Comment on "Polarized Raman Study of Aligned Multiwalled Carbon Nanotubes"

In a recent Letter [1] the polarization dependence of the Raman signal of aligned multiwalled nanotubes was reported and analyzed in terms of a nonresonant polarizability theory. The spectra presented by Rao *et al.* [1] show remarkable antisymmetric contributions to the scattering process. We measured the Raman-tensor invariants of multiwalled nanotubes and, in contrast to Ref. [1], found the antisymmetric part to be zero within experimental error.

In Fig. 1 of their Letter the authors show backscattering Raman spectra in four different polarizations. The spectrum in *YX* polarization was found to have twice the intensity of the *XY* polarized one. Antisymmetric scattering, i.e., $\alpha_{ij} \neq \alpha_{ji}$, by phonons is possible under resonant conditions, but rarely observed experimentally. Under nonresonant conditions Raman tensors are necessarily symmetric [2]. Rao *et al.*, however, state that E_{2g} modes are expected to contribute in *YX* but not in *XY* geometry. Similarly, they predict the intensities of the E_{1g} mode in *YX* and *XY* to be different. The discrepancies in the encountered polarizability theory are, however, not the main point of our comment.

The antisymmetric contribution to the Raman process in multiwalled nanotubes can be checked on unoriented tubes with the help of linearly and circularly polarized light. In backscattering the three Raman-tensor invariants are given by [3]

$$\begin{aligned} \text{isotropic part } \bar{\alpha}^2: &\quad 45\bar{\alpha}^2 = I_{\parallel} - \tfrac{2}{3} I_{\circlearrowleft\circlearrowleft}, \\ \text{symmetric anisotropy } \gamma_s^2: &\quad 6\gamma_s^2 = I_{\circlearrowleft\circlearrowleft}, \\ \text{antisymmetric anisotropy } \gamma_{as}^2: &\quad 5\gamma_{as}^2 = I_{\perp} - \tfrac{1}{2} I_{\circlearrowleft\circlearrowleft}, \end{aligned} \tag{1}$$

where $I_{\parallel}$ is the intensity measured in linear parallel polarizations on randomly oriented samples, $I_{\perp}$ in crossed polarizations, and $I_{\circlearrowleft\circlearrowleft}$ in corotating circular polarizations. The intensity in contrarotating polarizations $I_{\circlearrowleft\circlearrowright}$ provides a check on the experimental error. The quantities in Eq. (1) are accepted as being different from zero only if they are $> 3\Delta I = 3|(I_{\parallel} + I_{\perp}) - (I_{\circlearrowleft\circlearrowleft} + I_{\circlearrowleft\circlearrowright})|$ [3]. The Raman spectra on unoriented multiwalled nanotubes were excited with $\lambda = 514$ nm. For carrying out Raman experiments with linearly and circularly polarized light without change in the illumination level a setup similar to the one in Ref. [3] was used.

In Fig. 1 we show Raman spectra of multiwalled nanotubes in the different linear and circular polarizations. In arbitrary units the tensor invariants are $45\bar{\alpha}^2 = 1.1$, $6\gamma_s^2 = 3.1$, and $5\gamma_{as}^2 = 0.3$; the experimental error is $3\Delta I = 0.5$. The ratio $\bar{\alpha}^2/\gamma_s^2 = 1/20$ indicates that the Raman process in multiwalled tubes has fully symmetric

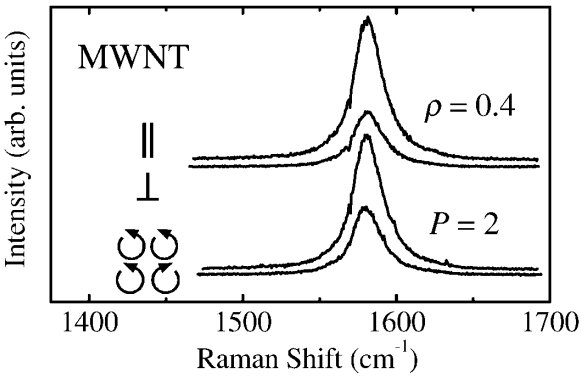

FIG. 1. Raman spectra in $\parallel$, $\perp$, $\circlearrowleft\circlearrowleft$, and $\circlearrowleft\circlearrowright$ polarizations. The depolarization ratio $\rho = I_{\perp}/I_{\parallel}$ and the reversal coefficient $P = I_{\circlearrowleft\circlearrowleft}/I_{\circlearrowleft\circlearrowright}$ are given.

A_1 and traceless E contributions. In contrast, the antisymmetric part γ_{as}^2 is found to be zero within experimental error or at least very small. Antisymmetric scattering cannot explain the spectra observed by Rao *et al.*

There is, however, a simple explanation for the difference in *XY* and *YX* intensities reported in Ref. [1]: The inset of Fig. 3 shows the *YY* intensities ($\theta_m = 90°$) obtained by (i) rotating the polarization while keeping the sample fixed and (ii) rotating the sample while keeping the polarization fixed. Of course, these two procedures must give the same intensity (the second one is preferred in polarized Raman measurements). Instead, a factor of ≈ 1.7 was found suggesting a problem with the experimental setup. When scaling the *XY* Raman spectrum with 1.7 the intensities in the two crossed polarizations are almost the same. Another questionable experiment is shown in Fig. 2 (lower trace) of the Letter; the depolarization ratio of disordered graphite ρ was measured as $\rho = 1$. As is long known in Raman spectroscopy an E_{2g} mode has a depolarization ratio $\rho = 0.75$ [2].

S. Reich and C. Thomsen
Institut für Festkörperphysik
Technische Universität Berlin
Hardenbergstrasse 36, 10623 Berlin, Germany

Received 25 April 2000
PACS numbers: 78.30.–j, 63.22.+m, 78.30.Na, 78.66.Tr

[1] A. M. Rao, A. Jorio, M. A. Pimenta, M. S. S. Dantas, R. Saito, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. Lett. **84**, 1820 (2000).
[2] M. Cardona, in *Light Scattering in Solids II,* edited by M. Cardona and G. Güntherodt, Topics in Applied Physics Vol. 50 (Springer-Verlag, Berlin, 1982), p. 19.
[3] J. Nestor and T. G. Spiro, J. Raman Spectrosc. **1**, 539 (1973).

 0031-9007/00/85(16)/3544(1)$15.00