Origin of the unusual dependence of Raman $D$ band on excitation wavelength in graphite-like materials

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We have revisited the still unresolved puzzle of the dispersion of the Raman disorder-induced $D$ band as a function of laser excitation photon energy $E_L$ in graphite-like materials. We propose that the $D$ mode is a combination of an optic phonon at the $K$ point in the Brillouin zone and an acoustic phonon whose momentum is determined uniquely by the double resonance condition. The fit of the experimental data with the double-resonance model yields the reduced effective mass of $0.025 m_e$ for the electron-hole pairs corresponding to the $A_2$ transition, in agreement with other experiments. The model can also explain the difference between $\omega_S$ and $\omega_{AS}$ for $D$ and $D^*$ modes, and predicts its dependence on the Raman excitation frequency. © 2001 American Institute of Physics.

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I. INTRODUCTION

Carbon based materials, ranging from highly oriented pyrolytic graphite, diamond-like carbon films, fullerenes, and carbon nanotubes have been the subject of extensive studies over the past two decades because of their numerous technological applications. Raman spectroscopy is a powerful non-destructive probe for characterizing different forms of carbon materials-diamond, crystalline graphite, glassy carbon, hydrogenated amorphous carbon, fullerenes, and nanotubes. Raman spectra of these materials give considerable information on the nature of chemical bonding ($sp^2$ vis-a-vis $sp^3$) and relative abundance of $sp^2$ and $sp^3$ bonds, residual stresses, crystallite size, and dopants. There is a long-standing puzzle in the Raman spectra of graphitic materials. Single crystals of pristine graphite ($D_{1h}$ space group symmetry) have two in-plane Raman active $E_g$ modes: one at 42 cm$^{-1}$ and the other at ~1582 cm$^{-1}$ ($G$ band). In the presence of disorder, an additional Raman band (called $D$ band) is observed at ~1350 cm$^{-1}$ for a laser excitation energy of 2.41 eV (wavelength 514.5 nm), irrespective of the kind of carbon material.\textsuperscript{1,2,4}

The important features of the Raman spectra associated with the disorder-induced $D$ band are as follows: (i) The $E_L$ dependence of the $D$-band frequency is essentially independent of the type of carbon involved. It occurs in all $sp^2$-hybridized disordered carbon materials, powdered and randomly oriented crystalline graphite, glassy carbon, boron-doped highly ordered pyrolytic graphite, carbon black, multicomponent carbon films, hydrogenated amorphous carbon and, more recently, in carbon nanotubes.\textsuperscript{2} (ii) The frequency of the $D$ band shifts upward with increasing excitation laser energy\textsuperscript{5} $E_L : \omega_D = 1279$ cm$^{-1}$ for $E_L = 1.17$ eV and $\omega_D \sim 1410$ cm$^{-1}$ for $E_L = 3.54$ eV (\textasciitilde 40 cm$^{-1}$/eV). Figure 1 shows the data from various measurements made on various kinds of disordered carbon\textsuperscript{2,4} and carbon nanotubes.\textsuperscript{3} (iii) The frequency of the associated second order ($D^*$) band ($\sim 2700$ cm$^{-1}$ for $E_L = 2.41$ eV) also shifts up with increasing $E_L$. The dispersion $d\omega_{D^*}/dE_L$ is almost twice that of $d\omega_D/dE_L$. (iv) The $E_L$-dependent second order $D^*$ band is observed in Raman spectra of single crystal graphite even though the first order disorder induced $D$ mode is absent.\textsuperscript{5} (v) The $D$-band intensity decreases as $E_L$ increases from 1.16 to 4 eV. In contrast, the intensity of the $G$ band is maximum at $E_L \sim 5$ eV.\textsuperscript{6} The $D$ band is not observed with excitation energies $E_L > 4.2$ eV as shown in Fig. 2, which displays Raman spectra of graphite powder (with a small amount of sodium sulphate for internal intensity calibration) using $E_L = 2.54$ and 4.82 eV. The lines marked by asterisks are from internal vibrational modes of sulphate ions. The intensities have been normalized with respect to the sulphate mode at 980 cm$^{-1}$. The data in the inset taken from Wang, Alsmeyer, and McCreery\textsuperscript{2} show the intensity ratio of $D$ band with respect to that of $G$ band for 1.16$<E_L<$4 eV. The decrease of this intensity ratio as $E_L$ increases has been seen by others as well.\textsuperscript{4} In other words, the resonance excitation profile of the $D$ band will show a maximum at $E_L$ less than 1.16 eV, which is very different from the $G$-band behavior. These experimental observations are crucial to arrive at the correct explanation for the origin of the $D$ band. (vi) The peak positions of the $D$ and $D^*$ bands observed in Stokes ($\omega_S$) and anti-Stokes ($\omega_{AS}$) are not the same: $\Delta \omega_S = \omega_{AS} - \omega_S = 7$ cm$^{-1}$ for the $D$ mode and $>\omega_{AS} - \omega_S = 28$ cm$^{-1}$ for the $D^*$ mode when $E_L = 2.41$ eV. In order to make sure that this anomalous difference between Stokes and anti-Stokes peak positions of the $D$ and $D^*$ bands is genuine, it was seen in the same experiment that $\Delta \omega \sim 0$ for the $G$ band, as is usually expected.

It is surprising that even after 20 years of experimental observation,\textsuperscript{1} the origin and dispersion of the $D$ band is still not quantitatively understood. Tuinstra and Koenig\textsuperscript{1} attrib-
We have also considered disorder-induced double resonance near a gap of ≈1 eV in the graphite band structure to result in the dependence of the phonon wave vector $q$ and hence the phonon frequency $\omega$ on the energy of the exciting laser light. Very recently, Thomsen and Reich (TR)\textsuperscript{12} have wrongly questioned the existence of such a gap of ≈1 eV in the electronic structure of graphite. They have also used double resonance using the electronic linear bands at $K$ point in the Brillouin zone. The serious difficulty with their calculations is that the calculated intensities of the $D$ mode for different incoming photon energies do not decrease as $E_L$ increases. On the contrary, the calculated intensity for $E_L = 4$ eV is higher than for $E_L = 2$ eV (see Fig. 3 of Thomsen and Reich\textsuperscript{13}). This is completely opposite to the experiments shown in Fig. 2. There is another difficulty we have with the TR’s calculation. As given by their Eq. (4), the magnitude of $q$ increases with $E_L$. For optic branch along $\Gamma K$ direction, the phonon frequency $\omega$ is a decreasing function of $q$ and hence $\omega$ should decrease with increasing $E_L$ which is contrary to the experiments.

In this article, we present a model based on double resonance which can address all the novel features associated with the $D$ mode. Keeping in mind that the acoustic phonon branches are strongly coupled to the high-frequency optic branches at the $K$ point in graphite,\textsuperscript{14} we propose that the $D$-mode is a combination of an optic phonon at the $K$ point in the Brillouin zone and an acoustic phonon whose momentum is determined uniquely by “double resonance” condition.\textsuperscript{14} In usual second order scattering, if the optic phonon is described by a wave-vector $q_1$, and the acoustic phonon by a wave-vector $q_2$, conservation of quasimomentum requires $q_1 + q_2 = 0$, where $q_1$ and $q_2$ can span the entire Brillouin zone. Since $D$ mode is disorder induced, we suggest that $q_1$ is fixed at the $K$ point of the Brillouin zone (maximum in the density of photon states)\textsuperscript{9} and the magnitude of $q_2$ is determined by the double resonance condition.\textsuperscript{14} The quasimomentum conservation is achieved by disorder scattering. In a double resonance process, real (not virtual) transition takes place between two electronic states with emission of a phonon. Since the electronic states have dispersion, phonons of appropriate wave vectors are needed to keep the electronic transition real. Double resonance has
been seen for optic phonon overtones in GaAs,\textsuperscript{15} 2\Gamma\textsubscript{12} optic phonons\textsuperscript{16} in Cu\textsubscript{2}O and for two acoustic phonons in Ge.\textsuperscript{17}

II. MODEL

Following Martin and Falicov,\textsuperscript{14} we will discuss the two-phonon Raman scattering arising from an iterated one-phonon scattering in second order.\textsuperscript{14} Near resonance condition, the incident photon is absorbed to create an electron-hole pair, with electron occupying the real conduction band states and hole in the real valence state. Assuming the parabolic dependence of the electron-hole pairs in directions perpendicular to K\textsubscript{H}, the wave vector of the electron or hole \( \mathbf{k} \) created by a photon of energy \( E_{\text{L}} \) can be written as \( E_{\text{L}} = \Delta + \hbar^2 k^2/2\mu \) where \( \mu \) is the reduced mass (1/\( \mu \) = 1/\( m_e^* \) + 1/\( m_h^* \)). \( m_e^* \) and \( m_h^* \) are the electron and hole effective masses and \( \Delta \) is the band gap at K point in the Brilliouin zone. We will now address the nature of critical point involved in the resonance Raman scattering of D band.

We recall that the D-mode intensity increases as \( E_{\text{L}} \) is decreased from 4.2 up to 1.16 eV, suggesting that the D-band excitation profile has a maximum below 1.2 eV. We suggest that the appropriate band gap associated with the resonance of the D mode is at \( \sim 0.8 \) eV where a maximum is seen in the optical reflectivity measurements on graphite.\textsuperscript{18,19} This gap is associated with the energy difference between \( E_1 \) and \( E_3 \) bands at the K point of the Brillouin zone as shown in the band structure of graphite [Fig. 3(a)] taken from Refs. 19–21. The wave vector is in the basal plane. The bands shown here are the 4-\( \pi \) bands in three-dimensional (3D) graphite. Recall that a single sheet of graphite has 2-\( \pi \) bands with linear dispersion and Fermi level passes through the point of interaction (K point) as depicted in Fig. 3(b). Band structure calculations treating the interlayer coupling as a small perturbation find a small gap at K point in the Brillouin zone. The optical transition between \( E_1 \) and \( E_3 \) is termed as A\textsubscript{2} transition. Within the Slonczewski–Weiss–McClure band model\textsuperscript{20} the energies of these optical transitions are mainly determined by the overlap interaction parameter \( \gamma_1 \sim 0.4 \) eV for nearest-neighbor atoms on successive layers\textsuperscript{21} and energy of A\textsubscript{2} transition is \( \sim 2\gamma_1 \). Thomsen and Reich\textsuperscript{12} have, therefore, wrongly questioned the existence of a gap \( \sim 0.8 \) eV in the 3D band structure of graphite as suggested Sood et al.\textsuperscript{6}

The mechanism we suggest is that the electron in the conduction band (or the hole in the valence band) is scattered by an optic phonon, changing the electron state from \( k \) to \( k' \). Another acoustic phonon scatters this electron at \( k' \) and \( k'' \), followed by an impurity (disorder) scattering from \( k'' \) to \( k''' \) and the electron-hole recombine to produce the scattered photon with a frequency shift given by \( \omega = \omega_{\text{op}} + \omega_{\text{ac}} \). As mentioned before, we propose that the optic phonon involved correspond to the maximum in the density of phonon states at the K point in the Brillouin zone (shown by a solid dot in the phonon dispersion of graphite in Fig. 3) and the wave vector \( q \) of the acoustic phonon is so chosen to satisfy the double resonance condition. This Raman process involving disorder mediated two-phonon scattering is fifth order in perturbation theory and will have four energy denominators as explicitly written by Kauschke \emph{et al.}\textsuperscript{22} out of which two energy denominators will be the same. The resultant expression for the Raman matrix element is to be integrated over \( k, k', k'', \) and \( k''' \). The Raman intensity will be maximum when all the three denominators resonate simultaneously. It can be shown\textsuperscript{14–17} that the magnitude of \( q \) satisfies the condition for Stokes Raman scattering, for \( \Delta + \hbar\omega_{\text{op}} < E_{\text{L}} < \Delta + \hbar\omega_{\text{op}} + \hbar\omega_{\text{ac}} \),

\[
q_s = \left( \frac{\sqrt{2\mu}}{\hbar} \right) \left[ (E_{\text{L}} - \Delta)^{1/2} + (E_{\text{L}} - \Delta - \hbar\omega_{\text{op}})^{1/2} \right].
\] (1)

For \( E_{\text{L}} > \Delta + \hbar\omega_{\text{op}} + \hbar\omega_{\text{ac}} \) another resonance becomes possible for

\[
q_s = \left( \frac{\sqrt{2\mu}}{\hbar} \right) \left[ (E_{\text{L}} - \Delta - \hbar\omega_{\text{op}})^{1/2} + (E_{\text{L}} - \Delta - \hbar\omega_{\text{op}} - \hbar\omega_{\text{ac}}(q))^{1/2} \right].
\] (2)

For a given \( E_{\text{L}} \), the two-phonon Raman peak position for Stokes scattering will be given by

\[
\omega_s = \omega_{\text{op}}(K) + \omega_{\text{ac}}(q_s)
\] (3)

with \( q_s \) given by Eqs. (1) or (2). For \( \Delta \sim 0.8 \) eV and \( E_{\text{L}} > 1.16 \) eV, Eq. (2) is the appropriate relation to be used. In graphite, there is a peak in density of states around 1230 cm\textsuperscript{-1} corresponding to the optic phonon frequency at the K point in the Brillouin zone.\textsuperscript{13} We therefore, take \( \omega_{\text{op}}(K) \) to be 1230 cm\textsuperscript{-1}.

Regarding the acoustic phonon, it has been seen that the acoustic phonon branch corresponding to the branch marked T in the phonon dispersion relation of graphite shown in Fig. 4 is strongly coupled to the optical phonon.\textsuperscript{13} We take \( \omega_{\text{ac}}(q) = \nu_{\text{TA}} q \) where \( \nu_{\text{TA}} \) is the transverse acoustic phonon velocity (= 1.23 \times 10^{4} \text{ m/s}) Since \( \omega_{\text{ac}} \ll \omega_{\text{op}} \), one can simplify Eq. (2) and write

\[
\omega_{\text{ac}}(q_s) = q_s
\nu_{\text{TA}} = 2
\nu_{\text{TA}} \left( \frac{\sqrt{2\mu}}{\hbar} \right) (E_{\text{L}} - \Delta - \hbar\omega_{\text{op}})^{1/2}.
\] (4)

The solid line in Fig. 1 is a fit to Eqs. (3) and (4), with \( \Delta \) and \( \mu \) as adjustable parameters and \( \omega_{\text{op}} = 1230 \) cm\textsuperscript{-1}. The
values obtained are $\Delta = 0.85 \pm 0.05$ eV and $\mu = 0.025 \ m_e$. Taking the electron and hole effective mass to be the same, $m^*_e = 0.05 \ m_e$, which is in excellent agreement with these values obtained from other experimental measurements like cyclotron resonance.\textsuperscript{23} We also tried to fit the data in Fig. 1 using Eq. (4), with $\omega_{op}$ also as an adjustable parameter along with $\Delta$ and $\mu$. In this case the fit is also very good with parameters, $\omega_{op} = 1211 \ \text{cm}^{-1}$, $\Delta = 0.75$ eV, and $\mu = 0.026 \ m_e$. The values of the parameters in both cases being in reasonable agreement with those obtained from other experiments gives us confidence in the double resonance model to understand the origin of $D$ band.

Recent Raman measurements on ion-implanted highly oriented pyrolytic graphite by Tan, Deng, and Zhao\textsuperscript{7} show that the peak positions in the Stokes and anti-Stokes spectra for the $D$ band are different, with $\omega_{AS} > \omega_{S}$. In our model, using the disorder-induced double resonance, the wave vector of the phonon in anti-Stokes Raman scattering for the $D$ mode will be given by

\begin{equation}
q_{AS} = \left( \frac{2\mu}{\hbar} \right) \left( (E_L - \Delta + \hbar \omega_{op})^{1/2} \right.
+ \left. (E_L - \Delta + \hbar \omega_{op} + \hbar \omega_{ac}(q))^{1/2} \right)
\end{equation}

in place of Eq. (2). Therefore

$$
\Delta_D = \omega_{AS} - \omega_S
$$

\begin{equation}
= 2v_{TA} \sqrt{\frac{2\mu}{\hbar T}} ((E_L - \Delta + \omega_{op})^{1/2} - (E_L - \Delta - \omega_{op})^{1/2}].
\end{equation}

For the $D^*$ mode, two optic phonons and two acoustic phonons will be involved. This process will not require disorder-induced scattering to conserve momentum. In this case $\Delta_{D^*} \approx 2 \Delta_D$. Putting in the values for $\Delta = 0.85$ eV and $\mu = 0.025 \ m_e$ as obtained from the fit of Fig. 1, $\omega_{AS} - \omega_S$ for $D$ mode $= 13 \ \text{cm}^{-1}$ ($E_L = 2.41$ eV) while the difference ob-

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