Origin of Strong G' Band in Raman Spectrum of Carbon Whiskers

Jian Dong, Wanci Shen and Feiyu Kang
Department of Materials Science and Engineering, Tsinghua University
Beijing 100084, P.R.China

Introduction

Generally, in the Raman spectrum of graphitic materials and some nongraphitic materials, the E_{2g} intralyer C-C stretch band (G band, located at 1582 cm^{-1}) is the most intensive in all bands. For certain kinds of nongraphitic materials, such as glass carbon and milled graphite, the D mode caused by the disorder of carbonaceous materials replaces G band and becomes the most intensive one. However, when one kind of carbon whiskers with original structure is characterized by Raman spectroscopy, its G' band (overtone of D band) becomes the most intensive. Polarized micro-Raman measurements show that intensity of all modes is orientation dependent.

Experimental

The carbon whiskers are prepared in 2100° (more information in reference [1]).

The Raman spectra of graphite whisker are recorded by the Dilor Super Labram with a typical resolution of 0.5~2cm^{-1} in a back-scattering geometry at the room temperature. The system consists of a holographic notch filter for Rayleigh rejection and a microscope with 100 × objective lens, allowing a spatial resolution of ~ 1.0 μm. The laser excitation wavelengths are 488.0 nm of an Ar^+ laser, and 632.8 nm of a He-Ne laser. Polarized Raman spectra were excited with 632.8 nm excitation from almost the same spot in the same graphite whisker.

Results and discussion

Scanning electron microscopy micrograph (Fig 1) shows that the diameter of the whiskers is ca. 1 μm, and length is about 10 μm. Transmission electron microscopy micrograph (Fig 2) shows that carbon layers are normal to the axis of the whiskers. HREM also shows that the surface is a frill-like structure, in other words, the carbon layers in the brim of the whisker are folded every several layers and most of the free edge carbon atoms disappear. Selected electron diffraction indicates the whisker composed a series of cones, and apex angle is about 135°. It is inferred from such structure that the whiskers grow by the declination mechanism. In their paper [2], Double and hellawell suggested that a cone can be formed from a flat circular sheet which is first cut radially and then curved so that the cut edges are made to overlap one another (Fig 3.a), the apex angle (α) of the cone so formed is determined by the extent of the overlap, and the overlapped regions themselves are rotated relative to one another by an angle (θ) such that:

$$\sin(\alpha/2)=(2\pi-\theta)/\pi$$

If the sheet is continuous then a cone-helix type cylinder is produced (Fig 3.c) in which each successive spiral layer is rotated relative to the layers above and below it by the overlap angle (θ).

The whiskers are stacked from parallel conical carbon layers so that there must be some stacking faults. Hereby the successive carbon layers should be stacked in an optimum coincidence configuration to realize the best fit. Thus α and θ is not arbitrary, as has been shown in flaky graphite, this represents one of the lowest energy coincidence configurations for a "c" axis rotation fault in graphite. The apex angle 135° is in good agreement with the value predicted by Double and hellawell, which has not been measured until now. Other values have been measured in the experiments. Therefore, The rotation angle of whisker is about 27.8°. Fig 4 is the schematic diagram of two overlapped layers with rotation angle 27.8°. The new lattice parameter is also noted.

Figure 5 shows Raman spectra of carbon whisker with 488 nm excitation. It is noted that the intensity of G band ($I_{G'}$) is about 7 times that of D band (I_D). In addition, D band is more intensive than G band, while for VGCF heated treated at 2100°, its G band is obviously more intensive than D band. Therefore, the formula that can calculate the in plane crystallite size L_a in term of the I_d/I_G can not be applied for the present whiskers. A sharp peak is found at 146.57 cm^{-1}, which might be caused by the frilled like structure. The assignment of the peaks is shown in Table 1.

Fig 6 shows that Raman spectra of carbon whisker with 488 and 632.8 nm excitation ranging from 1000 to 4000 cm^{-1}. It indicates that G' is still the most intensive band, which is not excitation wavelength dependent.

Figure 7 shows the polarized Raman spectra of graphite whisker measured in different configuration. The intensities of almost all Raman peaks in the spectra obtained with polarized parallel to the carbon layers are considerably larger than those polarized normal to the carbon layers. For G' band, when polarized incident is parallel to the carbon layers $I_{G'}$ is about 10 times that in the case that polarized incident is normal to the carbon layers. The polarization dependence shows that D, G and G' etc. is in plane modes.

G' band is associated with phonon pairs at K point of Brillouin zone having opposite wave vectors. Generally the phonon dispersion curves are related to the structure of the carbonaceous materials. As shown in Fig 4. Compared with graphite, carbon whiskers represent one of the lowest energy coincidence configurations for "a" axis ration fault in graphite. The lattice structure of carbon whisker will be changed, while there is no change in the single layer. The shape of Brillouin zone also will be changed. Therefore, more phonon pairs take part in the Raman process. In the end, the high intensity of G' band is related to the disclination in carbon whiskers.

Conclusions

The Raman spectra of one kind of graphite whiskers have been measured in the range of 100~7000 cm-1. The intensity of the overtone (2D) located at 2700 cm-1 is found to be the most intensive band in the spectra. The high intensity of G' band is related to the disclination in carbon whiskers..

References

1. Jian Dong et al., New origin of spirals and new growth process of carbon whiskers Carbon (accepted)

2. D.D. Double and A. Hellawell, Cone-helix growth forms of graphite ACTA METALLURGICA 22 (1974) 481.

Acknowledge

We are grateful for the experimental fund of Tsinghua University.

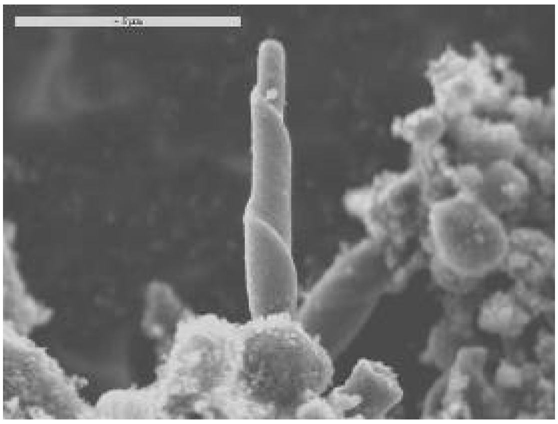

Fig 1 SEM micrograph of carbon whisker

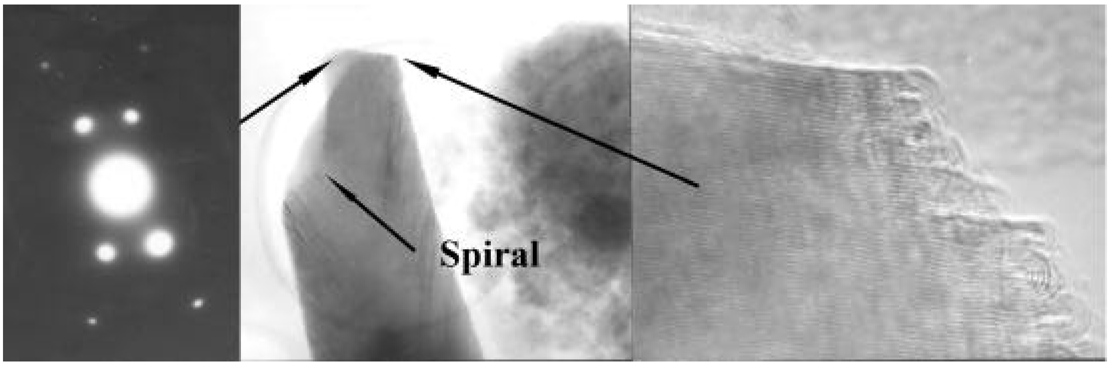

Fig 2 TEM micrograph of carbon whisker

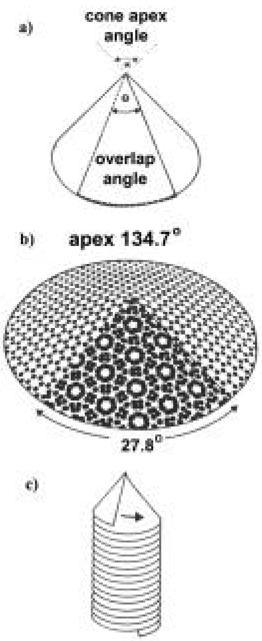

Fig 3.a, b, schematic diagram of disclination, c, the growth model in term of disclination mechanism.

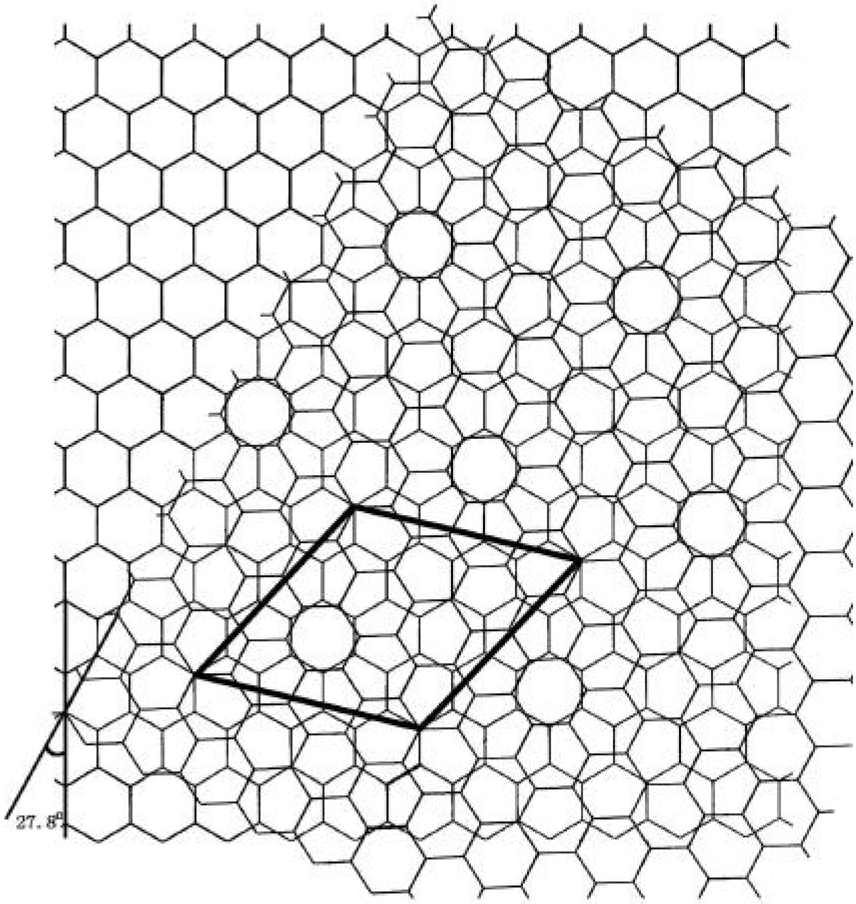

Fig 4 Schematic diagram of stack sequence of carbon layers in term of diclination

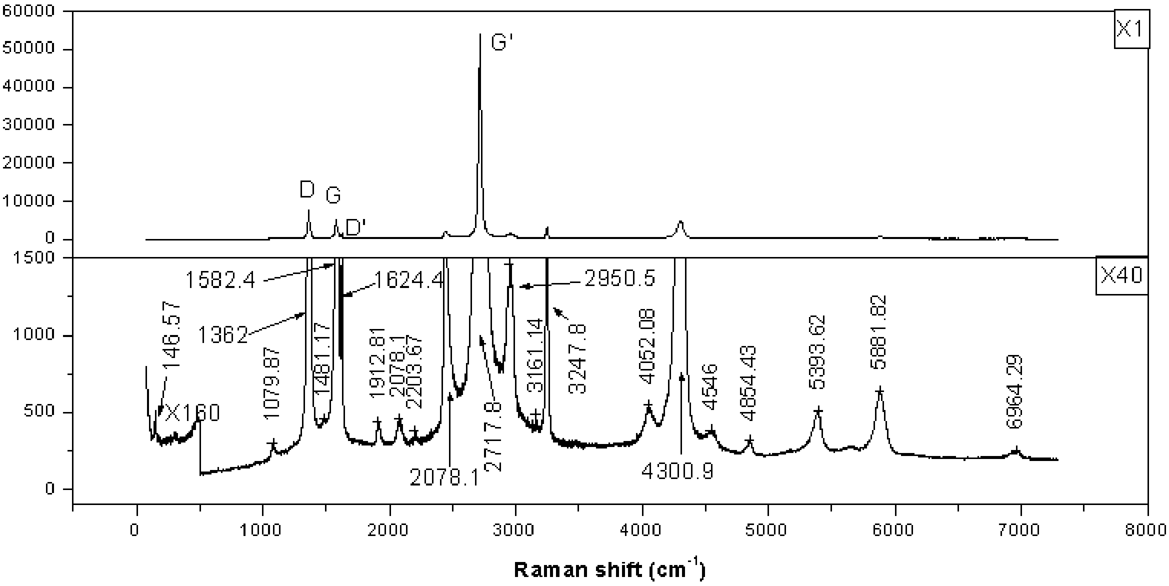

Fig 5 Raman spectra of carbon whisker with 488 nm excitation

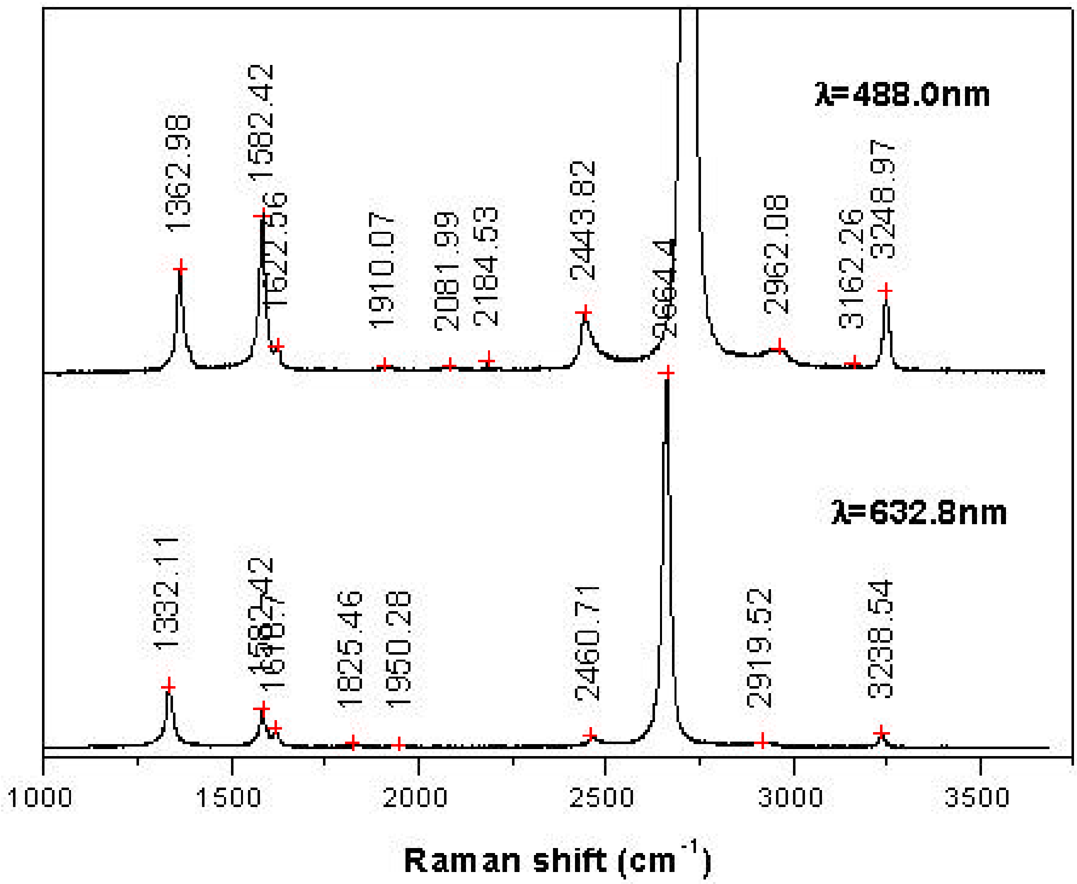

Fig 6 Raman spectra of carbon whisker with 488 and 632.8 nm excitation

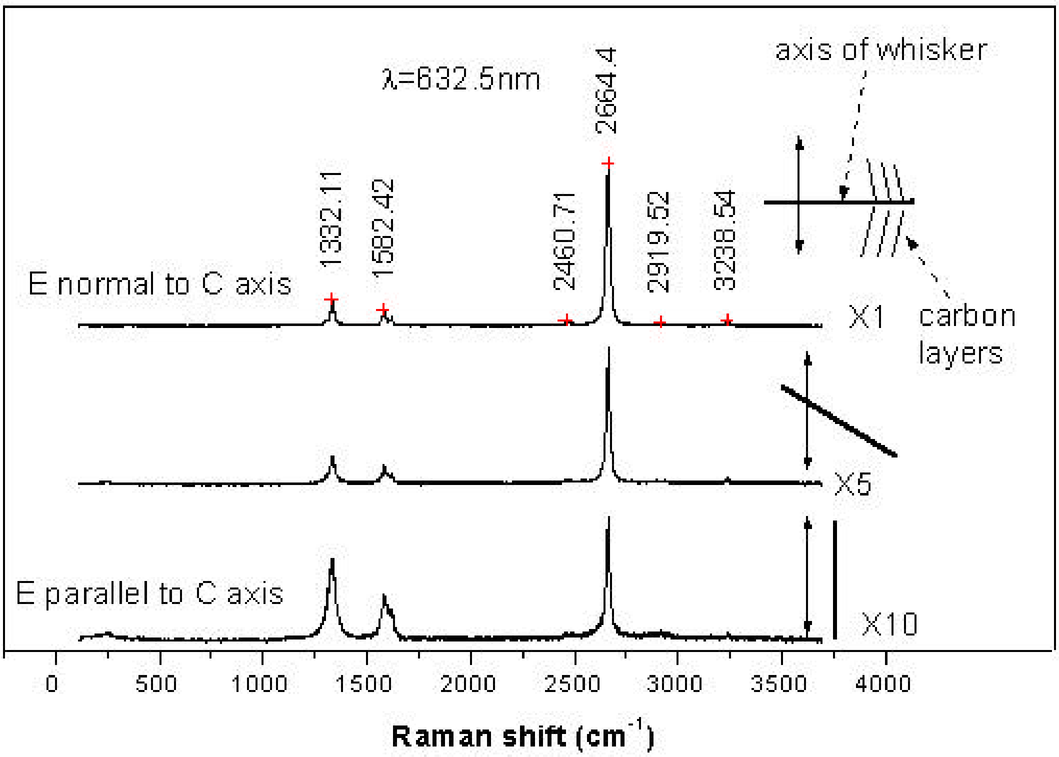

Fig 7. Polarized Raman spectra of carbon whiskers.

Table 1 the assignment of all of the bands of carbon whiskers

$\Delta\nu$ (cm^{-1}) λ=488.0nm	Assgnt.
146.7	?
1079.87	?
1361.98	D
1481.17	?
1582.4	G
1624.45	D’
1912.81	?
2078.1	?
2203.67	?
2717.84	2D
2950.55	D+G
3161.14	2G
3247.77	2D’
4052.08	3D
4300.94	2D+G
4546	D+2G
4854.43	2D’ +G
5393.62	4D
5881.82	2D+2G
6964.29	4D+G