More about the Raman modes

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It is shown that the soft mode among the (24p–3) optical modes propounded by Raman has the characteristics of high phonon magnification factor and is also a caustic at phase transition.

THE heat pulse experiments[1,2] have demonstrated that phonons are focused in certain directions and defocused in certain other directions, even when one starts with an incoherent source of phonons with isotropic angular distribution of wave vectors. The phonon magnification factor (PMF) A has been defined by Taylor *et al.*[1,2], as the ratio of the solid angle in the wave vector space to the solid angle in the group velocity space:

$$\frac{1}{A}=\frac{\mathrm{d}\Omega_s}{\mathrm{d}\Omega_q}=\frac{\sin\theta_s \mathrm{d}\theta_s \mathrm{d}\phi_s}{\sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi}, \tag{1}$$

where (θ_s, ϕ_s) denote the polar angles of the group velocity vector and (θ, ϕ) those of the wave vector. Earlier Jacob Philip and Viswanathan[3] had evolved a computer-based numerical method to evaluate the phonon focusing for crystals. The PMF has been studied earlier by Viswanathan and his students[4–6] for acoustic waves for a large number of crystals. The phonon focusing effect is best demonstrated experimentally by the ballistic phonon imaging technique devised by Northrop and Wolfe[7,8].

While these studies have focused on acoustic modes, very little work has been carried out for phonon focusing for optical modes. Northrop and Wolfe[7,8] have also studied the phonon focusing for optical modes. We define the magnification factor A_{op} for the optical modes as

$$\frac{1}{A_{\mathrm{op}}}=\frac{\mathrm{d}s_x\mathrm{d}s_y\mathrm{d}s_z}{\mathrm{d}q_x\mathrm{d}q_y\mathrm{d}q_z}=\frac{s^2\sin\theta_s\mathrm{d}s\mathrm{d}\theta_s\mathrm{d}\phi_s}{q^2\sin\theta\mathrm{d}q\mathrm{d}\theta\mathrm{d}\phi}. \tag{2}$$

Since this quantity involves the Jacobian $J=(\partial(s_x, s_y, s_z)/\partial(q_x, q_y, q_z))$ of the transformation from the group velocity space to the wave vector space, it is clear that the phonon magnification factor is inversely proportional to the Jacobian of the transformation between the two sets of variables.

This note investigates how the phonon magnification factor A_{op} for optical modes behaves near a phase transformation. It was shown earlier by Viswanathan[9] that the group velocity of the waves vanishes for (24p–3) optical modes. According to Raman[10,11], for these modes, equivalent atoms in adjacent cell vibrate either with the same phase or with opposite phase. Since the group velocity is inversely proportional to the frequency distribution $f(\nu)$ of phonons, these modes further have singularities in the frequency spectrum. Representing the wave vector $\mathbf{q}$ in the reciprocal space $\mathbf{q}=\theta_1\mathbf{b}_1+\theta_2\mathbf{b}_2+\theta_3\mathbf{b}_3$ where $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ are the basic vectors of the reciprocal space, these modes correspond for the set $(\theta_1, \theta_2, \theta_3)$ to the values $(0, 0, 0)$; $(\pi, 0, 0)$; $(0, \pi, 0)$; $(0, 0, \pi)$; $(0, \pi, \pi)$; $(\pi, 0, \pi)$; $(\pi, \pi, 0)$ and (π, π, π).

These modes are well known as zone centre or zone boundary modes in the literature. Their importance in solid state physics stems from the fact that all phase transitions, ferroelectric or antiferroelectric, correspond to soft modes associated with any one of these wave vectors.

As stated earlier, the group velocity $(\mathrm{d}\omega/\mathrm{d}q)$ for these optical modes vanishes. If in addition, the second derivatives $(\partial^2\omega/\partial q_x\partial q_y)$ vanish all or more especially the determinant of these quantities vanishes, the zone centre-boundary modes will further have the characteristics of a caustic. Here, we find under what conditions, these modes will turn into a caustic for phonon propagation.

This dispersion equation for a crystal with p atoms in the unit cell is given by[12,13]:

$$x^{3p}+s_1x^{3p-1}+\ldots+s_rx^{3p-r}+\ldots+s_{3p-1}x+s_{3p}=0, \tag{3}$$

where we write $x=\omega^2$.

We try to evaluate the second derivative of ω with respect to q at the zone centre or any one of the zone boundary points. Differentiating the above equation twice with respect to q and noting that at these points $(\mathrm{d}\omega/\mathrm{d}q)=0$, we get

$$2\omega\frac{\mathrm{d}^2\omega}{\mathrm{d}q^2}=-(X/Y), \tag{4}$$

$$\text{where } X=x^{3p-1}\frac{\mathrm{d}^2s_1}{\mathrm{d}q^2}+\ldots+x\frac{\mathrm{d}^2s_{3p-1}}{\mathrm{d}q^2}+\frac{\mathrm{d}^2s_{3p}}{\mathrm{d}q^2}, \tag{5}$$

$$\text{and } Y=3px^{3p-1}+s_1(3p-1)x^{3p-2}+\ldots+2s_{3p-2}x+s_{3p-1}. \tag{6}$$

We shall now suppose that the mode $\omega=\omega_1$ is the soft mode and it tends to zero in the limit $T\to T_c$, where T_c is the critical temperature for the phase transition. In the limit $x_1\to 0$, we obtain

$$2\omega_1\frac{\mathrm{d}^2\omega_1}{\mathrm{d}q^2}=\frac{-\left[\frac{\mathrm{d}^2s_{3p}}{\mathrm{d}q^2}+x_1\frac{\mathrm{d}^2s_{3p-1}}{\mathrm{d}q^2}+O(x_1^2)\right]}{[s_{3p-1}+O(x_1)]}, \tag{7}$$

Now s_{3p} is the product of all the roots of the equation with a sign factor and may be written as

$$s_{3p} = (-1)^{3p}\Pi\omega_r^2 = \omega_1^2 F, \quad (8)$$

where $F = (-1)^{3p}\omega_2^2\omega_3^2 \ldots \omega_{3p}^2$. (9)

From this we find that

$$\frac{d^2 s_{3p}}{dq^2} = 4\omega_1 \frac{d\omega_1}{dq}\frac{dF}{dq} + 2\omega_1 \frac{d^2\omega_1}{dq^2} F$$

$$+2\left(\frac{d\omega_1}{dq}\right)^2 F + \omega_1^2 \frac{d^2 F}{dq^2}. \quad (10)$$

Since $(d\omega/dq) = 0$, at these critical points, we have

$$\frac{d^2 s_{3p}}{dq^2} = 2\omega_1 \frac{d^2\omega_1}{dq^2} F + \omega_1^2 \frac{d^2 F}{dq^2}. \quad (11)$$

Again s_{3p-1} is the sum of products of all the roots of eq. (3) taken $(3p-1)$ at a time with a sign factor of $(-1)^{3p-1}$.

We group it into terms involving $\omega_1{}^2$ and another term not involving it. We write

$$s_{3p-1} = \{\omega_1^2 F_2 + (-1)^{3p-1}\omega_2^2\omega_3^2 \ldots \omega_{3p}^2\}$$

$$= \omega_1^2 F_2 - F. \quad (12)$$

In the limit when $\omega_1 \to 0$, we have $s_{3p-1} \to -F$.

And further in the limit when $(d\omega/dq) = 0$, one can find that

$$\frac{d^2 s_{3p-1}}{dq^2} \to 2\omega_1 \frac{d^2\omega_1}{dq^2} F_2 - \frac{d^2 F}{dq^2}. \quad (13)$$

Hence from eq. (7) we find that

$$2\omega_1 \frac{d^2\omega_1}{dq^2} = -(A/B), \quad (14)$$

where $A = -\Bigg[2\omega_1 \frac{d^2\omega_1}{dq^2} F + \omega_1^2 \frac{d^2 F}{dq^2} + \omega_1^2$

$$\times\left(2\omega_1 \frac{d^2\omega_1}{dq^2} F_2 - \frac{d^2 F}{dq^2}\right) + x_1^2 \frac{d^2 s_{3p-2}}{dq^2}\Bigg] \quad (15)$$

and $B = (-F + \omega_1^2 F_2)$, (16)

$$\text{or } \frac{d^2\omega_1}{dq^2} = \frac{\omega_1}{4F_2}\frac{d^2 s_{3p-2}}{dq^2}. \quad (17)$$

In the same way we can show that

$$\frac{\partial^2\omega_1}{\partial q_x \partial q_y} \to \frac{\omega_1}{4F_2}\frac{\partial^2 s_{3p-2}}{\partial q_x \partial q_y}. \quad (18)$$

It follows that all the second derivatives of ω_1 with respect to q_x, q_y, q_z tend to zero as ω_1 or $|T-T_c|^{1/2}$. This result is stronger than saying that the determinant of the second derivatives vanishes. It is clear that the phonon magnification factor becomes infinite or in practical cases large due to scattering, as the transition temperature may still be different from the temperatures of the ballistic regime.

It was shown by the Viswanathan[9] that any initial disturbance in the crystal after a long time asymptotically settles into a superposition of the $(24p-3)$ normal modes with an amplitude proportional to $t^{-3/2}$. The effect of an initial disturbance is evaluated as an integral near the saddle point for which $(\partial\omega/\partial q_x) = 0$ $(x = x, y, z)$. When the second derivatives $(\partial^2\omega/\partial q_x \partial q_y)$ vanish for a particular frequency, this treatment needs modification. In this case the third order terms in the expansion of ω near the zone boundary or zone centre vectors make contributions to the integral which varies far more slowly than what the $t^{-3/2}$ law might suggest. (For example, an integral in one variable that would normally yield $t^{-1/2}$ will now vary as $t^{-1/3}$.) The amplitude will be much higher than $t^{-3/2}$ or in other words, these modes in addition to being singularities in the frequency spectrum are also caustics. When a phase transition takes place, the mode that becomes soft has high magnification factor besides being a caustic.

1. Taylor, T., Maris, H. J. and Elbaum, C., *Phys. Rev. Lett.*, 1969, **23**, 416.
2. Taylor, R., Maris, H. J. and Elbaum, C., *Phys. Rev.*, 1971, **3**, 1462.
3. Philip Jacob and Viswanathan, K. S., *Phys. Rev.*, 1978, **B17**, 4969.
4. Viswanathan, K. S. and Pushpahasan, A., *Pramana*, 1985, **24**, 875.
5. Viswanathan, K. S., in Proceedings of XIII Winter School of Theoretical Physics held at Karpaacz, 1987, Springer-Verlag, Poland, p. 301.
6. Viswanathan, K. S. and Narasimha Iyer, V., *J. Phys.*, 1987, **C20**, 5261.
7. Northrop, A. and Wolfe, J. P., *Phys. Rev.*, 1980, **B22**, 6196.
8. Northrop, A. and Wolfe, J. P., *Phys. Rev. Lett.*, 1979, **43**, 1424.
9. Viswanathan, K. S., *Proc. Indian Acad. Sci.*, 1953, **37**, 424.
10. Raman, C. V., *Proc. Indian Acad. Sci.*, 1943, **18**, 237.
11. Raman C. V., *Proc. Indian Acad. Sci.*, 1947, **26**, 339.
12. Born, M. and Huang, K., *Dynamical Theory of Crystal Lattices*, Oxford, 1954.
13. Maradudin, A. A. *et al.*, *Theory of Lattice Dynamics in the Harmonic Approximation*, Academic Press, New York.

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