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## THEORY OF THE RESONANCE RAMAN EFFECT IN CRYSTALS

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**Résumé.** — Étude théorique de la relation entre l'intensité de la diffusion Raman et la fréquence excitatrice, dans le cas où cette fréquence est voisine d'une raie ou d'une bande d'absorption du cristal diffusant. On discute les cas des diffusions Raman spontanée et stimulée. Pour la diffusion par les niveaux électroniques d'atomes d'impuretés dans les cristaux, on trouve que l'intensité Raman atteint une valeur maximale constante quand le coefficient d'absorption à la fréquence d'excitation est très supérieur à l'inverse de la longueur de l'échantillon. On admet que, dans ce cas, l'absorption est produite par des transitions permises des atomes d'impureté eux-mêmes. Pour la diffusion Raman par vibrations du réseau, on étudie les effets de la proximité entre la fréquence d'excitation et la limite d'absorption électronique intrinsèque. On trouve que le rendement de l'effet Raman augmente brusquement lorsque la fréquence excitatrice tend vers la limite d'absorption, par valeurs inférieures. Ce rendement tombe à une valeur constante et faible pour des fréquences supérieures à cette limite, tandis que le coefficient d'absorption augmente rapidement dans cette région. La fréquence d'excitation la plus efficace est celle pour laquelle le coefficient d'absorption commence à augmenter notablement, à partir de sa valeur nulle au-dessous de la limite.

**Abstract.** — The dependence of the Raman-scattered intensity on exciting frequency is investigated theoretically for the case where this frequency is close to an absorption line or absorption band of the scattering crystal. Both spontaneous and stimulated Raman scattering are discussed. For scattering by electronic levels of impurity atoms in crystals, it is found that the Raman intensity achieves a constant maximum value when the absorption coefficient at the exciting frequency is much larger than the inverse sample length. It is assumed that the absorption in this case is produced by allowed transitions of the impurity atoms themselves. For Raman scattering by lattice vibrations, the effects of proximity of the exciting frequency to the intrinsic electronic absorption edge are investigated. It is found that the Raman efficiency increases steeply as the exciting frequency approaches the absorption edge from below. The efficiency falls to a small constant value for frequencies above the edge, while the absorption coefficient increases rapidly in this region. The optimum exciting frequency to use is the frequency at which the absorption coefficient begins to rise significantly from its zero value below the edge.

**I. Introduction.** — A common feature of theoretical expressions for the Raman scattering efficiency of a substance is the presence of terms which either diverge or become relatively large when the frequency of the exciting radiation is equal to an allowed optical transition frequency of the substance. This predicted increase in the intensity of the scattered light, known as the resonance Raman effect, is very familiar in the realm of Raman scattering from liquids, and good agreement is found between theory and experiment [1]. With the increased range of exciting frequencies now becoming available, it is of interest to consider the theory of the analogous phenomenon for crystal scatterers.

The proximity of the exciting frequency to an allowed transition frequency of the scattering substance may lead to a significant absorption of the exciting radiation. The scattered radiation may also be attenuated. These factors offset the increased scattering efficiency to some extent, and they must be allowed for in a realistic theory.

In section II we treat resonance effects in the ordinary, or spontaneous, Raman scattering inten-

sity. We include scattering both by the electronic states of impurity atoms in crystals, as first observed by Hougen and Singh [2] and by lattice vibrations. Stimulated Raman scattering is considered in section III, and the implications of the theory are discussed in the final section.

**II. Spontaneous Raman scattering.** — 1. GENERAL SCATTERING FORMULA. — Consider the right-angle Raman-scattering experiment illustrated in figure 1. The exciting radiation is assumed to be in a narrow parallel pencil, as from a laser source.

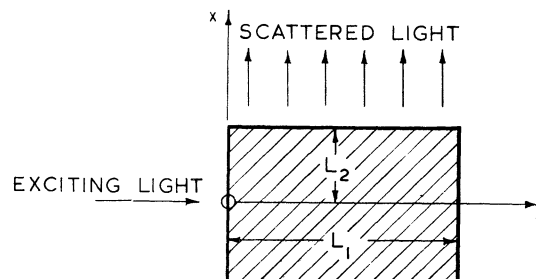


FIG. 1. — Right-angle Raman-scattering experiment.

Let the exciting and scattered radiation have frequencies  $\omega_1$  and  $\omega_2$ , and complex refractive indices  $N_1$  and  $N_2$ , respectively. Resolving the  $N$ 's into real and imaginary parts

$$N_1 = n_1 + i\alpha_1 \quad \text{and} \quad N_2 = n_2 + i\alpha_2, \quad (1)$$

and the intensity absorption coefficients at  $\omega_1$  and  $\omega_2$  are

$$\alpha_1 = 2\omega_1 \kappa_1/c \quad \text{and} \quad \alpha_2 = 2\omega_2 \kappa_2/c. \quad (2)$$

Let  $I_1(z)$  be the magnitude of the Poynting vector of the exciting radiation, and let  $I_2(x, z)$  be the energy in the scattered radiation produced per unit time and unit cross-sectional area, between the front face of the crystal and co-ordinate  $z$ . We suppose for simplicity that the detector of the scattered radiation collects light from a small solid angle  $d\Omega$  independent of the point from which the scattered light originates. The quantity  $I_2(x, z)$  refers only to the detected part of the scattered radiation.

The scattering efficiency of the crystal is characterized by a quantity  $R$  defined to be the radiative energy at frequency  $\omega_2$  scattered into  $d\Omega$  in unit volume of crystal and in unit time, divided by the energy flux of the exciting radiation. The dependence of  $R$  on  $\omega_1$  and  $\omega_2$  will be discussed in subsequent sections. The equations for the spatial dependence of  $I_1$  and  $I_2$  are

$$\left. \begin{aligned} dI_1(z)/dz &= -RI_1(z) - \alpha_1 I_1(z), \\ dI_2(x, z)/dx &= -\alpha_2 I_2(x, z), \\ dI_2(0, z)/dz &= RI_1(z). \end{aligned} \right\} \quad (3)$$

The solution for the total scattered and detected radiative energy  $I_2(L_2, L_1)$  with the boundary condition  $I_2(0, 0) = 0$  is

$$I_2(L_2, L_1) = [RI_1(0)/(R + \alpha_1)] \exp(-\alpha_2 L_2) \{1 - \exp[-(R + \alpha_1)L_1]\}. \quad (4)$$

The quantity attains a maximum value of  $[RI_1(0)/\alpha_1] \exp(-\alpha_2 L_2)$  when  $L_1$  is much greater than  $1/\alpha_1$ , assuming that  $\alpha_1$  is much larger than  $R$ .

If the crystal is strongly absorbing at  $\omega_2$  the 180° backward scattering arrangement shown in figure 2 may be preferable. With a slight redefinition of the various quantities to take account of the diffe-

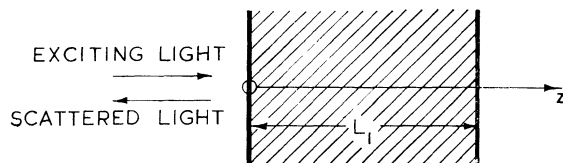


FIG. 2. — Backward-scattering experiment.

rent geometry, the total scattered energy produced at the exit surface ( $z = 0$ ) is

$$I_2(0) = [RI_1(0)/(R + \alpha_1 + \alpha_2)] \{1 - \exp[-(R + \alpha_1 + \alpha_2)L_1]\}. \quad (5)$$

For sufficiently large  $L_1$ , and assuming that  $\alpha_1$  and  $\alpha_2$  are much larger than  $R$ , the limiting value of  $I_2(0)$  is  $RI_1(0)/(\alpha_1 + \alpha_2)$ . A scattering geometry similar to that of figure 2 has been used by Khaikin and Bykov [3] in an unsuccessful attempt to detect Raman scattering from superconducting lead.

2. ELECTRONIC RAMAN EFFECT. — The analytic form of  $R$  for atomic energy levels is well known. We consider a crystal of volume  $V$  containing  $N$  identical impurity atoms. When  $\omega_1$  and  $\omega_2$  are well removed from resonance with the atomic transition frequencies,

$$R = \frac{Ne^4 \omega_2^2 n_2 d\Omega}{Vm^4 \omega_1^2 c^4 n_1} \left| \sum_j \left\{ \frac{\mathbf{e}_1 \cdot \mathbf{p}_{ij} \mathbf{e}_2 \cdot \mathbf{p}_{jf}}{E_j - E_i - \hbar\omega_1} + \frac{\mathbf{e}_2 \cdot \mathbf{p}_{ij} \mathbf{e}_1 \cdot \mathbf{p}_{jf}}{E_j - E_i + \hbar\omega_2} \right\} \right|^2 \quad (6)$$

(see e.g. reference [4]; in terms of the quantities of this reference,  $n_1 R/n_2 = \omega_2 S/(\omega_1 L)$ ). It is assumed that only the atomic ground state is populated in thermal equilibrium, and  $i, j$  and  $f$  refer to the ground, virtual intermediate, and final states of the atom. The energy conservation requirement is  $E_f - E_i = \hbar\omega_1 - \hbar\omega_2$ . The  $\mathbf{p}_{ij}$  and  $\mathbf{p}_{jf}$  are electronic momentum matrix elements between the subscripted states, and  $\mathbf{e}_1$  and  $\mathbf{e}_2$  are the unit polarization vectors of the exciting and scattered radiation. We concern ourselves only with the Stokes component of the scattered light.

When  $\hbar\omega_1$  is close to  $E_j - E_i$  for one of the terms in the summation over  $j$ , a resonance occurs in the first term in the bracket of (6), and this term dominates the summation (we assume that the transitions  $i \rightarrow j$  and  $j \rightarrow f$  are allowed; i.e.  $\mathbf{p}_{ij}$  and  $\mathbf{p}_{jf}$  are non-vanishing). It is important in this situation to take account of the breadth of the transition  $i \rightarrow j$  caused by the finite lifetime of the electronic state  $j$ . This can be done by subtracting a small imaginary part  $i\hbar\Gamma_j$  from the denominator of the first term in (6). If we further replace  $E_j - E_i$  by  $\hbar\omega_j$  in this term, the Raman efficiency close to resonance becomes

$$R = \frac{Ne^4 \omega_2^2 n_2 d\Omega}{V\hbar^2 m^4 \omega_1^2 c^4 n_1} \frac{|\mathbf{e}_1 \cdot \mathbf{p}_{ij} \mathbf{e}_2 \cdot \mathbf{p}_{jf}|^2}{(\omega_j - \omega_1)^2 + \Gamma_j^2}. \quad (7)$$

We envisage an experiment in which  $\omega_1$  is close to resonance, but  $\omega_2$  is far from any absorption region and  $\alpha_2$  can be neglected. Since  $R \ll \alpha_1$ , (4) and (5) are now virtually identical, and

$$I_2 = (RI_1(0)/\alpha_1) [1 - \exp(-\alpha_1 L_1)]. \quad (8)$$

For a Lorentzian absorption line,

$$\alpha_1 = \frac{2\omega_1 \kappa_1}{c} = \frac{N 4\pi e^2}{V\hbar m^2 \omega_1 c n_1} \frac{|\mathbf{e}_1 \cdot \mathbf{p}_{ij}|^2 \Gamma_j}{(\omega_j - \omega_1)^2 + \Gamma_j^2} \quad (9)$$

and

$$\frac{R}{\alpha_1} = \frac{e^2 \omega_2^2 n_2 d\Omega |\mathbf{e}_2 \cdot \mathbf{p}_{jf}|^2}{4\pi \hbar m^2 \omega_1 c^3 \Gamma_j}. \quad (10)$$

Thus  $R/\alpha_1$  is essentially constant when  $\omega_1$  lies close to  $\omega_j$ . The term  $1 - \exp(-\alpha_1 L_1)$  in (8) has a maximum value of 1 for  $\alpha_1 L_1 \gg 1$  and decreases significantly from unity only when  $\alpha_1 L_1 < 1$ . Thus for a crystal of given length, the Raman-scattered intensity increases as  $\omega_1$  approaches resonance and attains its maximum value of  $RI_1(0)/\alpha_1$  when the exciting radiation is all absorbed or scattered within the crystal. Provided that this condition is satisfied the scattered intensity is independent of  $\omega_1$ . For a half line-width  $\Gamma_j$ , about of  $20 \text{ cm}^{-1}$ ,  $R/\alpha_1$  is typically of order  $10^{-6}$ , assuming a unit solid angle  $d\Omega$ .

We comment at this point on the discussion of the resonance Raman effect in crystals given by Grechko and Ovander [5, 6, 7]. The result of this work (see particularly [7]) can be written

$$R = \frac{1}{v(\omega_1)} \frac{A}{\omega_1^2 (\omega_j - \omega_1)^2 + T^2} \tag{11}$$

where  $A$  is slowly-varying,  $v(\omega_1)$  is the velocity of propagation of the energy in the exciting radiation and  $T$  measures the strength of the interaction between the radiation and the atomic transition  $i \rightarrow j$ . In the notation used here

$$T^2 = \frac{N 2\pi e^2}{V \epsilon_1 \hbar m^2 \omega_1} |\mathbf{e}_1 \cdot \mathbf{p}_{ij}|^2 \tag{12}$$

where  $\epsilon_1$  is the real background dielectric constant at frequency  $\omega_1$  produced by all the transitions apart from  $i \rightarrow j$ . Ovander takes  $v(\omega_1)$  to be the group velocity at frequency  $\omega_1$ . However, Brillouin [8] has shown that the group velocity loses its significance in an absorbing region, and the velocity of energy transport  $v_E$  must be calculated from first principles. Consider first the limit  $T \gg \Gamma_j$ . For this case [9],

$$v_E = \frac{2T^2 \Gamma_j / \alpha_1}{(\omega_j - \omega_1)^2 + T^2} \tag{13}$$

(in terms of the quantities  $L$ ,  $\Lambda$  and  $\Gamma$  of [9]  $\alpha_1 = 1/L$ ,  $T = \Lambda/2$ ,  $\Gamma_j = \Gamma/2$ ). Putting  $v(\omega_1) = v_E$ , (11) becomes

$$R = \alpha_1 A / 2T^2 \Gamma_j \omega_1^2 \tag{14}$$

in agreement with the frequency dependence given by (10) when the form of  $A$  is substituted. The final result of Ovander [7] agrees in outline, though not in detail, with (14) above, the differences being due to the different expressions used for  $v(\omega_1)$ . In any case, the strength of the scattered radiation is determined by  $R/\alpha_1$  as discussed above, and not by  $R$  alone. Ovander's basic relation (11) is valid only in the limit  $T \gg \Gamma_j$ . On the other hand, the final result (10) of the present calculation is valid for all relative values of  $T$  and  $\Gamma_j$ .

3. LATTICE VIBRATION RAMAN EFFECT. — The analytic form of  $R$  for the optic vibrations of a

homopolar lattice having two atoms in the unit cell (e.g. diamond) has been given by Loudon [10], and the problem of resonance Raman scattering is partially treated in this reference. Suppose that  $\omega_1$  is close to the frequency  $\omega_0$  of the forbidden electronic energy gap, and let the direct optical transition across the gap be an allowed process. The dominant contribution to the scattering then arises from the interactions of the radiation and the lattice vibrations with the electrons in the two bands on either side of the gap. We therefore use a two-band model for the electronic structure of the crystal. Let the conduction band and the valence band be parabolic with reduced effective mass  $\mu$  and wave-vector  $K$ . Then

$$R = \frac{2e^4 \omega_0^2 n_2 (v_0 + 1) d \Omega}{\hbar^3 m^4 d^2 \rho \omega_1^2 c^4 \omega_0 n_1 V^2} |\mathbf{e}_1 \cdot \mathbf{p}_{0\alpha} \Xi_{\alpha\alpha} \mathbf{e}_2 \cdot \mathbf{p}_{\alpha 0}|^2 I^2 \tag{15}$$

where

$$I = \sum_K \{ [(\omega_0 - \omega_2 + \hbar K^2 / 2\mu) (\omega_0 - \omega_1 + \hbar K^2 / 2\mu)]^{-1} + [(\omega_0 + \omega_1 + \hbar K^2 / 2\mu) (\omega_0 + \omega_2 + \hbar K^2 / 2\mu)]^{-1} \} \tag{16}$$

(in terms of the quantities of reference [10],  $n_1 R / n_2 = \omega_2 N_2 / \omega_1 N_1 L$ ). Here

$$\omega_0 = (\omega_1 - \omega_2)$$

and  $v_0$  are the optic lattice vibration frequency and Bose-Einstein factor,  $d$  is the lattice constant and  $\rho$  is the crystal density. Both the interband momentum matrix element  $p_{0\alpha}$  and the deformation potential  $\Xi_{\alpha\alpha}$  have been assumed independent of  $K$ .

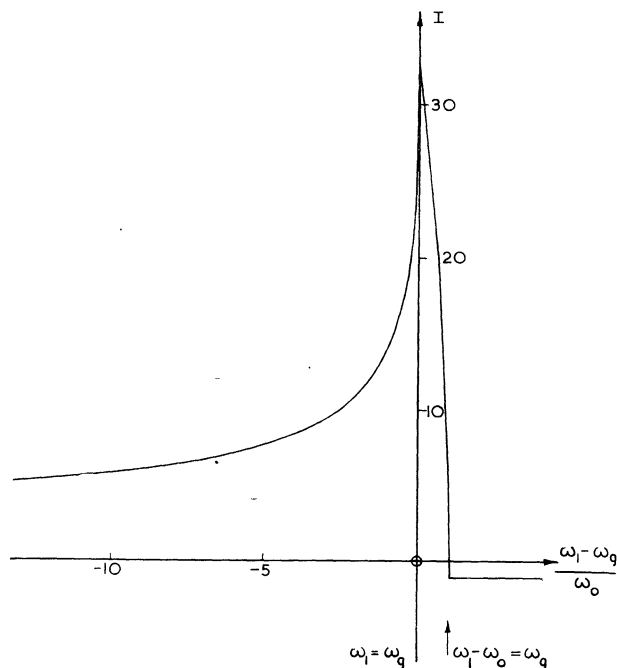


FIG. 3. — Variation of  $I$  with frequency close to the band edge. The Raman efficiency is proportional to  $I^2$ .

The summation in (16) can be evaluated by first converting it to an integration, and figure 3 shows the dependence of  $I$  on  $\omega_1$ . Here  $I$  is measured in units of  $V(2\pi)^{-2} (2\mu/\hbar)^{3/2} \omega_B^{-1/2}$ , where  $\omega_B$  is the sum of the frequency breadths of the valence and conduction bands. The numerical magnitudes  $\omega_g = 20,000 \text{ cm}^{-1}$ ,  $\omega_B = 40,000 \text{ cm}^{-1}$  and  $\omega_0 = 400 \text{ cm}^{-1}$  have been used.

It is seen that the scattering efficiency  $R$ , proportional to  $I^2$ , increases rapidly when  $\omega_1$  is increased to approach to within two or three times the phonon frequency  $\omega_0$  of the gap frequency  $\omega_g$ . Now  $\alpha_1$  is zero for  $\omega_1 < \omega_g$  in an ideal crystal, and the scattered intensity given by (4) is  $RI_1(0)L_1$ . When  $\omega_1$  is further increased to become larger than  $\omega_g$ ,  $R$  falls rapidly to become zero for  $\omega_1$  close to  $\omega_g + \omega_0$ . For  $\omega_1 > \omega_g + \omega_0$ ,  $R$  has a small constant value. In addition,  $\alpha_1$  is proportional to  $(\omega_1 - \omega_g)^{1/2}$  for  $\omega_1 > \omega_g$ , and  $\alpha_2$  is proportional to  $(\omega_2 - \omega_g)^{1/2}$  for  $\omega_2 > \omega_g$ . Thus the scattered intensity should be small when  $\omega_1$  lies within the absorption band, and the optimum exciting frequency to use is  $\omega_g$ .

The above discussion is of course based on a simplified model. In a real crystal  $\alpha_1$  may have a complicated dependence on  $\omega_1$  due to exciton effects. Also, other bands apart from the two considered always contribute to  $R$ , and a constant background should be added to  $I$  in figure 3 to account for this. This does not however alter the conclusion that the best exciting frequency to use is the highest frequency at which  $\alpha_1$  is negligibly small.

Dissipation in the electron system can be allowed for as before by introducing an imaginary part  $i\Gamma$  in the frequency denominators of the Raman efficiency. As an example, if  $\Gamma$  is given the rather large value of  $\omega_0$ , then the value of  $I$  at  $\omega_1 = \omega_g$  is reduced by a little over 50 %.

**III. Stimulated Raman scattering.** — 1. **GENERAL SCATTERING FORMULA.** — For theoretical convenience we consider a stimulated Raman scattering experiment where the Raman crystal is placed in a Fabry-Perot cavity with the laser crystal which supplies the exciting radiation. The end mirrors of the cavity force the scattered light wave to build up with its direction of propagation parallel to the cavity axis, and it is not necessary to consider the propagation directions as being spread over a finite solid angle  $d\Omega$ . The arrangement of light beams in the crystal is similar to that of figure 2 except that the scattered light travels in the direction of positive  $z$ . In the spontaneous Raman effect, the most important experimental quantity is the total integrated intensity in the Raman line at frequency  $\omega_2$ , and the width of the line is of secondary importance. However, in the stimulated Raman effect the cavity mode of the

scattered light may be narrow compared with the width of the Raman line, causing a decrease in scattered intensity with increase of line width. Similar considerations apply in experiments where the Raman crystal is placed outside the laser cavity, and the exciting radiation is focused to increase its intensity.

Let  $I_1(z)$  and  $I_2(z)$  be the magnitudes of the Poynting vectors of the exciting and scattered radiation. The equations which described stimulated Raman scattering have already been derived [11]. With a slight generalization to take into account the finite linear absorption coefficient  $\alpha_1$ , the equations for the spatial dependence of  $I_1(z)$  and  $I_2(z)$  are

$$dI_1(z)/dz = -T'I_1(z)I_2(z)/I_2(0) - \alpha_1 I_1(z) \quad (17)$$

$$dI_2(z)/dz = TI_2(z)I_1(z)/I_1(0) - \alpha_2 I_2(z) \quad (18)$$

where

$$T' = \frac{48\pi^2 \omega_1 I_2(0)}{n_2 c^2} \text{Im} \left\{ \frac{\chi_{1122}^{(3)}(\omega_1, \omega_2, -\omega_2)}{N_1} \right\} \quad (19)$$

$$T = -\frac{48\pi^2 \omega_2 I_1(0)}{n_1 c^2} \text{Im} \left\{ \frac{\chi_{2211}^{(3)}(\omega_2, \omega_1, -\omega_1)}{N_2} \right\}. \quad (20)$$

Here, the  $\chi^{(3)}$  are third-order susceptibility tensors, whose properties are discussed in detail in reference [11]. The equations analogous to (17) and (18) in this reference are written in terms of electric field amplitudes rather than Poynting vectors, and the symbol  $\alpha_L$  is used in place of  $\alpha_2/2$ . We neglect here any transfer of energy between the exciting and scattered light beams caused by parametric coupling, and restrict attention to the stimulated Raman effect.

An approximate solution of (17) and (18) is easily found. The exciting beam in a stimulated Raman experiment is usually generated by a pulsed ruby laser, and  $I_1(0)$  is thus a large quantity. On the other hand, the initial scattered intensity  $I_2(0)$ , which must be non-vanishing for stimulated scattering to occur, is produced by spontaneous scattering and is therefore small. Now  $\omega_1$  is assumed to be close to resonance and the absorption coefficient  $\alpha_1$  is large for scattering by electronic levels of impurity atoms but may be negligibly small for scattering by lattice vibrations. Consider first the case of electronic Raman scattering. We assume that  $I_2(z)$  is sufficiently small for all  $z$  to ensure the validity of the inequality

$$T'I_2(z)/I_2(0) \ll \alpha_1. \quad (21)$$

The first term on the right-hand side of (17) is then negligible compared with the second, and the solution of (17) and (18) is

$$I_2(L) = I_2(0) \exp \{ -\alpha_2 L + (T/\alpha_1) [1 - \exp(-\alpha_1 L)] \} \quad (22)$$

where  $L$  is the crystal length. For amplification to occur at frequency  $\omega_2$  we must have

$$T > \frac{\alpha_1 \alpha_2 L}{1 - \exp(-\alpha_1 L)} \quad (23)$$

The maximum attainable value of  $I_2(L)/I_2(0)$  is  $\exp(T/\alpha_1)$ , which occurs when  $\alpha_1 L \gg 1$  but  $\alpha_2 L \ll 1$ .

For scattering by lattice vibrations, both  $\alpha_1$  and  $\alpha_2$  may be negligible provided that  $\omega_1$  is smaller than the gap frequency  $\omega_g$ . The solution of (17) and (18) in this case is

$$\frac{I_2(L)}{I_2(0)} = \frac{T + T'}{T \exp[-L(T + T')] + T'} \quad (24)$$

The maximum value of  $I_2(L)/I_2(0)$  is now  $(T + T')/T'$ , which occurs for  $L(T + T') \gg 1$ .

**2. RELATION OF STIMULATED AND SPONTANEOUS SCATTERING EFFICIENCIES.** — We consider first the form of  $T$  given by (20), for the case of stimulated Raman scattering from electronic levels. We assume as in section II-2 that  $\omega_1$  is close to the frequency of an allowed transition  $i \rightarrow j$  of the impurity atom, but that  $\omega_2$  is well removed from any resonant absorption region. Thus  $\kappa_2$  can be neglected and  $N_2$  in (20) can be replaced by  $n_2$ . Close to resonance, one of the terms in the expression for  $\chi_{2211}^{(3)}$  given in reference [11] dominates, and (20) becomes

$$T = \frac{N 8\pi^2 e^4 I_1(0)}{V \hbar^3 m^4 \omega_2 \omega_1^2 c^2 n_1 n_2} \frac{|\mathbf{e}_1 \cdot \mathbf{p}_{ij} \mathbf{e}_2 \cdot \mathbf{p}_{ji}|^2}{(\omega_j - \omega_1)^2 + \Gamma_j^2} \frac{\Gamma_j}{(\omega_j - \omega_1 + \omega_2)^2 + \Gamma_j^2} \quad (25)$$

where  $\hbar\omega_j = E_j - E_i$  and the linewidth of the Raman-scattered radiation has now been given a finite value  $2\Gamma_j$  in accordance with the remarks at the beginning of section III. The other quantities in (25) are as defined previously. Comparing (25) with equation (7) for the spontaneous scattering efficiency,

$$T = R \frac{8\pi^2 c^2 I_1(0)}{\hbar \omega_2^3 n_2^2 d\Omega} \frac{\Gamma_j}{(\omega_j - \omega_1 + \omega_2)^2 + \Gamma_j^2} \quad (26)$$

This relation between  $R$  and  $T$  can be shown to hold quite generally, independent of the nature of the scatterer and whether or not  $\omega_1$  lies close to resonance. If the cavity mode of the scattered light is centred at the frequency  $\omega_1 - \omega_j$  and has a breadth narrow compared to  $\Gamma_j$ , then the final term in (26) reduces to  $1/\Gamma_j$  and

$$T = R \frac{8\pi^2 c^2 I_1(0)}{\hbar \omega_2^3 n_2^2 d\Omega \Gamma_j} \quad (27)$$

The factor multiplying  $R$  on the right-hand side depends weakly on  $\omega_1$  in the neighbourhood of resonance, and  $T/\alpha_1$  therefore has similar properties to  $R/\alpha_1$  given by (10). For a crystal of given length, the amplification  $I_2(L)/I_2(0)$  given by (22) increases as  $\omega_1$  approaches  $\omega_j$ , but attains a constant maximum value of  $\exp(T/\alpha_1)$  when  $\alpha_1$  is sufficiently large for the inequality  $\alpha_1 L \gg 1$  to be valid. It is assumed here that the crystal is transparent at frequency  $\omega_2$ .

The value of  $T$  for stimulated Raman scattering by lattice vibrations can be obtained from (15), (16) and (27) (with  $\nu_0 = 0$ , see [4]). As in spontaneous scattering, the efficiency close to resonance is proportional to  $I^2$ , where  $I$  has the form illustrated in figure 3. If  $\alpha_1$  and  $\alpha_2$  are negligible the amplification is given by (24) and in order for this to be a maximum the inequality  $L(T + T') \gg 1$  must be satisfied. It is thus advantageous to have  $\omega_1$  as close as possible to  $\omega_g$  without causing  $\alpha_1$  to become significant. Neglecting  $\kappa_1$  and  $\kappa_2$  in (19) and (20) and using

$$\text{Im } \chi_{1122}^{(3)}(\omega_1, \omega_2, -\omega_2) = -\text{Im } \chi_{2211}^{(3)}(\omega_2, \omega_1, -\omega_1),$$

the maximum amplification is

$$\frac{T + T'}{T'} = \frac{\omega_2 I_1(0) + \omega_1 I_2(0)}{\omega_1 I_2(0)} \quad (28)$$

**IV. Conclusions.** — The intensity of Raman-scattered radiation can usually be enhanced by choosing the exciting frequency to be close to an absorption line or band of the crystal. For scattering by electronic levels, the Raman intensity achieves its maximum value when the exciting frequency is sufficiently close to resonance for virtually all the exciting light to be absorbed or scattered in the scattering crystal. Further increase in the absorption coefficient does not produce any change in the scattered intensity. It is assumed here that the frequency of the scattered light lies in a transparent region of the spectrum. For scattering by lattice vibrations, the exciting frequency is usually chosen to be smaller than the forbidden energy gap, leading to negligible absorption of the exciting beam. The Raman efficiency increases steeply as the exciting frequency approaches the absorption edge. When the exciting frequency is increased to lie above the absorption edge, the Raman efficiency falls sharply to a small frequency-independent value, while the absorption coefficient rises with a square-root dependence on frequency. The largest scattering therefore occurs when the exciting frequency lies just below the absorption edge. The above remarks apply to both spontaneous and stimulated Raman scattering.

A common experimental difficulty is that the

available sources of exciting radiation all have frequencies which are higher than the forbidden energy gap frequency of a crystal whose lattice vibration Raman frequencies one would particularly like to determine. In this situation, it may be worthwhile to try to detect Raman scattering by reflection as illustrated in figure 2. Reference to figure 3 shows that the Raman efficiency falls by a factor of about 40 in changing from an exciting frequency of about  $4\,000\text{ cm}^{-1}$  below the absorption edge to frequency above the edge. Suppose that the absorption coefficients at the two frequencies are 0 and  $1\,000\text{ cm}^{-1}$  respectively. Then, if the Raman crystal is  $0.25\text{ cm}$  long, the total Raman-scattered intensity decreases by a factor of  $10^4$  when the exciting frequency is changed from below to above the absorption edge. Although the scattered intensity is much smaller when the exciting frequency lies in the absorbing region, it may be possible to detect the reflected Raman light in favourable cases, and with some experimental ingenuity.

The first successful measurement of this type has recently been carried out by Russell [12] on the first-order Raman line of silicon. The exciting frequency lay in the region of absorption caused by indirect electronic transitions, but below the relatively much stronger absorption associated with direct transitions across the forbidden gap.

We have confined attention in this paper to the variations in the strength of Raman scattering as the exciting frequency is varied slightly in the region of an absorption line or absorption edge. The overall proportionality of the Raman efficiency to the fourth power of the exciting frequency is well known. It arises from the linear dependence on frequency of the momentum matrix elements in (6) and (15). The fourth-power law has been checked experimentally for quartz and calcite [13], using exciting frequencies far removed from the absorption edges, so that the resonance effects discussed here play no part in the measurements.

### Discussion

M. HARDY. — What would be the situation for alkali halides where the dominant absorption is that of narrow exciton bands ?

M. TAYLOR. — Does the treatment of scattering from atoms also apply to the scattering from excitons ?

M. GIORDMAINE. — For the case of stimulated Raman scattering, in which the  $\omega_1$  field is intense, it may become necessary to take into account a population of the intermediate state  $j$  due to real transitions  $i \rightarrow j$ .

M. THEIMER. — Do you have a simple physical argument which explains the pronounced difference between the "atomic" and the vibrational resonance Raman effect in your theory ?

M. BURSTEIN. — I am rather puzzled that there is such a sharp drop off of the Raman scattered intensity in the case of the lattice vibration scattering. Certainly there are interband transitions beyond the band edge which, from an intuitive point of view, should allow continued scattering. What is the physical basis for the cut-off ?

It should be possible to have a relatively sharp density of states at the band edges by applying a magnetic field. As you know, this has the effect of reducing the three-dimensional bands to one-dimensional sub-bands which, in the absence of damping, have infinite density of states at the band edge.

Many of us are interested in the strength of the matrix elements for first order Raman scattering.

In your treatment of one phonon scattering in semiconductors, you make use of the deformation potential, I gather that you are only considering the contributions from a single pair of valence and conduction bands. In obtaining a more realistic estimate of the scattering matrix elements, one should include all of the interband transitions. Furthermore, on the basis of your treatment, one has, in effect, an additional method for obtaining information about direct band edges and indirect band edges, assuming of course that one has an intense source with continuously varying frequency. Using such a source one can measure the intensity of the scattered radiation as a function of frequency and thereby obtain a structure related to the variety of interband transitions.

In the atomic case, it seems to me that, when the exciting frequency coincides with the resonance absorption line :

1) One shall have a "real" transition of the electron to the excited state.

2) The electrons will make transitions to the lower excited level by a radiative ("fluorescence") transition. Does this not complicate the picture of resonance Raman scattering ?

Perhaps the two phenomena became identical i.e., they are one, and the same theory, except perhaps that the fluorescence transition represents the imaginary part and the Raman transition represents the real part of the polarizability terms that characterize the observed effects.

M. BIRMAN. — 1) In regard to question asked about effects caused in the theory by taking account of exciton states (as in ionic crystals where they are, sharp, of high intensity, and often far displaced from the electronic band absorption edge)

I should mention that Gangerly and I (at New York University) are examining the theory of such effect.

2) Did you use in your theory the full Raman tensor including the *real, antisymmetric* parts which you showed, in your 1963 (*Proc. Roy. Soc., A*, **275**) paper were nonvanishing in principle ?

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