Thermal expansion of single-walled carbon nanotube (SWNT) bundles: X-ray diffraction studies

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Thermal expansion coefficient in single-walled carbon nanotube bundles was determined as (−0.15 ± 0.20) × 10⁻⁵ (1/K) for the tube diameter and (0.75 ± 0.25) × 10⁻⁵ (1/K) for the triangular lattice constant by means of x-ray scattering between 300 K to 950 K. The value for the intertube gap was (4.2 ± 1.4) × 10⁻⁵ (1/K), which is larger than 2.6 × 10⁻⁵ (1/K) for the c-axis thermal expansion in graphite. The results reveal the presence of a remarkably larger lattice anharmonicity in nanotube bundles than that of graphite. The small value for the tube diameter is consistent with the seamless tube structure formed by a strong covalent bond between carbon atoms comparable to that in graphite.

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Single-walled carbon nanotubes (SWNTs) can be obtained, for example, in soot after arc-discharge or laser ablation of graphite containing metal catalyst. 1−5 Transmission electron microscopy (TEM) and x-ray diffraction (XRD) measurements of the soot clarified that the tubes are close-packed into bundles and form a triangular lattice. 4 Thermal expansion of the lattice constant and tube diameter is interesting because it gives us the nature of carbon-carbon bond and intertube interaction in the SWNT bundles. However little has been known so far experimentally. In the present note, we report, to the best of our knowledge, for the first time a determination of the thermal expansion coefficient for the increasing and decreasing temperature, respectively. The graphite (002) peak of the impurity shows a remarkable T-dependence and the estimated thermal expansion coefficient of interlayer spacing is 2.6 × 10⁻⁵ (1/K), consistent with reported values for graphite. 10 In contrast, that of the SWNT sample may be found to be very weak, indicating that the thermal expansion was almost constant because the desorption has almost completed. After this measurement, the sample was heated again. The XRD patterns, in this case, were very similar to those for the decreasing temperature, as expected.

Figure 3 shows the T-dependence of XRD patterns for the well heat-treated sample sealed within the capillary, where Q is the amplitude of the scattering wave vector defined by Q = 4π sin θ/λ. Because the sample has been well heated under a dynamic vacuum, the XRD patterns were essentially the same for the increasing and decreasing T. The graphite (002) peak of the impurity shows a remarkable T-dependence and the estimated thermal expansion coefficient of interlayer spacing is 2.6 × 10⁻⁵ (1/K), consistent with reported values for graphite. 10 In contrast, that of the SWNT sample may be found to be very weak, indicating that the thermal expansion

![Figure 1](image.png)

**FIG. 1.** Temperature dependence of XRD patterns in an SWNT bundle. The sample was placed in a furnace and evacuated to ~10⁻⁶ Torr during the measurements. The x-ray wavelength is λ = 1.0025 Å. The peaks denoted by * are not due to the sample. Left and right figures show the measurements performed with increasing and decreasing temperature, respectively.
of the SWNT bundle is much smaller than that for the graphite interlayer spacing.

Now, we simulate the XRD patterns of SWNT bundle in order to estimate the thermal expansion coefficient for the tube diameter and lattice constant. Here we use a homogeneous charged cylinder model for each tube, which is closed-packed into a triangular lattice. It should be noted that this model cannot include the "in-plane" carbon-carbon bond structures, although it can reproduce the low-Q diffraction intensity which gives us information on the tube diameter and lattice constants.

Figure 4 demonstrates how to obtain the XRD pattern from the simulation. The diffracted intensity is a multiplication of the tube form factor, Bragg peak intensity, and Lorentz factor. In the SWNT materials, the Bragg peaks are so broad that the resultant XRD pattern is strongly modulated by the tube form factor given by the zeroth-Bessel function, \( J_0(RQ) \). Therefore, because the Bessel function has the nodes whose position is inversely proportional to the tube diameter \( 2R \) as shown in Fig. 4, the dips \( Q_{\text{dip}} \) in the observed pattern, corresponding to the nodes of \( J_0(RQ) \), can give us the mean diameter with an accuracy of \( \sim 0.1\% \). Figure 5 shows the \( T \)-dependence of \( Q_{\text{dip}} \), giving \( \alpha_D = (-0.15 \pm 0.20) \times 10^{-5} \) (1/K) for the thermal expansion coefficient of the tube diameter. This is compared with the in-plane values, \((0 \pm 0.1) \times 10^{-5} \) (1/K) in multiwalled carbon nanotube \(^{11}\) in the same temperature domain, and also those for the in-plane thermal expansion in graphite. \(^{10}\)

Assuming the zero thermal expansion for the tube diameter, we simulated the XRD patterns for several values for the thermal expansion coefficient for the triangular lattice constant. From the comparison with those taken at 300 K and 950 K experimentally, we obtained \( \alpha_L = (0.75 \pm 0.25) \times 10^{-2} \) (1/K) as the most probable value for the averaged thermal expansion coefficient between 300 K and 950 K. The comparison between the simulated patterns and the observed ones is shown in Fig. 6.
FIG. 6. Comparison of the observed data at 300 K and 950 K with simulated patterns, where the thermal expansion of the tube diameter and lattice constant were chosen as $0 \times 10^{-5}$ (1/K) and $0.75 \times 10^{-5}$ (1/K), and the lattice constant and the tube diameter are 16.60 Å and 13.62 Å at 300 K, respectively.

The estimated absolute values for the tube diameter and lattice constant in this simulation are $2R = 13.62 \pm 0.01$ Å and $a = 16.6 \pm 0.1$ Å at 300 K, respectively. The obtained tube diameter is consistent with a rough evaluation from the radial breathing mode in Raman spectra, $\sim 14$ Å. The intertube gap, $d = a - 2R$, is 3.0 Å. The corresponding thermal expansion for the gap is estimated to be $\alpha_g = (2R \alpha_d + d \alpha_g)/(2R + d)$. This value is substantially larger than $2.6 \times 10^{-5}$ (1/K) along the c-axis of graphite. Because the thermal expansion is related to lattice anharmonicity, this result indicates that the anharmonicity in SWNT bundle is larger than that in graphite.

In the present analysis, it should be noted that the used values for the tube diameter and the lattice constant are “averaged” values over the sample and did not take account of the distribution. Thus, the simulated patterns could not completely reproduce the observed ones. For example, the fitting around $Q \sim 0.8$ (1/Å) in Fig. 6 seems to be improved by taking into account the existence of the bundles with different tube diameters and lattice constants. However, we believe that such a more sophisticated treatment would give essentially the same thermal expansion coefficients as the present analysis.

In conclusion, the thermal expansion of the tube diameter and lattice constant were determined as $(-0.15 \pm 0.20) \times 10^{-5}$ (1/K) and $(0.75 \pm 0.25) \times 10^{-5}$ (1/K), respectively. The small coefficient for the tube diameter indicates the strong carbon-carbon bonds comparable to that of graphite. The thermal expansion coefficient for the intertube gap is $(4.2 \pm 1.4) \times 10^{-5}$ (1/K), which is much larger than that of graphite, indicating the larger lattice anharmonicity.

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