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Fundamentals, overtones, and combinations in the Raman spectrum of graphite

Yasushi Kawashima
Department of Mechanical Engineering, Faculty of Engineering, Tokai University, Hiratsuka, Kanagawa 259-12, Japan

Gen Katagiri
Toray Research Center, Inc., Otsu, Shiga 520, Japan

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Raman spectra of highly oriented pyrolytic graphite (HOPG) and pyrolytic graphite (PG) have been investigated in the region between 200 and 7000 cm^{-1}. The high signal-to-noise ratio measurements reveal the existence of new bands in the fundamental and the higher-order regions. The excitation wavelength (λ) dependence of Raman spectra is also studied using 457.9-, 488.0-, and 514.5-nm excitation. It is found that the λ dependence of Raman bands is classified into three types, i.e., upward shifted, insensitive, and downward shifted bands; with the increase of the excitation wavelength. The ratios of the relative intensities of Raman bands against the E_{2g} mode (1580 cm^{-1}) between the edge and the basal planes ($\bar{I}_{\text{edge}}/\bar{I}_{\text{basal}}$) are examined. The fundamental and higher-order modes which become Raman active by degradation of translational symmetry increase their relative intensities in the edge plane. On the other hand, the overtone and combination modes satisfying the wave-vector selection rule by the combination of nonzero wave vectors with opposite sign show similar relative intensities between the basal and the edge planes. The assignments of Raman bands is conducted using the λ dependence and $\bar{I}_{\text{edge}}/\bar{I}_{\text{basal}}$ for HOPG and PG. Most of the Raman bands in the higher-order region can be successfully assigned as the overtones and combinations between *G*, *D*, and *D'* modes. It is suggested that the additional fundamental modes exist at 810 and 1080 cm^{-1} which are due to features in the density of states other than the 1355- and 1620-cm^{-1} modes. These fundamentals show λ dependence opposite to the 1355-cm^{-1} mode. Although some of the observed fundamentals or higher-order modes for HOPG ($\sim$1480 and 1754 cm^{-1}) and PG (1469 cm^{-1}) in this work cannot be completely explained by the existing density-of-states calculation, it is definitely denied that they are due to adsorbates, oxidized species, and other impurities.

I. INTRODUCTION

Single-crystal graphite belongs to the D_{6h} symmetry and has vibrational modes $2E_{2g}$, $2B_{2g}$, E_{1u}, and A_{2u}.[1-6] Only the $2E_{2g}$ modes are Raman active. Highly oriented pyrolytic graphite (HOPG) shows these two E_{2g} modes at 42 and 1581 cm^{-1},[1,4] but also exhibits three distinct second-order features at $\sim$2440, $\sim$2730, and $\sim$3240 cm^{-1}.[4,7] The first-order spectrum of microcrystalline graphite shows additional bands at around 1360 and 1620 cm^{-1} not observed in single-crystal graphite.[1,3,4]

The appearance of the additional features in the fundamental region has been explained by several workers.[1,4,7-15] Tuinstra and Koenig have attributed the 1360-cm^{-1} band to an A_{1g} mode which becomes Raman active due to the finite crystal size.[1] The second-order bands have been assigned to the combined density of states of two phonons of equal and opposite nonzero wave vector by Nemanich and Solin.[4] Furthermore, the first-order additional bands have been interpreted as fundamentals corresponding to high density of phonon states because of their having counterparts in the second-order Raman spectrum of single-crystal graphite.[4] The appearance of such Raman forbidden fundamentals has been explained on the basis of the wave-vector selection-rule relaxation that results from finite-crystal-size effects.[4,9-11] Some workers have considered such Raman-forbidden bands to be ascribed to the existence of specific vibrations due to $\mathrm{C}\overline{\cdots}\mathrm{O}$ or C=C groups of surface oxidized species.[12,13] The assignments of the Raman-forbidden bands to high density of states are consistent with the following facts: (1) the overtones can be found in the spectrum of HOPG without observing the fundamentals; (2) the intensities of fundamentals are smaller than those of the overtones in pyrolytic graphite (PG). But, the peak positions in the density of states calculated using several models[4,8-10] do not agree with those of the corresponding bands observed in the Raman spectrum of graphite. Furthermore, several peaks in the calculated density-of-states spectra[4,8-10] have not been observed at the corresponding positions in the Raman spectrum of graphite.

In order to give a more complete explanation for the Raman scattering of graphite, it is necessary to detect the other bands corresponding to peaks in the density of states by higher signal-to-noise ratio measurements and to determine their mode frequencies accurately. The condition for the appearance of Raman-forbidden fundamentals corresponding to features in the density of states has not been completely clarified. However, overtones and combinations corresponding to the combined high density of states of phonons with nonzero wave vector possibly become observable if the sum of their wave vectors balances the change in wave vector of the scattered photon.[16] The high-order spectra are expected to enable one to notice the existence of Raman-forbidden fundamentals attributed to features in the density of states not observed in the first-order spectra and furthermore to reveal a

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combination of the high density of states that becomes observable. The 1360- and 1620-cm^{-1} bands become observable not only in microcrystalline graphite but also in the edge plane due to the breakdown of translational and local lattice symmetries.[14] These bands are considered to be related to the presence of the crystalline edge rather than small microcrystallites.[14,15] Other bands corresponding to peaks in the density of states are expected to become observable at the edge plane with the high signal-to-noise ratio measurement. The peak positions of other bands attributed to features in the density of states possibly depend on excitation wavelength λ similar to the 1360-cm^{-1} band.[17,18] The λ dependence of the Raman peak frequency will also be useful for the assignments of the higher-order bands, since higher-order bands should follow the sum of the λ dependence of the fundamentals.

In this work, Raman spectra of HOPG and PG are presented in the fundamental and the higher-order regions. The excitation wavelength dependence of the Raman spectra is also investigated using 457.9-, 488.0-, and 514.5-nm excitation and is utilized for the interpretation of the assignment. In addition, Raman spectra of PG edge plane are examined. The effect of the crystalline edge can be discriminated by the comparison of relative intensities of Raman bands against E_{2g} mode in PG edge plane with those in PG basal plane. On the basis of the results, we discuss the origin of the Raman bands observed in the fundamental and higher-order region.

II. EXPERIMENT

Raman scatterings from HOPG and PG were obtained at room temperature in a helium atmosphere with 457.9-, 488.0-, and 514.5-nm excitation. The scattered light polarized parallel to the incident radiation was dispersed by a double-grating monochromator (Jobin Yvon, Ramanor U-1000) and detected by a cooled photomultiplier tube (Hamamatsu R943-02). Although relatively high laser power (50–100 mW) and long accumulation (20 h) were required for the measurements of Raman spectra with the high signal-to-noise ratio, no spectral change due to the damage of samples was observed in the course of repeated measurements. The edge planes of PG were prepared by the previously described method.[14] The polarizations of both the incident and scattered lights were kept parallel to the graphitic planes.

III. RESULTS AND DISCUSSION

The Raman spectra of HOPG cleaved basal plane, and the basal and the edge planes of PG in the region between 200 and 7000 cm^{-1} are shown in Fig. 1. The Raman spectrum of HOPG basal plane shows distinguishable peaks at 1480, 1754, 2050, 2180, 3170, 4050, 4320, ~4820, ~5400, and 5900 cm^{-1}, in addition to the E_{2g} band (1581 cm^{-1}) and overtone bands at 2434, 2736, and 3248 cm^{-1} which have been attributed to overtone scatterings from features in the density of states.[4] The 1480-cm^{-1} band has already been observed for Graphon carbon black and assigned to $C\overline{\cdots}O$ vibrations of surface carboxylates or related oxidized species.[12] However, this is an observation in the Raman spectrum of HOPG. We suggest later that the 1480-cm^{-1} band is not due to surface oxidized species but inherent in the graphite lattice vibrations.

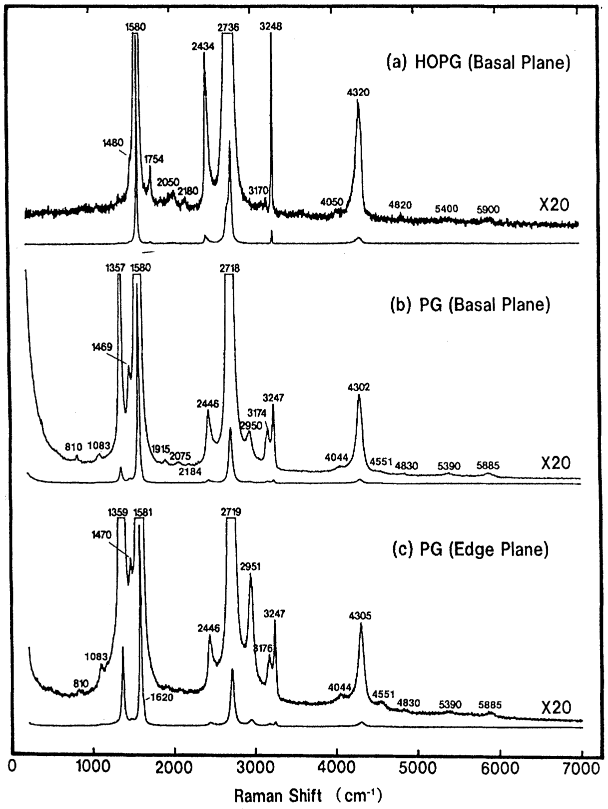

FIG. 1. Raman spectra of graphite with 488-nm excitation. Laser power at the sample was 50–100 mW; spectral resolution, 10 cm^{-1}. Spectra (a), (b), and (c) are obtained for HOPG basal plane, PG basal, and edge planes, respectively.

In the Raman spectrum of PG basal plane, in addition to E_{2g} band (1580 cm^{-1}), additional Raman-forbidden fundamentals (1357 and 1621 cm^{-1}) (Refs. 1 and 20) and overtones (2446, 2718, and 3247 cm^{-1}), fundamental and higher-order bands can be observed at 810, 1083, 1469, 1915, 2075, 2184, 2950, 3174, 4044, 4302, 4551, 4830, 5390, and 5885 cm^{-1}. The Raman spectrum of PG edge plane shows peaks at the same positions as those of PG basal plane. The relative intensities of the 1083-, 1357-, 2950-, and 4550-cm^{-1} bands to the E_{2g} band in PG edge plane are stronger than those in PG basal plane. The 1621-cm^{-1} band can be clearly observed in PG edge plane. The 2950-cm^{-1} band has already been assigned to a combination of 1357- and 1621-cm^{-1} bands or 1357-cm^{-1} and E_{2g} bands.[4,19,20] Both the peaks observed at 3170 and 3174 cm^{-1} for HOPG and PG, respectively, seem to be an observation of overtone of 1580-cm^{-1} band, implying that signal-to-noise ratio of the present Raman spectra is considerably higher than those of the spectra obtained heretofore.

Raman peak positions for the basal and the edge planes

TABLE I. Relative intensities to the E_{2g} band of peaks in PG basal and edge plane spectra.

$\Delta\nu$, cm^{-1}	Relative intensity		
$\lambda=488.0$ nm	PG (basal) $\bar{I}^{\mathrm{PG}}_{\mathrm{basal}}(\Delta\nu)=I_{\Delta\nu}/I_{E_{2g}}$	PG (edge) $\bar{I}^{\mathrm{PG}}_{\mathrm{edge}}(\Delta\nu)=I_{\Delta\nu}/I_{E_{2g}}$	$\bar{I}^{\mathrm{PG}}_{\mathrm{edge}}(\Delta\nu)/\bar{I}^{\mathrm{PG}}_{\mathrm{basal}}(\Delta\nu)$
810	~0.0015	~0.0013	~0.87
1083	0.0014	0.0028	2.00
1357	0.076	0.40	5.26
1469	~0.0083	~0.0075	~0.90
1620		~0.022	∞
2446	0.014	0.016	1.14
2718	0.27	0.29	1.07
2950	0.0088	0.036	4.09
3174	0.0098	0.012	1.22
3247	0.017	0.022	1.29
4044	0.0017	0.0034	2.00
4302	0.020	0.023	1.15
4550		0.0024	∞
4830	~0.00041	~0.00046	~1.12
5390	0.00087	0.00088	1.01
5885	0.0011	0.0012	1.09

of PG and the relative intensities with respect to the E_{2g} band of Raman bands in the edge and basal planes ($\bar{I}_{\mathrm{edge}}$, $\bar{I}_{\mathrm{basal}}$), are shown in Table I. It also includes the values of $\bar{I}_{\mathrm{edge}}/\bar{I}_{\mathrm{basal}}$, revealing that the bands at 1083, 1357, 2950, and 4550 cm^{-1} increase their relative intensities in the edge plane.

The Raman spectra in the region between 200 and 7000 cm^{-1} of PG basal plane obtained with 457.9-, 488.0-, and 514.5-nm excitation are shown in Fig. 2. Although some bands have been reported to be dependent on λ,[17] it is found that the λ dependence is more widely observed for Raman spectra of graphites. The bands observed for PG can be divided according to the λ dependence of peak position into the following classes: (1) 1357-, 2718-, 2950-, 4044-, 4302-, 4551-, 5390-, and 5885-cm^{-1} bands that shift to lower frequency with increasing λ; (2) 810-, 1083-, 1469-, and 2446-cm^{-1} bands that shift to higher frequency with increasing λ; and (3) 1580-, 1621-, 3174-, and 4830-cm^{-1} bands that are insensitive to λ. Here the frequencies indicated are the values in the case of 488-nm excitation. The peak positions for each excitation are listed in Table II, which also includes the inclinations $\delta(\Delta\nu)/\delta\lambda$ of the linear relations and the assignments. The magnitude of all the band shifts has a linear dependence on excitation wavelength. As indicated in Table II, the 1357-, 1580-, and 1620-cm^{-1} bands are referred to as the *D*, *G*, and *D'* bands according to Ref. 17, respectively. It is noted that the Raman spectrum of HOPG also shows λ dependence and can be interpreted in a similar manner to PG. Though the *G* band at 1580 cm^{-1} is assigned to E_{2g} mode, we suggest later that the *G* band also includes a mode corresponding to a high density of states.

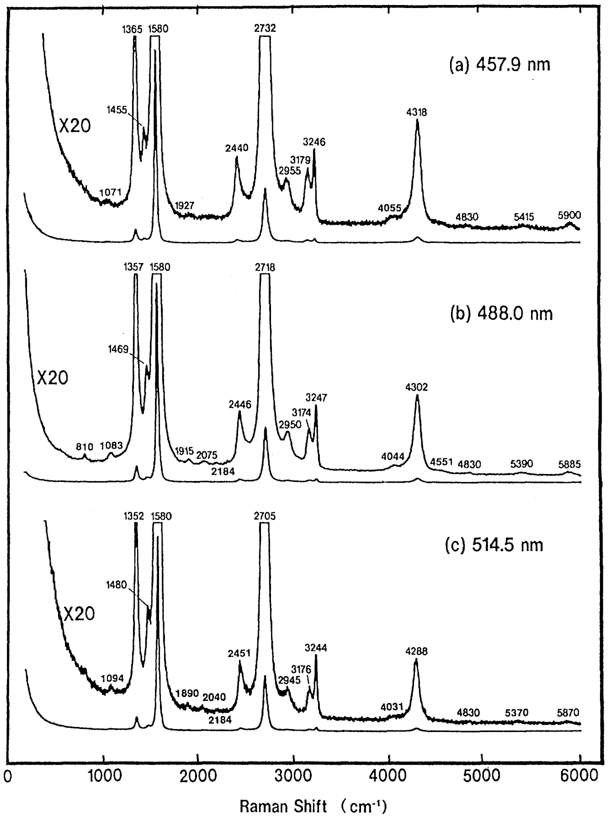

FIG. 2. Raman spectra of basal plane PG with (a) $\lambda=457.9$ (b) 488.0, and (c) 514.5 nm. Laser power at the sample was 50–100 mW; spectral resolution, 10 cm^{-1}.

TABLE II. Peak positions, $\Delta\nu$ (cm^{-1}), of basal plane graphite for $\lambda=457.5-514.5$ nm, the magnitude of the band shifts, $\delta(\Delta\nu)/\delta\lambda$, and the assignments. (*) Determined on the edge plane of PG. $\delta(\Delta\nu)/\delta\lambda$ was obtained using the least-squares fitting.

$\Delta\nu$, cm^{-1}					
HOPG	PG			$\delta(\Delta\nu)/\delta\lambda$ cm^{-1}/nm	Assgnt.
$\lambda=488.0$ nm	$\lambda=457.9$ nm	$\lambda=488.0$ nm	$\lambda=514.5$ nm		
	~803*	~810*	~820*	0.30	
	1071*	1083*	1094*	0.41	
	1365	1357	1352	−0.23	D
~1480	1455	1469	1480	0.44	?
1580	1580	1580	1580	0	G
	1623*	1621*	1622*	~0	D'
1754					?
	~1927	1915	~1890	−0.65	?
2050		2075	2040	−1.32	?
2180		~2184	~2184	~0	810+D
2434	2440*	2446*	2451*	0.19	1083+D
2736	2732	2718	2705	−0.48	2D
	2955	2950	2945	−0.18	$D+G$
3170	3179	3174	3176	~0	2G
3248	3246	3247	3244	~0	2D'
4050	~4055*	~4044*	~4031*	−0.42	3D?
4320	4318	4302	4288	−0.53	2$D+G$
	4558*	4551*	4544*	−0.25	$D+2G$
~4820	~4830	~4830	~4830	~0	2$D'+G$
~5400	5415	5390	5370	−0.80	4D
~5900	5900	5885	5870	−0.53	2$D+2G$

Before we investigate new bands observed in the first- and second-order region, we first examine the assignments of the third- and fourth-order bands using λ dependence of the peak positions.

The 4320-cm^{-1} band has already been observed for HOPG.[15] However, the peak position has not been accurately determined because of the low signal-to-noise ratio measurement. The 4320-cm^{-1} band shifts with λ at the same rate of the 2D band and its frequency is almost equal to the sum of those of the 2D and G bands ($2736+1580=4316$ cm^{-1}). A possible assignment is $2D+G$ which is the same as that reported in Ref. 15. The frequency of the 4320-cm^{-1} band is close to that of the H-H stretching mode (~4156 cm^{-1}). However, this band cannot be due to adsorbed H_2 species, because the frequency of the H-H stretching mode is expected to be independent of λ. In addition, the Raman frequency of the adsorbed species is expected to be lower than that of the free molecules, since the force constant becomes smaller by adsorption.

The 4551-cm^{-1} band shifts with λ at the same rate of the D band and its frequency is consistent with the sum of those of the D and 2G modes ($1357+3170=4527$ cm^{-1}), implying that it is the combination, $D+2G$. The 4830-cm^{-1} band is independent of λ and can be attributed to the combination of λ insensitive 2D' and G modes. The sum of the frequencies of 2D' and G (4822 cm^{-1}) is nearest to the 4830-cm^{-1} value comparing with those of combinations of 3D' (4863 cm^{-1}), $D'+2G$ (4781 cm^{-1}), and 3G (4743 cm^{-1}). The 5390-cm^{-1} band shifts with λ at quadruple the rate of the D band and its frequency is close to ($4\times1357=5428$ cm^{-1}), implying that it is a 4D band. The 5885-cm^{-1} band shifts with λ at twice the rate of the D band and its frequency is almost equal to the sum of the frequencies of the 2D and 2G bands ($2736+3170=5906$ cm^{-1}). A possible assignment is $2D+2G$.

The frequency of the 4044-cm^{-1} band agrees with those of the G+2446-cm^{-1} ($1580+2446=4026$ cm^{-1}), D'+2446-cm^{-1} ($1620+2446=4066$ cm^{-1}), and 3D ($1357\times3=4071$ cm^{-1}) modes. As seen from Table II, though the 4044-cm^{-1} band shifts to lower frequency with increasing λ, and the G and D' bands are insensitive to λ and the 2446-cm^{-1} band shifts to higher frequency with increasing λ. The 4044-cm^{-1} band can be assigned to the 3D band that should shift to lower frequency with increasing λ. However, $\delta(\Delta\nu)/\delta\lambda$ of the 4044-cm^{-1} band is much smaller than three times that of the D band which should be estimated for the 3D band.

The assignments of third- and fourth-order bands observed in the spectra of HOPG and PG are listed in Table II. We note that the combinations including the D and D' modes ($D+D'$, $D+2D'$, and $D'+2D$) are not definitely observed in both the edge and the basal planes. The absence of these combinations modes is considered to be due to the difference in the origin of the Raman-forbidden fundamentals (D and D') and the overtones (2D and 2D'). On the other hand, the combinations including the G mode ($D+G$, $2D+G$, $D+2G$, $2D'+G$, and $2D+2G$) are widely observed. It may be one of a crucial problem to clarify the way of combination between the fundamentals, in order to understand the lattice dynamics of graphite.

It is concluded from Table II that the shift of the peak frequency in the higher-order bands follows the sum of the λ dependence of each fundamental. For example, the magnitudes of the $2D$- and $4D$-band shifts are twice and quadruple that of the D band shift, respectively. The $2G$ band is λ insensitive, and $D+G$, $2D+G$, and $2D+2G$ bands follow the shift of D or $2D$ band, since the G band is λ insensitive.

In Table I, we note that the values of $\bar{I}_{\mathrm{edge}}/\bar{I}_{\mathrm{basal}}$ of the Raman-forbidden fundamentals and the higher-order modes including one Raman-forbidden fundamental such as the D, D', $D+G$, and $D+2G$ bands are much larger than unity. $\bar{I}_{\mathrm{edge}}/\bar{I}_{\mathrm{basal}}$ of the higher-order modes that consist of overtone and G modes, i.e., the $2D$, $2D'$, $2D+G$, $2D+2G$, and $2D'+G$ bands, are almost equal to unity. The $\bar{I}_{\mathrm{edge}}/\bar{I}_{\mathrm{basal}}$ can be utilized for discriminating between the modes containing one Raman-forbidden fundamental attributed to a feature in the density of states, and overtone and combination modes satisfying the wave-vector selection rule.

Although we tentatively assigned the 4044-cm^{-1} band to the $3D$ mode, this assignment is not straightforward. The following three possibilities can be considered as the origin of the $3D$ band. One is the combination $(2D+D)$ between the overtone of the two D modes with nonzero wave vector and the D mode which becomes Raman active due to relaxation of wave-vector conservation. Another is the overtone $(D+D+D)$ of the Raman-active D mode. These two types of scattering can occur only in the crystalline portion which has some kinds of crystalline imperfection degrading translational symmetry. The other is the combination of the three D modes $(3D)$ with nonzero wave vector satisfying wave-vector conservation. In this case, the scattering can occur regardless of crystalline imperfection.

The Raman spectrum for HOPG shows the $3D$ band in spite of the absence of the D band and its relative intensity against the E_{2g} band is almost equal to that of PG. These results indicate that only the last type of scattering occurs in HOPG and also in PG basal plane. The value of $\bar{I}_{\mathrm{edge}}/\bar{I}_{\mathrm{basal}}$ for the $3D$ band in PG is as large as 2.0, implying the contribution of the D band which becomes Raman active in the edge plane. This suggests that the $3D$ mode can contain all three types of scattering $(2D+D)$, $(D+D+D)$, and $(3D)$ in the edge plane. However, a ratio containing the $(D+D+D)$ type scattering seems to be less, because the value of $\bar{I}_{\mathrm{edge}}/\bar{I}_{\mathrm{basal}}$ for the $2D$ band (1.07 in PG) suggests that the $2D$ band is composed of $(2D)$ and $(D+D)$ with the ratio 1:0.07 in the edge plane. On the other hand, as already mentioned, the magnitude of the $3D$-band shift is much smaller than expected from the shift of the D band. The reason for such contradiction still remains to be clarified, as well as the assignment of the $3D$ band.

We examine the assignments of new bands observed in the first- and second-order regions on the basis of the properties of Raman-forbidden fundamentals deduced from the third- and fourth-order spectra.

The 810- and 1083-cm^{-1} bands are scarcely observed in HOPG basal plane. These bands are considered to be fundamentals attributable to features in the density of states. The value of $\bar{I}_{\mathrm{edge}}/\bar{I}_{\mathrm{basal}}$ of the 1083-cm^{-1} band is 2.0, indicating that the appearance of this band is related to the existence of the edge similarly to the D and D' bands. However, $\bar{I}_{\mathrm{edge}}/\bar{I}_{\mathrm{basal}}$ of the 810-cm^{-1} band is almost equal to unity.

The 1480-, 1915-, 2075-, and 2184-cm^{-1} bands are observed both in HOPG and PG basal planes and their relative intensities with respect to E_{2g} band are almost equal between HOPG and PG basal planes. Hence these bands are considered to be not fundamentals but overtones or combinations satisfying the wave-vector conservation rule. The 1480-cm^{-1} band has already been attributed to $\mathrm{C}\overset{\cdots}{\cdots}\mathrm{O}$ vibrations of surface oxidized species.[12] However, such interpretation cannot satisfactorily explain the fact that its relative intensities in HOPG basal, PG basal, and edge planes are almost equal. The 1480-cm^{-1} band has some properties in common with an overtone and a combination of fundamentals attributed to the strong density of states, e.g., the band has the same relative intensities in PG basal and edge planes and is observable in HOPG basal plane. The assignment of the 1480-cm^{-1} band as overtone (2×740 cm^{-1}) is inconsistent with the fact that the fundamental cannot be observed at 740 cm^{-1}. A possibility for this band is a combination, but it cannot be assigned to a combination of the fundamentals such as 810-, 1083-, 1357-, and 1621-cm^{-1} bands.

Though the 1915-cm^{-1} value is in agreement with the sum of the frequencies of the 810- and 1083-cm^{-1} bands, it is estimated from Table II that the 810+1083-cm^{-1} band has λ dependence opposite to that of the 1915-cm^{-1} band. The λ-insensitive 2184-cm^{-1} band is possibly assigned to a combination of the 810- and 1357-cm^{-1} bands ($810+1357=2167$ cm^{-1}) having opposite λ dependence. We will discuss the possibility of combinations between the fundamentals later. We could not observe a combination of fundamentals attributable to the 2070-cm^{-1} band in the spectra of HOPG basal plane, PG basal, and edge planes such as the 1480- and 1915-cm^{-1} bands.

The 1754-cm^{-1} band is observed only in HOPG basal plane. In the PG spectra, however, the peak corresponding to the 1754-cm^{-1} band may disappear behind the base of peak at 1580 cm^{-1} because of its weak intensity. The band also can be attributed to overtone- or combination-type scattering of two phonons satisfying wave-vector conservation relations. However, there is no combination of fundamentals attributable to the 1754-cm^{-1} band both in PG basal and edge planes. On the other hand, the 1754-cm^{-1} value is very near to the frequencies of overtones of the ir-active A_{2u} and optically inactive B_{2g} zone-center modes. However, the possibility that the 1754-cm^{-1} band is the overtone of the A_{2u} or B_{2g} mode may not be the case, because the former is considered to be the "in-plane" mode, while the others are "out-of-plane" modes.

The calculated "in-plane" density of states obtained with the Nicklow, Wakabayashi, and Smith (NWS)[8] or Young and Koppel (YK)[21] model by Nemanich and Solin shows four strong features (see Figs. 4 and 7 in Ref. 4).

The 810-, 1083-, 1357-, and 1621-cm^{-1} bands are probably attributed to these four strong features, respectively. Then the 1083- and 1357-cm^{-1} bands correspond to strong peaks (at ~1340 and 1470 cm^{-1}) in the density of states, respectively, which are due to flatness of the phonon dispersion curves at the zone boundary from K to M of Brillouin zone.

Although the 1480-, 1754-, 1915-, and 2070-cm^{-1} bands have some properties in common with an overtone and a combination of fundamentals attributed to features in the density of states, these bands cannot be assigned using the four fundamentals (810-, 1083-, 1357-, and 1621-cm^{-1} bands). We need to consider the existence of additional fundamentals not attributed to features in the calculated density of states to make the assignments of 1480-, 1754-, 1915-, and 2070-cm^{-1} bands.

The 2446-cm^{-1} band has been tentatively assigned to (2×1223 cm^{-1}),[4] although the expected fundamental is not observed definitely at 1223 cm^{-1} in the published results as well as this work. Here we present another possibility for the assignment of the 2446-cm^{-1} band using the fundamentals described above. We note that the sum of the frequencies of the 1083-, and 1357-cm^{-1} bands ($1083+1357=2440$ cm^{-1}) is very close to the 2446-cm^{-1} value. The assignment of the 2446-cm^{-1} band as a combination of the density-of-states features corresponding to critical points in the different phonon dispersion curve does not require the existence of the 1223-cm^{-1} band. The assignment is also supported by the λ dependence of the 1083- and 1357-cm^{-1} bands. The inclination $\delta(\Delta\nu)/\delta\lambda$ of the 2446-cm^{-1} band (0.19 cm^{-1}/nm) is almost equal to the sum of those of the 1083- and 1357-cm^{-1} bands ($0.41-0.23=0.18$ cm^{-1}/nm). Although the 2446-cm^{-1} band has already been attributed to an overtone mode on the grounds that it shows polarization dependence of total symmetric character,[4] the polarization dependence can be a necessary but not a sufficient condition because it is probable that the combination mode has total symmetric character as the overtone mode. In addition, we note in the existing phonon dispersion curves that most of phonons corresponding to points at the zone boundary between K and M of Brillouin zone contributes to strong features in the density of states. Since both the 1083- and 1357-cm^{-1} bands probably arise from critical points in the phonon dispersion curves at zone boundary from K to M of Brillouin zone, the 1083- and 1357-cm^{-1} bands can yield a combination mode which satisfies the wave-vector selection rule by the combination of nonzero wave vectors with opposite sign. It is also probable that the 810- and 1357-cm^{-1} bands can combine with each other, similarly to the 1083- and 1357-cm^{-1} bands.

The 3170- and 3174-cm^{-1} band in HOPG and PG spectra seem to be overtones of the E_{2g} band. The observation of the features at 3170 and 3174 cm^{-1} is also considered to be evidence for overtone scatterings from the features at ($3170/2=1585$ cm^{-1}) and ($3174/2=1587$ cm^{-1}) in the density of states. However, a peak corresponding to the 1585- or 1587-cm^{-1} band cannot be distinguished from the 1580-cm^{-1} band in the spectra for HOPG and PG. We suggest that the peak at 1580 cm^{-1} (G band) consists of a first-order feature in the density of states in addition to E_{2g} mode. In fact the weak peak corresponding to the saddle-type critical point of the phonon dispersion curve at M can be found at a frequency near 1580 cm^{-1} in the existing density of states (see Fig. 4 in Ref. 4).

The 810- and 1083-cm^{-1} bands assigned to fundamentals in the density-of-states spectrum have λ dependence opposite to that of the D band. The fundamentals attributable to features in the density of states are divided according to their λ dependence into the following classes: (1) the band (1357 cm^{-1}) that shifts with λ to lower frequency; (2) the band (810 and 1083 cm^{-1}) that shifts to higher frequency; (3) the band (1621 cm^{-1}) that is insensitive to λ. Such λ dependence is too complicated to explain by the existing calculations.[17,18] In addition, since the weak features in the spectra have some λ dependence such as the D band, these features can definitely be attributed not to adsorbates or other impurities but to modes inherent in the graphite lattice vibrations.

IV. SUMMARY

Raman spectra of HOPG and PG have been studied with the excitation wavelength between 457.9 and 514.5 nm. Several very weak features which have not been reported are found in the fundamental and the higher-order regions. The λ dependence of the Raman peak frequencies is widely observed for Raman bands of graphite besides D, $2D$, and $D+G$ modes,[17] and is classified into three types, i.e., upshifted, insensitive, and down-shifted bands, with increasing the excitation wavelength. Although the origin of such peculiar λ dependence has not been understood, it is useful for the characterization of the higher-order scattering, since it is demonstrated that the λ dependence of the higher-order bands follow that of the fundamentals.

The ratio of the relative Raman band intensities between the edge and the basal planes ($\bar{I}_{\text{edge}}/\bar{I}_{\text{basal}}$) can be utilized for the discrimination between fundamental and higher-order modes becoming Raman active at the crystalline edge by degradation of translational symmetry, and overtone and combination modes that satisfy the wave-vector selection rule by the combination of nonzero wave vectors with opposite sign.

It is suggested that the 810- and 1083-cm^{-1} modes are due to features in the density of states in addition to the 1357- and 1621-cm^{-1} modes. It is also proposed that the combination mode between 1083- and 1357-cm^{-1} modes can be another candidate for the assignment of the 2446-cm^{-1} mode, which has been tentatively assigned to the overtone mode of the supposed fundamental expected at around 1223 cm^{-1}.[4] However, observed features in this work cannot be completely explained by the existing density of states calculation. It is necessary to modify the calculation in order to explain the phonon spectrum of graphite. It is also important to investigate Raman spectra in a variety of graphite materials with signal-to-noise ratio as high as the present work.

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