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XAFS study on RbC$_{60}$

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The Rb K-edge XAFS spectra for the stable phase of RbC$_{60}$ which is a quasi one-dimensional polymer were measured in the temperature range from 14.6 to 210 K in order to clarify the origin of the metal-insulator transition around 50 K. The distances and mean-square relative displacements between the Rb atom and the neighboring C atoms determined by XAFS exhibited no change around 50 K, implying that the metal-insulator transition originates from the SDW instability.

Keywords: Rb K-edge XAFS, quasi 1D polymer, metal-insulator transition, spin density wave, charge density wave, lattice distortion

1. Introduction

The stable phase of RbC$_{60}$ was found to be a quasi one-dimensional (1D) polymer with an orthorhombic structure of a space group of *Pmnn* (No. 58) (Stephens *et al.*, 1994). The C$_{60}$ molecules formed chains along *a* axis through a [2+2] cycloaddition. The ESR showed the metallic behavior above 50 K and the insulating behavior below 50 K (Chauvet *et al.*, 1994). Further, RbC$_{60}$ possesses the other insulating metastable-phase prepared by rapid cooling after annealing at high temperature (Chauvet *et al.*, 1994); the phase was monoclinic, $P2_1/a$, and the C$_{60}$ molecules formed a dimer through a single C-C bond (Oszlanyi *et al.*, 1996).

The metal-insulator (M-I) transition in the stable phase of RbC$_{60}$ attracted many researchers because of the interests in the physical properties of the quasi-1D metal. Either possibility of charge density wave (CDW) or spin density wave (SDW) instability is suggested as the origin for this transition (Chauvet *et al.*, 1994). For the CDW insulating state, the ground state should be nonmagnetic state accompanied by the lattice distortion through the electron-phonon interaction (Peierls transition). On the other hand, when the SDW instability due to spin-spin interaction leads to the insulating state with the antiferromagnetic ground state, the lattice distortion should not occur.

In the present study, we have measured Rb K-edge XAFS for RbC$_{60}$ from 14.6 to 210 K in order to clarify the origin of the M-I transition. An indication for the lattice distortion was examined around 50 K from the temperature dependence of the distances and the mean-square relative displacements between the Rb atom and the neighboring C atoms in C$_{60}$ determined by the XAFS.

2. Experimental and data analysis

The RbC$_{60}$ sample was prepared by annealing stoichiometric quantities of C$_{60}$ and Rb under 10^{-3} Torr at 723 K for 929 h. The Raman spectrum for this sample exhibited an Ag(2) peak at 1459.4 cm^{-1}. The differential scanning calorimetry (DSC) exhibited an endothermic peak around 420 K, in consistent with the DSC for the stable phase of RbC$_{60}$ (Granasy *et al.*, 1995). X-ray powder diffraction pattern was in good agreement with the simulation calculated from the atomic coordinates for the stable phase of RbC$_{60}$ reported by Stephens *et al.* (1994). These results showed that the sample was the stable phase of RbC$_{60}$.

Rb K-edge XAFS spectra were measured in the transmission mode from 14.6 to 210 K at BL-10B of Photon Factory in High Energy Accelerator Research Organization (KEK-PF). The XAFS oscillation $\chi(k)$ was extracted from the XAFS spectrum by eliminating the back ground using Victreen formula, the cubic spline method and McMaster coefficients (McMaster *et al.*, 1969). The threshold energy E_0 was evaluated from the inflection point of Rb K-edge: 15.2012 keV at 14.6 K. The radial structure function $\Phi(r)$ was obtained

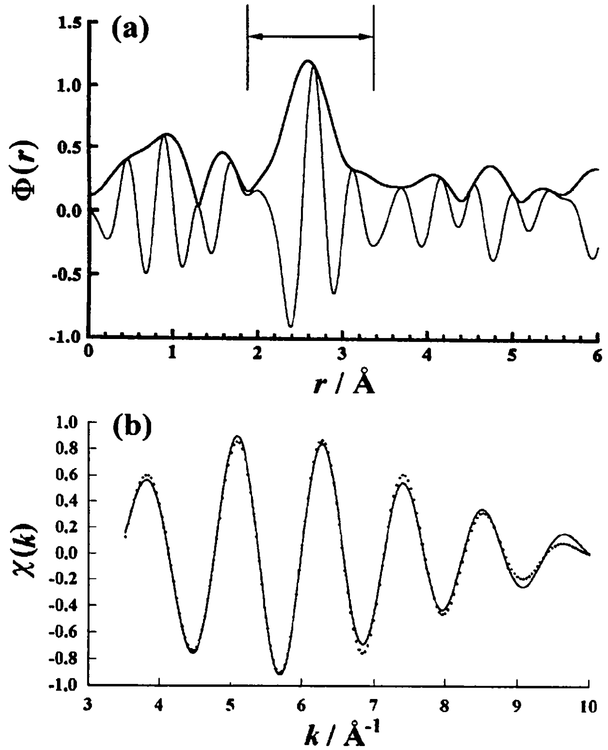

Figure 1

(a) $\Phi(r)$ at 14.6 K. The thick and thin lines refer to the magnitude and imaginary part of $\Phi(r)$. The range shown by an arrow was Fourier- transformed. (b) The closed circles and solid lines refer to the experimental XAFS obtained by an inverse-Fourier transform of $\Phi(r)$ at 14.6 K and the XAFS calculated with the structural parameters at 14.6 K.

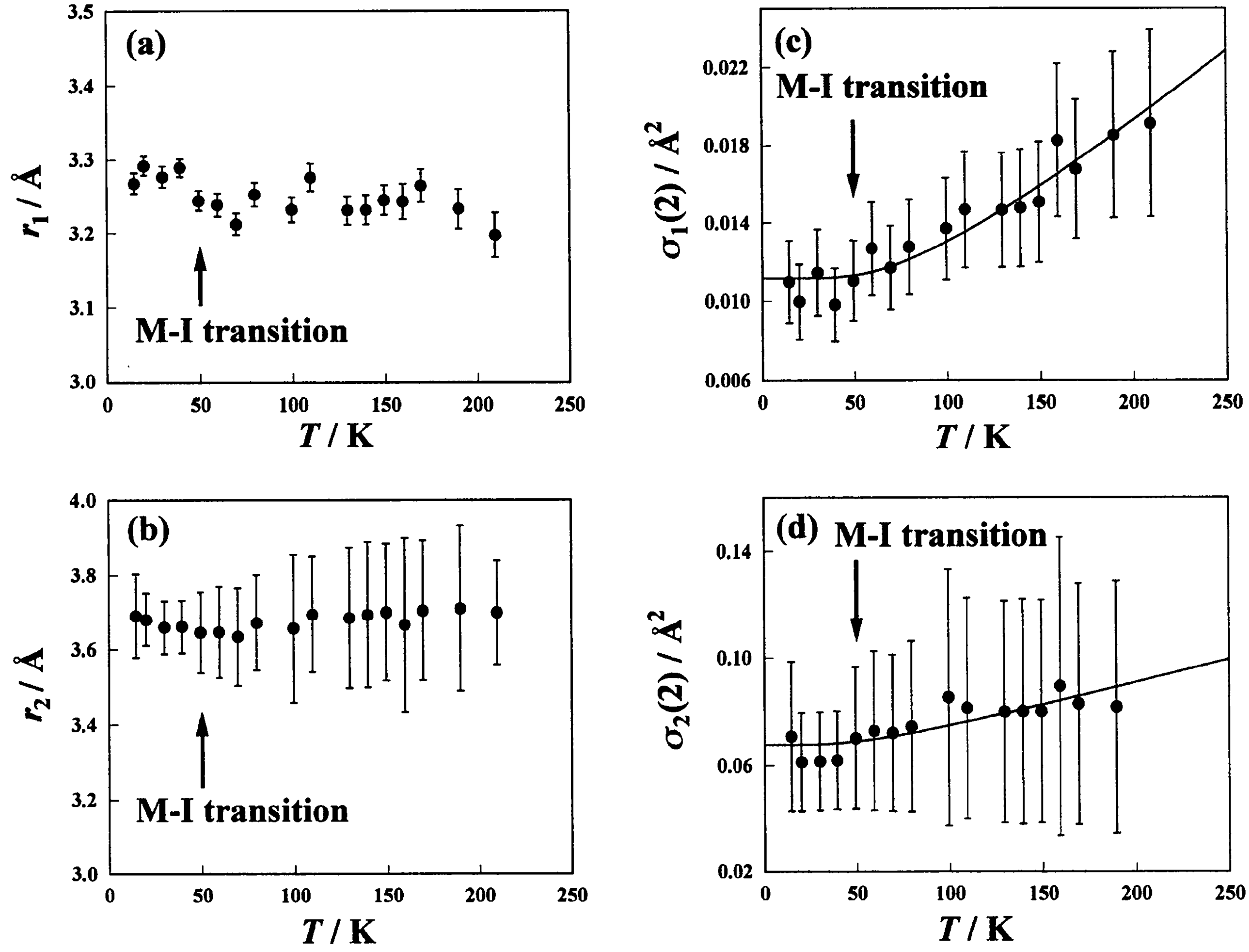

Figure2

Temperature dependence of (a) r_1, (b) r_2, (c) $\sigma_1(2)$ and (d) $\sigma_2(2)$.

by a Fourier transform of the $k^3\chi(k)$ in the k-region from 1.96 to 10.0 Å^{-1}. The structural parameters were determined by a least-squares fitting to the $\chi(k)$ in the k-region from 3.5 to 10.0 Å^{-1} derived by the inverse-Fourier transform of $\Phi(r)$ with XAFS formula within the harmonic approximation (Ishii, 1992). The $\chi(k)$ at 14.6 K was obtained from the $\Phi(r)$ in the r-region from 1.87 to 3.35 Å, and those above 14.6 K were also obtained from the $\Phi(r)$ in the similar r-region. The mean free path, $\lambda(k)$, of photoelectron and the shift, ΔE, from the E_0 were also parameterized along with the distances and mean-square relative displacements between the Rb atom and the neighboring C atoms in the XAFS data analysis at 14.6 K. The $\lambda(k)$ and ΔE above 14.6 K were fixed to the values at 14.6 K. The theoretical values reported by McKale *et al.* (1988) were used for the backscattering amplitudes of atoms and the phase shifts. The programs "XAFS93" and "MBF93" developed by one of the authors (Maeda) were used for the XAFS data analysis.

3. Results and Discussion

The imaginary part of the $\Phi(r)$ obtained by a Fourier transform of $k^3\chi(k)$ at 14.6 K exhibits a pronounced peak around 2.7 Å [Fig. 1(a)]. The Rietveld analysis of X-ray diffraction pattern at 300 K for RbC_{60} showed that the Rb atom was surrounded by six C_{60} molecules (Stephens *et al.*, 1994), and that the Rb-C distances below 4.0 Å which contribute to the $\Phi(r)$ around 2.7 Å were distributed to four types of distances with the coordination number of C atoms, N = 4: 3.525, 3.713, 3.734 and 3.759 Å. Two shell fittings were performed with the Rb-C distance of 3.525 Å and an average distance of 3.735 Å for the latter three types as initial parameters. The N of C atoms were fixed to four for the first shell and twelve for the second shell. The distance, r_1, and the mean-square relative displacement, $\sigma_1(2)$, between the Rb atom and the first neighboring four C atoms were 3.27(1) Å and 0.011 (1) Å^2 at 14.6 K, respectively. The distance, r_2, and the mean-square relative displacement, $\sigma_2(2)$, between the Rb atom and the second neighboring twelve

C atoms were 3.7(1) Å and 0.07(3) Å^2 at 14.6 K, respectively. The XAFS spectrum calculated with these parameters well reproduced the experimental XAFS [Fig. 1(b)]. The r_1 was fairly smaller than that from the Rietveld analysis of X-ray diffraction, 3.525 Å. This reason should further be studied. The r_2 was consistent with that by the Rietveld analysis, 3.735 Å. The large $\sigma_2(2)$ reflects the Rb-C distribution.

As seen from Fig. 2(a) and (b), the r_1 and r_2 were almost constant from 14.6 to 210 K. Clear changes were not observed for both r_1 and r_2 around 50 K. Fig. 2(c) and (d) show the temperature dependence of $\sigma_1(2)$ and $\sigma_2(2)$, respectively. Both $\sigma_1(2)$ and $\sigma_2(2)$ increased with an increase in temperature according to the Einstein model (solid lines): the Einstein temperatures θ_E = 242(4) K for $\sigma_1(2)$ and 161(1) K for $\sigma_2(2)$. The θ_E for the $\sigma_1(2)$ was almost consistent with those for the $\sigma(2)$ between the tetrahedral site Rb atom and the first neighboring C atoms in Rb_3C_{60} (209 K) and Rb_6C_{60} (223 K) (Kubozono *et al.*, 1997a, 1997b). The large deviation from the Einstein model was not observed for both $\sigma_1(2)$ and $\sigma_2(2)$ around 50 K, showing that the lattice distortion did not occur through the M-I transition; even if the lattice distortion was too small to influence the r_1 and r_2, the increase in $\sigma_1(2)$ and $\sigma_2(2)$ should be observed when the lattice distortion (Peierls distortion) occurs. Therefore, we have concluded that this transition is caused by the SDW instability but not by the CDW instability.

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