LIGHT SCATTERING WITH LASER SOURCES, Part II

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THIS article is meant to be a continuation of last year's in the SPEX SPEAKER, XIII, No. 2. So I will not try to duplicate explanations given there and maintain identical terminology. In this article I would like to review the promising contributions to essentially new scattering phenomena opened up in 1968 through the application of laser excitation. Only because of space limitations will I ignore developments in more conventional Raman spectroscopy such as rotational spectra of gases and vibrational spectra of liquids. While I intend to dwell mainly on studies of solids, let me commend the research in process on liquids and gases which is progressing at a rapid pace. A good deal of fine work is being conducted pertaining to absolute cross sections for Rayleigh, rotational, and vibrational transitions, local field effects, resonance phenomena, etc.

Before embarking on more fundamental questions, I would like to bring up a subject that had supposedly been thrashed out many years ago. It relates to the angular dependency of intensity of Raman scattering in liquids. If one thinks of the Raman effect as mainly the emission of light by a light induced electric dipole or electric quadrupole, the total intensity should depend on angle:

$$I = I_0(a + b\cos^2\theta) \qquad (1)$$

The ratio of b to a is related to the familiar depolarization ratio of the Raman scattered light, an old result theorized by Placzek. We can see that Eq. (1) is completely symmetrical in θ, i.e. $I(\theta) = I(-\theta)$; in particular the Raman intensity in the forward and backward directions has to be the same. Experiments in this country have verified theory. However, Russian scientists, mostly through publications in Optics and Spectroscopy (1) have reported a pronounced forward enhancement in the Raman effect. It is very hard to understand such an enhancement, unless polariton effects or coherent scattering by a number of molecules create a forward anomaly. Polaritons, never identified in liquids as far as we know, would only affect those lines that are simultaneously Raman and infrared active. This is not so for the general observations reported. The coherent scattering by many molecules, of an inherently incoherent phenomenon like the Raman

effect looks a little far fetched to me. Another explanation, i.e. the coherent scattering (laser phenomenon) of Raman radiation, would require threshold powers of the order of tens of kilowatts to appear. It is too early to say whether the experiments are right or wrong but if they are right an explanation must be conjured up.

In September 1968 an international meeting in New York on "Light Scattering Spectra of Solids" was held. Here many new interesting effects were presented; they will be summarized in a Conference Proceedings edited by G.B. Wright. Another 1968 highlight was the Debye Memorial Symposium on light scattering at Cornell. Some of the subjects discussed at those meetings at New York and Cornell encompassed: Rayleigh scattering in critical mixtures and opalescence, Doppler shifting of Rayleigh radiation and determination of diffusion velocities of large particles in solution, determination of selection rules and acousto-optical coefficients from Brillouin Spectra in single crystals, observation of spin wave scattering from impurities in crystals, Raman effect in single crystals, etc.

With all this new information announced in 1968 I have exercised my bias in choosing but a few subjects to highlight. Included are Rayleigh wing scattering, phonons in solids, scattering from metals, electronic Raman effect, mixed excitations and resonance scattering.

Rayleigh Wing Scattering

THIS scattering, appearing as a large (up to ~ 100 cm^{-1}) broadening of the Rayleigh scattering mostly in liquids, has now been observed in high pressure gases as well (2). Until recently we have been assuming that this Rayleigh wing scattering whose strength bears a one-to-one relationship with the Kerr effect (3), was due to hindered rotation of non-spherical molecules (those for which pure rotational Raman effect in the gas phase was allowed). The disturbing evidence against that model was, however, that the measured Kerr effect of such spherical top molecular substances as CCl_4 was relatively large, even though no pure rotational Raman effect is allowed. In 1968 even more confusing re-

sults appeared: Rayleigh wing scattering was observed in high pressure noble gases (Kr and Ar) (2) and liquids so close to spherical that no possibility of hindered rotation exists (4, 5a). Clearly, another explanation was in order.

The Rayleigh wing spectrum is now thought of as arising from different relaxation phenomena, one of them being the old Debye's rotation of an asymmetric molecule in a viscous medium (5). The Rayleigh wing spectrum of pressurized noble gases seems, however, to be of different origin. It is now thought to arise from a translational Raman scattering. Its origin can be understood (2) by a simple model: imagine two rare gas molecules (or any two molecules for that matter) on a collision course. As they approach one another their electronic shells start deforming progressively, i.e. they mutually polarize each other and their change of polarizability gives rise to a spectrum which is continuous and of low frequency. The intensity of this translational scattering falls off exponentially with frequency so, displayed logarithmically, the spectrum becomes a straight line. Any deviations from this straight line are thus readily observed. Photon counting electronics with provision for logarithmic read-out has proved ideal for making such measurements (5a).

This translational Raman effect is probably a common feature for the Rayleigh wing spectrum of all liquids and gases. For gases at low pressure it will probably be difficult to observe since its intensity should be proportional to the square of the pressure of the gas. One of the properties of this spectrum, is that it should be completely depolarized (ρ=.75) like the hindered rotation spectrum which is superimposed on it. A careful study of Rayleigh wing spectrum as the "rotational" wings of Raman lines (6) will undoubtedly bring forth a wealth of new understanding of relaxation mechanisms in liquids and pressurized gases.

Raman Effect in Metals

ONE exciting new observation made in 1968 was the observation of Raman effect in metals (7). The scattering quasi-particles in this case were phonons.

Most metals contain only one atom per unit cell. There will thus be only three degrees of freedom per unit cell corresponding to the acoustical modes, so no one-phonon Raman effect will be allowed for these metals, even though Brillouin scattering is theoretically possible. Other metals, however — most semi-metals, as well as intermetallic compounds — have more than one atom per unit cell and the extra degrees of freedom will then appear as optical phonons.

Conceptually, it is easy to observe the Raman effect in metals. Examine a metal or intermetallic compound with more than one atom per unit cell and measure the Raman scattering. There are a "few" unanticipated annoyances, however, that one has to contend with. The most vexing of them is that since the dielectric constant of a metal is purely imaginary light does not penetrate the metal. Put another way, all the light will be reflected before it has a chance to interact with the optical phonons. In practice, the real world is not that bad; light does penetrate the metal to about a few

tenths or hundredths of angstroms; interaction occurs, but the scattering volume is very small. To overcome this problem one can increase the effective power of the laser by focusing the beam on the metal, while the sample is made one of the mirrors inside the laser cavity (7). Although this method proved successful in the experiments, three new difficulties surfaced. Rayleigh scattering is proportional to the laser power in the sample so even though one is using a double monochromator with low scattering properties Rayleigh scattering imposes a limit on the maximum laser power. It goes without saying that if the sample is not polished very, very carefully, non-shifted laser scattering from the imperfect surface will flood the spectrometer with laser light burying the weak phonon scattering. This condition may be eased with a triple monochromator or a predispersor monochromator coupled with the normal tandem spectrometer. A second experimental difficulty encountered in this experiment is that, since the sample is inside the laser cavity, a lot of laser fluorescence will be collected in the spectrometer. This problem will not be fully solved even with a triple spectrometer. The third problem encountered in the observation of the phonon-Raman effect of metals is that the metal itself might fluoresce. This fluorescence in metals (8), if proved to be general and as strong as seen in recent experiments, will obscure future observations.

To show the difficulty of these observations we shall describe quickly how results were finally obtained (7). a) Metal samples with more than one atom per unit cell were selected; b) sample surfaces were polished to as good optical finish as possible; c) the sample was put inside the laser cavity with the laser focused on its surface; d) as a further precaution against instrumental scatter, a premonochromator was set in front of a Spex double spectrometer; e) the spectrum was scanned slowly enough to permit integration times of the order of 300 seconds. To speed up observations, measurements were centered around the phonon frequencies located from prior neutron diffraction measurements.

Results already obtained in my laboratory by L. Fraas on beryllium, tin, bismuth, chromium and niobium appear especially promising.

Raman Effect of Phonons

IN 1968 many papers appeared on the scattering of light by phonons. The selection rules obtained from group theory, the effect on the selection rules of optical activity in the crystal and the effect of simultaneous Raman and infrared activities of phonons for uniaxial crystals seem now to be pretty well understood. Although group theoretical selection rules apply (it would be funny otherwise), optical activity can, apparently, "mess up" the selection rules; but if the effect is recognized one can extract the right results. When a vibrational mode — phonon — in a crystal is both infrared and Raman active it may split into two phonons: a longitudinal (electric polarization $\vec{P}$ parallel to propagation direction $\vec{k}$) and a transverse ($\vec{P} \perp \vec{k}$) phonon. Even though they correspond to the same mechanical vibrational mode, the two offspring phonons scatter at different frequencies. Furthermore, a one-to-one correspondence relates how big the LO—TO splitting is for a certain mode and how strongly it

absorbs in the infrared. One fundamental result of this longitudinal and transverse mode splitting is that, from the relative intensities of the two modes, one may obtain that very important quantity in non-linear optics: the electro-optical coefficient (9, 10).

As the phonon structure, selection rules, etc. of simple crystals become better understood, investigations of more complicated crystals begin to look worthy of study. Until now the group theoretical and identification "tour de force" has been the study and identification of all the phonons of YAG (yttrium aluminum garnet) with its 160 atoms per unit cell and 80 atoms per primitive cell, i.e. 240 degrees of freedom (11).

The main trend, however, in 1968 (and we expect more of the same in '69), has been to use the phonon structure as a tool to understand physical effects such as ferroelectricity, phase transitions, etc. just as the vibrational Raman effect was and still is relied on as a tool to determine molecular structure.

Let us now look at phase transitions and how the study of the phonon structure can help us there. The easiest phase transition to observe and relate to phonon spectrum is melting since phonon structure of most substances is very sensitive to it. In the liquid phase only scattering at the internal vibrational frequencies of each molecule may be observed. The external modes, i.e. the modes corresponding to whole molecules moving in relation to other molecules, which appear at low frequencies in solids, disappear altogether in liquids (except for Rayleigh wing continuum); also an internal mode which, in the liquid corresponds to a single frequency, in a solid might split into two, three or more frequencies depending on how many molecules comprise the unit cell. The disappearance of this splitting of the internal modes corresponds exactly to a disappearance of order (melting) in a crystal.

Also easily observed through phonon structure is a solid-solid phase transition occurring at a certain critical temperature where the crystal changes its structure but not its state. For instance, $BaTiO_3$ at temperatures above $110°C$ is cubic, each atom centered in a cube, i.e. crystal structure O_h; the same $BaTiO_3$ at temperatures between $\sim4°C$ and $110°C$ changes to a tetragonal structure C_{4v} and below $4°C$ to an orthorhombic structure D_2. If we study the Raman effect of this crystal as a function of temperature we might expect that above $110°C$ no first order Raman effect would occur (every atom remains at the center of a cube); between $110°C$ and $4°C$ the spectrum should show the proper number of shifted frequencies each with the calculated polarizability tensors for a C_{4v} structure, etc.

The design of an experiment to tie the phonon structure to phase transitions would seem straightforward – until the work is actually performed. Recently, however, experimental data on $BaTiO_3$ have been substantiated.

Ammonium halides have proved to be easier to work with than $BaTiO_3$ because they have no domain structure and the absence, too, of a strong two-phonon process which confuses the picture of the one-phonon process under study. Al-though the spectra of ammonium halides are complicated by their large number of atoms per unit cell, their spectra do change as predicted as they undergo phase transitions. The correlation is not perfect, however. At temperature ranges of about $5 - 10°$ below and above the phase transition, one still sees the frequencies corresponding to the previous phase; even though the critical temperature T_c has been reached and the phase change has occurred, remnants of the prior order apparently linger. This order, which may have been evidenced by a particular Raman line, eventually disappears with increasing or decreasing temperature away from T_c. $KNO_3(I) \longleftrightarrow KNO_3(II) \longleftrightarrow KNO_3(III)$ was also studied in 1968 (13).

Phase transitions are associated with still another effect, the so-called soft mode. A soft mode is one which shifts its frequency with temperature; as the temperature approaches T_c, its shift tends towards zero. A typical example of a soft mode is that of a ferro-electric, the frequency of which obeys a relation like

$$\omega^2 = \kappa(T_c - T) \tag{2}$$

True, all the other modes of a crystal will also follow a frequency change with temperature; they are all related to the volume expansion of the crystal. The magnitude of the shift of the soft mode, however, will change dramatically, many times that of other shifts. Often the soft mode is actually responsible for the phase transition rather than vice-versa. For it corresponds to a movement that actually drives the solid from one structure to another. In the phase transition of $SrTiO_3$, for instance (14), the soft mode will, at the phase transition, double the size of the unit cell and the frequencies that are seen in the new structure are those that in the old structure corresponded to the edge of the Brillouin zone.

In two cases, in which the soft mode behavior of ferro-electric crystals $BaTiO_3$ and KDP (15) were studied the soft modes were found and their frequency obeyed Eq. 2 but the mode was over-damped, i.e., it did not show itself as a line but instead as a characteristic continuum of an over-damped oscillator, overlapping the Rayleigh line.

Resonance Raman Effect

CLASSICALLY, Raman spectra arise from the scattering of light by an induced oscillating dipole, the inducing field being that of laser radiation of frequency ω_L:

$$\underline{P} = \alpha \underline{E} = (\alpha_0 + \alpha_1 \cos\omega_M t) E_0 \cos\omega_L t$$
$$= \alpha_0 E_0 \cos\omega_L t + \tfrac{1}{2}\alpha_1 E_0 \cos(\omega_L + \omega_M)t + \tag{3}$$
$$\tfrac{1}{2}\alpha_1 E_0 \cos(\omega_L - \omega_M)t$$

The α is simply the polarizability of the molecule which may be modulated by the characteristic frequency of the medium ω_M.

If, instead of relying on classical theory, one calculates the scattering phenomenon more exactly from a quantum mechanical model he has to do a time dependent perturbation calculation in which the perturbing field is the time-varying electric field of light. What this perturbation does to the ground state of a system is mix it with all the possible excited states of the molecule. A simplified picture of the phe-
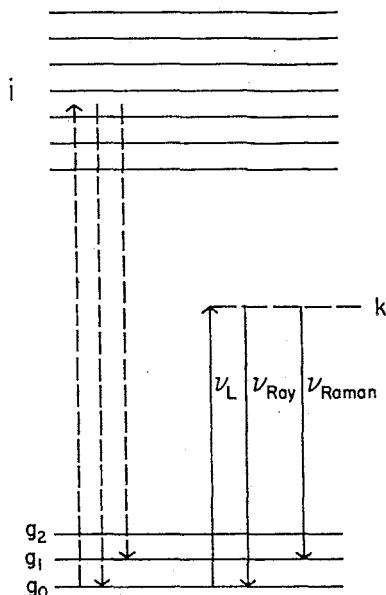
Fig. 1 A typical energy level diagram for a scattering process; g_0, g_1, g_2 correspond to vibrational levels of the ground state g. The i's are all other electronic levels of the material. In full lines we describe semi classically the scattering process, i.e., light is absorbed from the ground state to a virtual state k from which it decays into g_0 (Rayleigh scattering) or g_1 (Raman Stokes lines). The dashed lines give the real quantum mechanical description of the scattering process.

nomenon is shown in Fig. 1. Imagine a system made up of an electronic ground state g to which one can associate vibrational states g_0, g_1, g_2, . . . and of many electronic excited states i. If the exciting laser frequency ω_L is less than all $(E_i - E_g)/\hbar$ then the substance is transparent to the laser light. The scattering then can be thought of as a virtual process consisting of absorption of the laser light by the ground state g_0. Absorption will take it to a virtual level k and reradiate light returning to g_0 (Rayleigh scattering) or to g_1 (Raman-shifted), for instance. This process is shown in Fig. 1 as unbroken vertical lines. The true quantum mechanical picture is, however, that shown by dashed vertical lines; upon application of the perturbation, mixing of the ground electronic state g with all excited states i will occur and those excited states i that by selection rules can combine simultaneously with g_0 and g_1 will contribute to the strength of the Raman vibrational transition $g_0 \to g_1$. The polarizability α will then be expressed as

$$\alpha \sim \sum_i \frac{A_{g_0 i} \quad A_{i g_1}}{(\omega_i - \omega_L)(\omega_i - \omega_L \pm \omega_{01})} + c.c. \quad (4)$$

One can write the intensity of the scattered radiation as

$$I_R = \frac{64 \pi^4 \nu^4}{3C^3} [\alpha]^2 I_L \quad (5)$$

Where ν, the frequency of the scattered radiation α, is given in (4) and I_L is the laser intensity.

So if one varies the frequency of the incident radiation, ignoring the frequency dependence of α (this can be done

when $\omega_M \ll \omega_i - \omega_L$) the intensity of the scattered radiation is proportional to the fourth power of the frequency as shown in Eq. 5. This is the same result as for the Rayleigh scattering and as we know, it is responsible for the blueness of the sky and the beauty of the red sunsets. If one, however, starts getting close to resonance by approaching actual absorption wavelengths of the material, the denominators in the expression for α start blowing up, see Eq. 4, and the intensity starts going up faster than ν^4. This was one of the big unsuspected advantages attained by Rasetti in 1929-30 when he switched to the 2537A mercury line to excite Raman spectra in crystals; scattering intensity rose even faster than ν^4. More recently, the same enhancement allowed the observation of the Raman effect of F-centers in alkali-halides (16).

The importance of a careful study of the resonance behavior on Raman intensity is thus manifest but assuming Raman spectra are gotten, how does one determine which electronic excited states i in the system are really responsible for the coupling of the electromagnetic radiation field to the excitation (phonons, vibrations, rotations, etc.) in a sample? The problem has been in the mind of many experimentalists and theoreticians for many years. In particular Brandmuller's group in Germany and the Russians did a lot of work on resonance enhancement in liquids before lasers were known.

Some puzzling resonance results began appearing with the application of laser sources. Ionized argon-krypton lasers, in fact, emit so many laser lines in the visible (see table #1) that resonance work becomes a natural for them. Fig. 2 shows the resonance behavior of the intensity ratio of one phonon to two phonon processes in CdS (17). From the frequency measured we know that the scattering is done by longitudinal optical phonons (LO). The remarkable fact in these results is that essentially the whole resonance behavior of those LO phonons can be explained by assuming only one
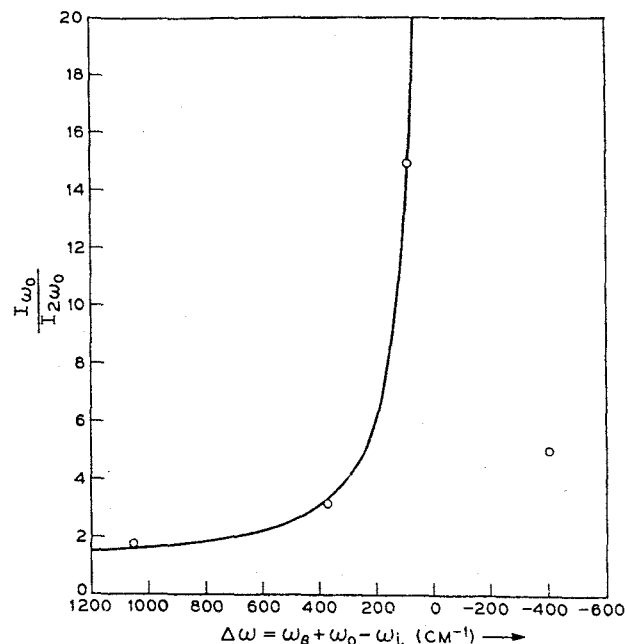

Fig. 2 Plot of the intensity ratio of one to two phonon processes in CdS showing the resonance behavior of the longitudinal phonon at the exciton frequency (17).

i state in Eq. 4 and the frequency of that state almost co-incides with that of an exciton* in CdS. This means that near resonance the mechanism responsible for coupling of electro-magnetic radiation to the LO phonon in CdS seems to involve the exciton while all the other excited states (conduction band, etc.) play no significant role in Raman scattering efficiency.

More interesting results yet are shown in Fig. 3. Plotted there are the resonance curves of the optical phonons in ZnSe and CdS (18). Again the results show that in both crystals LO phonons resonate at the frequency of the exciton but the TO phonons which correspond to the same vibrational modes resonate in a completely different way. Raman excitation mechanisms for LO and TO phonons are thus shown to be completely different even though they correspond to the same mechanical vibration.
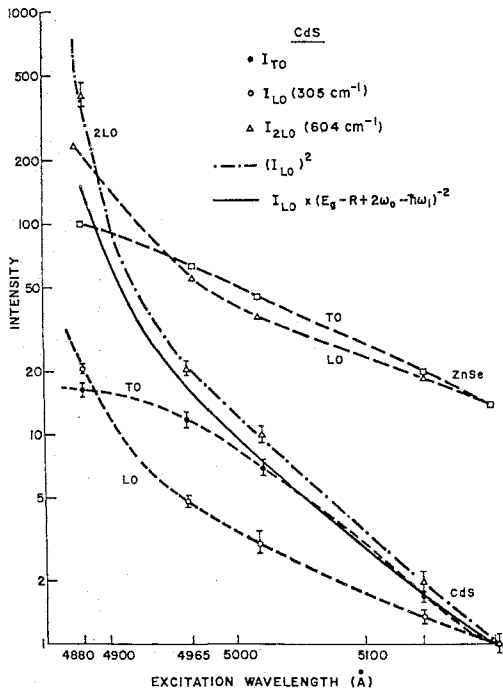

Fig. 3 Resonance behavior of the phonon processes in CdS and ZnSe. In it we see the difference in resonance behavior between the LO and TO phonons which correspond in each crystal to the same mechanical motion (18).

Another odd phenomenon occurs when the frequency of the laser falls fully into an absorption band. Here multiple phonon processes start to appear. Fig. 4 demonstrates the Raman scattering of CdS with different exciting frequencies; we can see that when the crystal is excited with the 4765Å argon laser radiation scattering appears at the frequencies of one, two . . . seven phonon processes (19). Only LO (no TO phonons) appear superimposed on the CdS fluorescence. In this case again the resonance is due to coupling of the phonons to the excitons or to the "dressed exciton," the polaron.

* An exciton is a hydrogen atom-like electron hole pair result-ing from the removal of an electron from the valence to conduction band.
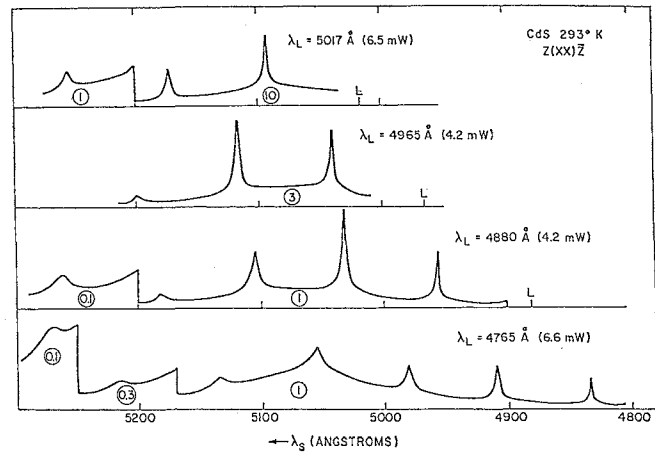

Fig. 4 Multiple phonon resonant Raman effect of CdS. Below resonance only one and two phonons show up; with 4765A excitation up to 7 LO phonons Raman processes appear (19).

I would like to emphasize the importance of continued study of resonance behavior to the real understanding of the coupling mechanisms responsible for the Raman effect. Different quasi-particles and even different phonons may show different resonant behavior as the exciting line ap-proaches different absorption valleys.

Electronic Raman Effect

JUST as molecular vibrationals cause Raman scattering, transitions between electronic levels in a sample cause scattering, too. The systems in which those electronic tran-sitions have been studied are those which have low lying electronic levels close to the ground state. For those tran-sitions the Raman shift is small: $\Delta\nu \sim 20$ to 3000 cm^{-1}.

Almost ideal subjects for the study of the electronic Raman effect are those of a rare-earth or transition ion imp-urity in a crystal. Imagine a Ce^{+3} ion implanted in a LaCl$_3$ lattice for instance. The ground state of the Ce^{+3} is the degenerate state $^2F_{5/2}$ while the next electronic state of the ion, the $^2F_{7/2}$ state, lies only ~ 2000 cm^{-1} above the ground state. Imagine further this Ce^{+3} ion substituting for a La^{+3} ion in LaCl$_3$. The cerium will now be subject to the influence of the electric field of all the chlorine and lanthanum ions surrounding it. A strong electric field will, of course, produce splitting and shift of spectral lines, the well known Stark effect. The difference in this Stark effect from the common gas case is that the electric field varies with direction in the crystal even though it has the same value for specified direct-ions given by the symmetry of the crystal. For instance the ground state $^2F_{5/2}$ of the Ce^{+3} ion, in this case of the LaCl$_3$ structure, splits into three different levels due to the crystal electric field while the first excited stage splits into four (see Fig. 5). So if the Raman effect of Ce^{+3} is observed one should see two low frequency shifted lines $\Delta\nu \sim 2 - 200$ cm^{-1} and four lines at around 2000 cm^{-1}, considering only transitions initiating in the lowest ground state sublevel. As one does the

cm^{-1}

2359
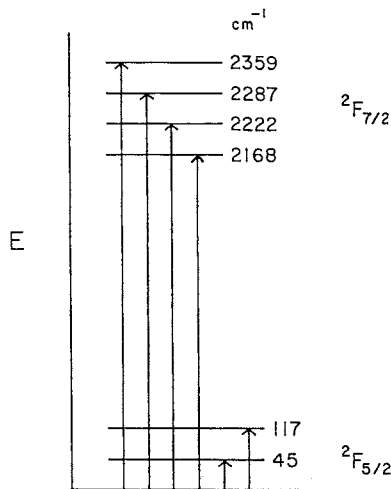2287 $^2F_{7/2}$
2222
2168

E

117
45    $^2F_{5/2}$

Fig. 5 Energy level diagram of the Stark splitting of the Ce^{+3} ion in a LaCl$_3$-type lattice showing the possible Raman transitions. The $^2F_{5/2}$ is split into three Stark components while the $^2F_{7/2}$ is split into four components.

experiment in a CeCl$_3$ crystal (20) at liquid helium temperatures this is exactly what is observed, (see Fig. 6) two Raman shifted lines at 39 and 112 cm^{-1} and another group of four at 2130, 2175, 2264 and 2321 cm^{-1} corresponding to the crystal field Stark split components of the $^2F_{5/2}$ and $^2F_{7/2}$ states of the Ce^{+3} ion. Naturally, if the Ce^{+3} is implanted into another crystal, such as CaF$_2$, the Stark splittings will be different since the electric field seen by the ion have different strengths and symmetry. A cursory look at the Raman scattering will furnish the number and the frequencies of the Stark-split components of the free ion levels.

Since an experiment of this kind involves Raman scattering again we can conclude that its selection rules should arise from a polarizability tensor just like in the vibrational Raman effect. However, big differences exist between the polarizability tensors associated with the electronic Raman effect and those of the vibrational Raman effect. In the first place, all the tensors associated with vibrational Raman effect are symmetric, i.e. it does not make any difference if you measure
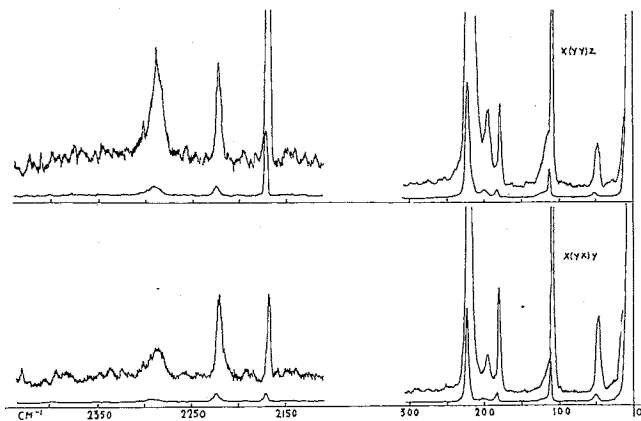

Fig. 6 Electronic Raman effect of Ce^{+3} in CeCl$_3$. Shown are the yx and yy components of the polarizability tensor. The extra low frequency lines represent phonons.

an α_{xy} or α_{yx} spectrum since $\alpha_{xy} = \alpha_{yx}$, $\alpha_{xz} = \alpha_{zx}$, etc. For the electronic Raman effect this is not so; quite a few tensors are pure antisymmetric, i.e. $\alpha_{xy} = -\alpha_{yx}$, etc., some are symmetric i.e. $\alpha_{xy} = \alpha_{yx}$, and some are asymmetric i.e. $\alpha_{yx} \neq \alpha_{xy}$, etc. Accordingly, more measurements are necessary to construct the complete polarizability tensor. The other big difference is that the tensors for the electronic Raman effect are more complicated, having more components different from zero than those for the vibrational case. Again a complete understanding requires more measurements than in the vibrational case.

In short, the electronic Raman effect of impurity ions in crystals should develop into a field worthy of deeper study. From it we can calculate all the crystal field Stark-split components of low lying states of the implanted ion, their frequencies, and the polarizability tensors associated with each transition. Since we can measure each polarizability tensor component and their relative magnitudes for each transition, such studies will allow detailed theoretical calculations of electric field parameters, wave functions, etc. It will become a live field, I believe, one which will lead to a better understanding and perhaps design of new laser materials.

We have discussed up to now Raman effects of well defined quasi-particles, i.e., Raman effect of phonons, vibrations in molecules, plasmas, etc. Imagine now two different excitations like a phonon and a plasmon which would have the same frequency, if they did not interact. When they interact, their energies will repel each other but in the interacting region they are not pure phonons or pure plasmons anymore. In molecular spectroscopy this is the well known Fermi resonance effect. The general phenomenon is known as mixed excitation.

Scattering From Mixed Excitations

A typical dispersion curve for a mixed excitation is shown in Fig. 7a. In this plot the ordinate is the frequency and the abscissa is a quantity such as wave vector, magnetic field, carrier concentration or any other quantity on which the frequency of at least one of the coupled excitations depends. The simplest case is that of the polariton discussed last year in my SPEAKER article. Here ω_1 and ω_2 are the LO and TO frequencies of a crystal, the abscissa is the wave vector of electro-magnetic radiation and, since the frequency of light varies linearly with wave vector, the dashed diagonal line is the dispersion relation of light. Were there no interaction of light with phonons, the three dashed lines would represent the complete picture of the simultaneous dispersion curves of all three excitations. Since, however, light interacts with the TO phonons the dispersion curves do not cross and the unbroken lines depict the resulting dispersion curves after the interaction. This means that if we excite Raman scattering in the forward direction and vary the observation direction, by simple conservation of momentum we vary the wave vector of the excitation observed and the frequencies observed should follow the unbroken lines of Fig. 7a. Such polariton experiments have been performed for a number of solids

such as GaP, ZnO and SiO_2, (21) and even when the number of phonon modes is large one can quantitatively predict the real dispersion curves for the interacting excitations. If in Fig. 7a we examine the solid lines (the real interacting dispersion curves) we can ask ourselves whether those full curves correspond to phonons, light or what. Fig. 7b gives a qualitative answer to this question. At large g the lower solid line ω^- corresponds to pure phonon and ω^+ corresponds to electromagnetic radiation. At g = 0, ω^+ corresponds to mechanical motion (phonon) while ω^- corresponds essentially to light and everywhere else in the middle they correspond to mixed light-phonon excitation, i.e. polariton.

Now let us examine phonon-plasmon coupling; again the ordinate in Fig. 7a is frequency but now the abscissa is the square root of density of free charge. The plasma frequency is proportional to the square root of density of free charges so the dashed line which before was the dispersion relation of light now relates the plasma frequency with carrier concentration. As the carrier concentration increases the plasma frequency will tend towards the TO phonon and the LO will start moving towards the dispersion curve which the plasma would have had without interaction. This plasma-phonon interaction will also follow the same qualitative features of Fig. 7b, i.e. at low concentrations ω^- will correspond essentially to the plasmon mode and ω^+ to the pure LO mode.
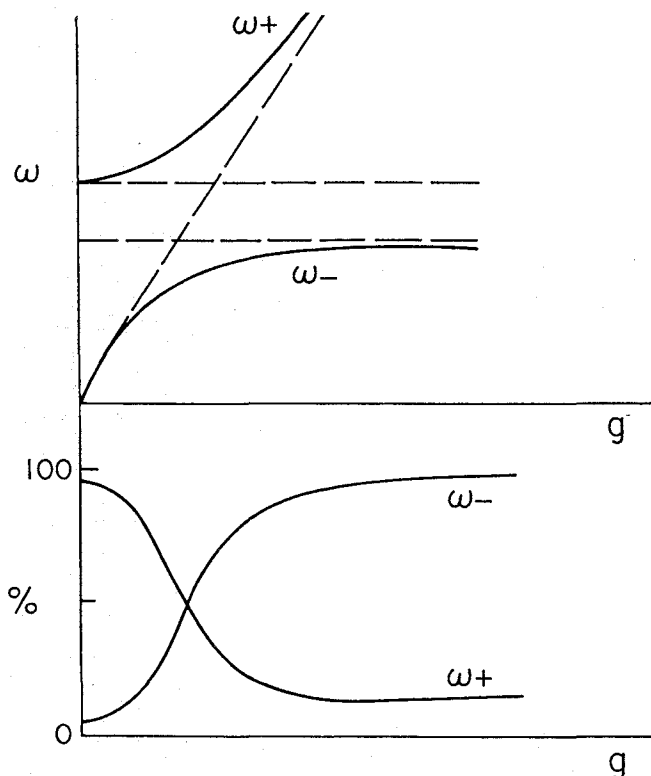

Fig. 7 The upper curves depict the dispersion relation of mixed excitation in solids. The ordinate is frequency; the abscissa g is a variable on which the frequency depends. For a plasma, g is the square root of the impurity concentration; for phonons, g is the wave vector; for Landau Levels, g is the magnetic field, etc. The lower curves show the percentage of phonon contribution for ω^- and ω^+.

At very high concentration ω^- will be pure mechanical and ω^+ will be pure plasmon and mixed excitations in between (22).

Still another example of mixed excitation is the Landau levels-phonon coupled system. The Landau level frequency, or the classical cyclotron frequency of a charged particle in a magnetic field, is linearly proportional to B so now in Fig. 7a the abscissa is the magnetic field B and the picture becomes essentially that of the phonon-plasmon coupling.

Two more facts relating plasmon-phonon coupling interactions should be pointed out. In GaAs scattering of phonons corresponds to off-diagonal tensor components; its spectrum is thus completely depolarized when the polarizations of the laser and scattered radiations are in the (100) directions. Plasma scattering, on the other hand, corresponds to diagonal tensor components resulting in a completely polarized spectrum. As the two excitations mix with one another, the polarizations beautifully follow what one expects from Fig. 7b.

Arising from pure phonons, the ω^+ spectrum, at low carrier concentrations, is completely depolarized. As the carrier (impurity) concentration is increased, plasma interactions begin and the spectrum becomes more polarized. Ultimately, a carrier concentration is reached where ω^+ is converted to pure plasma which gives rise to a completely polarized spectral feature (23).

Secondly, not only may mixed excitation be characterized by different tensors but they may have completely different frequency dependences, too. For instance, in the scattering of a plasma-phonon mixed excitation the intensity of the phonon (away from resonance) is proportional to ν^4 so at 10μ laser excitation the phonon cross section drops down 10^5 times from its intensity at 5000 A. The other excitation, the plasma, might have a cross section independent of frequency so it would show the same cross section at 10μ as at 5000 A. This means that if the mixed plasmon-phonon mode is being observed at 10μ we will see only the plasmon contribution of the mixed mode. In summary, the observed frequencies will at first follow the ω^- curve in Fig. 7a. As the carrier concentration increases eventually the frequency will jump to the upper ω^+ curve.

All kinds of such mixed excitations are being seen and studied today and more of them will be found and studied in the near future. One reason why these excitations — plasmon, Landau levels, spin-flip, single particle scattering in semiconductors, etc. — will be studied is the ease of observation. In general the cross-section of all those basic electron-light scattering mechanisms is proportional to the Thompson cross-section and this can be as many as 11 orders of magnitude larger than phonon-cross-sections.

Choosing to ignore indiscriminately in this article all non-linear optical phenomena, I did not intend to underplay their importance or the highly significant contributions made to their understanding during 1968 especially in the fields of hyper and stimulated Raman scattering. To include these,

however, would easily double the length of this article. Suffice it to say that all inelastic scattering research will continue at an increasing pace to provide us with a clearer picture of the structure and properties of matter.
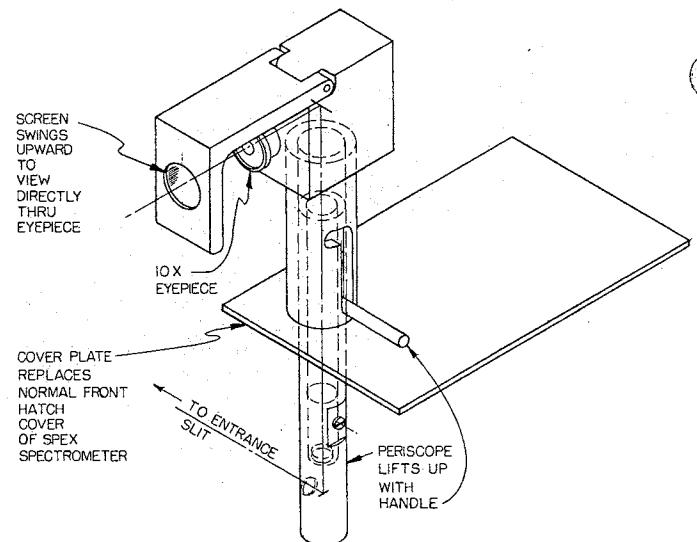
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