

Comment on "Rotational Ordering Transition in Single-Crystal C_{60} Studied by Raman Spectroscopy"

In a recent Letter van Loosdrecht, van Bentum, and Meijer [1] presented a detailed temperature-dependent Raman study of a C_{60} single crystal. They reported a discontinuous change in frequency and linewidth of the C_{60} Raman lines at the fcc to sc phase transition [2] near 252 K. The strongest change they observed is for the H_g vibration at 1564 cm^{-1} (high T , fcc phase) jumping in frequency to 1575 cm^{-1} (low T , sc phase) within a very narrow temperature interval. The increase in frequency is accompanied by a drastic steplike decrease ($\approx 8\text{ cm}^{-1}$) in linewidth. The authors of [1] attributed the hardening of the 1564-cm^{-1} mode to the volume change [2] near the phase transition implying that a value of 1575 cm^{-1} is characteristic for this mode in the sc phase.

We argue here that instead this behavior is most likely due to a combined effect of nearly overlapping peaks from C_{70} impurities and a drastic change in relative intensities between C_{60} and C_{70} Raman peaks at the phase transition. It is important to clarify this issue because of the implications for the vibrational modes in doped C_{60} [3].

In Fig. 1 we present Raman spectra of a C_{60} , C_{70} , and a mixed C_{60} and C_{70} sample ($\approx 10:1$) in the range of the H_g vibration of C_{60} near 1575 cm^{-1} . The measurements were performed using similar conditions as in [1]. Before recording the spectra all samples had been exposed to air. Except for curve (b), the shape of the Raman features in the spectra suggests a superposition of lines. For a C_{60} single crystal (a) the Raman feature is centered at 1573 cm^{-1} in agreement with the value of $1575 \pm 2\text{ cm}^{-1}$ for air-exposed films [4] and powder [5]. Note the line at 1564 cm^{-1} in the spectrum of the C_{70} film (b) which has the largest absolute intensity in the entire spectrum. Evidently the room-temperature Raman feature of the C_{60}/C_{70} film (c) is composed of two lines centered at 1565 (C_{70}) and 1575 cm^{-1} (C_{60}). At 12 K (d), there is an obvious redistribution in relative intensity, with the C_{60} component having increased dramatically. It thus appears that the jump in frequency reported in [1] is actually due to an increase in intensity of the 1575-cm^{-1} C_{60} peak with respect to the C_{70} line at 1564 cm^{-1} .

The frequency of the 1575-cm^{-1} H_g C_{60} vibration is not characteristic of only the sc phase. The same frequency was also measured at room temperature for air-exposed films [4] which are in the fcc phase [2], as well as for powders and C_{60}/CS_2 solutions [5]. Furthermore, we observed similar relative intensity changes for the peaks at 771 cm^{-1} (C_{60})/ 768 cm^{-1} (C_{70}) and 709 cm^{-1} (C_{60})/ 706 cm^{-1} (C_{70}); these peaks were also interpreted as having a discontinuous change in frequency at the phase transition [1]. Independent evidence for C_{70} im-

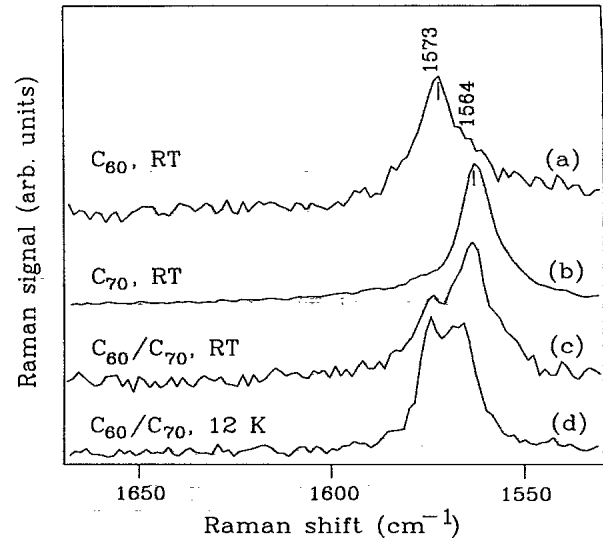


FIG. 1. Unpolarized Raman spectra: (a) C_{60} single crystal at room temperature (RT). (b) C_{70} film at RT. (c) C_{60}/C_{70} film at RT. (d) C_{60}/C_{70} film at 12 K.

purities in the spectra of [1] comes from the features at $\approx 262\text{ cm}^{-1}$ and $\approx 1450\text{ cm}^{-1}$ in their Figs. 2(b) and 2(c) which are characteristic of C_{70} only [4, 5].

We thus suggest that at room temperature, vacuum-kept C_{60} crystals containing a small amount of C_{70} show a broad Raman feature at $\approx 1564\text{ cm}^{-1}$ because of the relatively intense C_{70} peak and the broad (due to rotation) peak of C_{60} . In the low temperature, ordered sc phase the free rotation of the C_{60} molecules is hindered, like in air-exposed samples. This leads to an increase in C_{60} peak intensity and to the apparent, drastic frequency shifts and linewidth changes reported in [1].

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Received 16 April 1992

PACS numbers: 63.20.Hp, 78.30.Hv, 81.30.Hd

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