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 Brillioun 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 ω_S and ω_{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 pyrolitic 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 nondestructive 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_{6h}^4 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).[1] 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.[1–4]

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 pyrolitic graphite, carbon black, multicomponent carbon films, hydrogenated amorphous carbon and, more recently, in carbon nanotubes.[3] (ii) The frequency of the *D* band shifts upward with increasing excitation laser energy[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 ($\cong$40 cm^{-1}/eV). Figure 1

shows the data from various measurements made on various kinds of disordered carbon[2,4] and carbon nanotubes.[3] (iii) The frequency of the associated second order (*D**) band (~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.[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.[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[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.[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 (ω_s) and anti-Stokes (ω_{AS}) are not the same:[7] $\Delta\omega_S = \omega_{AS} - \omega_S = 7$ 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,[1] the origin and dispersion of the *D* band is still not quantitatively understood. Tuinstra and Koenig[1] attrib-
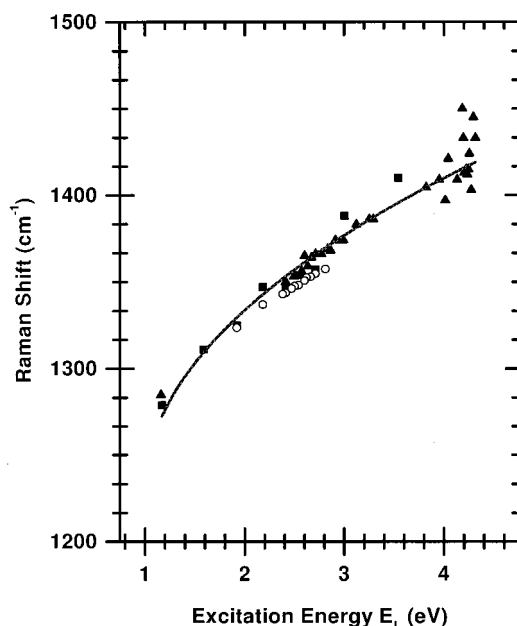

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FIG. 1. D-mode frequency dependence on excitation energy for different forms of carbon-disordered carbon (see Ref. 2) (filled squares), glassy carbon (see Ref. 4) (filled triangles), and carbon nanotubes (see Ref. 3) (open circles).

FIG. 2. Raman spectra of graphite at $E_L = 4.82$ and 2.54 eV. The inset shows the intensity ratio of D band to that of G band as a function of E_L as reported by Wang and co-workers (see Ref. 2). The peaks marked by asterisks are the internal vibrational modes of sulphate ion for use as internal intensity calibrant.

uted the D mode to the A_{1g}-type mode of a finite graphite crystallite with symmetry lower than D_{6h} of graphite, which corresponds to a longitudinal acoustic mode for the infinite lattice. Nemanich and Solin[8] and Lespade, Al-Jishi, and Dresselhaus[9] have invoked the breakdown of wave-vector selection rules due to disorder or finite size of crystals and correlated the D-band features with the density of states of graphite. These models, however, cannot explain the strong dispersive nature of the D mode as a function of E_L. The observation of second order D^* band for single crystal graphite which shows no disorder-induced D mode also rules out the explanation of the dispersion to crystallite size selective resonance Raman scattering process which occurs in polyacetylene. The recent studies[4,10] explained the dispersion of the D mode following Baranov et al.,[11] who attributed the dispersion of the D band in terms of the coupling between electrons and phonons with the same wave vector near the K point of the Brillouin zone. This model has a serious drawback in that it does not justify the reasons for the coupling and cannot address the resonance of the D mode at $E_L < 1$ eV, as well as the difference in ω_{AS} and ω_S for the D and D^* modes.

Almost three years back,[6] we proposed 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 ω on the energy of the exciting laser energy. Very recently, Thomsen and Reich (TR)[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
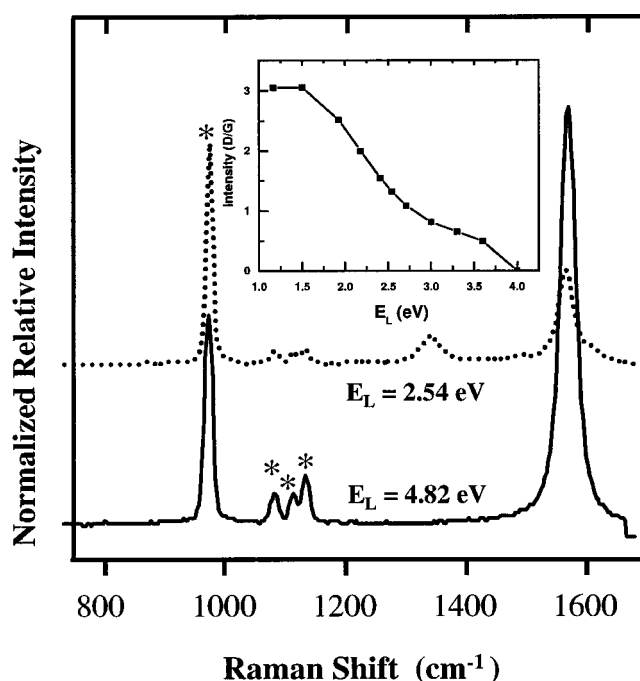
as E_L increases. On the contrary, the calculated intensity for $E_L = 4$ eV is higher than for $E_L = 2$ eV (see Fig. 3 of Thomsen and Reich[12]). This is completely opposite to the experiments as shown in Fig. 2. There is another difficulty we have with the TR's calculation. As given by their Eq. (4), the magnitude of q increases with E_L. For optic branch along ΓK direction, the phonon frequency ω is a decreasing function of q and hence ω 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,[13] 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.[14] In usual second order scattering, if the optic phonon is described by a wave-vector $\mathbf{q}_1$ and the acoustic phonon by a wave-vector $\mathbf{q}_2$, conservation of quasimomentum requires $\mathbf{q}_1 + \mathbf{q}_2 = 0$, where $\mathbf{q}_1$ and $\mathbf{q}_2$ can span the entire Brillouin zone. Since D mode is disorder induced, we suggest that $\mathbf{q}_1$ is fixed at the K point of the Brillouin zone (maximum in the density of photon states[9]) and the magnitude of $\mathbf{q}_2$ is determined by the double resonance condition.[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
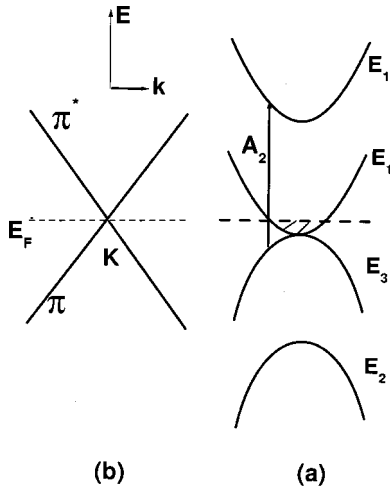
FIG. 3. (a) Schematic band structure of graphite showing the four π bands at the K point of the Brillouin zone. The wave vector **k** is perpendicular to the c axis. (b) Schematic of the single graphene sheet at the K point. Dashed liens denote the Fermi energy.

been seen for optic phonon obertones in GaAs,[15] $2\Gamma_{12}$ optic phonons[16] in Cu_2O and for two acoustic phonons in Ge.[17]

II. MODEL

Following Martin and Falicov,[14] we will discuss the two-phonon Raman scattering arising from an iterated one-phonon scattering in second order.[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 KH, the wave vector of the electron or hole **k** created by a photon of energy E_L can be written as $E_L = \Delta + \hbar^2 k^2/2\mu$ where μ 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 Δ is the band gap at K point in the Brillioun 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_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 ~ 0.8 eV where a maximum is seen in the optical reflectivity measurements on graphite.[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-π bands in three-dimensional (3D) graphite. Recall that a single sheet of graphite has 2-π 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_2 transition. Within the Slonczewksi–Weiss–McClure band model[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[21] and energy of A_2 transition is $\sim 2\gamma_1$. Thomsen and Reich[12] have, therefore, wrongly questioned the existence of a gap ~ 0.8 eV in the 3D band structure of graphite as suggested Sood et al.[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 $\omega = \omega_{op} + \omega_{ac}$. 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 et al.,[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[14–17] that the magnitude of q satisfies the condition for Stokes Raman scattering, for $\Delta + \hbar\omega_{op} < E_L < \Delta + \hbar\omega_{op} + \hbar\omega_{ac}$,

$$q_s \left(\frac{\sqrt{2\mu}}{\hbar} \right) [(E_L - \Delta)^{1/2} + (E_L - \Delta - \hbar\omega_{op})^{1/2}]. \tag{1}$$

For $E_L > \Delta + \hbar\omega_{op} + \hbar\omega_{ac}$, another resonance becomes possible for

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

For a given E_L, the two-phonon Raman peak position for Stokes scattering will be given by

$$\omega_s = \omega_{op}(K) + \omega_{ac}(q_s) \tag{3}$$

with q_s given by Eqs. (1) or (2). For $\Delta \sim 0.8$ eV and $E_L > 1.16$ eV, Eq. (2) is the appropriate relation to be used. In graphite, there is a peak in density of states around 1230 cm^{-1} corresponding to the optic phonon frequency at the K point in the Brillouin zone.[13] We therefore, take $\omega_{op}(K)$ to be 1230 cm^{-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.[13] We take $\omega_{ac}(q) = v_{TA}q$ where v_{TA} is the transverse acoustic phonon velocity ($= 1.23 \times 10^4$ m/s). Since $\omega_{ac} \ll \omega_{op}$, one can simplify Eq. (2) and write

$$\omega_{ac}(q_s) = q_s v_{TA} = 2v_{TA} \left(\frac{\sqrt{2\mu}}{\hbar} \right) (E_L - \Delta - \hbar\omega_{op})^{1/2}. \tag{4}$$

The solid line in Fig. 1 is a fit to Eqs. (3) and (4), with Δ and μ as adjustable parameters and $\omega_{op} = 1230$ cm^{-1}. The
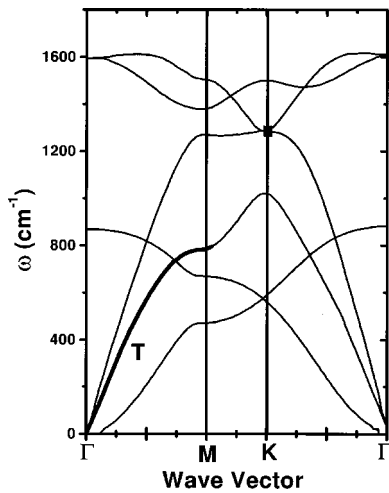
FIG. 4. Phonon dispersion curves in graphite calculated along certain high symmetry axes as given by Mathews *et al.* (see Ref. 10).

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.[23] We also tried to fit the data in Fig. 1 using Eq. (4), with ω_{op} also as an adjustable parameter along with Δ and μ. In this case the fit is also very good with parameters, $\omega_{op} = 1211$ 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[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

$$q_{AS} = \left(\frac{\sqrt{2\mu}}{\hbar} \right) \{ (E_L - \Delta + \hbar\omega_{op})^{1/2}$$
$$+ [E_L - \Delta + \hbar\omega_{op} + \hbar\omega_{ac}(q)]^{1/2} \} \tag{5}$$

in place of Eq. (2). Therefore

$$\Delta_D = \omega_{AS} - \omega_S$$
$$= 2 v_{TA} \sqrt{\frac{2\mu}{\hbar^2}} [(E_L - \Delta + \omega_{op})^{1/2} - (E_L - \Delta - \omega_{op})^{1/2}]. \tag{6}$$

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 $\Delta_{D*} \sim 2\Delta_D$. 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 $= 13$ cm^{-1} ($E_L = 2.41$ eV) while the difference ob-

served experimentally[7] is ~ 7 cm^{-1}. In the case of the D^* mode we find the difference to be 26 cm^{-1} which is very close to the experimentally observed value of 28 cm^{-1} of Tan, Deng, and Zhao.[7] Recent Stokes and anti-Stokes measurements by Zhang *et al.*[24] on carbon nanotubes also show a difference in the peak position of the D band in Stokes and anti-Stokes spectra and this difference is excitation laser energy dependent, very similar to the predictions of our model.

In conclusion, we have addressed the long standing problem of the dispersion of the Raman D band as a function of laser excitation energy using a simple model based on disorder-induced two-phonon scattering and the double resonance. The fit of the experimental data in this model yields the reduced effective mass of the electron-hole pair associated with the π bands at the K point. This is in reasonable agreement with the values obtained from other experimental probes. As a corollary, this model can also explain the different recently observed in the peak positions of the D and D^* bands in Stokes and anti-Stokes spectra.

ACKNOWLEDGMENTS

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