OBSERVATION OF AN ANOMOLOUSLY SHARP FEATURE IN THE 2ND ORDER RAMAN SPECTRUM OF GRAPHITE*

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The second order Raman spectrum of graphite is shown to exhibit an anomolously sharp feature at an energy higher than twice the energy of the first order Raman line. This feature is compared to the 2667 cm⁻¹ band in the second order Raman spectrum of diamond and is discussed in terms of a two-phonon bound state and ordinary overtone scattering. Also this feature serves to discriminate between current lattice dynamics calculations of graphite.

Cohen and Ruvalds (CR)¹ have ascribed a sharp peak at 2667 cm⁻¹ in the two phonon Raman spectrum of diamond^{2,3} to a two phonon bound state. The phenomenological theory which they employed was subsequently successfully adapted to other important problems in condensed matter physics, most notably to explain the second order Raman spectrum of superfluid He⁴ in terms of a two roton resonance.⁴ However the bound phonon concept has been repeatedly challenged.^{5,6,7} Recently Uchinokura et al.,⁵ (USM) suggested that all of the anomalous features of the 2667 cm⁻¹ band of diamond including its occurrence at an energy slightly (\approx 2 cm⁻¹) above twice the energy of the first order Raman line could be accounted for by anomolies in the phonon dispersion curves of diamond. That suggestion was in part verified by the calculations of Tubino and Birman.⁷ However the position of the 2667 cm⁻¹ band has only been quantitatively accounted for by CR. In this letter we report on observations of an anomalously sharp feature at the maximum of the second order Raman spectrum of graphite which has characteristics very similar to the above mentioned feature in diamond. In addition because graphite is the prototype lamellar material there have been many (recent) calculations of its phonon dispersion curves.²¹³ Unfortunately these several calculations are mutually inconsistent. Our Raman measurements provide additional information with which to discriminate between the present calculations.

Polarized Raman spectra of single crystal graphite (SCG) and highly oriented pyrolytic graphite (HOPG) were obtained using argon laser excitation lines and the back scattering geometry in which the incident and scattered radiation propagate along the "c" axis. To remove possible contaminants the HOPG samples were heated to 1000K for several hours in flowing He gas and then cleaved for Raman measurements. Several samples of HOPG and SCG were measured. The Raman spectra obtained from SCG and HOPG samples were indistinguishible.

In this paper we shall focus on the $3000-3300 \text{ cm}^{-1}$ region of the second order spectra and on the first order spectra which are shown in Figure 1. The details and

analysis of the full second order spectrum will be discussed elsewhere.¹⁴ Notice from Figure 1 that the peak at 3248 cm⁻¹, in the second order spectrum is upshifted by fully 86 cm⁻¹ from 2 ω_R where $\omega_R = 1581$ cm⁻¹ is the observed first order Raman frequency. (All samples examined whether HOPG or SCG yielded a first order line at 1581 ± 1 cm⁻¹ a value slightly higher than that reported by Brillson, et al.¹⁵ and Tuinstra and Koenig.¹⁶) The 3248 cm⁻¹ mode is also polarized. In contrast, the first order feature is depolarized and is therefore attributed to scattering from

the Γ_5 (E_{2g}) zone center intralayer vibration in agreement with the work of Brillson et al.¹⁵ Most intriguing about the spectra of Figure 1 is the fact that the 3248 cm⁻¹ second order feature has a full width at half maximum (FWHM) of 10 ± 1 cm⁻¹ and is thus considerably sharper than the first order line the FWHM of which is 14 ± 1 cm⁻¹.

The sharpness of the 3248 cm⁻¹ feature may suggest that it is a first order Raman line that arises from impurities. While the temperature dependence of the intensity of a Raman feature can usually be used to distinguish the origin as to first or second order, this cannot be easily accomplished for modes with large Raman shifts. The most likely impurity to give rise to a mode near 3248 cm^{-1} would be hydrogen. Molecules with hydrogen bonded to a carbon atom which is triply bonded to another atom (e.g., HCN) yield a H-C mode at ~3300 cm⁻¹ that would be Raman active¹⁷, however this configuration seems unlikely in graphite. Other configurations of H-C bonding yield bond stretching frequencies near 3000 cm⁻¹ (e.g., benzene exhibits a mode at 3062 cm⁻¹).¹⁷ To further confirm that the 3248 cm⁻¹ band is an intrinsic second order feature of graphite, we note its dependence on crystallite size.^{14,18} Specifically that feature evolved from a sharp peak to a step drop with decreasing crystallite size in contrast to the behavior anticipated if the 3248 cm⁻¹ band was a local impurity mode. The above arguments and the fact that the Raman spectra of HOPG and SCG are identical in our opinion supports the interpretation that the 3248 cm⁻¹ mode is a

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Fig. 1 Polarized first (I₁) and second (I₂) order room temperature Raman spectra of highly oriented pyrolytic graphite. The spectra were excited with 550 mW of 4880 Å Argon ion laser radiation and were recorded with spectral slit widths of 6.2 cm⁻¹ and 5.5 cm⁻¹ respectively. Laboratory axes are labeled x, y, and z with z parallel to the crystal "c" axis. The abscissa is marked in wavenumbers but is linear in wavelength.

second order feature of the Raman spectra of graphite.

As noted above there have been numerous lattice dynamics calculations of the phonon dispersion curves of graphite during the past two decades. These calculations have a common theme. The available neutron scattering results which to date have been experimentally limited to the region $\omega \leq 400 \text{ cm}^{-1}$ ¹¹ are fit with a multiparameter model. More recently Raman and IR data on the zone center optic phonons¹⁵ 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 $g(\omega)$ and from it the temperature dependence of the specific heat and in some cases the elastic constants. Unfortunately, all of the lattice dynamics calculatele experimental data which is thus not restrictive enough to distinguish between different models.

The most recent attempt to calculate the phonon dispersion curves of graphite is that of Mani and Ramani.⁸ While they find that the maximum one phonon energy is at the M point of the hexagonal Brillouin zone (BZ) not at the Γ point, this energy according to them is ≈ 1830 cm⁻¹. Also there is no evidence in the calculated curves for a critical point at $\approx 3248/2$ cm⁻¹ = 1624 cm⁻¹. Thus the second order Raman spectrum deduced from the model of Mani and Ramani would terminate at ≈ 3660 cm⁻¹ and have no distinct feature at 3248 cm⁻¹ in contrast to our experimental results. Rafizadeh⁹ has analyzed the lattice dynamics of graphite using various models for the carbon-carbon interaction potential. Of the four models addressed only one, labeled model 4, would exhibit a sharp critical point at ~3250 cm⁻¹ and that model essentially reproduces the results of Nickow et al.¹¹ Earlier calculations of the lattice dynamics of graphite carried out by Yoshimori and Kitano¹³ and by Young and Koppel¹²

yield phonon dispersion curves for which the maximum energy in the zone is at the Γ point and thus would not exhibit any structure above 2 Γ in the 2 phonon density of states.

Nicklow et al.¹¹ recently extended the seminal neutron scattering studies of graphite by Dolling and Brockhouse¹⁹ and applied an axially symmetric Born-Von Karman force constant model to their data to obtain the phonon dispersion curves. Using their model we have calculated the phonon dispersion curves for HOPG. Our results for the region 1540 cm⁻¹ $\leq \omega \leq 1630$ cm⁻¹ are shown in Figure 2. Slight (≈ 1 cm⁻¹) splittings of the two fold degenerate Λ and Σ lines and the four fold degenerate Λ lines are not shown in Figure 2. The second order Raman spectrum of the region in question will have approximately the same shape as the two phonon density of states²⁰ which for $\omega > 2 \omega_R$ results solely from overtones. Therefore we also show in Figure 2 the two phonon (or equivalently the one phonon) density of states $g_2(\omega)$ calculated from the phonon dispersion curves. Notice that in the 3000 - 3300 cm⁻¹ region the spectral distribution $g_2(\omega)$ of Fig. 2 exhibits a strong asymmetric feature that yields a cutoff at ~3250 cm⁻¹. In addition, since $g_2(\omega)$ is

the overtone density of states, $I_2(\omega)$ will contain the Γ_1^{T}

species of the D_{6h}^4 space group and thus yield a polarized feature in the second order Raman spectrum. This is because the direct product of an irreducible representation with itself always contains the identity representation.²¹ While as shown in Fig. 1 a polarized asymmetric feature is observed at ~3250 cm⁻¹ in the second order Raman spectrum of graphite, the width of the observed feature, ~10 cm⁻¹, is much less than the calculated width of ~25 cm⁻¹. It is possible but unlikely that the Raman matrix element varies sufficiently rapidly in the region of the peak



Fig. 2 Optic mode phonon dispersion curves and density of states for HOPG. The dots represent the Monte Carlo calculated density of states and the solid line is to guide the eve.

to remove the discrepancy between $g_2(\omega)$ and $I_2(\omega)$.

The 3248 cm⁻¹ feature has many characteristics in common with the 2667 cm⁻¹ band of diamond. It is sharp relative to the rest of the second order spectrum, exhibits a Γ_1^{*} symmetry, is upshifted from $2\omega_R$ and is at the upper extremum of the two phonon spectrum. To clarify further the similarity between the sharp two phonon peaks in graphite and diamond we now discuss critical point (C.P.) analyses of the respective $g_2(\omega)$.²² Uchinokura et al.,⁵ argued that the maximum phonon energy in the BZ of diamond was not at the Γ point but rather along the Δ or A lines. In that case the maximum would yield a P_3 C.P., the Γ point a fluted F₂ C.P., and a P₂ C.P. (incorrectly labeled F_2 by USM) would occur at a frequency between P_3 and F_2 . Thus the peak in $g_2(\omega)$ for diamond would in principle occur between P_2 and P_3 close to but slightly upshifted from $2\omega_R$. For graphite the dispersion curves of Figure 2 yield two P_3 C.P.'s at the essentially degenerate maxima along Σ , two P_2 C.P.'s at the almost degenerate saddle points along T and a combination of $F_1 + P_0 + F_2 +$ P₃ C.P.'s at the Γ point. Again the sharp peak in $g_2(\omega)$ will occur between the P₂ and upper P₃ C.P.'s not at the Γ point at which the effects of the C.P.'s tend to cancel. The "anomalous" shape (i.e., the rise above Γ along Λ and Δ) of the phonon dispersion curves of diamond was attributed by Tubino and Birman to strong second neighbor interactions relative to the first neighbor interaction.⁷ Here again graphite mimicks diamond; the optic mode phonon dispersion curves of graphite are quite sensitive to the second neighbor force constant. For instance using the model of Nicklow et al., there is a critical value of the second neighbor force constant below which the calculated phonon dispersion curves have an absolute maximum at the

Γ point.14

Consider now the possiblity that the 3248 cm⁻¹ band of graphite results from a two-phonon bound state. Recall that CR ascribed the 2667 cm⁻¹ feature of diamond to a bound state of two zone center phonons. We think it is unlikely that the 3248 cm⁻¹ feature is a bound state of two zone center phonons since the binding energy would be 84 cm⁻¹ or fully 5% of the single phonon energy. Such a relatively large binding energy necessitates an unrealistically large anharmonic contribution to the total energy and would most likely produce a bound state broadened beyond recognition. It is possible however that the feature in question is a bound state of two phonons at the maximum along the Σ line since the lattice dynamics calculations are sufficiently imprecise to accommodate a small (≤ 10 cm) binding energy. In this case one might expect to observe two peaks in the vicinity of ≈ 3250 cm⁻¹ one due to the shape of $g_2(\omega)$ and one from the bound state. However, since we cannot predict the relative intensities or widths of the above mentioned peaks it is conceivable that $l_2(\omega)$ would contain either an unresolved pair or a single peak.

It is remarkable that the second order band at 3248 $\rm cm^{-1}$ is much sharper than the first order Raman line. To our knowledge no such observation has been previously reported. For instance, in the case of diamond, the 2667 $\rm cm^{-1}$ feature is more than 3 times as broad as the 1332 $\rm cm^{-1}$ first order feature. At present it is not clear whether the 3248 cm⁻¹ band results from ordinary overtone scattering, a two phonon bound state or a combination of both.

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