LIGHT SCATTERING WITH LASER SOURCES

S. P. S. PORTO

Department of Physics and Electrical Engineering

University of Southern California, Los Angeles, Calif.

WHEN light passes through matter weak random scattered radiation appears. In the early 16th Century, Leonardo da Vinci prophetically suggested scattering by particles of air as the explanation for the blueness of the sky. This idea was pursued by many scientists including Newton and Tyndall who tried with only limited success to identify the particles responsible for the scattering. Maxwell, studying the careful measurements of Lord Rayleigh [1], finally proved that the molecules themselves turn the sky blue. After three centuries of thought, a correct and unambiguous explanation to all known properties of scattering—frequency dependence, critical opalescence, index of refraction, etc.—became a reality. Then came the anti-climax that usually follows the insertion of the last jagged piece in a jig-saw puzzle: most physicists turned their attention elsewhere.

A few didn't. In 1922 Brillouin [2] predicted that if monochromatic radiation was allowed to scatter from an optical medium, side bands would appear. He went on to theorize that the bands would result from a Doppler shift due to the generation of a sound wave produced by the light wave as it encountered molecules in its path. The frequency shift would be a function of the angle of observation and of the sound velocity in the medium. In 1923 Smekal [3] considered, in the Bohr theory approximation, the scattering of light by a system having two quantized energy levels and predicted the effect to be discovered in 1928 by Raman [4]. Working independently in Russia, Mandelstam and Landsberg [5] discovered the same phenomenon in quartz: appearance of lines in the spectrum in addition to those from the source. (The Russians, believing that their work actually antedated Raman's identify the effect as "combinational scattering"). In 1930 Gross [6] confirmed the theory of Brillouin, demonstrating that the Doppler-shifted frequencies appeared as predicted for both liquids and solids.

The implication of line shifting was at once evident and a flurry of new enthusiasm broke out. By 1934, more than 500 papers related to the Raman effect had been published and by the early forties this number had increased to a few thousand.

In 1934, Placzek [7] wrote a lengthy and excellent review paper on the Raman effect. Just as Maxwell's explanations of Rayleigh scattering 35 years earlier had resulted in a virtual halt to further work in this area, Placzek's paper seemed to mark the end of an era in frequency-shifted spectra. Most fundamental Raman problems seemed now to be so well understood that research ground to a halt and pertinent papers in the Physical Review virtually disappeared. The Raman effect developed instead as a tool for the structural physical chemist. Only a handful of devoted physicists, notably groups under Krishnan, Raman and Baghavantam in India, Welsh in Canada, Mathiew in France and Stekhanov in Russia, remained to keep the flame of fundamental research barely flickering.

Light scattering research was adrenalized once again in this decade with the invention of laser sources. Not only was the physical chemist handed a new, more powerful, and cleaner source but, equally important, the physicist was furnished with means for testing rigorously the theories of Placzek, Rayleigh and Brillouin. Phenomena such as directional effects in scattering processes and inelastic scattering from very small cross sections which had previously defied measurement could now be studied easily with laser sources. The great level of current enthusiasm in such investigations is evident from the impressive number of laboratories and scientists engaged in related light scattering experiments.

In this paper we shall attempt to develop from very simple arguments the origin of the most common scattering mechanisms. Without pretending to be thorough — this would require a large book — we shall "island hop" from subject to subject in the hope of attracting more visitors to these research shores.

IF an electric field E is applied to a medium having polarizability α, a polarization (most commonly, but not necessarily, a dipole) P will be induced obeying the relation:

$$\underline{P} = \underline{\alpha}\underline{E} \text{ or } \begin{array}{c} P_x \\ P_y \\ P_z \end{array} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \quad (1)$$

where α is a tensor. If the field is applied in a certain direction i, the polarization can be induced in a different direction j. In the study of light scattering, E is the field associated with an electromagnetic radiation and it can, without loss of generalization, be expressed as $E = E_o \cos \omega_L t$ where ω_L is the source, or laser, frequency.

Since the atomic or molecular dimension is of the order of angstroms and the laser frequency is of the order of thousands of angstroms the usual approximation that the electric field is slowly varying across the molecular dimensions (Born approximation) is valid but on top of this is the fact that the field is constant over many molecular dimensions. What we actually sample when we apply light to matter is an average polarization and an average polarizability of all those molecules:

$$\langle \underline{P} \rangle = \langle \alpha \rangle \underline{E} \qquad (2)$$

Each molecule has a polarizability tensor $\alpha^{(i)}$ associated with it so if we neglect interaction between molecules:

$$\langle \underline{P} \rangle = \langle N\alpha^i \rangle \underline{E} = V \langle \delta \rangle \langle \alpha^i \rangle \underline{E} \qquad (3)$$

i.e., the average polarizability of the medium can be approximated by averaging the product of the volume V, the density of the sample and the polarizability of each molecule α^i.

We know also from electromagnetic theory that a permanent polarization such as a dipole will not interact with radiation but an oscillating dipole will emit or absorb light so that in order to observe a scattering phenomenon we have to look for oscillating polarization, an electric dipole for instance.

Rayleigh and Brillouin scattering

In eq. (3) let us concentrate on density fluctuations and assume that the polarizability tensor associated with each molecule is a diagonal (trace) tensor i.e., only α_{xx}, α_{yy} and $\alpha_{zz} \neq 0$. We can write those fluctuations in density as

$$\delta\rho = \left(\frac{\partial \rho}{\partial P}\right)_S \delta P + \left(\frac{\partial \rho}{\partial S}\right)_P \delta S \qquad (4)$$

i.e., the density will fluctuate with pressure or with entropy S. The pressure fluctuations of the density are those which propagate through the material while the entropy of thermal fluctuations will not propagate. Propagating pressure fluctuations will scatter the incoming photon at a displaced frequency and give rise to the Brillouin scattering while entropy fluctuations will give rise to the Rayleigh scattering. Imagine that a sound, or acoustical wave, characterized by a frequency ω_B and sound velocity V_B, travels through a medium. When this sound wave scatters a photon both energy and momentum must be conserved:

$$E_L = E_S \pm E_B \ or \ \omega_L = \omega_S \pm \omega_B \quad and$$

$$\underline{k}_L = \underline{k}_S + \underline{k}_B \qquad (5)$$

The conservation of momentum diagram for all scattering processes is shown in Fig. (1). If we can assume small dispersion, i.e., $n(\omega_L) \cong n(\omega_S)$ from Fig. (1) we obtain

$$|\underline{k}_B| \simeq 2 |\underline{k}_L| \sin \frac{\theta}{2} \ or \qquad (6)$$

$$|k_B| = \frac{\omega_B}{V_B} = 2 \frac{\omega_L n}{C} \sin \frac{\theta}{2} \ or$$

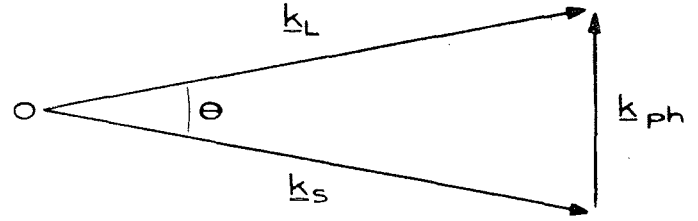$$\omega_B = 2 \frac{V_B n}{C} \omega_L \sin \frac{\theta}{2}$$

Fig. 1—Conservation of momentum diagram in any scattering experiment, K_L, K_s and K_{ph} are respectively the wave vectors of the laser light, the scattered light and of the phonon or of any scattering quasiparticle.

So the Brillouin frequency shift obeys a Bragg or grating diffraction law and its measurement at a given angle and excitation frequency provides a measure of the sound velocity in the medium. Since the sound velocities in condensed matter are of the order of a thousand meters/sec, ν_B is of the order of 3-10 kMHz or about .1 - .3 cm^{-1} for 90° scattering with a visible laser excitation source. Experimentally, Brillouin and Rayleigh spectra are studied by observing the scattering with a Fabry-Perot interferometer [8], a high resolution spectrograph, [9] or by photobeating electronic techniques [10]. Since the normal line width of an argon laser is of the order of .15 cm^{-1} and that of a He-Ne is of the order of .05 cm^{-1} much care has to be exercised to mode select the laser so that its line-width is less than that of the Brillouin line (~700 MHz).

From the way in which we arrived at the Brillouin and Rayleigh scattering as fluctuations in density, we can see that both Brillouin and Rayleigh lines are completely polarized. By relating the fluctuations in pressure and entropy to known thermodynamic quantities C_P and C_V one obtains the well-known Landau-Placzek relation between the intensities of the Brillouin and Rayleigh scatterings:

$$\frac{I_B}{I_R} = \frac{C_V}{C_V - C_P} \qquad (7)$$

For instance for water, where $C_V \cong C_P$, most of the intensity observed in the "Rayleigh" line, in low resolution instruments, corresponds to the two Brillouin components. Fig. (2) shows a high [9] resolution spectrum of the Rayleigh and Brillouin spectra of water.

Generalized Raman effect

For the purposes of this paper we shall designate as Raman effects all those inelastic light scattering phenom-

ena in which the scattering mechanism produces a change in the polarizability tensor associated with each molecule, as viewed in our laboratory frame of reference.

Rotational Raman effect

To each molecule we can associate a polarizability tensor which is tied to the symmetry axis of the molecule: x, y, z. Let us diagonalize this tensor and call the new tensor diagonals α_1, α_2, α_3. In a completely spherical molecule $\alpha_1 = \alpha_2 = \alpha_3$ so if the molecule rotates, the tensor, viewed in the laboratory axis x', y', z' stays constant. No change or modulation of the polarizability occurs during the rotation and without a change no oscillating dipole develops so this rotation will be inactive in scattering.

If $\alpha_1 \neq \alpha_2$, for instance, as in the case of a linear molecule, the polarizability viewed in the laboratory system will change when the molecule rotates and the rotational Raman effect can be observed. The selection rules for the rotational Raman effect are $\Delta J = 0, \pm 2$ because each component of the tensor viewed in the laboratory system is equal to the sum of the components in the molecular system of reference multiplied by a factor containing two cosine functions. The rotational Raman effect is completely depolarized $(P = .75)$ and the $\Delta J = 0$ selection rule predicts an undisplaced scattering (Rayleigh) which is polarized. The rotational frequencies are inversely proportional to the molecular moments of inertia and the rotational displacements are of the order of 1 cm⁻¹.

To observe the rotational Raman effect high resolution spectrographs have been used almost exclusively up to date. Due, however, to the fact that the Rayleigh scattering is so highly polarized while the rotation Raman effect is depolarized, one can foresee coupling a laser source to a single monochromator (a double monochromator will not be needed because in the right geometry the Rayleigh line is weak) and photoelectric techniques as the ideal way to observe rotational Raman effects [11].

Anisotropy Raman scattering in liquids

This kind of scattering is quite commonly known as the "Rayleigh wing" scattering and is observed in liquids. It is, in one way, very closely related to the rotational Raman effect and in another related to the Kerr effect in liquids. This anisotropy scattering is due to the fact that in a liquid the molecules sampled by the laser beam are rotating in a viscous medium and that one views a changing polarizability in the laboratory system of reference. This changing polarizability is due to this "overdamped rotation" and also to changes in instantaneous aggregation states of the molecules. "Overdamped rotation" gives rise to the same kind of polarizability changes responsible for the rotational Raman effect but instead of discrete levels, the resulting spectrum is a low frequency continuum centered around the laser exciting frequency.

Debye [12] has worked out details of this anisotropy scattering predicting a Lorentzian line shape for the scattering with a width that is dependent on the volume of the molecule, the temperature and the shear viscosity. For most liquids the half width of this anisotropy scattering is of the order of 5-10 cm⁻¹ but recent measurements [13] show deviations from the predicted Lorentz shape.

This anisotropy scattering, even though hardly explored today, should generate much information on the
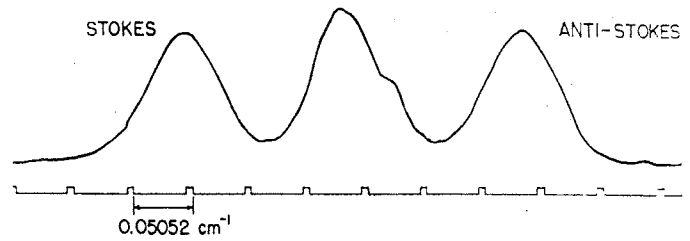

Fig. 2—Brillouin scattering of water taken from Ref. 9 showing the two Brillouin components (outside lines) and the Rayleigh line of water. The Rayleigh line for water shown in the picture is almost all coming from scattering of particles suspended in the sample since for pure water the Rayleigh scattering should be very small.

angular correlation functions in liquids so badly needed to understand nonlinear optical effects, like self focusing, which are dependent on the Kerr effect.

Vibrational Raman effect in molecules

This is the oldest kind of Raman effect known and can be simply understood as a modulation of the polarizability tensor components due to a vibration of the molecule. Classically, if the polarizability is modulated, or if it changes with a vibration of the molecule

$$\alpha = \alpha_o + \frac{\partial \alpha}{\partial q_m} q_m = \alpha_o + \alpha_1 \cos\omega_M t \quad so \qquad (8)$$

$$P = (\alpha_o + \alpha_1 \cos\omega_M t) (E_o \cos\omega_L t)$$

$$= E_o \alpha_o \cos\omega_L t + \alpha_1 E_o [\cos(\omega_L + \omega_M) t + \cos(\omega_L - \omega_M) t]$$

We see from eq. (8) that the polarization P will radiate energy at the frequencies $(\omega_L - \omega_M)$ and $(\omega_L + \omega_M)$, the anti-Stokes and Stokes-Raman vibrational frequencies, besides the Rayleigh scattering discussed before.

Group theory predicts the number of frequencies which are Raman, or infrared active, for all molecules provided that the shape of the molecule or its "point group" is known. Group theory also predicts for each normal mode those polarizability tensor components which are changing during the vibrational motion measured by the Raman effect. By counting the number of modes which are Raman and infrared allowed, and measuring the depolarization of the Raman lines, one can gain considerable knowledge about the shape of the molecule under investigation. All completely symmetric molecular vibrations (such as the "breathing" motions) are characterized by changes in the diagonal components of the polarizability tensor and their scattering is polarized (depolarization ratio is close to zero); in all other normal modes changes are found mostly in the off-diagonal terms of the polarizability tensor or have the trace of the tensor equal to zero. Associated scattering is depolarized (depolarization ratio = .75).

It is interesting to mention here the "vibrational overtone" Raman effect. Selection rule for a vibrational Raman effect is $\Delta v = \pm 1$; an overtone Raman effect means that we are observing a process in which $\Delta v = \pm 2$. This new selection rule can arise from two different causes: the mechanical anharmonicities of the harmonic oscillator or a non-linear term in the polarizability i.e., $\partial^2 \alpha / \partial Q^2 \neq 0$. In either case a sharp line corresponding to $\Delta v = \pm 2$

appears with the Raman displacement in general being a little less or equal to twice the Raman displacements for the $\Delta v = \pm 1$ transition.

Raman scattering by phonons

The main difference between the vibrational Raman effect in liquids and in solids is that in liquids light is scattered by the changes of polarizability associated with a normal mode in the molecule. In solids, such as NaCl, if a pair Na^+ - Cl^- oscillates, the sodium is so tightly bound to all of its Cl^- nearest neighbors that the change of position of this Na^+ ion will induce a corresponding movement of all those Cl^- ions in a continuing chain reaction. The molecule NaCl thus loses its identity as the vibration becomes a wave propagating the whole crystal. Characterized by a discrete phase velocity v, a frequency ω and a wave propagation vector k, this wave is called a phonon. It is a normal mode of the crystal. By contrast, we can consider the Raman effect in liquids as one in which $|k| = 0$, i.e., no phonon propagation occurs.

In practice for liquids we have to conserve only energy in the Raman scattering process, for solids both energy and momentum or, more properly, energy and wave vector k must be conserved. Another difference which is very important between Raman spectroscopy of liquids and solids is that where the liquid molecules are randomly oriented in relation to the laboratory system of reference all the unit cells of a solid are oriented in the same manner. No difference exists in solids, between the laboratory and the crystal systems of reference. Imagine that we calculate from group theory that a primitive cell of a solid has a vibration in which the only changing components in the polarizability tensor are xy and yx. To observe the Raman effect of that phonon, we first arrange the polarization of the incoming laser radiation parallel to the x axis and observe the scattered light with its polarization in the y direction or vice-versa, since only those two geometries would give non-zero results for the equation:

$$(9)$$

$$\underline{P} = \alpha \underline{E} \quad i.e. \quad P_x = \alpha_{xy} E_y \quad and \quad P_y = \alpha_{yx} E_x$$

So in very elegant ways we can, for a solid, determine all the Raman-active phonons and with each we can associate a polarizability tensor and a definite symmetry. Fig. (3) shows a typical example for MnF_2. MnF_2 belongs to the D_{4h} point group and group theory predicts four Raman active modes: $1A_{1g}$ (with α_{xx}, α_{yy}, $\alpha_{zz} \neq 0$), $1E_g$ (α_{yz}, α_{xz}, α_{zy}, $\alpha_{zx} \neq 0$), $1 B_{1g}$ (α_{xx}, $\alpha_{yy} \neq 0$) and $1B_{2g}$ (α_{xy}, $\alpha_{yx} \neq 0$). Fig. (3) shows the spectra observed for the different α_{ij} spectra, in complete agreement with the results of group theory [14].

The conservation of momentum plays a very important role in the understanding of the spectra of solids. First the frequency of a phonon—either in the acoustical or optical modes*—varies with momentum throughout the Brillouin zone (the maximum $k = 2\pi/a$ where a is the crystal lattice constant). For example, Fig. (4) shows how the frequency varies with momentum for two acoustical modes and two optical modes. With a visible source of light, where $|k| = v/c \cong 10^5 \ cm^{-1}$, a 90° scattering will

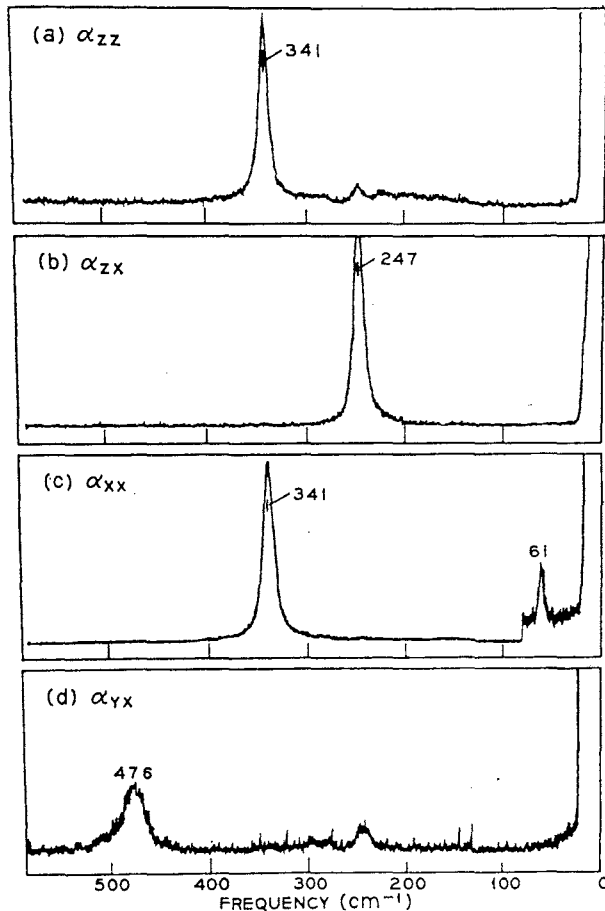Fig. 3—Raman scattering of MnF_2. In this crystal there is an A_{1g} vibration at 341 cm^{-1} with $\alpha_{xx,yy,zz} \neq 0$, a B_{1g} vibration, with $\alpha_{xx,-yy} \neq 0$, at 61 cm^{-1}, a B_{2g} line with $\alpha_{xy,yz} \neq 0$ at 476 cm^{-1} and an Eg vibration at 247 cm^{-1} with the $\alpha_{xz,yz} \neq 0$. (From Ref. [141]).
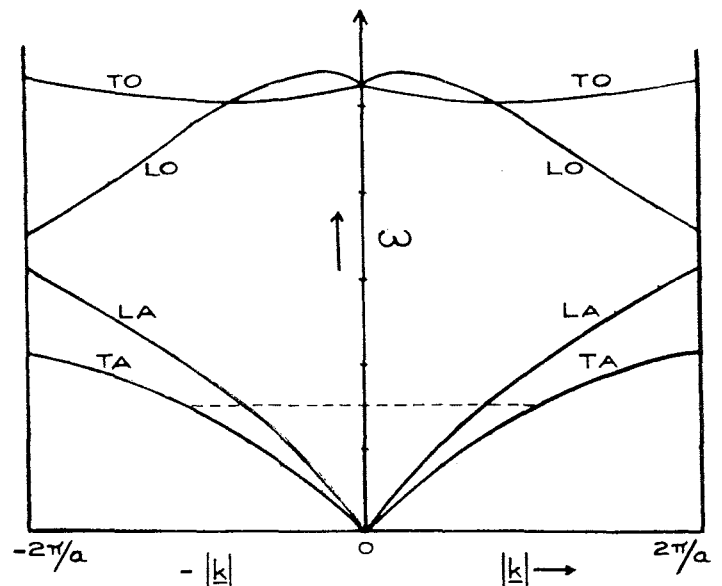
Fig. 4—Idealized dispersion curves of the acoustical and optical phonons of a crystal with two atoms per unit cell showing how the phonon frequencies change with wave vector.

*An acoustical phonon is like a sound wave in which all constituents in the unit cell vibrate in the same direction; in an optical phonon, they vibrate against one another. At $k = 0$ in solids the two are markedly different. At very large values of k, they may tend to merge.

create or destroy phonons with $|k| \cong 10^5 \ cm^{-1}$; in the scale of Fig. (4) this $|k|$ is very small so we often refer to the Raman effect measuring the $|k| \cong 0$ phonons. Let us examine the influence of this conservation of momentum in another case. In ZnO a doubly degenerate phonon of symmetry E_1 is present. It is both Raman and infrared active. When infrared active in the x direction its polarizability tensor components xz and zx are different from zero. On the other hand, when the phonon is polarized in the y direction the yz and zy polarizability components are different from zero [15]. Imagine that we are looking at the xz polarizability component of this E_1 line in ZnO: if the light is incident in the z direction and the observation is made along the y direction, by conservation of momentum, a phonon is produced in the yz plane with x polarization (since we are measuring the xz component of the tensor). So this phonon has a propagation direction perpendicular to its polarization and is a transverse optical phonon (TO). If, still measuring the xz spectrum, the light is incident in the z direction and the observation is in the x direction we produce a phonon in the xz plane with x polarization. This observed phonon is both transverse (propagation perpendicular to polarization) and longitudinal (LO). Since the transverse and longitudinal phonons have different frequencies we observe two lines. So in the $z \ (xz)y$ spectrum we see only one line, the TO phonon, while in the $z \ (xz)x$ spectrum we see two E_1 lines, the TO and LO phonons. Figs. (5A) and (5B) show the $z \ (xz)x$ and the $z \ (xz)y$ spectra of ZnO with the conservation of momentum diagrams which explain them. [16]

Raman scattering by multiple phonon processes

If we expand the polarizability tensor as in eq. (8) and keep higher order terms:

$$(10)$$

$$\alpha = \alpha_0 + \frac{\partial \alpha}{\partial q_i} q_i + \frac{\partial^2 \alpha}{\partial q_i \partial q_j} q_i q_j$$

The production of two or more phonons will create a modulation in the polarizability and will scatter in a Raman-like process. Similarly, if the force constants between atoms are not that of harmonic oscillators but include terms like ax^3, bx^4 etc. the selection rules are relaxed and $\Delta n = \pm 2, \pm 3$ processes are now allowed. Again, this scattering process must conserve both energy and momentum and for a two-phonon process:

$$(11)$$

$$\omega_L = \omega_R \pm \omega_{PH1} \pm \omega_{PH2}$$

$$k_L = k_R + k_{PH1} + k_{PH2}$$

In liquids, only phonons with $k = 0$ exist and an overtone Raman effect is produced which, as indicated before, consists of sharp lines. In the case of two-phonon scattering in solids, the two phonons can be produced throughout the whole Brillouin zone with only the conditions that energy and momentum are conserved in the scattering and that the process has the correct polarizability tensor of the experiment. Since, as seen in Fig. (4), the frequency of a phonon may vary drastically with momentum, in general multiple phonon scattering results in broad bands. We can imagine two successive Raman processes i.e., where when one phonon is produced, the Raman light is scattered and when another phonon is produced this will cause a sharp two-phonon or overtone line. Two phonon spectra are usually broad even though most of their intensity comes from large $|k|$ phonons, because here the density of states may be larger than that for phonons with small $|k|$.

Aside from the breadth, which sometimes can be misleading, there are two other ways of recognizing that a spectral feature arises from multiple phonon scattering. First, group theory will tell you that the symmetry of the two-phonon process is the product of the symmetries of the two phonons involved. The symmetry of the two-phonon process is thus more complex than that involving one phonon; the former may even appear not to obey the symmetries allowed for the specific point group under study. Since the product of two symmetries quite often contains the most symmetric representation, A_1, the second order Raman spectra may appear superimposed on the A_1 spectra. Another way to recognize a second order Raman process is from its temperature dependence. The one-phonon Stokes intensity decreases with temperature as $(n+1)$ while the intensity of the two-phonon spectra, occurring at the same frequency, will vary with temperature obeying a law like $(n+1)^2$ where $n = (exp \ h\omega/KT -1)^{-1}$. The two-phonon process fades away quickly with decreasing temperature.

The old concept that in Raman spectra the strong lines represent one-phonon processes while the two-phonons
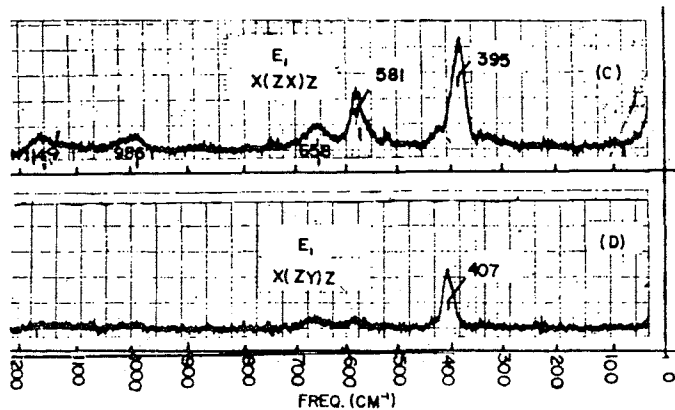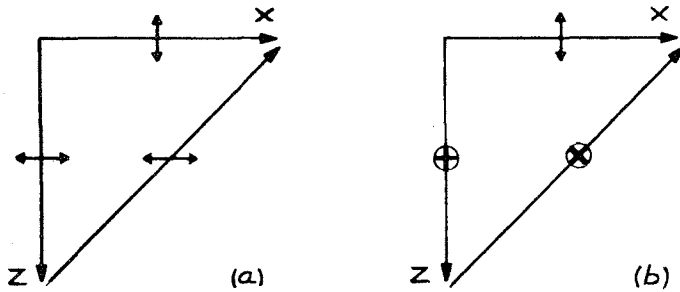

Fig. 5—Experimental demonstration of the conservation of momentum in an optical phonon scattering in ZnO. Fig. 5 (a) is the conservation diagram to show that in 5 (C) one obtains the scattering from the LO and TO phonons. Fig. 5 (b) explains the data of Fig. 5 (D) where the scattering is obtained from the TO phonon only. (From Ref. [16]).

give rise to broad and weak lines is very treacherous. In many substances like $BaTiO_3$, TiO_2, $KTaO_3$, some of the most prominent features of the Raman spectra are due to multiple phonon processes. Another fact to remember is that the $|k| \cong 10^5$ cm^{-1} acoustical phonon gives rise to the Brillouin spectrum with a frequency shift of the order of .1 cm^{-1}, while the two-phonon Raman scattering of the acoustical processes will extend to a few hundred cm^{-1}, since most of the Raman effect is due to phonons with $|k|$ near the edge of the Brillouin zone. See Fig. (4).

Fig. (6) shows part of the (xx) spectrum of TiO_2 where the sharp line at 143 cm^{-1} corresponds to a one-phonon process of symmetry B_{1g} ($\alpha_{xx}, \alpha_{yy} \neq 0$) while the broad and strong band at $\sim$234 cm^{-1} corresponds to the two-acoustical-phonon Raman scattering [14].
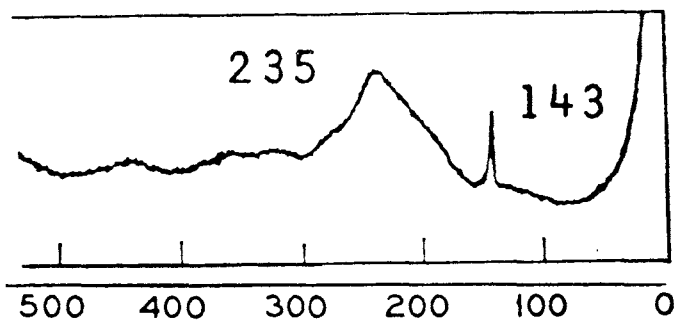

500   400   300   200   100   0

Fig. 6—Part of the xx spectrum of TiO_2 showing that the two phonon process at $\sim$235 cm^{-1} can be stronger than the one phonon B_{1g} scattering at 143 cm^{-1}. From Ref. [14].

In principle, the two-phonon process should provide considerable information on the dispersion relation ($|k|$ vs ω) of phonons, critical points in the Brillouin zone where the population of those phonons is maximum, etc. However, due in part to the poor state of the experimental work on second order Raman processes, we feel that most of the original promises have not as yet been fulfilled.

Raman effect of f-centers and impurities in crystals

Imagine a crystal like NaCl in which the first order Raman effect is forbidden for reasons of symmetry (each Na and Cl ion occupies a center of the cubic lattice). Should a Cl atom be removed and substituted by a vacancy in which an electron is trapped, an f-center is created. In the process the translational symmetry of the crystal is destroyed so that the Na$^+$ ions which are next-neighbors of the trapped electron are no longer at centers of cubes. First order Raman i.e., one-phonon interactions, are now allowed around the f-center. The same happens, for instance, when we substitute a Cl by Br or a Na by a K atom.

The problem of observing the Raman effect of f-centers is that we cannot introduce enough of them. By having just a few centers the Raman effect is distressingly weak. In NaCl, for instance, with 10^{17} f-centers/ml (one of every 100,000 Cl atoms) the first order Raman effect intensity of f-centers at 300°K is, at best, comparable to the weak two-phonon spectrum of the crystal. To observe the scattering from f-centers and to discriminate against the two-phonon processes, the temperature is lowered and the frequency of the laser excitation can then be chosen
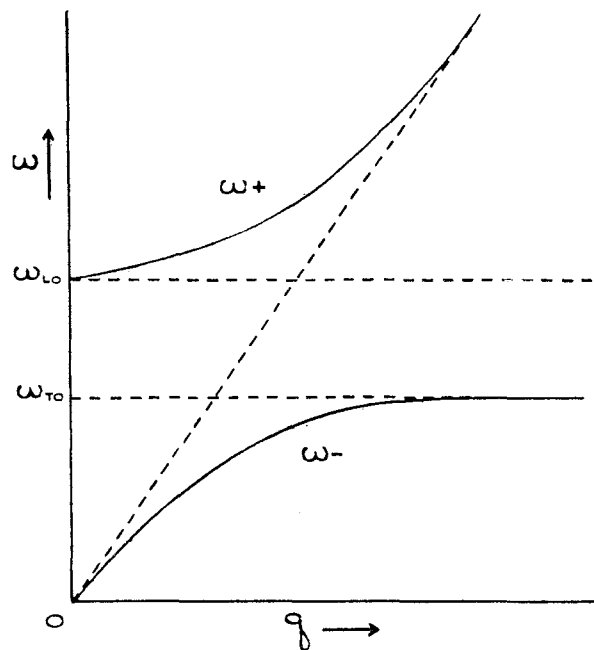

Fig. 7—Idealized dispersion curves of the coupled phonon - E. M. wave system (polariton) for the case of one infrared and Raman active phonon interacting with long wavelength light. The dashed lines are the dispersion of the uncoupled phonon and light waves. The solid curves are the dispersions of the coupled excitations.

to be close to the strong electronic absorption of the f-center so that the resonant denominator will increase the cross section of the Raman process [17].

A substitutional impurity Raman effect, in alkali-halides—as distinguished from an f-center—cannot make ready use of this resonant denominator because unlike f-centers, visible light absorption of the impure crystal does not change. However, much larger concentrations of the impurity than f-centers can be substituted in the lattice without appreciably disturbing the crystal symmetry. The total cross section can then be made sufficiently large for observation [18].

An interesting characteristic of both the f-center and impurity Raman effect is that the Raman active centers, or impurities, disturb the translational symmetry characteristic of a solid; conservation of momentum then loses its meaning and the $|k|$ of the phonon can, in essence, assume any value within the Brillouin zone. This means that, like in the two-phonon processes, the scattering results from phonons with all values of $|k|$ and the spectrum is broad, reflecting the density of states functions for all the allowed phonons, instead of the normally sharp one-phonon processes obtained for a solid where only the $|k| \cong 0$ phonons are sampled.

Raman effect of polaritons

Electromagnetic radiation passing through a crystal is characterized by a frequency ω, a velocity (c/n) and a wave vector k. For low frequency light, the dispersion relation (ω vs $|k|$) is a straight line passing through the origin. Imagine that in the same graph we plot the dispersion relation (ω vs $|k|$) of light and of an infrared active optical phonon with its LO and TO components. The k interval we are interested in is so small that we may consider that the phonon frequency itself is constant and

independent of $|k|$. As seen from the dashed lines of Fig. (7) the two dispersion relations will cross where the phonon and the electromagnetic radiation have the same frequency and wave vector. If this phonon is infrared active there will be an interaction of the electromagnetic radiation with the mechanical vibration and the excitation, around the interaction region, will be partially phonon and partially light. This mixed excitation in the interaction region is called the polariton and its dispersion relation is also shown in Fig. (7) as the full lines. As can be seen from the figure we have two branches of the polariton: the upper or quasi-photon branch ω^+, which in the limit $|k| \to 0$ tends toward the frequency of the LO mode and which has escaped observation up to date, and the lower or quasi-phonon ω^- which has been observed for GaP [19], ZnO [20] and quartz [21]. From Fig. (7) we see that the polariton exists only for very small values of $|k|$ so that in order to scatter from it we have to observe the Raman effect in the forward direction. Since this scattering process conserves momentum, in the forward direction a polariton with minimum $|k|$ will be produced. By observing the scattering let us say at 1°, 2°, 3° etc., from the forward region we can observe polaritons of higher and higher $|k|$ until the excitation becomes pure phonon for angles of the order of 10°. Fig. (8) shows the Raman effect of the polariton in ZnO [20] with the dispersion relation of the quasi-phonon polariton from 160 to 407 cm^{-1}.

Raman effect of spin waves or magnons

Spin waves are excitations characterized by dispersion relations (ω vs $|k|$) very much like those of phonons. They occur in magnetic materials whose atoms have non-zero spins oriented in an ordered manner. The spins of all the atoms of ferromagnets (such as iron and nickel) are parallel with the same orientation. This, of course, gives rise to their very high degree of magnetization. In an antiferromagnet (MnF_2, FeF_2) the spin of one of the magnetic ions is pointed in a definite direction while the next ion is pointed in exactly the opposite direction; although the total magnetization of an antiferromagnet is zero all the spins are still oriented. In a ferrimagnet the spins of next neighbors are also antiparallel like in an antiferromagnet but they are of different magnitude so that cancellation is incomplete and a magnetization remains, see Fig. (9). Exactly as in the case of phonons, if we now disturb the orientation of one spin, since they are all coupled, this misorientation will be felt by the next neighbors creating again a wave which will travel through all the spins. This process, or this wave, is called a spin wave or magnon. If we heat a magnetic material we can break up the spin ordering and destroy its magnetic properties. When cooling the sample, the temperature at which magnetic ordering takes place is called the Neel-Curie temperature. In Fig. (3) we see the room temperature spectrum of MnF_2 without any trace of spin wave scattering; by cooling the crystal below its Neel temperature ($\cong 70°K$) Raman scattering by spin waves appears [22]. Fig. (10) shows the dramatic appearance of the one and two-magnon processes in FeF_2 [22] as the temperature is lowered.

As in the case of phonons, the dispersion relations of magnons are not flat. The frequency of the broad two-magnon scattering does not, therefore, have to occur at twice the frequency of the one-magnon process since the two-magnon process consists of scattering by a pair of magnons throughout the Brillouin zone. The frequency

$\theta = .63°$

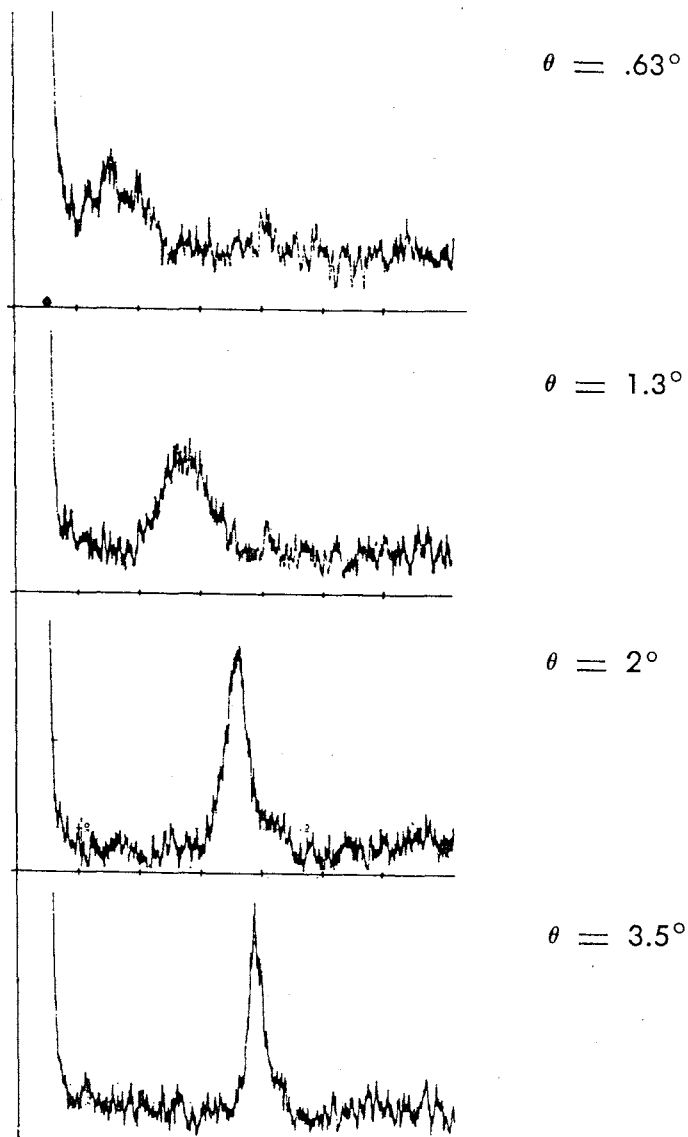$\theta = 1.3°$

$\theta = 2°$

$\theta = 3.5°$

Fig. 8—Experimental observation of the scattering of polaritons. One can see easily that the frequency shift changes with the angle of observation from the forward direction. At 3.5° from the forward direction the polariton is almost completely the TO phonon whose frequency is 407 cm^{-1}. At .63° it is 160 cm^{-1}. From Ref. [20].

distribution of the two-magnon process, like that of phonons, reflects the dispersion relation of the magnons in question and their density of states for the different points in the Brillouin zone [23].

Electronic Raman effect

The electronic Raman effect is light scattering by a material in which conservation of energy is furnished by the quantum jump of an electron from one electronic state to another. This effect has been known for a long time, as far as Raman effects go; it was discussed by Placzek in 1934, who also discussed the experiments done up to that time [7]. More recently the electronic Raman effect has been observed in solids, using mercury excitation, in which electronic transitions occurred between the Stark split levels of a rare earth ion in a crystal field [24]. Even more recently, electronic Raman transitions were observed between the ground and impurity levels, in semi-conductors [25].
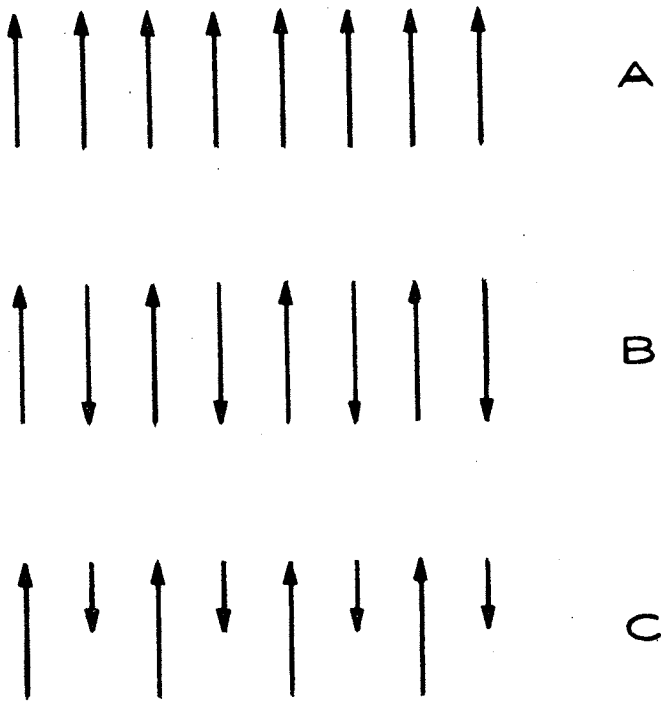
Fig. 9—Graphical representation of the spin alignment of (a) ferromagnetic materials, (b) antiferromagnets and (c) of ferrimagnets.
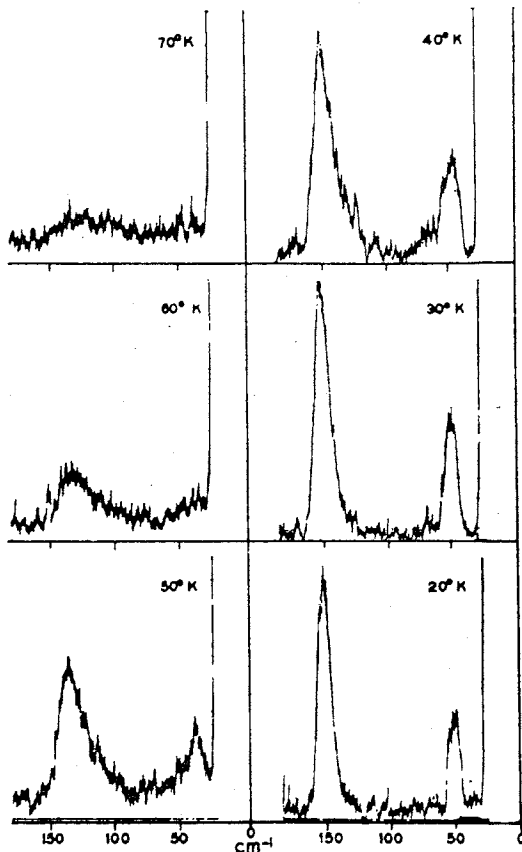

Fig. 10—The scattering from the one and two magnon states of FeF_2. FeF_2 becomes antiferromagnetic at ~70°K so the spins become oriented at that temperature and spin waves can propagate and scatter light. From Ref. [22].

It is interesting to speculate on what new information one might obtain from the Raman spectra of rare earth Stark split levels. Let us imagine doping a crystal of $LaCl_3$ with Pr^{+3}. In free Pr^{+3} all electrons in the same orbit have identical energy levels — degenerate in quantum mechanical parlance. The anisotropy of the crystal field of $LaCl_3$ will remove the degeneracy of the Pr^{+3} levels. The ground state of Pr^{+3} ($^3H_4$), for instance, will be split into six discrete levels each one of which can be characterized by a wave function ψ, an energy E, a crystal quantum number μ and a symmetry S in relation to all the operations of the crystal. So the electronic Raman effect of the Stark split levels of the $^3H_4$ state of Pr^{+3} will consist of five lines characterized by Raman displacements ΔE and polarizability tensors for each of the electronic transitions. These electronic Raman effect tensors, in general, will be more complicated than those arising from phonons in the same crystal but at the same time they will contain more information. From the form of the tensors for the different transitions we should be able to obtain many correlations such as energy levels with their respective quantum numbers and wave functions.

One might question the usefulness of the electronic Raman effect on the ground that most of the information can also be obtained from absorption and fluorescence spectroscopy. Perhaps so but the rebuttal is the same as can be given for phonons: in absorption or fluorescence arising from a dipole we measure but three possible components of a dipole vector; in Raman we measure nine components of a tensor and inherently we should extract much more information from the tensor.

Plasmon scattering

Imagine N free electrons inside a cube of volume A^3. Coulombic repulsions taking place between the electrons will cause the electrons to congregate around configurations of minimum free energy. Cooled to $0°$ K these electrons organize themselves like atoms in a crystal. Any external disturbance will then propagate itself through the medium as a wave called a plasmon.

The plasmon, like the other excitations studied, can be characterized by its frequency ω_P and its momentum $\mathbf{k}$ given by:

(12)

$$\omega_P = \left(\frac{2\pi\rho e^2}{EM^*}\right)^{\frac{1}{2}} \quad and \quad |\underline{k}| = \left(\frac{4\pi\rho e^2}{kT}\right)^{\frac{1}{2}}$$

where ε is the dielectric constant, ρ the plasma density and M^* is the effective mass of the electrically charged particle. For a gas, $\varepsilon \cong 1$ and for a semiconductor, $\varepsilon \cong 10$. So for a gas plasma $\omega \cong 10^1 - 10^4$ cm^{-1}; for a semiconductor plasma $\omega \cong 10^2 - 10^7$ cm^{-1}; for metals $\omega \cong 10^8$ cm^{-1}.

Let us scatter a laser beam from the plasma. We are going to transfer momentum in the scattering process from the light wave to the plasma; if the scattering experiment is done for instance at 90° the momentum transferred is $\cong 10^5$ cm^{-1} and if the scattering is observed in the forward direction the transferred momentum $\mathbf{k}$ drops towards zero. The important thing in the scattering process is that the momentum has to be transferred to the plasmon and we

have to have allowed plasmons with the required $|k|$. If the $|k|$ to be transferred in a scattering experiment is larger than the allowed $|k|$ for the plasmon, we have no scattering from those plasma waves.

Fig. 11—Light scattering from a gaseous hydrogen plasma at the ruby laser frequency. On 11(a) the scattering was observed at small angles for the plasma as well as the Rayleigh scattering. At large angle, 90°, and large $|k|$ transfer, we see the Doppler broadened scattering of the elementary scattering particles and not the collective excitations. From Ref. [26].

We can imagine qualitatively that in a scattering process the $|k|$ transfer measures the "lattice spacing" between electrons. Large $|k|$ transferred corresponds to large frequencies or small interparticle distance intervals probed. If the collective system, like a gas plasma, involves particles far away from each other its frequency and momentum (wave-vector) are small. To detect it we have to probe with a small momentum transfer.

If in a certain system the momentum transfer is smaller than the maximum allowed momentum of the plasmon we can detect the collective or plasma excitations. But if the momentum transfer is larger, we are probing smaller volumes. In a plasma, for instance, we are probing the velocity distribution of the individual scattering charges. This is beautifully illustrated in Fig. (11a and 11b) [26] which shows the near forward and 90° scattering of ruby laser light by a flash-produced H_2 plasma.

In the nearly forward scattering case of Fig. (11a) we see the Rayleigh and plasma-shifted frequencies. This scattering is similar to Brillouin scattering where the Rayleigh and plasma frequencies can be understood as propagating (pressure) and nonpropagating (entropy) fluctuations in the density of charges; the plasma shift observed is a function of $|k|$ similar to that in a Brillouin experiment. In Fig. (11b) scattering at 90°, we obtain

a spectrum for high values of $|k|$ from the Doppler-broadened scattering by the individual particles, in this case molecular or atomic hydrogen ions surrounded by an electron cloud.

In the above we have treated only gaseous or "free" plasmas, ones not coupled to the medium through which they flow. Let us now consider a plasma in a solid, say a semiconductor. Here the same "Brillouin-like" spectrum discussed above will appear, the electronic mass, M, substituted by an effective mass M^*. But a coupling of the host lattice with the internal electric field of the oscillating plasma will also take place. An externally or internally applied electric field will couple to the lattice and is, in effect, responsible for the LO-TO splitting of the optical vibrations. This coupling affects the dielectric constant of the material. In a plasma-free medium we can write the dielectric constant ε at low frequencies as:

$$ \varepsilon\,(\omega) \;=\; \varepsilon_\infty \,+\, \sum_i \; \frac{\omega_i^2\, S_i}{(\omega_i^2 - \omega^2)} \tag{13} $$

where ε_∞ is the dielectric constant far away from the optical phonon frequencies, ω_i is the frequency of the infrared active optical phonons (transverse, or TO modes) and S_i is the infrared intensity of each i mode. If we now add free carriers with a plasma frequency ω_P, Eq. (12), the dielectric constant expression has to be modified to

$$ \varepsilon\,(\omega) \;=\; \varepsilon_\infty \,+\, \sum_i \; \frac{\omega_i^2\, S_i}{(\omega_i^2 - \omega^2)} \,-\, \frac{\omega_P^2\, \varepsilon_\infty}{\omega^2} \tag{14} $$

The infinities of the dielectric constant define the frequencies of the TO, or transverse optical modes and from expression (14) we see that the plasma does not change these TO frequencies, so we can say that the plasma does not couple to the TO modes. The zeroes of the dielectric constant are the LO (longitudinal) mode frequencies and those are definitely modified by the plasma. As a matter of fact we have now for each TO mode two coupled LO plasmon modes with their frequencies, line widths, etc. completely dependent on the plasma frequencies.

The scattering from this coupled plasmon-longitudinal mode-lattice can be classified as a generalized Raman effect. Fig. (12) shows the Raman effect of GaAs [27] with different carrier concentrations in which the TO mode appearance is hardly affected while the LO-plasma modes are very dependent on carrier concentration.

Raman scattering of Landau levels

If a free electron is subjected to a magnetic field it will describe a circular trajectory with a radius and frequency determined by the magnetic field, electronic charge, mass of the particle and the dielectric constant of the medium. These "cyclotron orbits" inside a crystal are quantized and are called Landau levels. If we choose a crystal in which the effective electronic mass is small, for example in GaAs the effective electron mass is $\cong$ .07 and in InSb it is $\cong$ .01 of the rest electron mass, we can observe a large Landau splitting for relatively small magnetic fields.

The Landau levels of an electron in a magnetic field are equally spaced in energy, reflecting the fact that one can consider them as levels of an harmonic oscillator in
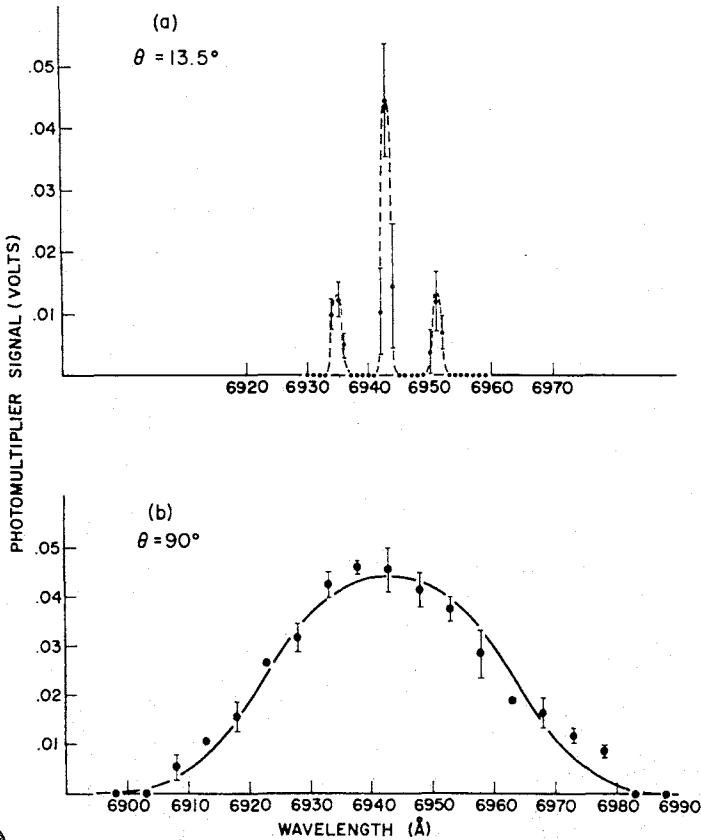
N = 2.3 × 10^15

7.4 × 10^16

3.9 × 10^17

9.5 × 10^17
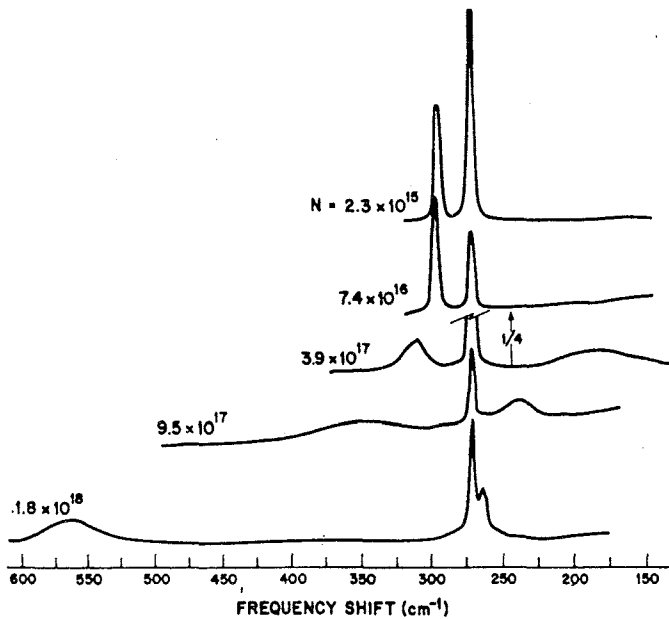
.1.8 × 10^18

FREQUENCY SHIFT (cm⁻¹)

Fig. 12—Scattering from coupled LO-plasma modes in GaAs, from Ref. [27]. On top for a low carrier concentration we see the LO and TO modes of GaAs. As the concentration of carrriers N is increased there is a coupling of the LO and plasma frequencies shown very clearly.

which the fundamental frequency is equal to the cyclotron frequency ω_C. Carrying the harmonic oscillator approximation further we can predict the Raman selection rules and cross-section for a harmonic oscillator. The selection rules are found to be $\Delta n = 0, \pm 2$ [28]. If we then include anharmonic terms, transitions with $\Delta n = \pm 1$ would be allowed but should naturally be weaker than the $\Delta n = \pm 2$ transitions. Recent experiments [29] in Raman scattering by Landau levels in InSb were performed and to a first approximation theoretical predictions of the properties of the scattering were observed. Disagreeing with predictions, the $\Delta n = \pm 1$ transitions were observed to be of the same strength as those with $\Delta n = \pm 2$. The harmonic oscillator theoretical approximation for the Landau levels has to be modified. In the same experiments [29] a "spin-flip" Raman transition, $\Delta s = \pm 1$, was also observed in these Landau levels.

Electric field induced Raman effect

If we apply an electric field to a collection of coupled harmonic oscillators we can induce a dipole proportional to the polarizability; vibrations which were only Raman active without the field now become infrared active. This is the well known effect of Stark-induced infrared absorption. One can also show that the electric field will shift all the levels of the harmonic oscillator by the same amount, so the transition frequency does not change nor do the Raman effect $\Delta n = \pm 1$ selection rules for the oscillator change. The electric field may, however, change the symmetry of the unit cell in such a way that it may pull the center atom of a cubic crystal of symmetry 0_h away from the center position making the symmetry of the cell a tetragonal C_{4v}, for example.

This small displacement of an atom in the unit cell may have drastic effects. Imagine that for reasons of symmetry a crystal has no first order Raman effect: by so slightly changing the symmetry the electric field makes the first order Raman effect allowed without affecting, in

first order, the vibrational frequencies of the field-free crystal.

If the change of symmetry is small, the new one-phonon Raman effect at first will be as strong as the two-phonon process until, hopefully, it will become so strong as to dominate the spectrum. Assuming that the new, induced, one-phonon process is only as strong as the no-field-allowed, two-phonon process, a clever way of separating the two has been found, [30]. The laser is allowed to continuously shine upon the crystal while the applied electric field is oscillated in a square wave of frequency ω, let us say 100 cycles/sec. The detection of the Raman effect is made with a synchronous amplifier set at the electric field frequency ω or at 2ω; the electronics then measure the difference between the field-on and field-off spectra and, while the two-phonon spectra obligingly cancel out, the newly allowed field-induced one-phonon spectra rise.

This technique may presage a new way of looking at the forbidden modes and at a host of new crystals while per se the results will furnish information on the effect of electronic fields, on vibrational mode frequencies, etc.

WE have tried to summarize today's research in the field of light scattering with laser sources. So extensive is the current work that all of us participating await eagerly each week's Phys. Rev. Letters to learn what new effects have been discovered or what unexplained details of the older ones have been clarified. It is an age of excitement in the light scattering field, brought about by the availability of the laser source.

References

[1] Lord Rayleigh: Phil. Mag. 47, 375, 1899, Coll. papers IV p. 397.

[2] L. Brillouin, Ann. Phys. (Paris) 17, 88, 1922.

[3] A. Smekal: Naturwiss. 11, 873, 1923.

[4] C. V. Raman: Indian J. Phys. 2, 387, 1928; C. V. Raman and K. S. Krishnan: Nature, 121, 501, 1928.

[5] G. Landsberg and L. Mandelstam: Naturwiss. 16, 57, 1928.

[6] E. Gross: Nature 126, 201, 400, 603, 1930.

[7] G. Placzek: Marx's Handbuch der Radiologie VI, 2, 209, 1934.

[8] In particular the Indian work published in the Ind. Acad. Sc. by R. S. Krishnan and others and in this country by D. H. Rank et al., and more recently with laser sources by R. Y. Chiao and B. Stoicheff: J. Opt. Soc. Am. 54, 1286, 1964.

[9] G. Benedek, J. B. Lastovka and K. Fritch, J. Opt. Soc. Am. 54, 1284, 1964; G. Minichino, R. O'Brien, G. J. Rosaseo and A. Weber: Bull. Am. Phys. Soc. 12, 1132, 1967. Both groups used laser sources.

[10] J. B. Lastovka and G. B. Benedek: Proc. Phys. Quantum Electr. Conf., Puerto Rico 1966, p. 231, M. G. Cohen and E. I. Gordon: Bell Syst. Tech. J. 44, 693, 1965 and H. Z. Cummins, N. Knable and Y. Yeh: Phys. Rev. Lett. 12, 150, 1964.

[11] A. Weber, S. P. S. Porto, L. E. Cheesman and J. J. Barrett: J. Opt. Soc. Am. 57, 19, 1967.

[12] P. Debye: "Polar molecules," Dover Publ., N.Y. 1929 Chapt. V.

[13] S. L. Shapiro and H. P. Broida: Phys. Rev. 154, 129, 1967.

[14] S. P. S. Porto, P. A. Fleury and T. C. Damen: Phys. Rev. 154, 522, 1967.

[15] R. Loudon: Adv. in Phys. 13, 423, 1964.

[16] T. C. Damen, S. P. S. Porto and B. Tell: Phys. Rev. 142, 570, 1966.

[17] J. M. Worlock and S. P. S. Porto: Phys. Rev. Lett. 15, 697, 1965.

[18] J. Hurrell, T. C. Damen, S. P. S. Porto and S. Mascarenhas: Phys. Lett. 26A, 194, 1968.

[19] C. H. Henry and J. J. Hopfield, Phys. Rev. Lett. 15, 964, 1965.

[20] S. P. S. Porto, B. Tell and T. C. Damen: Phys. Rev. Lett. 16, 450, 1966.

[21] J. P. Scott, L. E. Cheesman and S. P. S. Porto: Phys. Rev. 162, 834, 1967.

[22] P. A. Fleury, S. P. S. Porto, L. E. Cheesman and H. J. Guggenheim: Phys. Rev. Lett. 17, 84, 1966.

[23] P. A. Fleury, S. P. S. Porto and R. Loudon: Phys. Rev. Lett. 18, 658, 1967.

[24] J. T. Hougen and S. Singh: Phys. Rev. Lett. 10, 406, 1963; Proc. Roy. Soc. (London) A277, 193, 1964.

[25] C. H. Henry, J. J. Hopfield and L. C. Luther: Phys. Rev. Lett. 17, 1178, 1966.

[26] S. Ramsden and W. Davies: Phys. Rev. Lett. 16, 303, 1966.

[27] A. Mooradian and G. B. Wright: Phys. Rev. Lett. 16, 999, 1966.

[28] P. A. Wolff: Phys. Rev. Lett. 16, 225, 1966.

[29] R. E. Sluscher, C. K. N. Patel and P. A. Fleury: Phys. Rev. Lett. 18, 77, 1967.

[30] J. M. Worlock and P. A. Fleury: Phys. Rev. Lett. 19, 1176, 1967.

TABLE I: SCATTERING PHENOMENA

Type of Scatter	Instrumental Requirements		Principal Applications
	Optical	Laser Excitation	
Rayleigh	Fabry-Perot; Photobeating	Single mode, single frequency, low power	Critical opalescence; phase transitions; atmospheric propagation
Brillouin	Fabry-Perot; Photobeating; High-resolution spectrograph	Single mode, single frequency, low power	Phase transitions; velocity of sound; damping processes in sound transmission
Rotational Raman	High-resolution (0.0X cm⁻¹) spectrograph	High-power ion (1 watt)	Molecular structure of gases
Vibrational Raman	Double Grating Spectrometer	50 mW He-Ne	Molecular structure; force constants; chemical analysis and identification
Phonon	Double Grating Spectrometer	High-power ion	Lattice properties of and phase transitions in solids
Multiple Phonon	Double Grating Spectrometer	High-power ion	Anharmonicities of force constants in solids; critical points in the Brillouin zone
F-Center	Double Grating Spectrometer	High-power ion	Physics and analysis of lattice defects; phonon propagation in defective lattices
Polariton	Double Grating Spectrometer (forward scatter)	High-power ion	Coupling of phonons and light in the infrared
Spin Wave	Double Grating Spectrometer	High-power ion	Magnetic phase transition around Curie points; coupling of light with magnetic states
Electronic	Double Grating Spectrometer	High-power ion	Electronic energy levels of ions in solids
Plasmon	Double Grating Spectrometer	Ruby	Properties of gaseous, liquid, and solid plasmas; coupling of plasma with lattice modes
Landau levels	Single Grating Spectrometer	High-power CO_2	Cyclotron resonances and damping of nearly free electrons in solids
Field induced Raman	Double Grating Spectrometer	High-power ion	Electric field induced lattice deformation; "forbidden" Raman effects

A NU DIMENSION: RECIPROCAL CENTIMETERS

IN ADDITION TO READOUT IN WAVENUMBER (CM⁻¹ AND ΔCM⁻¹)

SPEX NEW ν 1401 DOUBLE SPECTROMETER ATTAINS

MORE THAN TWICE THE ACTUAL RESOLVING POWER OR
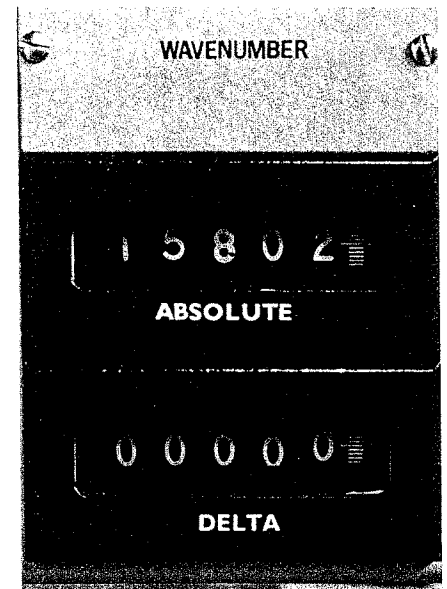
- - - - - - - - - TWICE THE LUMINOSITY OR

- - - - - - - - - TWICE AS MANY SCANS PER UNIT TIME OR

- - - - - - - - - TWICE THE SIGNAL:NOISE OR

- - - - - - - - - TWICE THE EFFECTIVE LASER POWER

AND ±0.5 CM⁻¹ ACCURACY

Also available is a complete Raman Spectroscopy System,
the RAMALOG, containing a laser source, sample illuminator,
the 1401 double spectrometer, detection, amplification and
recording instruments in compact, modular construction within
an attractive console.

SPECIALISTS IN SPECTROSCOPY