PHONON-LIKE LIGHT SCATTERING
IN POLYCRYSTALLINE CARBON STRUCTURES

A.P. NAUMENKO,[1] N.E. KORNIYENKO,[1] V.M. YASHCHUK,[1]
V.N. BLIZNYUK,[2] S. SINGAMANENI[3]

[1]Faculty of Physics, Taras Shevchenko National University of Kyiv
(4, Academician Glushkov Prosp., Kyiv 01601, Ukraine; e-mail: a_naumenko@univ.kiev.ua)

[2]Western Michigan University
(Kalamazoo, Michigan 49008, USA)

[3]School of Engineering Applied Sciences, Washington University
(St. Louis, MO 63130, USA)

A new type of inelastic light scattering in a disordered condensed matter is considered, in which, contrary to the conventional Raman scattering with fixed frequencies of vibrations, a shift of vibrational band positions is observed under variation of the excitation radiation frequency. This phonon-like scattering is inherent to intermediate states of the matter characterized by a "smeared" zone structure at the transition from individual non-correlated molecules of an amorphous material to a highly correlated structural state in single crystals. In particular, for different carbon structures, the intermediate structural states between graphite and diamond include some shares of sp^2 and sp^3 hybridizations. A defect band and additional ones (D and Ad bands, respectively) have been clearly detected in the Raman spectra of such carbon forms. The bands have a doublet frame with the "redistribution" of intensities between components of the doublet (at 1350 and 1375 cm^{-1}) in different structural modifications of graphite sensitive to the local environment of the corresponding chemical groups and to physical factors like pressure, temperature, and ionic implantation. The deconvolution of the composite bands into individual components has been performed through the subtraction spectra calculation. The origin of doublets and limitations of the applicability of a coupled double resonance concept are discussed. To determine the nature of the considered Raman bands, their fine structure and asymmetry are analyzed and compared with the behavior of similar bands in diamond-like hydrocarbon films and carbon metastable phases under high pressure.

1. Introduction

Graphite materials are excellent subjects for fundamental investigations directed toward finding the correlations between spectral features and a structural order due to a large number of structural modifications of graphite and a relatively small number of vibrational modes observed in their Raman scattering and IR absorption spectra. From inelastic neutron scattering experiments, one can find a dispersion of phonon branches in the whole Brillouin zone (BZ). However, only the states at the center of BZ are involved in the processes of first-order Raman scattering and IR absorption. A rather high accuracy of optical measurements allows the detection of features in vibrational spectra usually unobservable by diffraction techniques. In the case of superlattice structures, defects, or fine-dispersed powder samples, the non-centered vibrational modes resulting from phonon branches "folding" may be transformed to the "central" modes ($\mathbf{k} \cong 0$), thus allowing their registration in the first-order Raman and IR spectra. In the case of small-size domains with a random alignment of the crystalline axis, many vibrational states can be registered with optical spectroscopy techniques because of the violation of selection rules for the quasimomentum due to the strong smearing of their energy band structure. This essentially expands spectroscopic possibilities of optical methods. An essential feature of graphite materials' vibrational spectra is the high intensity of their forbidden bands (i.e., bands forbidden by selection rules for the space group D_{6h}^4 of graphite), comparable to or even exceeding the intensity of the fundamental bands [1, 2]. In this respect, the carbon materials differ from liquids, where the rules of selection for the symmetry point groups of molecules are not fulfilled because of the intermolecular interaction and thermal motion, which results, as a rule, in weak "forbidden" bands [3].

In spite of numerous spectral investigations of graphite materials, a less attention has been paid till now to a detailed study of the shape of spectral bands and their correlations with the corresponding structural features. Due to this fact, we have focused our present work on a detailed study of the spectral shapes of both allowed and forbidden bands. We distinctly revealed the bands with maxima at 1350 cm^{-1} and 1375 cm^{-1} in the forbidden spectra of some of carbon materials, by using an

Ar^+-laser ($\lambda_L = 514.5$ nm) as an excitation source. The essential dependence of the frequency of bands on the wavelength of the exciting radiation is one of the most interesting peculiarities of light scattering spectroscopy [4–7]. In particular, such a feature of inelastic light scattering was observed in a number of carbon materials, for example in disordered graphite, glassy carbon, and diamond-like and carbon films for fundamental bands at 1350, 1380, 1550, and 1600 cm^{-1} ($\lambda_L = 514.5$ nm) and for some overtones [4, 5]. The frequency shift of these bands is more than 40–50 cm^{-1} for a change in the excitation light frequency of 5×10^3 cm^{-1}. Moreover, in the majority of cases, the frequencies of the observed bands decrease with increase of λ_L [6, 7]. At the same time, as a rule, the frequencies of other narrower bands, for example 1582 and 1332 cm^{-1}, are neither displaced nor changed in lower limits. The generalization of experimental and theoretical data concerning this problem allows us to address a new type of scattering of light, namely the phonon-like scattering of light, contrary to the Raman scattering (RS) on molecule vibrations or phonons in perfect crystals. The phonon-like scattering, as a characteristic of disordered phases, is not described by a definite wave vector. In particular, such type of light scattering is a characteristic-like coordination.

2. Experimental Details

Because of the strong absorption in graphite at optical frequencies (the absorption coefficient is 2.4–2.6 cm^{-1} and the skin depth at $\lambda_L = 514.5$ nm is about 400 Å), we have used the Brewster backscattering geometry in our experiments. The light source used was a 514.5-nm and 488-nm Ar^+-laser with linearly polarized emission. A particular wavelength of an Ar^+ laser was selected with a prism located outside of a laser resonator, and a cylindrical lens was used to focus light on a 10×0.1 mm^2 spot. It is worth mentioning that the larger illuminated area can efficiently eliminate the local heterogeneity (more reliable data) and minimize the probability of radiation damage of the sample due to the resonance adsorption. The spectra were detected by an automated double spectrometer DFS-24 (LOMO, Russia) equipped with a cooled photomultiplier and a registration system working in the photon counting mode. In connection to the numerical analysis, the spectra were digitalized in a wide frequency range with a fixed increment (from 1 cm^{-1} up to 5 cm^{-1}). Because of the relatively small cross-section of Raman scattering (RS) in graphite materials and in order to obtain a more reliable information, an additional noise minimization technique was applied.

In particular, the relatively wide spectral windows of 3–5 cm^{-1}, long acquisition time, and optimized digital averaging of spectra with a variable spectral window were used for the weak signal amplification.

Single crystals of highly oriented pyrolytic graphite (HOPG), polycrystalline anisotropic and isotropic samples with various crystallite sizes L_a (from 200 to 1000 Å), flakes of natural graphite, samples of thermo-expanded graphite pressed at a pressure of 200 atm were investigated. In the case of anisotropic samples of single- or polycrystals, the RS spectra were collected under reflection from a fresh cleavage (along the crystalline planes) or from the sample edge, as a surface being perpendicular to the graphite planes [8]. Both spectra from the graphite plane and from the edges of a sample were studied. In the latter case, the exciting radiation has been polarized in a plane containing the optical axis c. Such a configuration is the most sensitive to out-of-plane vibration modes.

3. Results and Discussion

3.1. Doublet structure of forbidden bands and the phenomena of the distribution of intensities

Because of their strong sensitivity to the structure of materials, the studies of the forbidden bands may be more informative than the traditional investigations of the allowed band E_{2g} [1]. Typical Raman spectra of investigated graphite materials at different excitation wavelengths are shown in Figs. 1 and 2. We have carried out experimental investigations and comparative analysis of spectra in the range of the allowed E_{2g} G-band of graphite (1500–1650 cm^{-1}) and in the region of the forbidden D-band (1310–1410 cm^{-1}). All spectra were normalized to the maximum of intensity after the background subtraction. Some of the spectra are shifted along the Y-direction for clarity with an indication of the corresponding base lines. First of all, one can see that, in HOPG, a sharp Raman band with the maximum at 1580 cm^{-1} and the half-width of about 10 cm^{-1} is observed (Fig. 1). This band corresponds to the Raman active mode E_{2g} at the center of BZ, which is in agreement with [8]. The same narrow spectral band is also observed from the edges of graphite layers. These observations are in good agreement with [9]. From Figs. 1 and 2, one can also observe that, with increasing a degree of disorder, the allowed bands E_{2g} broaden, "move" to the high-frequency region by 5–7 cm^{-1} and cause a well-pronounced asymmetry on the high frequency
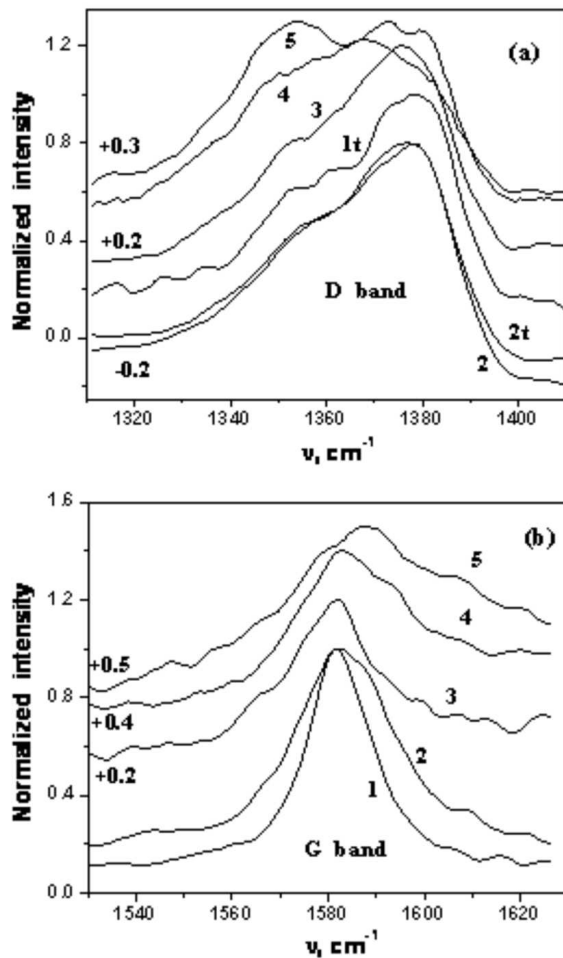
Fig. 1. Raman spectra of various forms of graphitic carbon in the region of "forbidden" D (*a*) and graphite G (*b*) bands normalized to the maximum of the intensity recorded under excitation with a wavelength of 514.5 nm for: (*1*) single crystal of highly oriented pyrolythic graphite (HOPG), (*2*) anisotropic graphite with the size of crystallites $L_a \approx 300$ Å, (*3*) natural graphite, isotropic graphite with the crystallite size of $L_a \approx 10^3$ Å, (*4*) and 200 Å (*5*). Symbol *t* shows Raman D bands registered under light scattering from the edges of corresponding samples. Some spectra are shifted along the vertical axis for clarity and corresponding values are indicated on the figure
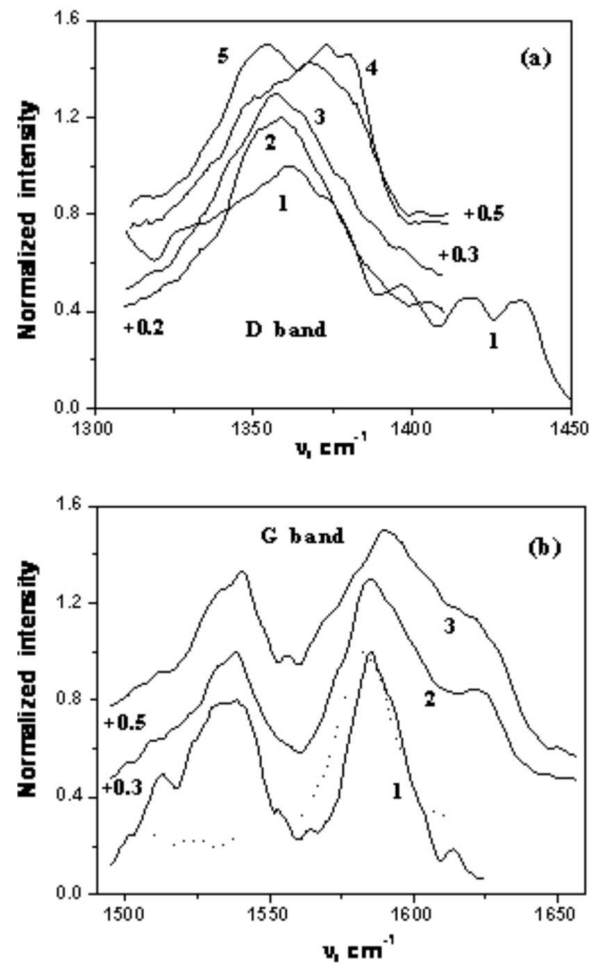
Fig. 2. Raman spectra of various graphite modifications in the region of D (*a*) and graphite G (*b*) bands normalized to the maximum of the intensity recorded under excitation with a wavelength of 488 nm for: anisotropic graphite with the size of crystallites $L_a \approx 300$ Å (curve *1*), isotropic graphite with the crystallite size $L_a \approx 10^3$ Å (curve *2*), and $L_a \approx 200$ Å (curve *3*). D bands of graphite samples with smaller (curve *4*) and greater (curve *5*) crystallite sizes (*a*), as well as the G band of anisotropic graphite (*b*, dashed line) recorded under the 514.5-nm excitation, are also shown for comparison. Some spectra are shifted along the vertical axis for clarity and corresponding values of the shift are indicated

side. For $\lambda_L = 488$ nm, a well-distinguished band at 1625 cm^{-1} appears on the high-frequency wing of the E_{2g}-band, while being practically not observable under the $\lambda_L = 514.5$ nm excitation.

The most significant changes of Raman spectra are observed in the forbidden bands near 1310–1410 cm^{-1}. For HOPG according to the selection rules, these bands should not be observed. However, in samples of anisotropic graphite with the crystallite size $L_a = 300$ Å,

these bands have intensities comparable with the intensity of the allowed band. For the majority of samples under study, the forbidden band intensities are generally higher than the intensity of the fundamental band E_{2g}. This seemingly paradoxical situation may be natural in graphite and can be explained by the high density of vibrational states (DOS) at K and M points on the border of BZ [1]. A similar situation is also observed in the Raman spectra of a high-temperature superconduc-

tor $YBa_2Cu_3O_x$ ($6 < x < 7$) under the intensive pulse excitation (38 kW/cm^2 with $\lambda_L = 488$ and 514.5 nm) [18]. However, when the laser beam intensity is lowered to a few kW/cm^2 or when the temperature is lower than 80° K, the intensity of the forbidden bands in this superconductor also essentially decreases.

A weak resolved doublet at 1350–1370 cm^{-1} in the Raman spectra of disordered graphite was reported. However, its structure has not been investigated in detail neither in [4] nor in subsequent papers [7–13] and so has not received an appropriate physical interpretation. The detailed investigation of the shapes of the forbidden vibrational bands in various graphite materials at $\lambda_L = 514.5$ nm (part of results is shown on Fig. 1) has allowed their decomposition into bands with maxima at 1350 cm^{-1} and 1375 cm^{-1} and the observation of the Raman intensity redistribution between these forbidden bands. This phenomenon is clearly manifested by a variation of the shape of the envelope band observed in different structural forms of graphite under the same experimental conditions. In particular, for the anisotropic and several isotropic graphite samples with the average domain size of $L_a = 200$–1000 Å, the most intensive band is the one at $\nu_{\max} = 1350$ cm^{-1}. While in other misaligned graphite samples (especially in the case of reflection of RS radiation from the edge), the band at 1375 cm^{-1} is more intensive. Contrary to the G-band behavior, the observed D-line is not sensitive to the degree of grain misalignment. Previously, these bands were observed individually in different types of diamond-like amorphous films and glassy carbons depending on the excitation wavelength λ_L. In the case of $\lambda_L = 514.5$ nm, there was a possibility to distinguish between vibration bands at 1380 cm^{-1} and 1540 cm^{-1} in amorphous films and 1350 cm^{-1} and 1590 cm^{-1} in glassy carbons [6]. However, we have presented a more detailed mathematical analysis of the spectra with the decomposition of the bands of diamond-like films [15] into two (as in [6]) and more constituent lines with a possibility of the variation of their individual position, intensity, shape, and width. The experimental Raman bands were separated (a sharp peak over relatively broad band) into two components at 1347 and 1375 cm^{-1} as the most realistic scenario. One should also note that similar lines along with the intensive band at 1332 cm^{-1} are often observed in Raman spectra of a crystalline diamond doped with boron [15].

The most significant feature observed in spectra recorded with $\lambda_L = 488$ nm is the appearance of an additional relatively strong band (Ad-band) located near the G band at 1540 cm^{-1} as shown in Fig. 2,b. This band also has a doublet structure with a shoulder observed on the higher frequency side (1510 cm^{-1}). In the case of $\lambda_L = 514.5$ nm due to a low overall intensity of the lines, only a small signature of these bands can be seen in the second derivative spectra (lower frequency side of a wide E_{2g} band of the subtraction spectra is discussed in the next section of this paper). Similar bands (i.e., tunable with the variation of an incident wavelength λ_L) but without a well-pronounced doublet structure were reported for diamond-like films [6]. In amorphous carbon without annealing, such variation of the G band position was observed in the range of 1500 to 1600 cm^{-1} [9]. We believe that, as in the latter case, the assignment of the bands to the G or Ad band was ambiguous. In polycrystalline diamond films with a sharp peak at 1332 cm^{-1}, the additional broad band near 1550 cm^{-1} was also observed and ascribed to the amorphous carbon [9]. In carbon and diamond-like films, simultaneously two forbidden bands D and Ad can be observed despite the fact of their significant overlap [17]. Various physical stimuli have been applied simultaneously with Raman spectroscopy experiments in order to reveal the nature of the observed bands. As a result of the carbon film exposure to a beam of Ar$^+$ ions, the 1366-cm^{-1} band is shifted to 1382 cm^{-1}, and the band at 1571 cm^{-1} to 1520 cm^{-1}. Under the bombardment of the same films with Xe$^-$ ions, the D band is observed at 1380 cm^{-1}. Under the Xe$^-$ bombardment, the Ad band is shifted from 1508 cm^{-1} to 1520 cm^{-1} [6, 17]. Under the annealing of amorphous carbon at 600 °C, the λ_L-dependent Ad band becomes narrower and is stabilized at 1600 cm^{-1}, probably being transformed into the G band [9]. Similarly, in the range corresponding to the position of the D, Ad, and G bands under appropriate resonance conditions, we have observed a doublet structure with the corresponding frequencies 1350–1375 cm^{-1}, 1510–1540 cm^{-1}, and 1590–1626 cm^{-1}. It is significant that the frequencies of the doublet components of the D and Ad bands remain practically unchanged, contrary to the E_{2g} band behavior as illustrated in Figs. 1 and 2.

3.2. Origin of the doublet structure of vibration bands of graphite materials

The existence of the doublet vibration bands was reported for graphite materials in many publications. For example, the high resolution spectra of the G band (1580 cm^{-1}) typically show a high-frequency shoulder at 1620 cm^{-1}, which is particularly well observed under $\lambda_L = 488$ nm (see Fig. 1) [4, 8, 11, 16]. In the overtone region of quasicrystalline graphite, a doublet band 2695–2735 cm^{-1} [4] (also at 2697–2739 cm^{-1} [5]) or a

band with a low-frequency shoulder near 2735 cm^{-1} has been reported [11,16]. In the same range of the spectra of glassy carbon, an intensive single line at 2720 cm^{-1} is observed, the frequency of which is strictly correlated with the position of the D band at 1360 cm^{-1} under variation of the crystalline size [5]. This observation confirms the interpretation of the 2720-cm^{-1} band as an overtone of the D band. Interestingly, a doublet overtone band (components at 2697 and 2739 cm^{-1} at $\lambda_L = 488$ nm) reported in [5] is, in fact, a manifestation of overtones of the components of the D band at 1350 cm^{-1} and 1375 cm^{-1} (also observed by us) and which can be tuned significantly with a variation of λ_L. The existence of the doublet structure and its frequency dependence have been explained in [5] through a coupled double resonance (CDR) concept. In accordance to this approach, the appearance of this doublet is caused by a splitting of the electronic π zone of 3D graphite due to interactions between neighboring graphite sheets. As a result, there are two wave vectors (for excited electrons $\mathbf{k}$ and for excited phonons $\mathbf{q}$) corresponding to resonance laser photons $\eta\omega_L$ which results in the appearance of two vibration frequencies corresponding to two known dispersion bands. However, as pointed in [5], the conditions of CDR are satisfied only for the phonon wave vectors larger than those of photons. Therefore, the effect can be observed in RS spectra of the first order only. In accordance to such a consideration, the existence of a forbidden D band in the fundamental frequency range reported in [4, 5] due to vibration states near K point of the Brillouin zone (in the KM direction) for highly disordered boundary regions of crystalline domains is possible. In these disordered regions, the graphite sheets are practically decoupled, and the dispersion equations for a single graphite layer can be used as a good approximation for the D band analysis [5]. Naturally, the D band and its overtone appear as a single line in this case (which is supported both by the theoretical consideration and by experimental observations [5]). This is the reason behind the doublet structure of the forbidden D band observed by us, not being explained in the framework of the CDR model. Nevertheless, the effect can find a reasonable explanation through closely located dispersion bands or the same phonon dispersion band considered at different points of BZ. In accordance to [11, 12], such a situation is realized for a weak 2450-cm^{-1} band having two components at 2435 cm^{-1} and 2468 cm^{-1} interpreted as the combination tones of the fundamental bands at 830, 850, and 1620 cm^{-1}.

The doublet structure of the D band ($\lambda_L = 514.5$ nm) has been observed in the spectra of all carbonaceous ma-

terials under study. Thus, for $\lambda_L = 488.0$ nm, the D band with maxima near 1357 cm^{-1} was practically simple, which is illustrated in Fig. 1,c, where the doublet D bands excited by $\lambda_L = 514.5$ nm were given for comparison. One can see that these single bands correspond to the low-frequency component with 1350 cm^{-1}. A small high-frequency shift of the D band under excitation at $\lambda_L = 488.0$ cm^{-1} is connected with a regular frequency shift, when λ_L is changed [4–6]. However, this shift is essentially smaller than the frequency interval of the observed doublet. Summarizing the above discussion, one can say that the doublet structure of the D, Ad, and G bands observed by us is probably associated both with the peculiarities of a structure of carbonaceous materials and with the resonance conditions of excitation of the Raman spectra. The fact of the existence of the overtone doublet structure in the RS spectra of graphite single crystals and the observation of three components in the overtone Raman spectra of hydrocarbon films [7], which are connected with a doublet structure in the fundamental region and the observation of the doublet structure 1350–1375 cm^{-1} in diamond-like films and even single diamond crystals [15], emphasizes the need for the additional analysis of the CDR conception and a more detailed explanation of the origin of the doublet band structure.

3.3. Subtraction spectra analysis

The phenomena of the intensity redistribution of forbidden peaks, which is observed as a change of line shapes in various structural forms of graphite, can be used for identifying the components of observed doublets. An approximate determination of the shape and the position of these constituting peaks can be done via the mathematical procedure of subtraction of the corresponding normalized spectra. The spectra were normalized to their maximal intensity after the preliminary subtraction of the background. Some of the subtraction spectra obtained under such a procedure are shown in Fig. 3.

In particular, the plot illustrates the extraction of the high frequency component (Fig. 3,a) and the low-frequency one (Fig. 3,b). One can see that the low frequency component is broader and has some low-frequency shift from the original position 1350 cm^{-1}. This fact can be identified by the existence of the third low-frequency component of the forbidden band. As a result, the subtracted bands in Fig. 3,b have broader shape and are shifted due to a combined contribution from two low-frequency components. Figure 3,a shows the subtraction spectra of the G band of isotropic graphite
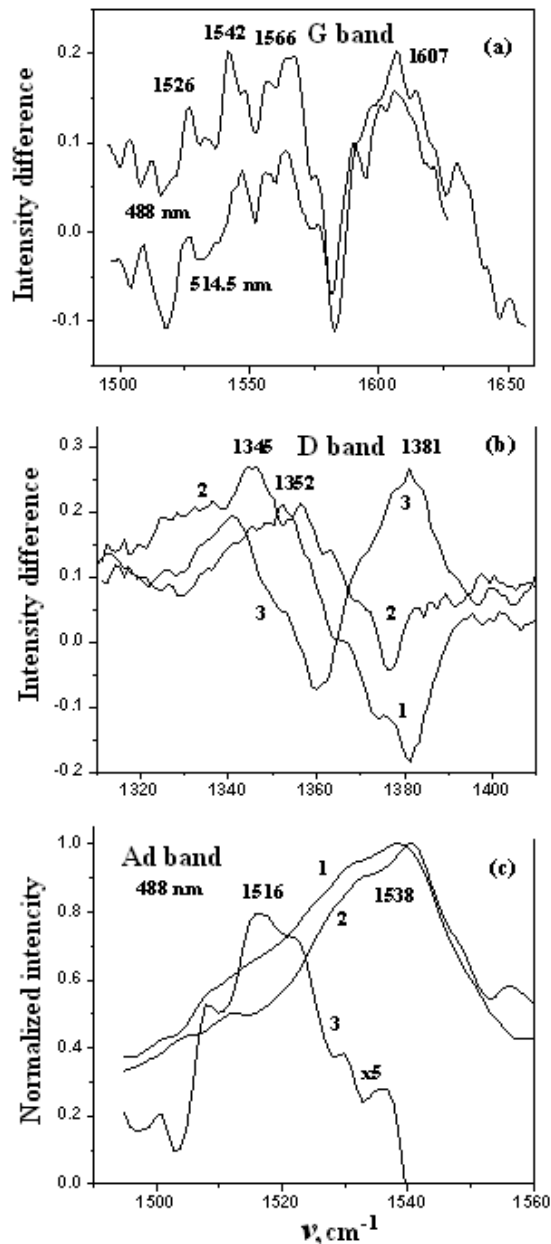
Fig. 3. G band (*a*), D band (*b*), and Ad band (*c*) portions of differential Raman spectra obtained by the subtraction of normalized spectra of various graphite materials: (*a*) two isotropic graphite samples with crystallite size L_a of 200 and 1000 Å ($\lambda_L = 488$ nm and $\lambda_L = 514.5$); (*b*) two isotropic graphite samples ($L_a \approx 200$–1000 Å) recorded under excitation with $\lambda_L = 514.5$ nm (curve *1*), isotropic and natural graphite (both for 514.5 nm) (curve *2*), and two isotropic graphite samples (200–1000 Å crystallite size) for excitation with $\lambda_L = 514.5$ and 488 nm, correspondingly (curve *3*); (*c*) normalized spectra of isotropic graphite ($L_a \approx 200$ Å) (curve *1*), anisotropic graphite ($L_a \approx 300$ Å) (curve *2*), and their differential spectrum magnified 5 times (curve *3*) recorded at $\lambda_L = 488$ nm

with various sizes of crystallites L_a. In accordance to the existing dispersion data for crystalline graphite, the maximum of the dispersion band of E_{2g} mode coincides with the center of BZ, which should appear in a pronounced asymmetry of the band versus the frequency and its bathochromic shift. In Fig. 3,*a*, the results of subtraction of G-bands of isotropic graphite characterized by crystallite size L_a are shown. As L_a decreases, the spectral bands in the G-band region should decrease because of the selection rules and the dimensional disclosing of the vibrational zone [5, 16]. It is well known that the maximum of the dispersion branch of E_{2g} mode is located at the center of BZ and manifests itself by an asymmetry of the band and a shift to the low-frequency region. However, as was discussed above, a high-frequency asymmetry was experimentally observed. This fact is explained by the relaxation of selection rules and the simultaneous presence of dipole-active E_{1u}-mode (1588 cm^{-1}) together with allowed $(E_{2g})_2$-mode. For an isotropic sample with $L_a = 200$ Å, the maximum of the Raman band is observed at $\nu_{\max} = 1587$ cm^{-1}, which is very close to the frequency of E_{1u} mode. The subtraction spectra in a vicinity of the G band display the vibrational states 1600 cm^{-1} and a wide spectrum of low-frequency vibrations. The high-frequency subtraction band is caused by the states of E_{1u} mode located near the minimum and the maximum of the dispersion branch placed at the center of BZ (point Γ) and at the point Σ along the $\Gamma - K$ direction, respectively [1, 16]. Note that the states close to the maximum of the E_{1u} branch (point Σ) are displayed as a shoulder at 1625 cm^{-1} of the G band (see Fig. 3,*a*) and as an overtone band at 3248 cm^{-1} [11, 16].

The low-frequency subtractive band corresponds to the additional Ad band. The subtractive band observed in the region of the additional Ad band is shown in Fig. 3,*c* and corresponds to a low-frequency component of the second doublet.

3.4. Analysis of the asymmetry and fine band structure

The easiest way to determine the origin of the forbidden bands at 1350, 1375, and 1540 cm^{-1} is based on the consideration of their phonon dispersion curves in a graphite single crystal along the directions of high symmetry [1, 16]. The band 1375 cm^{-1} can be described as that corresponding to the longitudinal acoustic (LA) mode at M point of BZ of graphite [1]. The frequency of the band at 1350 cm^{-1} is very close to the frequency of "merged" two optical (E_{1u}, E_{2g}) and one acoustical (LA)

modes at K point of BZ. The existence of the Ad band at 1540 cm^{-1} can be explained as a state of the E_{1u}-mode near M point [1, 16]. These vibrational states on the edge of the Brillouin zone can appear in the first-order Raman spectra, even when these vibrational states are folded on the center of BZ. This remains possible in the case of the formation of a polytypic structure or structural disorder. The high intensities of bands in the region of 1350–1375 cm^{-1} and 1510–1540 cm^{-1} can be explained by a high density of available vibrational states (DOS) in the corresponding areas in comparison with those of the $(E_{2g})_2$-mode at the center of BZ.

The existence of a sharp edge of the band and its asymmetry may be important for the correct interpretation of vibration spectra. For instance, the band at 3250 cm^{-1} observed in [16] has a high-frequency edge, which is in agreement with its common interpretation as an overtone of the 1625 cm^{-1} vibration state of mode E_{1u} near the maximum at Σ point of the dispersion curve along the ΓK axis of BZ [1]. On contrary, the band at 2450 cm^{-1} has a low-frequency edge [16]. Hence, this vibration should correspond to the minimum of the phonon dispersion curve. Therefore, they cannot be considered as the components of 830, 850, and 1620 cm^{-1} vibrations, as considered in [11], because each of the latter vibration states corresponds to the maximum of the dispersion curve. More likely, this band is located near the bottom of the zone near 1225 cm^{-1} frequency. The vibrational state, which is close in frequency and corresponds to the transverse acoustic (TA) branch at K point, cannot be assigned to this vibration (or at least it cannot contribute considerably to this vibration state) because of its location on the top of the zone. The actual vibration state is, probably, the state of mode E_{1u} near a deep minimum of the dispersion curve at K point of BZ. In favor of such assignment is a one-side-smeared asymmetric peak observed at 2450 cm^{-1} in graphite samples with the average domain size of 1 μm and even HOPG [16]. It worth mentioning that there is a considerable discrepancy of literature data concerning the behavior of dispersion curves of E_{1u} mode near the minimum at K point. We note also that, in comparison to a broader 2450 cm^{-1} band, the one at 3250 cm^{-1} is much narrower for the same sample, and its one-side broadening is observed only in samples with much more disordered crystallites with a size of 25 Å. The difference in the broadening behaviors of these bands is due to the uncertain nature of the quasimomentum conservation law here. It shows also a smooth or sharp $\omega(k)$ dispersion near the extremes of the dispersion curve. The above arguments can be

used for a more precise estimation of the phonon dispersion.

The observed fine structure of the 1350- and 1375-cm^{-1} doublet components can be also be used for interpreting the bands. In particular, for highly dispersed graphite materials (compressed samples of thermally expanded small-grain or colloidal graphite) and anisotropic graphite under light scattering from the edges, each of the 1350- and 1375-cm^{-1} bands is constituted with two elementary components (1350, 1358 cm^{-1} and 1370, 1379 cm^{-1}) in accordance to the second derivative spectra. The singlet structure of the second derivative spectra gives a hint of some regularity in the spectrum component positions constituting the broad vibration band. These observations support the idea of universality of the structure formation in dispersed graphite materials. The important things here are that the high-frequency component is more intense for the 1375-cm^{-1} band, while the low-frequency component is more intense for the 1350-cm^{-1} band. This interpretation is confirmed by the fine structure of the 1350–1375-cm^{-1} doublet. If we consider the secondary doublet structure to be caused by some physical factors (such as polytypic), the observed intensity correlation of the fine structure should confirm the dominant contribution from the LA mode to the 1375-cm^{-1} band. In the case of a considerable contribution to the 1350-cm^{-1} band from the states located close to the minimum of the optical modes, the low-frequency component should dictate its fine structure, which is in agreement with the observed spectra. The considerable contribution to the 1350-cm^{-1} band originates from the states close to the minimum of the optical modes near point K of BZ.

However, such interpretation may be not exhaustive. One should take several more arguments into account. Firstly, the DOS maximum should be "tethered" to some particular frequency while the observed spectral bands are frequency shifted, depending on the excitation wavelength. Secondly, the bands with wavenumbers of 1350 and 1370 cm^{-1} have been observed in the IR spectra of diamonds [18, 19]. The 1350-cm^{-1} band corresponds to a separate nitrogen impurity of the substitution type. In this case, according to an electron spin resonance data, an extra-electron is located on one of the C=C chemical bonds, extending its length up to 11%. As a result, the symmetry is decreased at least down to C_{3v}, when all vibrational states are allowed in IR and RS spectra. The band at 1370 cm^{-1} corresponds to aggregations of nitrogen plates in plane 100. A decrease in the linear sizes of graphite plates leads to an increase of the IR bands frequency to 1375 cm^{-1}, when the size reaches 200 Å [1]. In

some polycrystalline diamond films, an intensive band at 1332 cm^{-1} and a band at 1550 cm^{-1} have been observed simultaneously. The band at 1550 cm^{-1} may have the same origin as "our" Ad band [9]. Its intensity decreases with the increase of the excitation light frequency. Moreover, diamond-like samples synthesized from carbon vapor are characterized with a sharp diamond band at 1330 cm^{-1} [5–7]. In addition, the wide bands with variable maximum in the limits of 1440–1550 cm^{-1} are typically observed, although such states do not exist in the DOS of amorphous diamond [20]. Additionally, a sharp peak at 1375 cm^{-1} can be found in samples of diamond-like films with impurities [15]. All these results show that the observed bands cannot be interpreted as those resulting from the DOS maximum: the existence of the remaining vibrational state zone structure cannot be explained by the dispersion branch alone, but rather by the existence of wide bands which should be taken into account.

3.5. Origin of the observed bands and their frequency shift

In accordance to the CDR concept, the second-order Raman spectra may be characterized with spectral bands (not connected to DOS), whose positions are determined by dispersion branches of the electronic or vibrational zone structure and, under strong phonon dispersion conditions, may depend on the frequency (or wavelength) of the excitation light λ_L. This approach explains the variation of the frequency of overtone vibration bands in graphite single crystals under λ_L [5]. However, this interpretation is less straightforward in application to disordered materials (graphite or diamond like) due to the observed doublet structure of forbidden bands in the range of fundamental mode frequencies. One can name several reasons why the CDR concept cannot be used in the latter case. As mentioned above, the CDR concept is valid for a direct application to the first-order Raman spectra in the fundamental region and also for highly disordered phases for those zone structures, in which vibrational and electronic states are considerably smeared. Secondly, as reported in [6] for diamond-like films, the vibration states tunable with λ_L, which have corresponding frequencies of 1380 cm^{-1} and 1540 cm^{-1} at $\lambda_L = 514.5$ nm, were observed. For glassy carbons, the corresponding bands tunable with λ_L were observed at 1350 cm^{-1} and 1580 cm^{-1}. Therefore, the bands at 1350 cm^{-1} and 1380 cm^{-1} with frequencies close to D-band doublets observed by us appeared separately in different carbon dispersion data based on the CDR. The

bands' shift observed under conditions of ionic bombardment provides, in our view, an evidence that they originate from the structural peculiarities of the matter and not from the kinetics of the RS process [17]. Thirdly, the observed overtones at 2697 cm^{-1} and 2739 cm^{-1} in graphite single crystals correspond to the fundamental states of 1347.5 cm^{-1} and 1369.5 cm^{-1}, if we take the observed zero anharmonicity of a glassy carbon into account [5]. In consideration of the same difference in λ_L, the deviation from the doublets components' positions observed by us is negligible. Moreover, the observed value of this doublet splitting is 3 to 4 times smaller than the result of theoretical calculations reported in [5]. However, the usage of dispersion relations for single-layer graphite in highly disordered regions does not lead to a doublet splitting [5]. Depending on the heat treatment, the components with a frequency lower or similar to 1350 cm^{-1} or higher than 1370 cm^{-1} are observed near the D band position in carbon films [7]. These frequencies are also probably related to the structural peculiarities of the matter. Importantly, the half-width $\delta\nu$ of the above-mentioned low-frequency components varies with λ_L in the opposite way. In the initial film, $\delta\nu$ goes down with λ_L for $\nu < 1350$ cm^{-1}, while $\delta\nu$ increases with λ_L in an annealed film for $\nu < 1370$ cm^{-1} (the latter fact may justify for their different origin) [7].

All the above factors demonstrate that the CDR concept cannot explain all known experimental results and therefore needs a generalization and a development for disordered media. Due to the absence of the long-range order in disordered (amorphous) materials, they cannot be characterized with a particular momentum of the vibrational excitation. One of the existing concepts of the violation of selection rules in the RS process is based on the wave vector shift consideration: $D\mathbf{k} = \mathbf{k}_L - \mathbf{k}_S - \mathbf{q} = 0$, where $\mathbf{k}_L$ and $\mathbf{k}_S$ are the wave vectors of the incident and scattered (Stokes) radiation, $\mathbf{q}$ is the wave vector of a phonon. The concept introduces a correlation length Λ, which characterizes the spatial distribution of the normal mode. Under such approach, q is not a proper parameter of the normal mode, and a phase shift $\Delta k = 2\pi/\Lambda$ is allowed. In amorphous media in accordance to Shuker and Gamone, the normal vibration modes and the spatial time correlation are proportional to $e^{\mathbf{qr}}e^{-r/\Lambda}$ [1]. However, in the majority of publications on the vibrational states of disordered materials, all vibration states are considered to be localized in accordance to DOS [5]. For many intermediate states of matter between the extremes of the long-range order and the random arrangement of atoms, the vibration modes are delocalized in some spatial region Λ having

wave properties and dispersion bands with the width increasing under reduction of Λ. In the case of the presence of a residue of the existing zone structure of vibrational states, which is characterized with broad energy bands rather than dispersion curves $\omega(q)$, it is possible to talk in terms of phonon-like excitations and to consider peculiarities of light scattering on them. The distinguished feature of light scattering on such states is the possibility of a considerable variation (tuning) of the frequency of spectral bands in the range of considerable widths of energy dispersion bands. In this connection, we prefer to use a special term of phonon-like light scattering to underline the difference of the process from the traditional Raman scattering, where the frequencies of the bands are fixed. A collective zone structure of a crystal is, first of all, deviated near the boundary of BZ, which is manifested by a weakening of the overtone 2720 cm^{-1} and its practically disappearance with increase of the structural disorder. This is connected with a small wavelength for states near the BZ boundary. At the center of BZ, due to longer wavelengths of the corresponding excitations, the zone structure may be preserved probably for a longer time.

In the consideration of the phonon-like scattering of light, one should consider a possibility of the existence of various metastable structural states of carbon arising, in particular, under the application of a high pressure [3, 4]. Under a pressure $P > 15$ GPa, the G band became broader. Carbon samples loose their metal shine due to the development of a broader band gap structure. Under a pressure exceeding 35 GPa, a new "hybrid" state of carbon can be found due to the amorphization of the matter. A hysteresis can be observed in cycles with increasing and decreasing pressure. Simultaneously, the optical transmittance of carbon samples arises, and they became transparent in the visible range of light, when the pressure is increasing to 35–55 GPa, while the reduction of the pressure to $P = 5$ GPa is necessary for their transformation back to the non-transparent state. The disappearance of the vibration band at 3340 cm^{-1} corresponding to the maximum of the E$_{1u}$-mode at Σ-point in the overtone region of the spectra with the increase of the pressure has been also observed [6]. The authors explained this result by a shift of this maximum to the center of BZ due to a weakening of the coupling of second neighbors, which can lead to a gaufre transformation of the graphite layers before the formation of the amorphous phase with sp^3-bonding [5]. The broadening of the G band under high pressure conditions happens mainly due to an increase of the intensity of scattered light in the low-frequency side, where the contribution

from sp^3 bonds is more significant. In accordance to [1], nearly 15% of sp^3 bonds are observed in amorphous carbon. Note also that the intensity of the 1375-cm^{-1} band is higher in the Raman spectra recorded from the sample edge (Fig. 2). That is, first of all, true for the atoms on the border of the graphite layers, where the "free" (unemployed) bonds of carbon atoms can "couple" to the neighboring layers forming electronic configurations similar to the tetrahedral sp^3 hybridization. The existence of the sp^3 hybridization in disordered carbon materials is confirmed by several other facts noticed before. At first, we should note a monotonous increase of the D-band intensity with the degree of disorder [11–13]. Unlike the behavior of other bands in the region of the fundamental bands, overtones, and combination tones show the increasing intensity with the degree of disorder, which is followed by the decreasing intensity caused by the disappearance of the zone structure. The existence of sp^3 hybridization has also been confirmed by studies of the radial distribution of the electronic density and of the angular dependences of γ-quanta created during the annihilation of positrons and electrons in carbon materials participating sp^2 or sp^3 hybridization [17]. Observation of the 1350- and 1375-cm^{-1} bands in diamond materials undoubtedly demonstrates the important contribution of sp^3 hybridization in their Raman spectra.

4. Summary

In this work, we demonstrated how changes of the structure of graphite materials lead to the processes of composition of phonon branches, which, in turn, bring to the existence of special vibrational states located out of the center of the Brillouin zone and appear in the IR and Raman spectra of such materials. This phenomenon, as well as the violation of strict selection rules for the carbon systems, offers new broader applications to optical spectroscopy techniques. The intensity of the bands forbidden under strict selection rules for the space symmetry group D_{6h}^4 of graphite is nevertheless comparable to that of the allowed fundamental transitions and can be even stronger in some cases. Due to this fact, we could study, in detail, the shape of vibrational bands and reveal a doublet structure of diamond-like (D), additional (Ad), and graphite (G) bands. We have investigated the intensity and the spectral position of these bands depending on the wavelength of the exciting laser radiation λ_L. For the first time, the two components of the D band at 1350 cm^{-1} and 1375 cm^{-1} are clearly observed. Our structural study of a large number of various structural modifications of disordered graphite allowed the observa-

tion of the Raman intensity redistribution between these components depending on the degree of structural disorder. Doublet structures have been also observed for the Ad and G bands (1510–1540 cm^{-1} and 1590–1626 cm^{-1}, respectively). Similar bands were previously reported by us and other authors in diamond-like films. The detailed study of the individual components of the doublets has been executed via application of a subtraction procedure to the original Raman spectra. We demonstrate how the interpretation of the bands is possible in view of the existence of a sharp edge of the bands and their one-side "smearing" under a reduction of the crystallite size. Useful information about the existing fine structure of the band was extracted here from the second derivative spectra. We have demonstrated that the observed doublet structure cannot always be explained in the framework of the CDR concept, which was previously successfully employed for the interpretation of doublet overtone vibrational states at 2697–2739 cm^{-1} registered for a single crystalline graphite. Some of the doublet components can be observed independently in various carbon materials and, moreover, may move in their spectral position under influence of some physical factors such as the ion implantation or the external pressure. These observations show the relationship of the doublet components to the structure of the materials under study and not to kinematic peculiarities of the Raman scattering. The theory of disordered condensed matter has else to be developed to include the consideration of such processes. Summarizing the experimental and theoretical results of Raman spectroscopy studies of carbon materials, we can conclude that the D and Ad bands are caused by various types of chemical bonding, including sp^2 and sp^3 hybridizations, in graphite materials (i.e., they are especially sensitive to intermediate structural states between a graphite-like and diamond-like coordination). As a consequence, the intensity of the band at 1350 cm^{-1} is to be higher, when the contribution of sp^2 hybridization is predominant. On the other hand, sp^3 hybridization prevails in the case of maximum intensity of the 1375 cm^{-1} band. In a similar fashion, the intermediate carbon structures determine the behavior of the additional Ad band. The studies carried out by us and the analysis of the extensive literary data have allowed the formulation of a new concept of phonon-like scattering of light applicable to a wide class of disordered condensed media. This not very common type of dispersion of light is specific for substances that are characterized with broad energy bands and poorly defined wave vector, rather than narrow dispersive branches $\omega(q)$. On contrary to a normal Raman

scattering, where the frequencies of bands are fixed, the dependence of the positions and the intensities of vibrational bands on the experimental conditions (in particular, on the frequency of excitation radiation) is a typical feature of the phonon-like scattering processes. As we demonstrate in our study, carbon structures intermediate between graphite and diamond coordination (such as a range of metastable carbon structures formed under high pressures) with various contributions from sp^2 and sp^3 hybridizations make a significant contribution to the phonon-like Raman scattering. The intermediate states and the related phonon-like scattering of light are proven to be extremely sensitive to the conditions of the formation of carbon materials and to physical factors (ion implantation, thermal annealing, and radiation). Naturally, the intermediate structures of carbon possess specific electronic states, which may lead to specific resonance effects in Raman spectra observed by us and other authors. The effect reported here, involving the redistribution of the Raman intensity between the forbidden bands in the spectra of phonon-like scattering can be explained by the dependence of a residue of the zone structure on the structural modification of the matter. More studies both theoretical and experimental are needed to clarify the exact mechanisms of this phenomenon. The proposed concept and the obtained results may be useful for the investigation of metastable phases of amorphous carbon, scenarios of graphite-diamond transitions, and determination of the origin of high-temperature superconductivity.

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ФОНОНОПОДІБНЕ РОЗСІЯННЯ СВІТЛА
У ПОЛІКРИСТАЛІЧНИХ ВУГЛЕЦЕВИХ СТРУКТУРАХ

*А.П. Науменко, М.Є. Корнієнко, В.М. Ящук,
В.М. Близнюк, С. Сінгаманені*

Р е з ю м е

Розглянуто новий тип непружного розсіяння світла у невпорядкованих конденсованих середовищах, коли, на відміну від КР світла на коливаннях молекул та фононах з фіксованими коливальними частотами, відбувається зсув коливальних частот зі зміною частоти збудження. Це фононоподібне розсіяння світла притаманне проміжним станам упорядкування речовини із "замитою" зонною структурою при переході від молекул до кристалів, зокрема, для різноманітних вуглецевих структур, які є проміжними між графітовою та алмазною координацією та містять деякі частки sp^2- та sp^3-гібридизації. У дефектній (D) та додатковій (Ad) смугах чітко спостерігається дублетна структура та встановлений перерозподіл інтенсивностей між компонентами дублету 1350 і 1375 см$^{-1}$ для різних структурних модифікацій графіту. Виділення форм окремих складових компонент складних смуг здійснено у різницевих спектрах. Обговорюється природа дублетності коливальних смуг та обмеженість застосування концепції подвійного зв'язаного резонансу. Для встановлення природи аналізується асиметрія та тонка структура смуг, а також поведінка аналогічних смуг в алмазоподібних та вуглеводневих плівках та метастабільних фаз вуглецю при високих тисках.