

Double Resonant Raman Scattering in Graphite

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We find that the electronic dispersion in graphite gives rise to double resonant Raman scattering for excitation energies up to 5 eV. As we show, the curious excitation-energy dependence of the graphite D mode is due to this double resonant process resolving a long-standing problem in the literature and invalidating recent attempts to explain this phenomenon. Our calculation for the D -mode frequency shift ($60 \text{ cm}^{-1}/\text{eV}$) agrees well with the experimental value.

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Single incoming or outgoing resonances are widely known in Raman spectroscopy and frequently used to study the electronic and vibrational properties of crystals or molecules. They occur if the energy of the incoming or the scattered photon matches the transition energy of an allowed electronic transition leading to a large enhancement of the Raman cross section [1]. Closely related is the idea of double resonant Raman scattering, where, in addition to the incoming or outgoing resonances, the elementary excitation makes a real transition. Double resonances are much stronger than single resonances. They were, however, only observed under very specific experimental conditions: The energetic difference between two electronic bands was adjusted to the phonon energy by applying electric or magnetic fields, uniaxial stress, or by a proper choice of the parameters of semiconductor quantum wells [2–5]. Double resonant conditions were thereby realized for distinct excitation energies.

In this Letter we study the double resonant Raman process for linearly dispersive bands as in semimetals. We show that double resonances are responsible for the observation of the defect induced D mode in graphite and its peculiar dependence on excitation energy. The double resonance considered has a much stronger enhancement than simple incoming or outgoing resonances explaining why the defect mode (and its second order peak) is so strong compared to the graphite Γ point vibration.

The first order Raman spectra of graphite show besides the Γ point modes an additional defect induced peak, the so-called D mode [6–9]. The D mode is related to the finite crystallite size and disappears for perfect crystals [6,10]. Its frequency was found to shift with excitation energy at a rate of $40\text{--}50 \text{ cm}^{-1}/\text{eV}$ over a wide excitation energy range [7,11–13], a phenomenon which has not been understood for almost 20 years. Tan *et al.* found that there is a curious discrepancy between the Stokes and anti-Stokes frequencies of the D mode, which they were unable to explain [14]. Various groups have recently attempted to explain the unusual excitation-energy dependence which was found also for the second order spectra, where the mode shifts at approximately twice the rate and is not defect induced. Sood *et al.* proposed a disorder in-

duced double resonance above a gap $\Delta \approx 1 \text{ eV}$ in the band structure leading to a dependence of the phonon wave vector q and hence the phonon frequency on the energy of the incoming light E_1 as $q \sim (E_1 - \Delta)^{1/2}$ [12]. There is, however, no such gap in the electronic structure of graphite; it is a semimetal with valence and conduction band crossing the Fermi level at the K point of the Brillouin zone. Pócsik *et al.* introduced a new Raman mechanism for which the wave vector of the electron which is excited by the incoming resonant photon supposedly defines the wave vector of the scattered phonon [13]. This *ad hoc* $k = q$ quasiselection rule was applied to particular branches of the phonon band structure by Matthews *et al.* and Ferrari and Robertson [15,16]. However, these explanations required a mysterious coupling of the optical branches to a transverse acoustic branch in the phonon band structure or did not yield the correct shift of the D mode. Single resonances have not been identified in the graphite Raman spectra because the linear dispersion of the electronic bands allows these resonances to occur at all energies E_1 and for the entire D band independently of q . There is no reason why the quasimomentum where the electronic transitions occur is transferred selectively to the phonon seen in the Raman spectra, and it is impossible to understand the difference between Stokes and anti-Stokes frequencies. In other words, the “quasiselection rule” invoked by Refs. [13,15,16] has no physical basis and cannot explain the experimental observations.

To study the resonant Raman effect in a semimetal like graphite we first consider a one-dimensional example as depicted in Fig. 1, where we have shown two linear bands with different Fermi velocities which cross at the Fermi level. The peculiarity of this electronic dispersion is that, in addition to single resonances, a double resonant transition is possible for a wide variety of excitation energies. The first step of the double resonance for a particular incident laser energy E_1 is to create an electron-hole pair at the k point matching the energy difference between the conduction and the valence band ($i \rightarrow a$). It is obvious that for a monotonically increasing phonon dispersion $\omega_{\text{ph}}(q)$ there exists a (ω_{ph}, q) combination which can scatter the electron to a state on the second band ($a \rightarrow b$). This

is the phonon for which double resonance occurs. Then the electron is elastically scattered back by the lattice defects ($b \rightarrow c$) and recombines conserving k in the process ($c \rightarrow i$). For a larger incoming photon energy a larger phonon quasimomentum is required for this transition and hence a different phonon energy, if the phonon band is dispersive. The double resonance occurs also for two emitted phonons at twice the energy where quasimomentum is con-

served by equal and opposite q of the two emitted phonons, i.e., it is not defect induced. The anti-Stokes process for a particular incoming energy is seen to be doubly resonant at a larger phonon momentum (and hence energy) than the Stokes process.

For the linear bands in Fig. 1 we can calculate the Raman matrix element $K_{2f,10}$ explicitly by evaluating the usual expression [1]:

$$K_{2f,10} = M_f \mathcal{M}_{ba} \mathcal{M}_{cb} M_o \sum_{a,b,c} \frac{1}{(E_1 - E_{ai}^e - i\hbar\gamma)(E_1 - \hbar\omega_{ph} - E_{bi}^e - i\hbar\gamma)(E_1 - \hbar\omega_{ph} - E_{ci}^e - i\hbar\gamma)}. \quad (1)$$

Here $M_{o,f}$ are the (constant) transition matrix elements for the incoming and outgoing photons, $\mathcal{M}_{ba}, \mathcal{M}_{cb}$ represents the phonon or impurity which scatters the electron from state a to b and from state b to c , and γ , the broadening parameter, has been taken to be the same for all transitions. For a semimetal the electronic energies are $E_{ai}^e = |k|(v_2 - v_1)$ and $E_{bi}^e = \mp qv_{1/2}$, and $E_{ci}^e = |k|(v_2 - v_1)$ with $v_1 < 0$ and $v_2 > 0$ being the Fermi velocities. In one dimension the sum may be converted to an integral over k :

$$K_{2f,10} = \frac{M_f \mathcal{M}_{ba} \mathcal{M}_{cb} M_o (2\kappa_2 - q)}{(v_2 - v_1)^3 (\kappa_2 - q \frac{v_2}{v_2 - v_1}) (\kappa_2 + q \frac{v_1}{v_2 - v_1})} \times \int_0^\infty \frac{dk}{(\kappa_1 - k)(\kappa_2 - k)}, \quad (2)$$

with $\kappa_1 = (E_1 - i\hbar\gamma)/(v_2 - v_1)$ and $\kappa_2 = (E_1 - \hbar\omega_{ph} - i\hbar\gamma)/(v_2 - v_1)$. This integral is straightforwardly evaluated to

$$K_{2f,10} = \frac{aM_f \mathcal{M}_{ba} \mathcal{M}_{cb} M_o}{(\kappa_2 - q \frac{v_2}{v_2 - v_1})(\kappa_2 + q \frac{v_1}{v_2 - v_1})}, \quad (3)$$

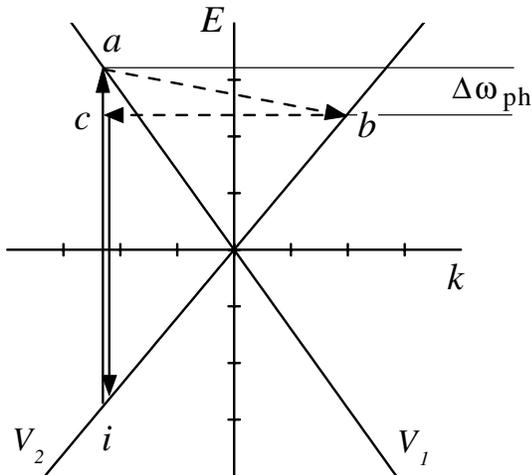


FIG. 1. Schematic Raman double resonance in one dimension for linearly dispersive bands with Fermi velocities v_1 and v_2 . For a given incident energy E_1 and a monotonically increasing phonon dispersion relation $\hbar\omega_{ph}(q)$ there is at most one q and $\hbar\omega_{ph}$ leading to double resonance. In this example the electron is scattered back to band 1 by an impurity.

where $a = \ln(\kappa_2/\kappa_1)(2\kappa_2 - q)/[(v_2 - v_1)^2 \hbar\omega_{ph}]$ is a slowly varying function of q . Physically Eq. (3) says that there is double resonance when the phonon quasimomentum is equal to

$$q = \frac{E_1 - \hbar\omega_{ph}}{v_2} \quad \text{or} \quad \frac{E_1 - \hbar\omega_{ph}}{-v_1}. \quad (4)$$

The double resonance is particularly strong since two terms in the denominator of Eq. (1) go to zero simultaneously, and much stronger than the incoming resonance considered by Refs. [13,15,16], where only one term in the denominator of Eq. (1) vanishes.

In Fig. 2 we plot $|K_{2f,10}|$ of Eq. (3) as a function of phonon quasimomentum for two incoming photon energies. For each photon energy there are two maxima, their separation depending on the Fermi velocities [Eq. (4)]. For different incoming E_1 the resonances occur at different q again as given by Eq. (4); for E_1 between 1 and 4 eV the center q varies between 0.13 and 0.6 \AA^{-1} (we chose as Fermi velocities $v_1 = -7$ and $v_2 = 6$ eV \AA adapted from graphite) as compared to ≈ 0.003 \AA^{-1} for a nondefect induced process excited at 3 eV. For a dispersive phonon, if it is single valued and increasing with q , there are two

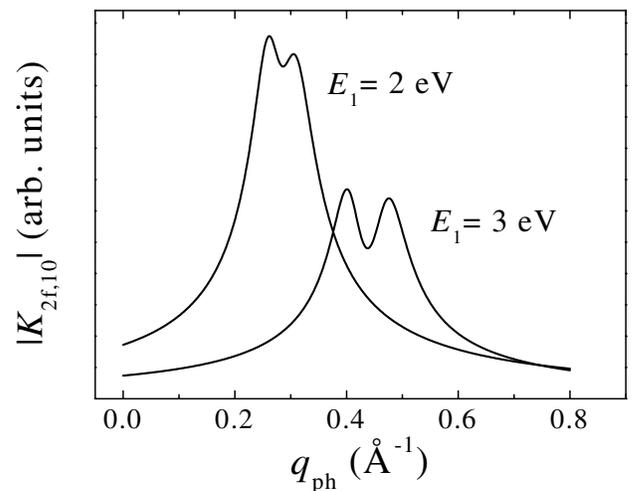


FIG. 2. The absolute magnitude of the Raman matrix element in Eq. (3) for two incident photon energies and a model dispersion. See text for details. By far the strongest enhancement occurs for the double resonance as given by Eq. (4).

pairs (q, ω_{ph}) which fulfill condition (4). To give a rough estimate for a hypothetical linear dispersion of an optical phonon we adapted from the K and Γ point values of graphite $\hbar\omega_{\text{ph}}^K = 1270 \text{ cm}^{-1}$ and $\hbar\omega_{\text{ph}}^\Gamma = 1580 \text{ cm}^{-1}$; the double resonance for an incoming photon energy at $E_1 = 3 \text{ eV}$ according to Eq. (4) occurs for the center $q = 0.44 \text{ \AA}^{-1}$, and hence $\hbar\omega_{\text{ph}} = 1350 \text{ cm}^{-1}$ is the phonon energy actually observed. For a different E_1 the phonon energy shifts accordingly. Note the large phonon quasi-momentum which can normally be observed only with neutron scattering. A difference in Stokes and anti-Stokes frequencies follows naturally from Eq. (4) when replacing ω_{ph} by $-\omega_{\text{ph}}$.

$$w(\mathbf{k}) = \{3 - \cos k \cdot \mathbf{R}_1 - \cos k \cdot \mathbf{R}_2 - \cos k \cdot (\mathbf{R}_1 - \mathbf{R}_2) + \sqrt{3} \sin k \cdot \mathbf{R}_1 - \sqrt{3} \sin k \cdot \mathbf{R}_2 - \sqrt{3} \sin k \cdot (\mathbf{R}_1 - \mathbf{R}_2)\}^{1/2}, \quad (5)$$

where $\mathbf{R}_{1,2}$ are the unit vectors of the graphene cell, $\gamma_0 = 3.03 \text{ eV}$, and $s = 0.129$ for a close approximation to the graphite band structure [17]. In the isotropic limit (for small k and neglecting s) the incoming transition occurs at $E_{ai}^e = E_c - E_v = \sqrt{3} a_0 \gamma_0 k$. Note, though, that for photon energies in the visible and higher the incoming resonance does not occur close to the K point, and the anisotropy of the band structure must be taken into account. For example, for $k = 0.23 \text{ \AA}^{-1}$ in the KM direction $E_{ai}^e = 2.7 \text{ eV}$, while in the $K\Gamma$ direction $E_{ai}^e = 3.2 \text{ eV}$.

To obtain a realistic as possible two-dimensional numerical evaluation of the sum in Eq. (1) we included for $E_{(a,b,c)i}^e$ the full electronic dispersion curves of Eq. (5) and integrated $|K_{2f,10}|^2$ over k space. The phonon dispersion in the energy range $(1270, 1620 \text{ cm}^{-1})$ we modeled by simple functions such that they represent closely the ones calculated from force constant [19] or *ab initio* [20] calculations. In particular, we fixed the Γ point frequency to 1580 cm^{-1} , the M and K point ones to 1480 and 1270 cm^{-1} , respectively, and included the overbending to 1620 cm^{-1} typical for the vicinity of the Γ point in graphite [10]. Our results are not dependent on the details of these curves. We then proceeded to evaluate Eq. (1) by searching the Brillouin zone for incoming resonances and, where we found them, by integrating $\{[E_1(\mathbf{k}^o) - [E_c(\mathbf{k}^f) - E_v(\mathbf{k}^o)] - \hbar\omega_{\text{ph}}(\mathbf{k}^f - \mathbf{k}^o) - i\hbar\gamma][\hbar\omega_{\text{ph}}(\mathbf{k}^f - \mathbf{k}^o) - i\hbar\gamma]\}^{-1}$ over \mathbf{k}^f in the entire Brillouin zone.

We plotted the Raman intensities $|K_{2f,10}|^2$ as a function of phonon frequency ω_{ph} for three different incident laser energies in Fig. 3. The peak is seen to shift to higher energies with increasing E_1 . In Fig. 4 we show the maxima of the intensities as a function of incident energy together with the experimental results on the D -mode's excitation dependence of various groups. The agreement is found to be excellent, in particular, in view of the fact that no unknown parameter was introduced in our derivation and no fitting was performed. The slope for the D -mode's excitation energy dependence calculated by our model if taken

After illustrating the principle of a double resonance with linearly dispersive electronic bands near the Fermi surface we now turn to a two-dimensional realistic description of the bands in graphite and demonstrate that our interpretation explains quantitatively the experimental dependence of the D mode in graphite on excitation energy. For the electronic bands it is sufficient to consider only the bonding and antibonding bands which, up to about 6 eV , are the only bands involved in real optical transitions. The asymmetries between bonding (lower sign) and antibonding (upper sign) states we took into account [17] according to $E_{c,v} = \pm\gamma_0 w(\mathbf{k})/[1 \mp s w(\mathbf{k})]$, where $w(\mathbf{k})$ is the tight binding band centered around the K point of the Brillouin zone of graphite [18]:

to be linear is $60 \text{ cm}^{-1}/\text{eV}$, the experimental slopes being slightly lower, ranging from 46 to $51 \text{ cm}^{-1}/\text{eV}$ [11,13,15]. The absolute values of the D -mode frequencies agree also excellently.

The relative strength of single and double resonances may be determined by the relative area A of the two-phonon peaks of the Γ point mode and the D mode, which are both Raman allowed. Experimentally we find $A_{2D}/A_{2\Gamma} \approx 40$ which independently confirms our interpretation of the shifting D mode as due to a double resonance. We obtained the difference in Stokes and anti-Stokes frequencies as $\approx 15 \text{ cm}^{-1}$ (for $E_1 = 2 \text{ eV}$) slightly depending on E_1 compared to $\approx 7 \text{ cm}^{-1}$ as reported in Ref. [14]. The remaining discrepancy suggests a somewhat too small slope of our model phonon dispersions or a slightly too large electron dispersion.

In conclusion, we investigated Raman double resonances, a mechanism which leads to a strong Raman signal at variable q vectors well within the Brillouin zone of solids. Our interpretation resolves the long-time not

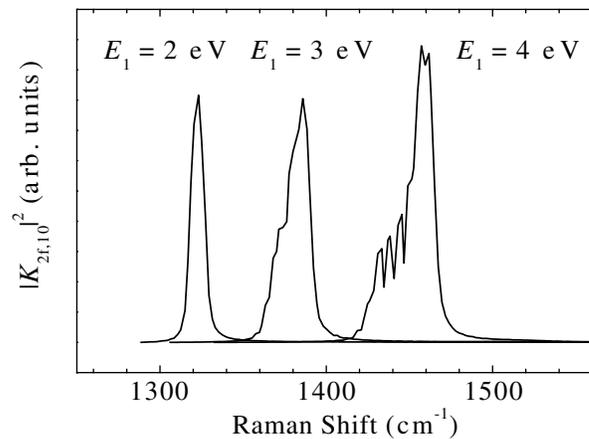


FIG. 3. Calculated Raman spectrum of the D mode in graphite for different incoming photon energies E_1 .

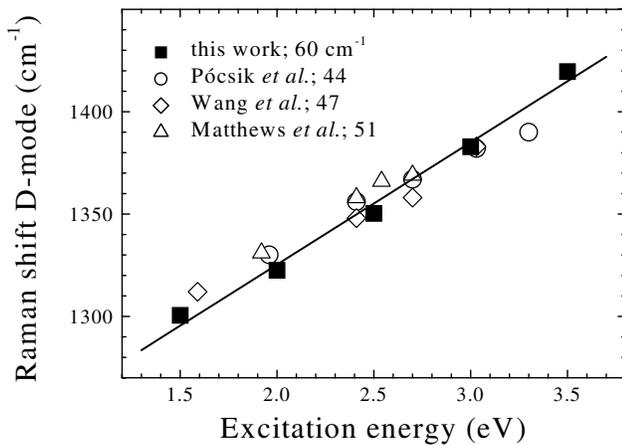


FIG. 4. Measured and calculated frequencies of the D band as a function of the excitation energy. The open symbols correspond to experimental data, and the closed squares to the calculated phonon energies in double resonance. The line is a linear fit to the theoretical values with a slope of $60 \text{ cm}^{-1}/\text{eV}$, the numbers give the corresponding slopes for the data.

understood excitation-energy dependence of the D mode in graphite. Using a realistic electron and phonon band structure we calculated the absolute value as well as the rate at which the D mode shifts without adjusting any parameter to $60 \text{ cm}^{-1}/\text{eV}$ compared to $\approx 50 \text{ cm}^{-1}/\text{eV}$ as observed experimentally. The recently introduced quasi-selection rule “ $k = q$ ” for the explanation of this phenomenon may be dismissed.

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