Can buckling account for the features seen in graphite’s Raman spectra?

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Raman scattering data were collected on graphite monochromator. Spectra were interpreted in terms of the space group P6₃/mmc, a subgroup of space group P6₃/mmc. The latter has commonly been used for the interpretation of Raman scattering data. Space group P6₃/mmc corresponds to the buckling of graphene sheets and is consistent with many spectral features. Both the first and second order scattering were considered. Many first order results (most notably the assignments of the band at 1350 and the peak at 1620 cm⁻¹) were found to agree with previous observations [Y. Kawashima and G. Katagiri, Phys. Rev. B 66, 104109 (2002)] carried out on highly oriented pyrolytic graphite samples. To check the consistency of the model, symmetry analysis was applied to the second order spectra. Also a simple test for buckling model was done.

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I. INTRODUCTION

Despite its nominally simple crystal structure the interpretation of the Raman and infrared spectra of graphite has been an active and controversial topic. The crystal symmetry of graphite is reported to be either P6₃/mmc (No. 194) or P6₃mc (No. 186). A more rare form, with rhombohedral space group symmetry R3m (No. 166) was also reported in ref. [1]. The symmetries of these different forms increase in order R3m → P6₃mc → P6₃/mmc: these symmetry groups share group-subgroup relationships. It is well known that, despite its virtually simple structure, a large number of features which seem to contradict the space group symmetry P6₃/mmc, have been observed in Raman spectra. Partially the problem has been that rather different types of ‘graphites’ were studied, as far as crystallite size and defects are considered. Despite that Raman spectra were commonly interpreted in terms of space group P6₃/mmc.

Still, the puzzling features of the Raman spectra of graphite are (i) the peak(s) at around 1355 cm⁻¹ (often labelled by D), (ii) peak at around 1620 cm⁻¹ (often labelled by D') (iii) the first overtones of the aforementioned modes (often labelled by 2D and 2D', respectively). If P6₃/mmc symmetry is assigned to graphite, the Brillouin zone centre modes transform as the irreducible representation (IRREP) 2A₂⁺ 2B₂⁺ 2E₁⁺ 2E₂⁻ 2E₂⁺, where A₂⁺ and E₁⁺ representations are infrared active, B₂⁺ is silent and E₂⁻ is the only Raman active representation. Thus, only two peaks, observable at xx, yy, xy and yx geometries, are expected (i.e., E₂⁻ modes can only be observed if the polarization vectors of both the incoming and scattered light are perpendicular to the hexagonal c axis). They were reported to appear at 42 and 1580 cm⁻¹ (the latter is commonly labelled as ‘G’ mode). However, the number of observed peak is generally greater. Now, it is interesting to note that in the case of P6₃/mmc symmetry the Brillouin zone centre modes transform as the IRREP 2A₁ 2B₁ 2E₁ 2E₂, where A₁ and E₁ symmetry modes are Raman and infrared active, B₁ mode is silent and E₂ mode is Raman active.

The first attempt to explain the D band were based on disorder, which was interpreted to cause an appearance of a totally symmetric mode. As is discussed below, this mode(s) is not totally symmetric and its origin is still not clear. Recent explanations are based on double resonance idea. The merits of the double resonance model are its ability to take the laser beam wavelength dependent positions of D and 2D bands into account. The first attempt to explain the D band were based on an idea that, due to the disorder, a Raman inactive mode became active. The intensity of this mode was reported to be dependent on particle size. In addition, the frequency of this mode was reported to increase with increasing laser light frequency. The corresponding changes occurred in the first overtone of the D band. To explain these features a double resonance Raman scattering model was developed. Several weak peaks were observed in Raman spectra, the most notable at 867 cm⁻¹, which was reported to correspond to the out-of-plane vibration. This model assumes that the D and D' bands are transverse optic Brillouin zone boundary (K point) and zone centre near Brillouin zone centre modes. The double resonance model further necessitates that the atom displacements occur in graphane sheets (in-plane vibrations). Occasionally, double resonance theory has been merited to take the slight difference in the anti-Stokes and Stokes positions into account. In this context one should be in mind that, in order to observe the high frequency overtones in anti-Stokes spectra, exceptionally high laser beam power densities were used in these studies (the highest powder densities were approximately 5000 times larger than the one used...
in this study. Although this type of considerations are interesting, we note that, in the case of the anti-Stokes spectra, the reported differences between the Stokes and corresponding anti-Stokes frequencies were, for different modes, positive, almost zero and negative, as was pointed out in ref. 8.

The purpose of this work was to reinvestigate a high quality graphite sample by Raman scattering technique. The first goal was to check if the buckling model can explain the first and second order spectra. The second goal was to consider to which extent the proposed double resonance model is consistent with the observed symmetry properties of $D$ and $D'$ bands.

II. EXPERIMENTAL

A pyrolytic graphite monochromator (Advanced Ceramics) sample was used in this study. Raman measurements were performed using a Jobin-Yvon T64000 spectrometer consisting of a double monochromator coupled to the third monochromator stage with 1800 grooves per millimeter grating (double subtractive mode). Prior to measurements, spectrometer was calibrated with Ne lamp. Acquisition time was adjusted to have a sufficient signal-to-noise-ratio. CCD detector was used to count photons. Backscattering measurements were carried out under the microscope. Also 90-degree scattering angle experiments (the angle between the incoming and scattered light was 90 degrees) were carried out. Raman spectra were excited using an argon ion laser. In the case of backscattering experiments, the laser beam power on the sample surface was 200 $\mu$W and the diameter of the laser beam spot was approximately 2 $\mu$m (the spot diameter was approximately 100 $\mu$m in 90-degree scattering angle measurements, and the power was 50 mW, so that the powder density was smaller than in the case of backscattering measurements). In a backscattering geometry the wavelength was 514.532 nm and in a 90-degree scattering angle measurements it was 487.986 nm.

III. RESULTS AND DISCUSSION

Selected regions of Raman spectra collected on $ab$-basal plane with an polarizer set parallel (labelled as $Z(XX)Z$) and perpendicular (labelled as $Z(XY)Z$) with respect to the incoming polarization direction are shown in Fig. 1 (a), (b) and (c). Particular attention was paid on the $D$, $D'$, $G$, $2D$, and $2D'$ modes. Here $Z$ and $Z$ refer to the incoming and scattered light propagation direction. Although the light propagation direction can be rather accurately determined at backscattering geometries, incoming light polarization direction with respect to hexagonal $a$ and $b$ axes was not known. The corresponding regions, obtained through right-angle geometry, are shown in Fig. 1 (d), (e) and (f). The intensity of $G$ mode at around 1580 cm$^{-1}$ was the same for $XX$ and $XY$ geometries (see Fig. 1 (a)), consistently with the idea that it belongs to the $E_{2g}$ symmetry (space group $P6_3/mmc$) or $E_2$ symmetry (space group $P6_3mc$). In contrast to the earlier reports (see, e.g., ref. 3), we could not see any other mode below 1580 cm$^{-1}$. Fig. 1 (b) shows the broad band centered at around 2750 cm$^{-1}$. We note that this band is consisted of several peaks and the intensity differs from zero in $XX$, $XY$, $ZZ$ and $ZY$ geometries. Now, it is of interest to consider the symmetries of the first overtone (second order scattering) in the case of the fundamentals belonging to the point group symmetries 6$\text{m}$ and 6$\text{mm}$. Only two-dimensional IRREPs need to be considered, since the first overtone of a one dimensional IRREP is always totally symmetric and can be distinguished by depolarization measurements. Now, the first overtone of the $E_{1u}$, $E_{1g}$, $E_{2u}$ and $E_{2g}$ modes transform as $A_{1g} \oplus E_{2g}$ and the first overtone of the $E_1$ mode transforms as $A_{1g} \oplus E_2$. Thus, if this band is due to the second order scattering of the Brillouin zone centre mode, it must belong to $E_{1u}$ (space group $P6_3/mmc$) or to $E_1$ symmetry (space group $P6_3mc$). To check if either assignment is correct two other experimental geometries were used. First one is the geometry where light propagates perpendicularly to the hexagonal $c$-axis, Fig. 1 (d)-(f). Consistently, $G$ mode was significantly weaker (if the polarization direction of the incoming or scattered light is strictly parallel to the hexagonal axis, the $G$ mode should have zero intensity. Deviations might be because of the folding of graphene sheets). The appearance of the mode at around 1355 cm$^{-1}$ is consistent with the space group $P6_3mc$. Basically, if this mode belongs to the $E_1$ symmetry, it should only be observed at the $XZ$ and $YZ$ geometries. Thus, this mode should not be observable at $ZZ$ geometry, in constrast to the experimental observations. Although partially this might be due to the aforementioned folding we decided to carry out 90-degree measurements.

If the buckling model alone is sufficient for explaining the appearance of $D$ and $D'$ bands (instead of the disorder, which activates non-Brillouin zone centre modes), one should see them at 90-degree measurements carried out on large graphene sheets (so that the effect of disorder as a dominant factor can be eliminated). Now, the phonon propagates parallel to the graphene sheet, by momentum conservation rule. The $G$ mode was observed (Fig. 2), since both the incoming and right-angle scattered light have a polarization component parallel to the $ab$ plane. The more interesting point is that now also the modes belonging to the $E_1$ symmetry modes should be observed. Thus, this experiment served as a test to clarify whether $D$ and/or $D'$ modes are due to the Brillouin zone centre modes or if they correspond to the disorder activated modes. As Fig. 2 reveals, $D$ and $D'$ bands were not observed, but $2D$ was observed. Rather common opinion is that $D$ mode is related to the Brillouin zone $K$ point mode (sometimes assigned to the totally symmetric mode), whereas $D'$ mode has sometimes been considered to belong to $B_1$ symmetry with wavevector
FIG. 1: Raman spectra collected on $ab$ plane at $Z(XX)\bar{Z}$ and $Z(XY)\bar{Z}$ geometries: (a) spectral region corresponding to the $D$, $G$ and $D'$ modes, (b) Spectral region corresponding to the $2D$ mode(s) and (c) $2D'$ modes. The corresponding Raman spectra collected on edge plane at $X(ZZ)\bar{X}$ and $X(YZ)\bar{X}$ geometries are shown in panels (d), (e) and (f). Spectra shown in red correspond to the setting where polarizer and polarizator were parallel to each other, whereas blue lines give the spectra collected on with polarizer perpendicular to the incoming polarization direction.

FIG. 2: Raman spectra collected on 90-degree scattering angle geometry, where phonon propagates along the graphene sheet. (a) spectral region between which should reveal also the $D$ and $D'$ modes, (b) Confirmation that $2D$ are observed at this geometry, too.

close to zero (Brillouin zone centre), see for example ref. 2. Now, the problem is that these assignments do not comfort with the polarization measurements. The first overtone of these modes should also be totally symmetric, in contradiction with the experiments. Now, the selection rules for phonons which can participate on double resonance scattering state that only totally symmetric modes can resonantly couple electrons within the same non-degenerate bands. The second possibility is that the phonon involved in the process should belong to the $B_1$ symmetry.

IV. CONCLUSIONS

The Raman spectra collected on graphite monochromator were interpreted in terms of two space group symmetries. The only observed first order lines were $G$ mode, and $D$ and $D'$ modes. It was concluded that although the weak, additional lines reported in literature probably do correspond to the buckling of graphene sheets, the $D$ and $D'$ modes are probably not due to the buckling. The latter feature was confirmed by 90-degree angle experiments. However, the situation is different for smaller crystal size materials. It was also confirmed that $D$ and $D'$ modes do not belong to the totally symmetric representation.
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