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HAL Id: jpa-00255255
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Submitted on 1 Jan 1997

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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\(_2\)C\(_{60}\), K\(_2\)RbC\(_{60}\) and Na\(_2\)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 \(\alpha(2)\) of the t-site Rb-C for Rb\(_2\)C\(_{60}\) has been observed around \(T_c\), while the increase in \(\alpha(2)\) has not clearly been observed for the o-site Rb-C in K\(_2\)RbC\(_{60}\). The local structure around Rb\(^+\) ion in non-superconducting alkali doped fullerene Rb\(_2\)C\(_{60}\) has also been studied to compare with that in superconducting fullerenes.

The temperature dependence of local structure around Rb\(^+\) ions in Rb\(_2\)C\(_{60}\) and Rb\(_2\)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 \(\alpha(2)\) 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\(_2\)C\(_{60}\), K\(_2\)RbC\(_{60}\), Na\(_2\)CsC\(_{60}\) and Rb\(_2\)CsC\(_{60}\). The present study is aimed to confirm the increase in \(\alpha(2)\) of the t-site Rb-C in Rb\(_2\)C\(_{60}\) 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\(_2\)C\(_{60}\), K\(_2\)RbC\(_{60}\), Na\(_2\)CsC\(_{60}\) and Rb\(_2\)CsC\(_{60}\) 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\(^{-5}\) Torr. The \(T_c\) of Rb\(_2\)C\(_{60}\), K\(_2\)RbC\(_{60}\) and Na\(_2\)CsC\(_{60}\) were 30, 23 and 12 K, respectively. Rb\(_2\)CsC\(_{60}\) 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\(_2\)C\(_{60}\), K\(_2\)RbC\(_{60}\), Na\(_2\)CsC\(_{60}\) and Rb\(_2\)CsC\(_{60}\) 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\(_2\)C\(_{60}\), a pronounced peak was observed around 2.6 Å. The peak can be assigned to the t-site Rb-C scattering. The distance \(r_{RB-C}\) and \(\alpha(2)\) 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) Å\(^2\) at 10 K. Figure 1 shows the \(\alpha(2)\) of the t-site Rb-C in Rb\(_2\)C\(_{60}\). The \(\alpha(2)\) 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 \(\theta_E\) is consistent with that of Rb\(_2\)CaC\(_{60}\), 212.5 K [2]. The \(\alpha(2)\) 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 K\(_2\)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 \(r_{OB-C}\) and \(\alpha(2)\) 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) Å\(^2\) at 16 K. The results show that the Rb\(^+\) ion occupies the center of this site and largely fluctuates. A large temperature dependency of \(\alpha(2)\) has also been observed. The increase 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 \(\alpha(2)\). Though the increase in \(\alpha(2)\) around \(T_c\) is suggested, it cannot clearly be confirmed.

The imaginary part in \(\Phi(r)\) of Na\(_2\)CsC\(_{60}\) at 13 K shows three pronounced peaks at 2.82, 3.39 and 3.83 Å. It is known that Na\(_2\)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, \(r_{\text{CsC}}\), 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 value of \(r_{\text{CsC}}\) in the o-site is almost constant below 40 K. The value of \(\sigma(2)\) is smaller than that of the o-site Rb-C in K\(_2\)RbC\(_{40}\). The value of \(\sigma(2)\) increases with an increase in \(T\). The values of \(r_{\text{CsC}}\) and \(\sigma(2)\) could not be determined above 40 K based on the sc structure.

![Figure 1](image1.png)

Figure 1: A plot of \(\sigma(2)\) versus \(T\) for the t-site Rb-C of Rb\(_3\)C\(_{40}\). The solid line shows the Einstein model.

![Figure 2](image2.png)

Figure 2: A plot of \(\sigma(2)\) versus \(T\) for the o-site Cs-C of Na\(_2\)CsC\(_{40}\).

![Figure 3](image3.png)

Figure 3: A plot of \(\sigma(2)\) versus \(T\) for Rb-Rb of Rb\(_3\)C\(_{40}\). The solid line shows the Einstein model.

It is well known that Rb\(_3\)C\(_{40}\) takes a bcc structure [6]. Two envelopes were observed in the magnitude of \(\Phi(r)\) of Rb\(_3\)C\(_{40}\). 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, \(r_{\text{Rb-Rb}}\), 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 Rb\(_3\)C\(_{40}\). 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 Rb\(_3\)C\(_{40}\), the o-site Rb-C in K\(_2\)RbC\(_{40}\) and the o-site Cs-C in Na\(_2\)CsC\(_{40}\). The \(\theta\) has been estimated from the \(\sigma(2)\) to be 125 K. The force constant between Rb\(^+\) ions has been estimated to be 23.1 Jm\(^{-2}\) 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 K\(_2\)RbC\(_{40}\) and Na\(_2\)CsC\(_{40}\) 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 K\(_2\)RbC\(_{40}\), but the behavior is not clear in comparison with that found for the t-site Rb-C in Rb\(_3\)C\(_{40}\). The increase in \(\sigma(2)\) around \(T_c\) has not been observed for a non-superconductor Rb\(_3\)C\(_{40}\).

References