Asymmetry in the Raman cross section from large temperature variation

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We show that in the presence of large temperature gradients the second-order Raman cross sections can show asymmetry around the optical-phonon frequency. This skewness as a function of Raman frequency is proportional to the temperature gradient and is traced to the form of the accoustical-phonon occupation. It thus provides an additional mechanism for this asymmetry in addition to the usual spatial variation considered previously.

The Stokes intensity R_S has been studied in solids under equilibrium conditions.[1] More recently, such measurements have been extended to systems far from global equilibrium (but possibly in local equilibrium, i.e., equilibrium within small microscopic regions) of which one manifestation is very large "temperature"[2] gradients. Laser annealing is an example of such a system. It is the purpose of this paper to focus on noticeable asymmetry in R_S observed for such large nonuniformity in the temperature.[2] We follow a previous study of Brillouin scattering,[3] where *acoustic* phonons (AP) at the center of the Brillouin zone (BZ) are involved, and extend it here to Raman cross sections with the corresponding *optical* phonons (OP) at the center of the BZ. While other mechanisms certainly exist for explaining such asymmetries in R_S (see, for example, Ref. 2) the one we propose has not been previously considered, and if its magnitude is competitive it could provide insight into higher-order Raman processes.

The Raman-Stokes intensity R_S, of any nonuniform collections of electrons and ions, can be written as[4]

$$R_S \approx \int d^3\vec{r} \int d^3\vec{r}\,' \sum_{\vec{l},\vec{l}\,'} n_\alpha n_\beta I_{\alpha\gamma\beta\delta}(\nu_L,\nu_S,\vec{u}_{\vec{l}}(\vec{r}),\vec{u}_{\vec{l}\,'}(\vec{r}\,'),\vec{r},\vec{r}\,')E_\gamma(\vec{r})E_\delta(\vec{r}\,') \;, \quad (1)$$

where $\hat{n}$ is a unit vector defining the scatterd light of frequency ν_S, $\vec{E}$ is the electric field of the incident light of frequency ν_L, $\vec{u}_{\vec{l}}$ are the displacements of the ions at lattice positions $\vec{l}$, and $I_{\alpha\gamma\beta\delta}$ is the Raman tensor[4] which contains both electronic and vibrational coordinates. In the usual way[4] we can next make expansions of I in the ionic coordinates $\vec{u}_{\vec{l}}$ (first order in $\vec{u}_{\vec{l}}$ is first-order Raman, etc.). The point we wish to make [in Eq. (1)] is that when the spatial variation of $\vec{E}(\vec{r})$ is of the scale of the nonuniformity it samples, the nonlocal dependence of I on $\vec{r}$ and $\vec{r}\,'$ might become very important.

While Eq. (1) is rigorous it is clearly intractable. To reduce it we make the following two assumptions: (1) The vibrational modes are unaffected by the global "temperature" nonuniformity, and their occupation obeys local statistics [with "temperature" $T(z)$, see below]; (2) the electronic contribution to I via the electron-ion interaction is also a local function of $T(z)$. (We consider nonuniformity in only the perpendicular direction z to the surface.) With these two assumptions first- or higher-order Raman intensities can be written in terms of local quantities, i.e., the scattering cross sections (see Fig. 1) are calculated as though the system were *uniform* with a local "temperature" $T(z)$. For example, for a surface with "temperature" profile $T(z)$ the differential first-order Stokes-Raman intensity $dR_S(z)$ at point z is given by[5]

$$dR_S(z) = \nu_S^3 R_L e^{-\alpha_L z}\delta(\nu_L-\nu_S-\omega_0)\sigma(\nu_L,\nu_S) \times [n(z)+1]dz \;, \quad (2)$$

where R_L is the incident laser photon flux, α_L the absorption coefficient at frequency ν_L, ω_0 the frequency of the Raman phonon, $\sigma(\nu_L,\nu_S)$ the Stokes-Raman cross section, and $n(z)$ the OP occupation at the center of the BZ.[5] We have neglected the local variation in $\alpha_L(z)$, which would otherwise modify

$$e^{-\alpha_L z} \to \exp\left[-\int_0^z \alpha_L(z')dz'\right] .$$

If d is defined as some characteristic length over which the "temperature" $T(z)$ shows appreciable variation, then the total signal is[5]

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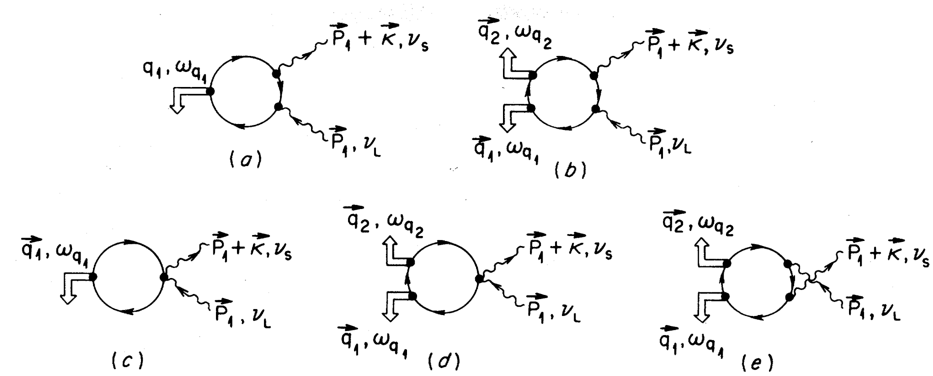

FIG. 1. (a) Feynman diagrams for the first-order Raman cross section σ_s in an emission of an optical phonon. The wiggly lines are the incoming and outgoing photons; the double solid line is the optical phonon and the single arrowed line the electron propagators. In more common treatments (Ref. 4) this graph is nothing more than the polarizability tensor $P_{\alpha\beta}(oj)$ in Eq. (7) of Ref. 4. The Raman cross section σ_s is calculated by squaring this contribution and averaging over the Boltzman ensemble (Ref. 4). (b) Second-order Raman cross section σ_s' for an emission of an optical phonon and acoustic phonon of wave vectors $\vec{q}_1$ and $\vec{q}_2$, respectively. This graph is the term $P_{\alpha\beta}(\vec{q},j,j)$ in Eq. (7) of Ref. 4. Both figures 1(a) and 1(b) correspond to the $\vec{J}\cdot\vec{A}$ coupling of the electron to the electromagnetic field. Note that both Figs. 1(a) and 1(b) do not include electron-electron interactions which further modify the electron contributions (i.e., the circle) to σ_s. (c) the same as Fig. 1(a) for ρA^2 coupling. (d) The same as Fig. 1(b) for ρA^2 coupling. (e) Example of additional contributions to σ_s' which relate via crossing symmetries. There are two for σ_s [Fig. 1(a)] and six for σ_s' [Fig. 1(b)].

$$R_S = \nu_S^3 R_L \delta(\nu_L - \nu_S - \omega_0) \times \int_0^\infty \sigma_S(\nu_L,\nu_S,z) \times [n(z)+1]\exp[-(\alpha_L+\alpha_S)z]\,dz\ , \tag{3}$$

where α_S is the absorption at the Stokes frequency ν_S. The type of spatial variation in $\sigma(z)$ and $n(z)$ of Eq. (3) has been considered previously[2,5,6] and will not be our primary interest here [see discussion following Eq. (4)]. We therefore imagine a probe laser of frequency ν_L such that the absorption takes place within a distance much smaller than d [i.e., $d(\alpha_L+\alpha_S) \gg 1$]. Then[5] Eq. (3) simplifies to

$$R_S = \frac{\nu_S^3 R_L \delta(\nu_L-\nu_S-\omega_0)\sigma_S(\nu_L,\nu_S)}{\alpha_L+\alpha_S}(n+1)\ . \tag{4}$$

We now turn to the particular effect (from the z dependence in the temperature) which is of interest here. Imagine first that Fig. 1 describes a Brillouin process, i.e., an emission or absorption of an AP. Even when we neglect the overall spatial variation in $\sigma(z)$ and $n(z)$ [as we did in arriving at Eq. (4)], the local derivative in the "temperature" introduces a modification in the AP occupation.[3] More explicitly, consider the Boltzmann equation for the acoustical branch (in the presence of a temperature gradient $\vec{\nabla}T$, summation over polarization is implicit). With the use of the usual transformation for the phonon occupation,[7] i.e.,

$$n(\vec{q}) = n_0(\vec{q}) - \frac{\partial n_0(\vec{q})}{\partial \omega_q}\phi_{\vec{q}}\ , \tag{5}$$

where $n_0(\vec{q}) = 1/(e^{\beta\omega_{\vec{q}}}-1)$, the standard Boltzmann equation for these acoustic phonons emerges,[7] i.e.,

$$-v_{\vec{q}_1}\cdot\vec{\nabla}T\frac{\partial n_0(\vec{q}_1)}{\partial T} = \beta\sum_{\vec{q}_2,\vec{q}_2'}\{\tfrac{1}{2}P_{\vec{q}_1,\vec{q}_2}^{\vec{q}_2'} \times[-\phi_{\vec{q}_1}+\phi_{\vec{q}_2}+\phi_{\vec{q}_2'}] + P_{\vec{q}_2',\vec{q}_2}^{\vec{q}_1}[-\phi_{\vec{q}_1}-\phi_{\vec{q}_2}+\phi_{\vec{q}_2'}]\}\ , \tag{6a}$$

where

$$P_{\vec{q}_1,\vec{q}_2}^{\vec{q}_2'} = \delta(\omega_{\vec{q}_1}-\omega_{\vec{q}_2}-\omega_{\vec{q}_2'})n_0(\vec{q}_2)n_0(\vec{q}_2') \times[1+n_0(\vec{q}_1)]D_{\vec{q}_1,\vec{q}_2}^{\vec{q}_2'}\ , \tag{6b}$$

$D_{\vec{q}_1,\vec{q}_2}^{\vec{q}_2'}$ is the matrix element connecting the three AP [for the additional channel of an OP and two

AP, see Eq. (9) below], $P_{\vec{q}_1,\vec{q}_2}^{\vec{q}\,'_2}$ defined in Eq. (6b) is the equilibrium transition rate,[7] and $v_{\vec{q}_1}=\partial\omega_{q_1}/\partial\vec{q}_1$. If the crystal possesses inversion symmetry, Eq. (6a) can be solved *exactly* for the zone-center ($\vec{q}_1=0$) AP. This follows from the appropriate symmetries of the scattering amplitude $D_{\vec{q}_1,\vec{q}_2}^{\vec{q}\,'_2}$ which, of course, includes both normal *as well* as umklapp processes. We get

$$\lim_{\vec{q}_1\to 0}\phi_{\vec{q}_1}=-\lim_{\vec{q}_1\to 0}\left[v_{\vec{q}_1}\cdot\frac{\vec{\nabla}T}{T}\right]\omega_{\vec{q}_1}\tau(\vec{q}_1)\ , \quad (7a)$$

where

$$\lim_{q_1\to 0}\tau(\vec{q}_1)=\frac{1}{\beta}\frac{\partial n_0(\vec{q}_1)}{\partial\omega_{\vec{q}_1}}\times\left[\sum_{\vec{q}_2,\vec{q}\,'_2}\left(\tfrac{1}{2}P_{\vec{q}_1,\vec{q}\,'_2}^{\vec{q}_2}+P_{\vec{q}_2,\vec{q}\,'_2}^{\vec{q}_1}\right)\right]^{-1}+O(1)\ . \quad (7b)$$

[From Eq. (6a), the correction to $\tau(\vec{q}_1)$ of Eq. (7b), as one moves slightly from the center of the BZ, is of order 1, i.e., $|\vec{q}_1|^0$.] Also, it is not hard to see that higher-order phonon-phonon scattering will only modify Eq. (6b) by bringing higher-order sums of higher-order scattering processes, e.g., $\sum_{\vec{q}_2,\vec{q}\,'_2,\vec{q}\,''_2}D_{\vec{q}_1,\vec{q}_2}^{\vec{q}\,'_2,\vec{q}\,''_2}$.[7] From Eqs. (5) and (7) we get

$$\lim_{\vec{q}_1\to 0}n(\vec{q}_1)+1=\lim_{\vec{q}_1\to 0}\left[n_0(\vec{q}_1)+1-\gamma(\vec{q}_1)v_{\vec{q}_1}\cdot\frac{\vec{\nabla}T}{T}\right]\ , \quad (8a)$$

where

$$\gamma(\vec{q}_1)=\omega_{\vec{q}_1}\tau(\vec{q}_1)\frac{\partial n_0(\vec{q}_1)}{\partial\omega_{\vec{q}_1}}\ . \quad (8b)$$

Clearly, $\vec{\nabla}T$ introduces asymmetry in the Brillouin cross section if $\gamma(\vec{q}_1)$ and $v_{\vec{q}_1}$ are *nonzero*. The finite-phase velocity of the AP ($\lim_{\pm q_1\to 0}v_{\vec{q}_1}=\pm v_S$, which equals speed of sound), the low energy of the excitations ($\omega_q=v_S q$) coupled with the singular structure of $n_0(\vec{q}_1)$, and the infinite lifetime $\tau(\vec{q}_1)$ (Refs. 8–13) ensure this. [Note that boundary scattering will make $\tau(\vec{q}_1)$ finite for $\vec{q}_1=0$ (Ref. 9).] The question we explore next is whether similar corrections can enter the optical-phonon Raman cross sections.[14]

The effect of $\vec{\nabla}T$ on the OP occupation cannot be as pronounced as for the AP for two reasons; OP have zero velocity at the BZ center and the excitations have finite energy (as $\vec{q}_1\to 0$). From Eq. (6) the correction is in fact *identically* zero at $\vec{q}_1\to 0$. One could imagine that the coupling between the OP and AP branches would impart indirectly a phase velocity to the OP. We show that this is not so. We identify the variable $\vec{q}_1$ with the OP and $\vec{q}_2$ with the AP. Equation (6a) only changes in that now $\phi_{\vec{q}_2}$ (AP branch) has a different functional form from $\phi_{\vec{q}_1}$ (OP branch). The second equation for this coupled system is

$$-v_{\vec{q}_2}\cdot\vec{\nabla}T\frac{\partial n_0(\vec{q}_2)}{\partial T}=\beta\sum_{\vec{q}_1,\vec{q}\,'_2}\{P_{\vec{q}_1,\vec{q}_2}^{\vec{q}\,'_2}[\phi_{\vec{q}_1}-\phi_{\vec{q}_2}-\phi_{\vec{q}\,'_2}]+P_{\vec{q}\,'_2,\vec{q}_2}^{\vec{q}_1}[\phi_{\vec{q}\,'_2}-\phi_{\vec{q}_1}-\phi_{\vec{q}_2}]+\mathrm{P}_{\vec{q}_2,\vec{q}_1}^{\vec{q}\,'_2}[\phi_{\vec{q}_1}+\phi_{\vec{q}\,'_2}-\phi_{\vec{q}_2}]\}\ . \quad (9)$$

It is again not difficult to show that at the center of the BZ, $\phi_{\vec{q}_1}$ is given *exactly* by Eq. (7). Although the coupled Eqs. (6) and (9) only allow for the channel where OP scatter off two AP, a full treatment does not change this conclusion. In fact, it can be readily seen that phonon-phonon scattering to any order with electron scattering included will also leave the OP occupation *unchanged* to order $|\vec{\nabla}T|$ (this follows from appropriate symmetries of the scattering amplitudes). Second order in $|\vec{\nabla}T|$ or ∇^2T contributions cannot introduce asymmetry in R_S and will not be considered here.

We have approached the effect of $\vec{\nabla}T$ on the OP via the Boltzmann equation in order to make direct contact with the work of Griffin on AP. Actually, R_S [Figs. 1(a) and 1(c)] can be written more rigorously than Eq. (4) by replacing the OP occupation numbers $\delta(\nu_L-\nu_S-\omega_0)(n+1)$ by the exact OP propagators $D(\vec{q},\omega)$ [see, e.g., Eq. (11) of Ref. 4]. As long as $D(\vec{q},\omega)$ has no discontinuity at $\vec{q}=0$, i.e.,

$$\lim_{\vec{q}\to 0}D(\vec{q},\omega)=\lim_{\vec{q}\to 0}D(-\vec{q},\omega)\ ,$$

the effect of $\vec{\nabla}T$ on the first-order R_S must vanish. (This is expected for the OP which differ from AP by their *finite* optical frequency $\omega(\vec{q}_1=0)=\omega_0$ and *zero-phase* velocity.) $\vec{\nabla}T$, however, can incur corrections of the form of Eq. (8) in second- and higher-order R_S [Figs. 1(b) and 1(d)]. To see this, consider the emission of two phonons. Then R_S gets corrected by

$$\Delta R_S=\frac{\nu_S^3}{\alpha_L+\alpha_S}R_L\sum_{\vec{q}_1,\vec{q}_2}[n(\vec{q}_1)+1][n(\vec{q}_2)+1]\delta(\vec{q}_2+\vec{q}_1+\vec{\kappa})\delta(\omega_{\vec{q}_2}+\omega_{\vec{q}_1}-\Omega)\sigma'_S(+\vec{q}_2,\vec{q}_1,\vec{p}_1,\vec{p}_1+\vec{\kappa}) , \quad (10)$$

with σ' the *second*-order Stokes-Raman cross section and where $\vec{p}_1$ is the momentum of the incident light, $\vec{\kappa}$ the momentum exchange, and $\Omega=\nu_L-\nu_S$. (Emission of a phonon and absorption of the other also have to be considered.)

Now light carries very small momentum ($\vec{\kappa}$ is small) and $\vec{q}_1=-\vec{q}_2-\vec{\kappa}\approx-\vec{q}_2$. It then follows that linear corrections in $\vec{\nabla}T$ again vanish (to *order* κ) *unless* one of the phonon occupations contains singular behavior. For example, the channel of two AP (of opposite momentum) combining to give the OP energy ω_0, or similarly the transverse and longitudinal AP near the zone edge along the [100] direction,[1] are both not relevant to $\vec{\nabla}T$ or ΔR_S. The only relevant channel is the convolution of the AP and OP (both at the center of the BZ) where the AP carry a singularity [Eqs. (5) and (7)]. It is tempting to dismiss Eq. (10) on the basis that the phase space of such contributions is very small (due to κ being small). We show next that the form of $\tau(\vec{q})$ (Refs. 8 and 9) and the singular nature of the AP occupation compensate for the small phase space and lead to a finite correction ΔR_S. (Finite here means a contribution which is not scaled by positive powers of v_S/c, or equivalently by positive powers of κ, where c is the speed of light in the media.) Since the $\vec{\nabla}T$ contribution comes entirely from the center of the BZ we write σ'_S as a leading small $\vec{q}_1$ and $\vec{q}_2$ expansion, e.g.,

$$\sigma'_S(+\vec{q}_2,\vec{q}_1,\vec{p}_1,\vec{p}_1+\vec{\kappa})\approx\Delta_S(\vec{p}_1,\vec{\kappa})\,|\vec{q}_2|^t\,|\vec{q}_1|^u(\vec{q}_2\cdot\vec{q}_1)^2 . \quad (11)$$

[The exponents t and u and the function Δ_S are discussed following Eq. (16).] The $\vec{\nabla}T$ contribution to the AP occupation $n(\vec{q}_2)$ is given by Eqs. (5) and (7). For the lifetime $\tau(\vec{q}_2)$ we use the form from Callaway,[9] i.e.,

$$\tau(\vec{q}_2)=\frac{1}{A\omega^4_{\vec{q}_2}+(B_1+B_2)T^3\omega^s_{\vec{q}_2}+v_S/L} , \quad (12)$$

where $\omega_{q_2}=v_Sq_2$ and $\omega_q=\omega_0$, A is the phonon impurity scattering, and B_1 and B_2 correspond to the umklapp and normal contributions to τ [note that B_1 contains the exponential temperature factor $e^{-\Theta/aT}$, where Θ is the Debye temperature and a is a characteristic constant of order 2 (see Refs. 7 and 9)]. The term v_S/L reflects corrections from *macroscopic* boundary scattering[9]; here we will take $L\to\infty$. The contribution of $\vec{\nabla}T$ to $n(\vec{q}_2)$ is

$$\lim_{\vec{q}_2\to 0} n(\vec{q}_2)=-\frac{\partial n_0(q_2)}{\partial\omega_{q_2}}\phi_{\vec{q}_2}=-\frac{k_B\vec{q}_2\cdot\vec{\nabla}T}{\hbar q_2^2[Av_S^4q_2^4+(B_1+B_2)T^3(v_Sq_2)^s+v_S/L]} . \quad (13)$$

Combining Eqs. (11), (13), and (10), we get

$$\Delta R_S=\frac{+\nu_S^3}{\alpha_L+\alpha_S}R_L[n(\omega_0)+1]\frac{k_B}{\hbar}\Delta_S(\vec{p}_1,\vec{\kappa})$$
$$\times\sum_{\vec{q}_1}(\vec{\kappa}+\vec{q}_1)\cdot\vec{\nabla}T\frac{|\vec{q}_1+\vec{\kappa}|^t\,|\vec{q}_1|^u}{|\vec{\kappa}+\vec{q}_1|^2[Av_S^4|\vec{\kappa}+\vec{q}_1|^4+(B_1+B_2)T^3(v_S|\vec{\kappa}+\vec{q}|)^s+v_S/L]}$$
$$\times[(\vec{q}_1+\vec{\kappa})\cdot\vec{q}_1]^2\delta(v_S|\vec{\kappa}+\vec{q}_1|+\omega_0-\Omega) . \quad (14)$$

The integral over $\vec{q}_1$ can be carried out. For a backscattering geometry (i.e., $\vec{\kappa}\approx-2\vec{p}_1$), we get

$$\Delta R_S=+\frac{\nu_S^3}{\alpha_L+\alpha_S}R_L[n(\omega_0)+1]\frac{k_B}{\hbar}\Delta_S(\vec{p}_1,\vec{\kappa})\frac{|\vec{\nabla}T|\,I(\kappa,\epsilon)}{v_S|\vec{\kappa}|\,\epsilon^{-t+1}[Av_S^4\epsilon^4+(B_1+B_2)T^3(v_S\epsilon)^s+v_S/L]} , \quad (15a)$$

where

$$I(\kappa,\epsilon)=\frac{1}{8|\vec{\kappa}|}[J_{1+u}(\kappa,\epsilon)(\kappa^6-\epsilon^2\kappa^4-\epsilon^4\kappa^2+\epsilon^6)+J_{3+u}(\kappa,\epsilon)(-3\kappa^4+2\epsilon^2\kappa^2+\epsilon^4)$$
$$+J_{5+u}(\kappa,\epsilon)(3\kappa^2-\epsilon^2)-J_{7+u}(\kappa,\epsilon)] , \quad (15b)$$

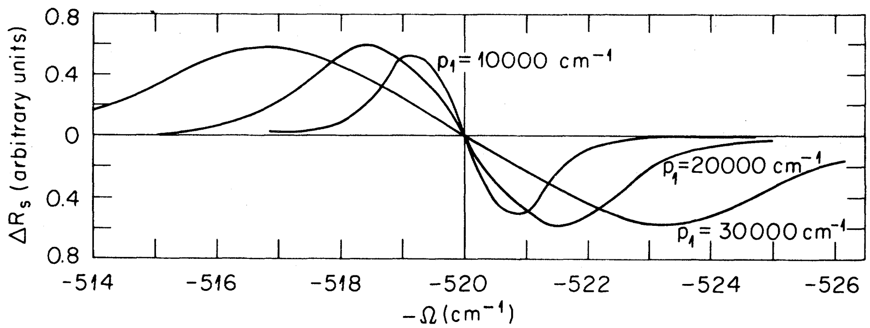

FIG. 2. Contribution to the Raman cross section ΔR_S from the emission of an optical and an acoustical phonon in the center of the Brillouin zone. The incoming wave number of the probing laser p_1 is set equal to 10000, 20000, and 30000 cm^{-1}.

where

$$J_a(\kappa,\epsilon)=\int_{\epsilon-\kappa}^{\epsilon+\kappa} q^a dq \tag{16}$$

and $\epsilon=|\Omega-\omega_0|/v_S$. For an absorption of an AP and an emission of an OP (i.e., $|\Omega|<\omega_0$) we get the negative of Eq. (15); thus ΔR_S is indeed asymmetric. For the exponent s we take the value of Callaway[9,15] ($s=2$). The exponents t and u are much more difficult to establish, and so in order not to overestimate we choose the least favorable values for the effect of $\vec{\nabla}T$ ($t=-1$ and $u=-2$). With these three exponents and setting $A=0$ and $L\rightarrow\infty$, we see that in Eq. (15a) $\kappa\epsilon^{s-t+1}=\kappa\epsilon^4$. Now ϵ is of the order of κ and comparison of the powers of κ and ϵ in Eqs. (15) and (16) leads to finite contribution from ΔR_S [indeed the small-phase space does get compensated by the structure of $n(q_2)$ of the AP; see the discussion preceding Eq. (11)].

Along with the exponents t and u it remains for us to establish the magnitude of $\Delta_S(\vec{p}_1,\vec{\kappa})$ in Eq. (11), which is indeed very difficult since it clearly depends on the details of higher-order electron-phonon interactions [see Figs. 1(b) and 1(d)]. We therefore will only briefly consider the magnitude of ΔR_S. We concentrate more on its dependence on ν_L (the probing laser's frequency). In Fig. 2 we display the asymmetry contribution of ΔR_S for three different ν_L.[16] The temperature $T(z)$ was set to 350 K and the temperature gradient to 5×10^5 K/cm.[17] Particularly striking is the change in the width of the asymmetry around the OP frequency $\omega_0=520$ cm^{-1}. We would like to add that this asymmetry is about the OP position and not an asymmetry in the Stokes—anti-Stokes ratio. It thus is different from that observed in Ref. 3. The experimentally observed asymmetry[2] was attributed to a geometrical variation in T largely parallel to the surface. Our contribution, from Eq. (15), come from variations in the temperature only along z. However, without an accurate estimate of $\Delta_S(\vec{p}_1,\vec{\kappa})$ we cannot tell whether it is competitive in magnitude with other considerations.[2] A *very rough* estimate in which we assume that the emission of the AP proceeds independently from the OP via the usual screened electron-phonon matrix element[7] and in which the symmetric line shape around the OP is approximated via a Lorentz linewidth of 3 cm^{-1} could possibly produce an asymmetric correction of the order of a percent away from the center OP line. Preferably, however, its signature [strong dependence on ν_L and $\vec{\nabla}T(z)$] should be experimentally verified. For example, in laser annealing (where large $\vec{\nabla}T$ are expected) major differences in $\vec{\nabla}T(z)$ exist in different time duration of the annealing pulse[15,18] which can help identify such ΔR_S contributions. Finally, one can aim experimentally for larger $\vec{\nabla}T$ at lower T [see Eq. (15a)] in the hope of encouraging enhancement of the asymmetry. The possibility of extracting the structure of Eq. (11) experimentally could then yield interesting information about higher-order Raman cross sections.

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[14]We would like to make here a brief connection between the exact result of Eq. (6) (in the center of the BZ) and apprxoimate relations throughout the BZ (Refs. 9—13). Following Callaway[9] we see that if α [Eq. (6) of Ref. 9] is set equal to our $\tau(\vec{q}_1)$, the two results are similar; but there is more to it than that. The displacement parameter $\lim_{\vec{q}\to 0}\lambda(\vec{q}_1)=-\beta' v_S^2 \vec{\nabla} T/T$ [Eq. (10) of Ref. 9], and therefore $\alpha=\tau_c(1+\beta'/\tau_N)=\tau_c+O(1)$, which is consistent with the $O(1)$ correction of Eq. (7b).

[15]In certain symmetry direction the exponent s can be larger (see Ref. 8). However, not to overestimate the effect of $\vec{\nabla} T$, we choose $s=2$.

[16]Note, from Eq. (15), that boundary scattering of the form of Eq. (12) is not expected to change these results drastically.

[17]Such temperature and temperature gradients are observed in model calculations (see Ref. 6) during the initial duration of the annealing laser pulse. We also caution that for this temperature the lifetime in Eq. (12) (and, in particular, its temperature dependence) is being extended beyond its true limit of validity (see Refs. 8 and 9).

[18]We should, however, note that the higher temperature gradients are accompanied (usually) by higher temperatures which, through Eqs. (12) and (15), tend to compensate. A better nomenclature would probably be ν_L.