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Aerographite phonon density of states affects double resonant Raman scattering

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ABSTRACT

Raman spectra of aerographite, graphite oxide, graphite flakes, and kish graphite were investigated with different laser excitation energies (wavelengths, \( \lambda \)), namely, 2.81 eV (442 nm), 2.41 eV (514 nm), 2.33 eV (532 nm), and 1.96 eV (633 nm). X-ray diffraction analysis showed that aerographite and graphite oxide are structurally disordered. The Raman spectra of both exhibit typical graphitic features, namely, G, D, \( \lambda \) for aerographite and graphite oxide. A physical explanation of this unexpected saturation is proposed within the double resonant Raman scattering model, taking into account the disorder-induced changes of the phonon density of states.

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I. INTRODUCTION

Carbon is an amazingly versatile element, owing to its three different hybridization states, \( sp^1, sp^2, \) and \( sp^3 \). Graphite is a three-dimensional layered material formed by stacking single graphene sheets with honeycomb structures made up of carbon atoms in \( sp^2 \) hybridization and features covalent \( \sigma \) and \( \pi \) bonds that are held together by weak interlayer van der Waals forces.1 Aerographite is an ultralightweight porous graphite aerogel, which consists of an interconnected network of tubular carbon foams, resulting in an ultra-low density of 0.18 mg/cm\(^3\) and a large specific surface area, which has demonstrated numerous potential applications in supercapacitors, lightweight batteries, water purification, and so on.2,4

Raman spectroscopy is a non-destructive experimental technique of choice to investigate graphite-like materials since Raman sharp spectral lines exhibit a wide variety of features corresponding to carbon allotropes and reflect fine structural information.1–20 Raman spectra of “plain” graphite and graphene are well understood in both their theoretical and experimental aspects. The main features in the Raman spectra of graphitic materials are the \( G \) (\( \sim 1580 \text{ cm}^{-1} \)) and \( D \) (\( \sim 1350 \text{ cm}^{-1} \)) bands.1,4,9–23 The G band (\( E_{2g} \) symmetry) corresponds to the doubly degenerate in-plane transverse optical (iTO) phonon modes at the first Brillouin zone center, originating from the in-plane stretching vibrations of the carbon–carbon bonds. The disorder-induced D band is due to the \( A_{1g} \) breathing mode of \( sp^2 \) rings. It involves an elastic scattering of the excited electrons by a defect (impurities or structural disorder within the graphitic structure) and an inelastic scattering of electrons by iTO phonons near the K point of the Brillouin zone.9–12

Graphite with significant defects shows additional disorder related bands, the \( D' \) at \( \sim 1620 \text{ cm}^{-1}, G' \) (also called 2D) at \( \sim 2710 \text{ cm}^{-1} \), and \( D + D' \) at \( \sim 2970 \text{ cm}^{-1} \) bands.

One of the most frequently studied features of the Raman spectra for graphite materials is the intensity ratio of G band and disorder-induced D band, \( I_G/I_D \). The appearance of D band was initially explained through a model based on the disorder-affected phonon density of states (PDOS).22 Moreover, the energy at which D band occurs (\( E_L \)) was shown to depend on the laser excitation energy (\( E_L \)). But \( E_D \) (in cm\(^{-1}\)) shifted with \( E_L \) (in eV) at a rate of...
40–50 cm$^{-1}$/eV, which was inconsistent with the proposed model. Both the appearance of the D band in graphitic materials and the laser energy dependence of D band were later explained through a double resonant Raman scattering model.\textsuperscript{9–12}

The ratio $I_D/I_G$ has been used to quantify the disorder in $sp^2$ graphitic systems. An empirical relation was developed for ordered graphitic systems with radiation-induced defects, relating the areal density of defects ($n_D$) and $E_L$ to $I_D/I_G$ as\textsuperscript{9–11,33}

$$n_D = 7.3 \times 10^3 \frac{I_D}{E_L^2} \left( \frac{I_D}{I_G} \right)$$

(1)

for low defect density and as

$$n_D = 5.9 \times 10^4 \frac{I_D}{E_L^4} \left( \frac{I_D}{I_G} \right)^{-1}$$

(2)

for high defect density. Here, $n_D$ and $E_L$ are in cm$^{-2}$ and eV, respectively. In both cases, $I_D/I_G \sim E_L^2$, and so $I_D/I_G \sim \lambda_L^2$, where $\lambda_L$ is the laser wavelength. However, a similar analysis has not been attempted for aerographte, as Raman spectra of aerographte at different laser excitation energies have not been reported in detail. Thus, systematic investigations of the Raman spectra of aerographte will deepen our understanding of this new form of carbon material and shed further light on other forms of graphite.

This paper presents a comparative study of the Raman spectra of aerographte and more common graphitic systems of graphite oxide, graphite flakes, and kish graphite. Kish graphite is obtained through precipitation on steel in the steel manufacturing process and it has a nearly ideal crystalline form. $I_D/I_G$ is studied under different laser excitation energies, from 1.96 to 2.81 eV. We show that the commonly used relationships, Eqs. (1) and (2), are no longer valid for highly disordered graphitic systems (aerographte and graphite oxide) over the whole range of $E_L$ used. The energy of the D band, however, still depends linearly on $E_L$, as expected for ordered graphitic systems. The explanation for the dependence of both, $I_D/I_G$ and $I_D$, on $E_L$ is sought in terms of a double resonant Raman scattering model. However, our measurements suggest that the defect-induced changes of the PDOS also need to be taken into account to explain the observed dependence of $I_D/I_G$ on $E_L$.

II. EXPERIMENTAL DETAILS

The carbon-based aerographte was synthesized using single-step chemical vapor deposition (CVD) in direct conversion from sacrificial zinc oxide based ceramic templates.\textsuperscript{23} First, ZnO tetrapods were fabricated using flame transport synthesis (FTS), with details given in Refs. 2 and 3. Aerographte was then fabricated through the CVD process, by growing graphitic carbon at 760 °C on the top of ZnO network while simultaneously removing the underlying ZnO template in the presence of toluene as the carbon source and H$_2$ as ZnO reducing agent. The porous ZnO network acts as a sacrificial template for aerographte, whose architecture is mainly determined by the structural morphology of the ZnO templates. Graphite oxide powder (with a diameter of 0.5–5 μm and a thickness of 1–3 nm) was supplied by ACS Material LLC. Graphite flakes (with 99% carbon basis, and a particle size of 300 μm) were purchased from Sigma-Aldrich. Kish graphite (Grade 200 with flake size: 0.7–2 mm, ultrapure: carbon >99.2%) was supplied by Graphene Supermarket. The graphite oxide, graphite flakes, and kish graphite were pressed into pellets using a laboratory press (International Crystal Laboratories) at the pressure of 4000 psi. The sample structure was investigated using a powder x-ray diffractometer (GBC Scientific Equipment LLC), using Cu-Kα radiation (λ = 0.154 nm). The diffraction patterns were collected at room temperature in the 2θ range from 10° to 80° with a step size of 0.02° and a scan speed of 1°/min. All samples were mounted onto x-ray diffraction (XRD) goniometer using a Kapton tape.

Raman spectra were collected on a confocal Raman microscope (Renishaw plc) in an ambient environment using a backscattering geometry with four different excitation lasers: 442 nm (excitation energy $E_L = 2.81$ eV, source power 19.5 mW) using the He–Cd laser; 514 nm ($E_L = 2.41$ eV, source power 73.8 mW) using the Ar ion laser; 532 nm ($E_L = 2.33$ eV, source power 33.6 mW) using the diode laser; and 633 nm ($E_L = 1.96$ eV, source power 13.0 mW) using the He–Ne laser. The laser was focused on the sample via a Leica 50× magnification objective (numerical aperture 0.75), using an exposure time of 10 s, and 1–10 accumulations in the extended mode. The laser beam power was adjustable from 10% to 100% of the source power. The power was adjusted to ensure the best signal-to-noise ratio (SNR) but without damaging the sample. Detection was achieved with an air-cooled charge-coupled device camera. The spectral resolution was 1 cm$^{-1}$. The calibration of a spectrometer was checked by using the line of a silicon sample at 521 cm$^{-1}$. The Raman peaks were fitted with the Lorentzian shape to obtain the intensity and energy of the peak in each absorption band. The background signal was fitted with a cubic function.

III. RESULTS AND DISCUSSION

The powder XRD patterns of graphite oxide and graphite oxide are shown in Fig. 1(a). There are several sharp peaks for the aerographte sample in the 2θ range of 10°–80°, which can be identified as peaks of residual ZnO at 32.3° (100), 36.8° (002), 40.2° (101), 48.0° (102), 57.1° (110), 63.3° (103), 66.8° (200), 68.3° (112), and 69.5° (201).\textsuperscript{21} A broad peak is also observed at 18°. It is possible that the background of the XRD spectrometer and the Kapton tape contribute to this peak.\textsuperscript{21} There are three broad XRD peaks for graphite oxide, at 11.4° (001), 22.6° (002), and 43.1° (100).\textsuperscript{34–41} The (002) peak is attributed to the orientation of the aromatic ring carbon reticulated layers in three-dimensional arrangement.\textsuperscript{3–4} The narrower and higher (002) peak reflects a better orientation of the aromatic layer slice.\textsuperscript{21} The (100) peak reflects the size of the aromatic layer slice, and a larger size results in a narrower and higher (100) peak.\textsuperscript{34–41}

The powder XRD patterns of graphite flakes and kish graphite are shown in Fig. 1(b). These patterns feature sharp peaks, indicating that the samples have no significant structural disorder. The XRD reflections are identical for both samples: 27.5° (002) and 55.5° (004). This indicates that graphite flakes and kish graphite are c-axis aligned, as expected for two-dimensional crystalline forms of graphite.
In summary, the XRD patterns show that aerographite and graphite oxide are structurally highly disordered, showing only very broad XRD features. Graphite flakes and kish graphite, on the other hand, give sharp XRD peaks corresponding to a graphitic structure. Therefore, they are structurally ordered. The marked difference in XRD patterns between these two groups of the samples will also be reflected in their Raman spectra.

Raman spectra of graphite oxide, graphite flakes, and kish graphite are displayed in Fig. 2 for different excitation energies. Kish graphite and graphite flakes have very similar Raman spectra, with well-defined sharp peaks. Graphite oxide, however, gives broader Raman peaks, which are not completely separated from each other. This is consistent with XRD data, where graphite oxide gave only broad features implying strong structural disorder while kish graphite and graphite flakes gave sharp XRD peaks (see Fig. 1). Regardless of these differences, all three samples exhibit the G band, the disorder-induced D band, the overtone 2D band, and further combination modes. Despite having sharp XRD peaks, graphite flakes and kish graphite contain substantial enough defects to produce the D band in Raman spectrum. These defects are linked to crystallite surfaces, resulting in the dependence of $I_D/I_G$ on crystallite size.5

There is a "blue-shift" (shift to higher frequency) with increasing laser excitation energy observed for the D and 2D bands (Fig. 4), whereas the position of the G band is essentially invariant. The magnitude of the 2D shift (∼98 cm$^{-1}$/eV) is approximately twice that of the D shift (∼46 cm$^{-1}$/eV). This is consistent with the assignment that the 2D band is the overtone of the D band.30 The dispersion is attributed to a disorder-induced phonon scattering process, which involves the combination of an optical phonon at the K point in the Brillouin zone and an acoustic phonon with a momentum that is determined by the double resonant enhancement condition.22,42,43

A three-stage model based on Raman spectra was reported to interpret the evolution of disorder among carbon atoms. This is dependent on the configuration of the $sp^2$ sites in $sp^2$-bonded clusters and the ratio of $sp^2$ and $sp^3$ hybridization, which control the positions, intensities, and widths of the G and D peaks for various forms of carbon from graphite to amorphous carbon.44,45 In stage two (nano-crystallite graphite to low $sp^3$ amorphous carbon), the second-order Raman bands are not well defined anymore, but a broad feature is present from ∼2300 cm$^{-1}$ to ∼3200 cm$^{-1}$ and is modulated by the 2D and 2D’ bands.44–47 This is exactly as observed for aerographite, again indicating a highly disordered structure. Thus, there is a good correlation between the results from the XRD measurements and the Raman scattering spectral studies.
We next focus on the dependence of $I_D/I_G$ on the laser excitation energy for aerographite. Comparison with other forms of graphite will help pinpoint the origin of the surprising deviation of its $I_D/I_G$ vs $E_L$ from the expected behavior described by Eqs. (1) and (2). Measurements on each spot of the sample were performed several times to obtain the uncertainty (expressed as mean square deviation). The values of $I_D/I_G$ were strongly dependent on the position on the sample at which the Raman spectrum was measured, as is evident in Fig. 5. This is not surprising, considering that the XRD spectrum reveals that the aerographite is a highly disordered system. However, this result further implies that the disorder in the aerographite is not homogeneously spread throughout the sample. Similar inhomogeneity in $I_D/I_G$ has been reported for graphene oxide.

To test if $I_D/I_G$ gives the same dependence on the laser excitation wavelength as reported in the literature for graphene and common forms of graphite [Eqs. (1) and (2)], $I_D/I_G$ is plotted against $\lambda_L^4$ in Fig. 6 for all samples measured. Each point in Fig. 6 is the average of several measurements taken on one spot on the sample. The dependence of $I_D/I_G$ on the position on the sample where the Raman spectrum is measured seems to be a common feature. This gives large data scattering also for structurally ordered materials.
samples with low values of $I_D/I_G$, i.e., kish graphite and graphite flakes. To establish if $I_D/I_G$ for the ordered graphitic samples indeed gives the expected proportionality to $\lambda_L^4$, values of $I_D/I_G$ were then averaged over all measurements for each laser wavelength separately and plotted again (Fig. 7). It is seen that $I_D/I_G$ scales linearly with $\lambda_L^4$, as expected for $sp^2$ graphite systems [Eqs. (1) and (2)]. The gradient of $I_D/I_G$ vs $\lambda_L^4$ averaged over both samples, is $1.2 \times 10^{-12}$ nm$^{-4}$.

Figure 8 shows the dependence of $I_D/I_G$ on $\lambda_L^4$ for aerographite and also for graphite oxide. Here, only measurements at one spot for each material are shown, to eliminate uncertainty associated with sample inhomogeneity. For both materials, a linear relationship of $I_D/I_G$ with $\lambda_L^4$ was obtained for three smaller laser wavelengths, $\lambda_L = 442, 514,$ and 532 nm. This is as expected for $sp^2$ graphitic materials. In this region, the gradient in $I_D/I_G$ vs $\lambda_L^4$ was $8.9 \times 10^{-12}$ nm$^{-4}$, larger than the gradient obtained for kish graphite and graphite flakes. However, this linear relationship no longer holds for $\lambda_L = 633$ nm. More specifically, $I_D/I_G$ vs $\lambda_L^4$ tends to saturate at the longest wavelength. To check that the apparent saturation does not in fact come from a power-law behavior of our data-points with exponent different than 4, the same $I_D/I_G$ ratio was re-plotted against wavelength in the inset to Fig. 8 using logarithmic scales. The experimental points apparently still do not make a straight line, excluding the possibility that they follow a unique power-law over the whole range of measured $\lambda_L$. The XRD results showed that both aerographite and graphite oxide have a highly disordered structure, with no clearly discernible XRD peaks (Fig. 1). On the other hand, kish graphite and graphite flakes have a highly ordered and orientated crystalline structure, with sharp XRD peaks. This suggests that the unexpected saturation of $I_D/I_G$ vs $\lambda_L^4$ at high $\lambda_L$ occurs because of structural disorder in aerographite and graphite oxide.

This phenomenon is also reflected in the shape of the Raman peaks. Aerographite and graphite oxide give broad D and G peaks that merge. The non-linearity in $I_D/I_G$ vs $\lambda_L^4$ cannot be an artifact of the merging of the bands for aerographite, as otherwise a non-linearity also would be obtained for the shorter wavelengths. This

![Raman spectra of aerographite excited by different excitation energies.](image1)

![Peak positions of the (a) D and (b) 2D bands as a function of excitation energy for aerographite. The lines are linear fits to the data.](image2)
lends support to treating the observed $I_D/I_G$ vs $\lambda_L^4$ for aerographite and graphite oxide as being genuinely nonlinear if longer laser wavelengths are used.

Further insight into these phenomena is obtained from the dependence of the Raman shift of the D (i.e., $E_D$) and G (i.e., $E_G$) bands on $E_L$ (Fig. 9). A linear relationship between $E_D$ vs $E_L$ for aerographite was obtained for all samples. The gradient of the $E_D$ vs $E_L$ for aerographite was $\sim 46 \text{ cm}^{-1}/\text{eV}$. The other materials have similar gradients: for graphite flakes, kish graphite, and graphite oxide, they are $\sim 42 \text{ cm}^{-1}/\text{eV}$, $\sim 43 \text{ cm}^{-1}/\text{eV}$, and $\sim 36 \text{ cm}^{-1}/\text{eV}$, respectively. In contrast to $E_D$, the $E_G$ of graphitic materials is almost constant with respect to $E_L$. Evidently, $E_D$ has the same dependence on laser energy for high and for low values of $E_L$ (or, equivalently, $\lambda_L$) for all samples. This behavior is in agreement with the dependence of $I_D/I_G$ on $E_L$ for kish graphite and graphite flakes, where a single linear $I_D/I_G$ vs $\lambda_L^4$ is obtained for all measured $\lambda_L$. However, this differs from the dependence of $I_D/I_G$ on $E_L$ for aerographite and graphite oxide, for which $I_D/I_G$ is linear at small $\lambda_L$, but it saturates for larger $\lambda_L$.

The occurrence of the D band in graphite has been successfully described by a model involving a double resonance Raman scattering process, in which the elastic scattering of an electron on crystal defects plays a key role. In this model, the electron dispersion relation for electrons near the Fermi level ($E_F$) is approximately linear, making “Dirac cones” (Fig. 10). An electron is excited by a laser photon (of energy $E_L$) to the next higher available energy level ($a$ in Fig. 10), leaving a hole at point $a$. The value of electron momentum, $k$, is determined by the electron dispersion relation and $E_L$. A larger value of $E_L$ results in the excitation of an electron at a higher value of $k$. This excited electron can exchange energy with a phonon of non-zero phonon momentum, $q$. It was shown that the phonons near the phonon symmetry point $K$ contribute to the D band and they are associated with large $q$. This large $q$ needs to be compensated by a large change of electron momentum, which is accomplished through inter-valley double resonant Raman scattering, as shown in Fig. 10. The energy of this
phonon ($E_{ph}$) is such that the electron moves to a real electron state at point $c$ in Fig. 10, defined by values of $q$ and $E_L$ and by the electron dispersion relation. The scale of $E_{ph}$ is grossly enlarged in Fig. 10, to make it visible there. After that, the electron emits a photon of energy $E_L - E_{ph}$ and occupies a virtual state at point $d$ in Fig. 10. Scattering on crystal defects then allows this electron to change its momentum, without changing its energy, so that it can recombine with a hole at point $a$ (dashed line in Fig. 10). The photon of energy $E_L - E_{ph}$ emitted in this double resonant Raman scattering is detected in Raman spectroscopy. Other options are also possible, in which two excited states of the electron are real states and one is a virtual state.1,4,9

D bands occur through an inter-valley double resonance Raman process. The probability of this process was reported to be proportional to the squares of the transition matrix elements for each of the transitions $a$-$b$, $b$-$c$, $c$-$d$, and $d$-$a$ in Fig. 10. In this model, increasing $E_L$ leads to a linear increase of $k$, which in turn leads to a linear increase of $q$ with $E_L$. As $E_{ph}$ increases approximately linearly with $q$ for this phonon near the $K$ point of symmetry, it follows that the energy of the Raman D peak ($E_D$) increases linearly with $E_L$.1,4,8,9 The linear relationship in $E_D$ vs $E_L$ is exactly what is obtained experimentally. This result could not be reproduced by the other models describing the occurrence of D peak.

A physical explanation for the saturation of $I_{D}/I_G$ vs $\lambda_L^2$ for aerographite and graphite oxide (Fig. 8) might be sought within the framework of the defect-induced double resonance Raman scattering model, because our measurements give a linear $E_D$ vs $E_L$ for the entire range of $E_L$ (i.e., $\lambda_L$) used (Fig. 9). A distinct difference between the samples showing the saturation in $I_{D}/I_G$ vs $\lambda_L^2$ (Fig. 9) and samples showing linear $I_{D}/I_G$ vs $\lambda_L^2$ in the entire range of $\lambda_L$ (Fig. 8) is that the former are highly structurally disordered. Therefore, disorder-induced effects can be singled out as potential underlying mechanisms for the observed $I_{D}/I_G$ vs $\lambda_L^2$. These might be disorder-induced changes of the density of states (DOS) or disorder-induced changes of the dispersion relation, each for electrons and for phonons.

A study of electron DOS produced by strong point defects for graphene showed an enhanced DOS near the Fermi level.26-31 The dispersion relation for this state was not given. What was important, however, is that the finite defect-related electron DOS was obtained only close to the Fermi level. A schematic diagram of the dispersion relation for the electron DOS is given in Fig. 10 by dotted lines, arbitrarily assuming a linear form for simplicity. In Raman experiments with high $E_L$, i.e., small $\lambda_L$, the electron will be excited to energy above the disorder-induced electron states ($a$-$b$ in Fig. 10). Subsequent interaction with a phonon will then result in the same double resonance Raman scattering effect as without defect-induced electron states ($b$-$c$-$d$-$a$). If $E_L$ is low enough, the electron can be excited to energies at which electron defect states exist close to the Fermi level. A possible double resonant Raman scattering can then be described by transitions $a'$-$b'$-$c'$-$d'$-$a$ in Fig. 10. This is a different process than that for high $E_L$ and it is a good candidate for explaining the saturation in $I_{D}/I_G$ vs $\lambda_L^2$ for aerographite and graphite oxide. However, a different $E_D$ vs $E_L$ dependence will then be obtained than for high $E_L$, because of different dispersion for the disorder-induced electron states. The experiment does not show such a transition in $E_D$ vs $E_L$ from high to low $E_L$ (Fig. 9). Therefore, disorder-induced electron density of states cannot be the mechanism for the observed saturation in $I_{D}/I_G$ vs $\lambda_L^2$ for aerographite and graphite oxide.

The linearity of the electron dispersion relation for disorder-induced electron states may also be altered by the structural disorder, which would in turn affect the Raman D band. However, this would affect the phonon momentum and energy of step $b'$-$c'$ in the double resonant Raman scattering (Fig. 10). Consequently, $E_D$ vs $E_L$ would no longer be linear, reflecting the non-linearity of the electron dispersion relation for disorder-induced states. Since the experiment shows otherwise, the effect of disorder on the electron dispersion relation can be ruled out as a mechanism for the observed saturation in $I_{D}/I_G$ vs $E_L$ at low $E_L$.

In addition to affecting the electron states, a high degree of the structural disorder will also affect the phonon states. The dispersion of the iTTO phonon near the $K$ point was approximated to be linear in the double resonant Raman scattering model, which ensured a linear $E_L$ vs $E_L$. A high degree of the structural disorder can affect this linearity, which in turn may affect $I_{D}/I_G$ vs $E_L$. However, this would then also be reflected in $E_D$ vs $E_L$ relationship, because the phonon energies would then no longer change linearly with $E_L$. As the experiment gives a linear $E_D$ vs $E_L$ relationship for all experimental values of $E_L$, the effect of structural disorder on the iTTO phonon dispersion near the $K$ point can be, therefore, excluded as a possible cause of saturation in $I_{D}/I_G$ vs $\lambda_L^2$ at large $\lambda_L$ (Fig. 8).
The structural disorder can also affect the PDOS, which exhibits a peak near the energy of the D band. The larger the magnitude of PDOS at \( E_D \), the greater is the probability for the electron–phonon interaction corresponding to step b–c in Fig. 10. An increase of \( E_L \) results in a proportional increase of \( E_D \) through the double resonant scattering process (Fig. 9), involving the phonons in step b–c with different values of PDOS. If PDOS in the vicinity of \( E_D \) is such that PDOS increases with \( E_D \) (i.e., \( E_L \)), \( I_D/I_G \) should increase with \( E_L \), providing PDOS as the dominant factor determining the change of \( I_D \) when \( E_D \) changes within the narrow range of values in our experiments. This condition would be valid when the range of \( E_D \) is much smaller than the width of the Raman band D, as is the case for aerographite and graphite oxide. PDOS for highly disordered graphite systems must then change at a lower rate with the phonon energy for the values of \( E_D \) corresponding to small \( E_L \), at which the saturation of \( I_D/I_G \) occurs.

To explore the viability of this mechanism, the dependence of PDOS on phonon energy near \( E_D \) needs to be established first. There are many reports on the phonon energy dependence of PDOS in graphitic systems. They are most often calculated for graphene, either numerically with the density functional theory (DFT) modeling or analytically using model potentials and experimentally obtained material parameters. It is difficult to distinguish which part of the PDOS exactly is associated with the occurrence of band D, if relying solely on the experimental \( E_D \) as the distinguishing parameter. DFT calculations typically overestimate phonon energies and the analytical approach makes approximations in the model potentials that also result in \( E_D \) differing from the experimental
values. This leads to inconsistencies between different reports regarding the region in PDOS curves that are associated with the band D. The most reliable way to ascertain this region would be to limit our consideration only to the works that report both PDOS and position of characteristic energies in PDOS near which Raman band D occurs.

Phonons near symmetry point K on iTO phonon branch were shown to be responsible for the double resonant Raman scattering leading to band D. As $E_L$ increases, these phonons move away from point K and their energy increases. The contribution to band D by the phonons between symmetry points K and $\Gamma$ (so-called inner phonons) is substantially higher than phonons between symmetry points K and $\Gamma$. This will help identify the energy range in PDOS responsible for band D.

Phonon dispersion and PDOS were calculated analytically for graphene in Ref. 51. Key symmetry points were indicated in both phonon dispersion and PDOS diagrams, which enables us to identify the PDOS region associated with the band D. From there, band D occurs at the descending branch of a peak in PDOS, between energies of iTO phonon branch at point M and LO phonon branch at point K. Analytical calculus for graphite also places band D to a descending branch of PDOS, just above the energy of the LO phonon branch at symmetry point M. Numerical DFT calculations for graphite show that band D occurs just above the energy of LO phonon branch at symmetry point K. This again places the band D at the descending branch of a peak in PDOS, same as the analytical calculus in Ref. 53. This is all consistent with our suggestion that the variation of the intensity of band D as $E_L$ changes within a limited range may be determined primarily by the variation of PDOS. As $E_L \propto E_{\lambda L}$ (Fig. 9) in double resonant Raman scattering; an increase of $E_L$ results in a decrease of PDOS value associated with band D, because $E_D$ lies on the descending branch of the peak in PDOS curve. Therefore, $I_D$ decreases with $E_L$. In our experiment, an increase of $E_L$ results in a decrease of $I_D/I_G$, considering $E_L \propto \lambda_L^{-1}$ (Figs. 6–8). This is consistent with PDOS being the dominant factor affecting the change of $I_D$ as $E_L$ changes within the narrow range of values in our experiment.

We now focus on the observed weaker decrease of $I_D$ with $E_L$ in the range of low $E_L$ values (i.e., a weaker increase of $I_D$ with $\lambda_L^2$ for high $\lambda_L$ values shown in Fig. 8) for highly structurally disordered graphite. The weaker change of $I_D$ with $E_L$ due to PDOS would require a more gradual dependence of PDOS on phonon energy. While there are no reports on PDOS for highly structurally disordered graphite, such more gradual dependence of PDOS is in fact expected. A disorder broadens the peaks in PDOS, as shown for the case of graphene. The broader peaks in PDOS would have a more gradual dependence of PDOS on phonon energy nearer to the top of the broad peak. This dependence will get stronger away from the peak top, at higher values of $E_L$, as $E_L$ increases. Therefore, disorder-induced change of PDOS is a plausible cause for the occurrence of the plateau in $I_D/I_G$ vs $\lambda_L^2$ at large $\lambda_L$ (Fig. 8).

IV. CONCLUSIONS

The Raman spectrum of aerographite was studied in comparison to the Raman spectra of graphite oxide, kish graphite, and graphite flakes. XRD measurements showed that the aerographite and graphite oxide were structurally highly disordered, while the kish graphite and graphite flakes were structurally ordered. All the samples give Raman bands characteristic for graphitic systems; however, the bands for the disordered samples are broadened, as expected. The intensity ratio of the D and G bands and its dependence on the wavelength of the excitation laser also show a distinct difference between these two groups of samples. The values of $I_D/I_G$ are an order of magnitude larger for the disordered samples. While $I_D/I_G$ increases linearly with laser wavelength for all wavelengths used for kish graphite and graphite flakes, it saturates at the longest wavelengths for aerographite and graphite oxide. However, all samples show a linear increase in the energy of the D band with the laser energy for all laser wavelengths used.

A physical explanation of these phenomena was sought within the framework of the double resonant Raman scattering model. Unlike the model based on the defect-affected PDOS previously proposed for the D band, this physical model can explain both the occurrence of D band and the dependence of its energy on the laser energy. However, our results suggest that the effects of defects on the PDOS also need to be taken into account within the framework of the double resonant Raman scattering model to describe the observed saturation in $I_D/I_G$ vs $\lambda_L$ at long laser wavelengths for highly disordered aerographite and graphite oxide.

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