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Temperature Dependence of Local Structure Around Rb^+ and Cs^+ Ions in Alkali Doped Fullerenes

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Abstract. Rb and Cs K-edge EXAFS spectra have been measured in the temperature range from 10 to 290 K, in order to investigate the temperature dependence of local structure around Rb^+ and Cs^+ ions in various alkali doped fullerenes. It has been found that the alkali metal ions in Rb_3C_{60} , $\text{K}_2\text{RbC}_{60}$ and $\text{Na}_2\text{CsC}_{60}$ occupy the center of the tetrahedral and octahedral sites of C_{60} crystals. The metal ion in the octahedral site exhibits a large fluctuation in comparison with that in the tetrahedral site. The increase in $\sigma(2)$ of the t-site Rb-C for Rb_3C_{60} has been observed around T_c while the increase in $\sigma(2)$ has not clearly been observed for the o-site Rb-C in $\text{K}_2\text{RbC}_{60}$. The local structure around Rb^+ ion in non-superconducting alkali doped fullerene Rb_6C_{60} has also been studied to compare with that in superconducting fullerenes.

The temperature dependence of local structure around Rb^+ ions in Rb_3C_{60} and $\text{Rb}_2\text{CsC}_{60}$ has been studied by Rb K-edge EXAFS in the temperature range from 10 to 300 K [1,2]. The results show that the Debye-Waller factor $\sigma(2)$ between the tetrahedral site (t-site) Rb^+ ion and the nearest neighboring C atoms of C_{60} increases around superconducting critical temperature T_c . Most of alkali doped fullerene superconductors take a fcc crystal structure, and the metal ions are intercalated into the t- and octahedral (o-) sites. It is generally considered that a larger alkali metal ion is located preferably at the o-site because the space is larger than the t-site. Recent EXAFS studies indicate that the o-site metal ion occupies the off-center of the o-site [3,4]. In the present paper we report the temperature dependence of local structure around Rb^+ and Cs^+ ions in Rb_3C_{60} , $\text{K}_2\text{RbC}_{60}$, $\text{Na}_2\text{CsC}_{60}$ and Rb_6C_{60} . The present study is aimed to confirm the increase in $\sigma(2)$ of the t-site Rb-C in Rb_3C_{60} around T_c by more detail Rb K-edge EXAFS measurement than that reported previously [1] and to clarify the temperature dependence of local structure around the Rb^+ and Cs^+ ions in alkali doped fullerenes.

The samples of Rb_3C_{60} , $\text{K}_2\text{RbC}_{60}$, $\text{Na}_2\text{CsC}_{60}$ and Rb_6C_{60} were prepared by annealing stoichiometric amounts of alkali metal and C_{60} for 1028 h, 1183 h, 216 h and 1032 h, respectively, at 450 °C under vacuum of 10^{-3} Torr. The T_c of Rb_3C_{60} , $\text{K}_2\text{RbC}_{60}$ and $\text{Na}_2\text{CsC}_{60}$ were 30, 23 and 12 K, respectively. Rb_6C_{60} does not exhibit superconductivity. These samples were confirmed to be almost single phase by X-ray powder diffraction. Rb and Cs K-edge EXAFS spectra of Rb_3C_{60} , $\text{K}_2\text{RbC}_{60}$, $\text{Na}_2\text{CsC}_{60}$ and Rb_6C_{60} were measured in transmission mode at the Photon Factory of the National Laboratory for High Energy Physics (KEK-PF). The programs "XAFS93" and "MBF93" developed by one of the authors (H.M.) were used for EXAFS data analysis.

In the imaginary part of the radial structure function $\Phi(r)$ of Rb_3C_{60} , a pronounced peak was observed around 2.6 Å. The peak can be assigned to the t-site Rb-C scattering. The distance $r_{\text{Rb-C}}$ and $\sigma(2)$ between the t-site Rb^+ ion and the nearest neighboring C atoms have been determined to be 3.290(4) Å and 0.0110(5) Å² at 10 K. Figure 1 shows the $\sigma(2)$ of the t-site Rb-C in Rb_3C_{60} . The $\sigma(2)$ increases with an increase in temperature T above 40 K. The curve calculated on the basis of Einstein model with Einstein temperature $\theta_E = 209$ K is shown in Fig. 1. The value of θ_E is consistent with that of $\text{Rb}_2\text{CsC}_{60}$, 212.5 K [2]. The $\sigma(2)$ deviates below 40 K from the curve. The value shows the maximum just below T_c . The result is consistent with that reported previously [1].

Two pronounced peaks were observed below 100 K in the imaginary part in $\Phi(r)$ of $\text{K}_2\text{RbC}_{60}$. The peak around 2.6 Å can be assigned to the t-site Rb-C scattering, while that around 3.0 Å to the o-site Rb-C scattering. The peak around 3.0 Å decreases drastically with an increase in T , and was not clearly observed above 100 K. The distance $r_{\text{Rb-C}}$ and $\sigma(2)$ between the o-site Rb^+ ion and the nearest neighboring C atoms have been determined to be 3.66(1) Å and 0.039(3) Å² at 16 K. The results show that the Rb^+ ion occupies the center of this site and largely fluctuates. A large temperature dependency of $\sigma(2)$ has also been observed. The decrease in peak-intensity of the o-site Rb-C scattering with an increase in T can be reasonably explained by the large temperature dependency of $\sigma(2)$. Though the increase in $\sigma(2)$ around T_c is suggested, it cannot clearly be confirmed.

The imaginary part in $\Phi(r)$ of $\text{Na}_2\text{CsC}_{60}$ at 13 K shows three pronounced peaks at 2.82, 3.39 and 3.83 Å. It is known that $\text{Na}_2\text{CsC}_{60}$ does not take an fcc structure but take an sc structure at low temperature [5]. It is also found from a neutron powder diffraction that Na^+ ion in the t-site ion is faced to one hexagon and three hexagon-hexagon fusions in neighboring C_{60} , while Cs^+ ion in the o-site is faced to six hexagon-hexagon fusions. From the simulation based on the structure, the peaks at 2.82 and 3.39 Å were assigned to the t-site Cs-C and o-site Cs-C scatterings, respectively.

The occupancy fraction of Cs⁺ ion has been estimated to be 70 % for the o-site and 30 % for the t-site. The distances between the Cs⁺ ion and the nearest neighboring C atoms, r_{Cs-C} , at 13 K have been determined to be 3.27(2) and 3.46(2) Å for the t-site, and 3.89(2) Å for the o-site. The r_{Cs-C} in the o-site is almost constant below 40 K. The value of r_{Cs-C} indicates that the o-site Cs⁺ ion occupies the center of this site in the same manner as the o-site Rb⁺ ion in K₂RbC₆₀. Figure 2 shows a plot of $\sigma(2)$ versus T for the o-site Cs-C. The value of $\sigma(2)$ is smaller than that of the o-site Rb-C in K₂RbC₆₀. The value of $\sigma(2)$ increases with an increase in T . The values of r_{Cs-C} and $\sigma(2)$ could not be determined above 40 K based on the sc structure.

Figure 2: A plot of $\sigma(2)$ versus T for the o-site Cs-C of Na₂CsC₆₀.

Figure 1: A plot of $\sigma(2)$ versus T for the t-site Rb-C of Rb₃C₆₀. The solid line shows the Einstein model.

Figure 3: A plot of $\sigma(2)$ versus T for Rb-Rb of Rb₆C₆₀. The solid line shows the Einstein model.

It is well known that Rb₆C₆₀ takes a bcc structure [6]. Two envelopes were observed in the magnitude of $\Phi(r)$ of Rb₆C₆₀. The first envelope corresponds to Rb-C scatterings. The second envelope can be attributed to the Rb-Rb scattering. The distance between Rb⁺ and the nearest neighboring Rb⁺ ions, r_{Rb-Rb} , at 10 K has been determined to be 4.093(3) Å. The value is consistent with that determined at room temperature by X-ray powder diffraction, 4.114 Å [6]. Figure 3 shows a plot of $\sigma(2)$ versus T for Rb-Rb in Rb₆C₆₀. The temperature dependency of $\sigma(2)$ exhibits a monotonous increase with an increase in T . The $\sigma(2)$ is smaller than those of the t-site Rb-C in Rb₃C₆₀, the o-site Rb-C in K₂RbC₆₀ and the o-site Cs-C in Na₂CsC₆₀. The θ_E has been estimated from the $\sigma(2)$ to be 125 K. The force constant between Rb⁺ ions has been estimated to be 23.1 J m⁻² from the $\sigma(2)$ above 30 K within the framework of classical approximation.

In the present study, we have found that the o-site Rb⁺ and Cs⁺ ions occupy the center of this site in K₂RbC₆₀ and Na₂CsC₆₀, respectively. These ions fluctuate largely in this site. The increase in $\sigma(2)$ of the o-site Rb-C around T_c is suggested for K₂RbC₆₀, but the behavior is not clear in comparison with that found for the t-site Rb-C in Rb₃C₆₀. The increase in $\sigma(2)$ around T_c has not been observed for a non-superconductor Rb₆C₆₀.

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