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SUMMARY

First and second order Raman and first order infra-red reflectance spectra of highly oriented pyrolytic graphite (HOPG) have been obtained for both $E \parallel c$ and $E \perp c$. From the infra-red measurement, the A_{2u} out of plane mode is identified for the first time and occurs at 868 cm^{-1} . The macroscopic effective changes of both the A_{2u} and E_{1u} modes have also been calculated. The second order Raman spectra have been recorded for graphite forms of various crystallite sizes. The second order Raman spectra of both HOPG and single crystal graphite exhibit an anomalously sharp feature at 3 248 cm^{-1} , which is, in fact, sharper than the first order zone center E_{2g} band at 1581 cm^{-1} . Of the six recent, and in some cases mutually inconsistent, lattice dynamics calculations on graphite, only that due to Nicklow et al. is compatible with the 3 248 cm^{-1} feature, and even that model does not provide a satisfactory explanation of the entire second order spectrum.

RESUME

Les spectres de réflection Raman de premier et second ordre et infrarouge de premier ordre ont été obtenus sur du graphite pyrolytique hautement orienté (HOPG) pour $E \parallel c$ et $E \perp c$. A partir des mesures infrarouge, le mode A_{2u} en dehors du plan est identifié pour la première fois et se produit à 868 cm⁻¹. Les changements macroscopiques effectifs des deux modes A_{2u} et E_{1u} ont aussi été calculés. Le spectre de second ordre Raman a été enregistré pour différentes variétés de graphite allant du monocristal de 3 mm à des poudres de noir de carbone dont la dimension des cristallites est de 16 Å. Le spectre Raman de second ordre du graphite monocristallin et de HOPG montre une anomalie aiguë à 3248 cm^{-1} qui est en fait plus accusée que la bande E_{2g} à 1581 cm⁻¹ du centre de zone de premier ordre. A propos des six récents calculs de dynamiques de réseau du graphite, et parmi des cas mutuellement incompatibles, seulement celui de Nicklow et al. [4] est compatible avec la raie à 3248 cm^{-1} , mais ce modèle ne donne pas d'explication satisfaisante pour la totalité du spectre de second ordre. Ce qui distingue le modèle de Nicklow est le fait que la courbe calculée de dispersion des phonons Σ et Γ part du centre de la zone pour atteindre des maxima pour 9 approximativement égaux à 0,6 et 0,4 respectivement. Nous avons observé un déplacement du phonon du phonon du centre de la zone E_{2g} vers les hautes fréquences avec la diminution de la taille des particules et attribué ce déplacement aux caractéristiques de la courbe de dispersion mentionnées plus haut et à une modification des règles de sélection des vecteurs d'onde pour la lumière diffusée. Nous opposerons nos résultats sur le graphite avec d'autres sur BN (à paraître) qui montrent aussi un déplacement vers les hautes fréquences du phonon du centre de la zone intraplanaire avec la diminution de la taille des particules.

Graphite, the prototype lamellar homopolar crystal has been the subject of numerous lattice dynamics calculations [1 - 6] during the past two decades. These calcula-

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tions have a common theme. The available neutron scattering results [4, 7] which, to date, have been experimentally limited to the region $\omega \leq 400 \text{ cm}^{-1}$, are fitted with a multiparameter model. More recently, Raman and IR data on the zone center optic phonons [8] have been included in the fit. Having obtained the parameters which produce the best fit, the model is used to calculate the phonon density of states and from it the temperature dependence of the specific heat and, in some cases, the elastic constants. Unfortunately, all of the lattice dynamics calculations carried out to date provide good fits to the experimental data, which is thus not restrictive enough to distinguish between different models. Moreover, a major problem with these calculations has been a lack of information on the IR active out-of-plane A_{2u} mode. We report here a study of the first and second order Raman spectra of graphite and of the first order IR reflectance. Our results, which include the properties of the A_{2u} mode, impose additional constraints on the lattice dynamics models of graphite.

Samples studied in this work included natural crystals, highly oriented pyrolytic graphite (HOPG) and various microcrystalline forms of graphitic carbon as well as bulk vitreous or "glassy" carbon. The average crystallite size L_a (*i.e.*, the range of order in the layer planes) was determined by X-ray diffraction measurements and from the first order Raman spectra using the method of Tuinstra and Koenig [9]. Measurements of HOPG with light incident along the c axis were made on samples freshly cleaved with a razor blade, while "a" axis measurements were made on a sample surface which was cut perpendicular to the layer planes and then polished.

Raman spectra of all samples were obtained at room temperature using argon laser excitation lines and the backscattering geometry. The spectroscopic apparatus is described elsewhere [10]. A Perkin-Elmer Model 180 Spectrophotometer operated in the double beam mode was used to record the IR reflectance spectra.

The three dimensional graphite crystal has space group symmetry D_{6h}^4 [11]. The isolated carbon layer has point group symmetry D_{6h} , the same as the point group of the crystal (at $\overline{k} = 0$). The correlation between the group



Fig. 1. The correlation of the zone center vibrational modes of graphite for a single layer and the 3-dimensional crystal structure. Raman or IR activity are indicated in the parentheses by R and IR, respectively.

theoretically derived irreducible representations of the vibrational modes of the isolated layer and those of the full crystal is illustrated in Fig. 1, in which the Raman and IR active modes are also identified. As can be seen from Fig. 1 it is the interlayer coupling which gives rise to first order IR active modes in graphite. Of the modes specified in Fig. 1, the E_{1u} optic mode has been observed at 1 588 cm⁻¹ [8], the E_{2g} rigid layer modes have to date defied detection by optical methods, and the B_{2g} modes are optically inactive. We report here properties of the A_{2u} mode.

The polarized reflectance spectra of HOPG are shown in Fig. 2. The $E \perp c$ spectrum shows a weak, sharp feature at 1588 cm⁻¹, in agreement with previous work [8], while the $E \parallel c$ spectrum yields a feature at 868 cm⁻¹ superposed upon a non-dispersive background reflectance. The $E \perp c$ spectrum of a polished face has also been obtained and is similar to that of the cleaved face except that (a) the reflectance is reduced, and (b) the feature at 1 588 cm⁻¹ is broadened. Both changes are attributed to surface damage produced by polishing. The ratio of the two $E \perp c$ spectra provides a quantitative measure of the sur-

TABLE 1

Reflectance spectrum	Mode symmetry	$(\mathrm{cm}^{\nu_{\mathrm{TO}}})$	S	γ	e _T *,†	$(cm^{\nu_{LO}^{\dagger}})$
Ellc	A 2u	867.8	0.004	0.001	0.08e	868.1
<i>E</i> ⊥ <i>c</i>	E _{1u}	1 587.0	0.031	0.003	0.41e	1 587.5

The parameters v_{TO} , S and γ obtained from the oscillator analysis of the $E_{\perp c}$ and $E_{\parallel c}$ reflectance spectra of graphite

+For details of the calculation of the effective charge, e_T^* , and the LO frequency, ν_{LO} , see ref. 12.

face damage. For analysis of the $E \parallel c$ spectrum the experimental reflectance was scaled by this ratio. The results of an oscillator analysis of the spectra of Fig. 2, the details of which are described elsewhere [12], are given in Table 1.

In Fig. 3 we show the first and second order Raman spectra of various forms of graphitic carbon. The feature at 1 581 cm⁻¹ is the E_{2g} intralayer vibration, while the feature at 1 355 cm⁻¹, which decreases in intensity with increasing crystallite size, has been attributed to a zone boundary phonon Raman activated by the breakdown of the wave vector selection rule [9]. Note that the spectra of Fig. 3 broaden and evolve continuously with decreasing crystallite size. This is evidence that all of the features are intrinsic



Fig. 2. The IR reflectance of graphite (a). The $E \parallel c$ spectrum has been normalized to account for surface damage. The oscillator fits to the data in the region of the phonon features are shown as dashed (------) lines in (b), while the solid lines are the data.



Fig. 3. First and second order Raman spectra of various graphite forms of carbon. The spectra were excited with the $4\,880$ Å radiation from an argon ion laser. Note that the abcissa is linear in wavelength rather than wave number.

to graphite. Of particular interest is the sharp band at 3 248 cm^{-1} in HOPG and the natural crystal. Not only is this band narrower (Γ = $10 \pm 1 \text{ cm}^{-1}$) than the first order band at 1581 cm^{-1} ($\Gamma = 14 \pm 1 \text{ cm}^{-1}$) but also it is upshifted by fully 86 cm^{-1} from the overtone of the first order band. This result is a direct indication that the maximum phonon energy for graphite does not occur at the zone center or Γ point, but at some finite value of the wave vector. Thus, at least one branch of the phonon dispersion curves has a positive slope at $\omega = 1.581 \text{ cm}^{-1}$, $\vec{k} \approx 0$. As further evidence for the rise in the phonon dispersion curve away from k = 0 we tabulate in Table 2 the dependence of the Raman shift of the first order E_{2g} mode on crystallite size. There is a

TABLE 2

Raman frequency for different graphitic forms of carbon

Graphitic form	La	1st order Raman shift (cm ⁻¹)
Natural crystals	3 mm	1 582
Pyrolytic	2 µm	1 582
Ultra carbon	$1 \mu m$	1 581
Fisher powder	130 A	1 583
Carbon rod	25 Å	1 585
Vitreous carbon		1 593

noticeable increase in the Raman frequency with decreasing crystallite size which is not attributable to the additional high frequency shoulder that broadens the mode. This behaviour of the first order line is similar to the behaviour of the intralayer mode of BN [13] and is, we believe, a consequence of the breakdown in the wave vector selection rule coupled with a phonon dispersion curve that rises away from the zone center.

Of the several recent lattice dynamics calculations for graphite, only that due to Nicklow et al. [4] exhibits a maximum phonon energy at finite k and is thus compatible with the Raman data. Indeed, a quantitative calculation of the two phonon density of states based on the model of Nicklow et al. vields a sharp feature ($\Gamma \simeq 25 \text{ cm}^{-1}$) at $3\ 250\ \mathrm{cm}^{-1}$ [14], remarkably close to the experimentally measured second order band. Unfortunately, the two phonon density of states calculated from the model of Nicklow et al. is not entirely compatible with the full second order Raman spectra of Fig. 3, most of the features of which cannot be definitively accounted for.

Finally, we note that not only do the available lattice dynamics calculations for graphite fail to satisfactorily account for the second order Raman spectrum, but also the different force field models employed yield an A_{2u} optic mode frequency that varies between 600 cm⁻¹ and 1300 cm⁻¹. It is interesting to note that the A_{2u} mode cannot be described in a simple valence force field model which includes only the usual bond stretching (k_r) and bond-bending (k_{θ}) forces [5]. The addition of other three-body forces e.g., $k_{rr'}$ and $k_{r\theta}$ does not remedy the problem. It is, in fact, necessary to consider an additional four-body force (k_{μ}) that is characterized by a "puckering" of the layer planes [5]. We note that k_{μ} is of the same order as k_r [12], an indication that this "puckering" force is not attributable to more distant neighbors, but rather is a characteristic of the unusual lattice properties of graphite.

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