a direct evidence for non-metallicity of Cs_1C_{60} . The sharp Fermi-edge cutoff observed at $x=0.6$ may be ascribed to an unknown new phase because pristine C_{60} and α -phase C_{60} should be insulative or semiconductive. Another interpretation of the experimental result takes into account of the ambiguity of estimated x 's. When considering the experimental error in determining x 's (0.2 - 0.3 in the region of small x), the sharp Fermi-edge cutoff at $x=0.6$ may be attributed to that of Cs_1C_{60} , suggesting the metallic nature of Cs_1C_{60} . Indeed, as found in Fig. 2, the photoemission intensity near E_F gradually increases and at the same time moves toward the

Fermi level from $x=0.2$ to $x=0.6$. Thus it looks very hard at present to extract a final conclusion with respect to the metallicity of Cs_xC_{60} . However, in spite of the two conflicting interpretations described above, the present experimental result on Cs_xC_{60} presents a clear evidence for the existence of a metallic phase in Cs_xC_{60} in the composition range of $0 < x \leq 1$, since contribution from metallic A_3C_{60} phase is entirely excluded in Cs_xC_{60} in contrast with the case of K_xC_{60} . Further experimental studies are needed to elucidate whether the metallic phase found in this study is Cs_1C_{60} or another new phase.

4. Conclusion

We found in the present comparative high-energy resolution photoemission study on A_xC_{60} (A; K and Cs) that Cs_xC_{60} ($0 \leq x \leq 6$) is an insulator or a semiconductor in all the composition range except for $0 < x \leq 1$. The photoemission spectrum of $x=0.6$ exhibits a sharp Fermi-edge cutoff indicative of a metallic nature of the compound. Although it is unknown at present whether the metallic edge is due to Cs_1C_{60} or another new metallic phase of Cs_xC_{60} ($0 < x \leq 1$), the present experimental result clearly indicates the existence of a metallic phase in Cs_xC_{60} .

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