which follows from (30). This calculation has however not been carried out and neither has the Born, Bradburn and Smith type of calculation been repeated during the period under review. Nevertheless, some progress has been made in the understanding of the structure in second-order Raman spectra in the last few years. This is largely due to advances in the theory of phonon densities of states, reviewed in the next section.

3.2. *Two-phonon Density of States and Raman Selection Rules*

Any structure which occurs in a second-order Raman spectrum reflects structure in the frequency dependence of the combined density of states of pairs of phonons with equal and opposite wave vector, or in the frequency dependence of the interaction which gives rise to the transition. Information about the structure of a phonon density of states can be obtained by means of an approach known as a critical-point analysis. When this information is combined with selection rules, it is possible to interpret the shape of the second-order continuous Raman spectrum. This approach is simpler to carry through than a Born and Bradburn type of calculation, and it correlates experiment and theory in a way not possible by the older method. Although only partial critical-point analyses of Raman spectra have so far been made, the method appears to hold great promise and we review it briefly.

For the sake of simplicity we restrict the discussion to the case of cubic crystals having two atoms in the unit cell (e.g. diamond, rocksalt, zinc blende) and thus six phonon branches. A critical-point analysis determines the amount and nature of the structure in the single- or two-phonon density of states. Consider first the single-phonon density of states. Let $\mathbf{k}$ be the phonon wave vector and $\omega(\mathbf{k})$ its frequency. A critical point is a point in $\mathbf{k}$-space where every component of $\nabla_{\kappa}\omega(\mathbf{k})$ is either zero or changes sign discontinuously. The importance of critical points arises from the circumstance that a plot of phonon density of states against frequency may exhibit a discontinuity of slope at a critical point. This property of critical points was first investigated by Van Hove (1953) and his work was later extended by Phillips (1956) (see also the review article by Maradudin *et al.* 1963). By making use of the methods of these authors, it is possible to locate all the slope discontinuities which occur in the single-phonon density of states, and to decide their shape. Some of the shapes which a slope discontinuity can have are illustrated by Loudon and Johnson (1964, table 2).

The discussion so far has been in terms of the single-phonon density of states. The critical-point method has been extended to deal with the two-phonon density of states by Loudon and Johnson (1964). We consider only the part of the second-order Raman spectrum due to lattice states in which two phonons are created. Since $\omega(\mathbf{k})=\omega(-\mathbf{k})$, the relevant two-phonon density of states is obtained from two-phonon dispersion curves constructed by adding together all pairs of phonon branches at each wave vector $\mathbf{k}$. At each $\mathbf{k}$ on the two-phonon dispersion curves constructed in this way the total wave vector of the two-phonon states is effectively zero, and every state is Raman active as far as the wave vector conservation rule is concerned. For six single-phonon branches there are 21 two-phonon branches, and their critical points and accompanying density of states slope discontinuities can be treated in exactly the same way as the corresponding phenomena on single-phonon branches. One can thus obtain a knowledge of the positions and shapes of all the slope discontinuities in the two-phonon density of states. The density of states histograms which result from lattice dynamics calculations are not sufficiently fine grained to show the critical points reliably, and the Born and Bradburn (1947) and Smith (1948) Raman spectrum calculations consequently do not display any sharp structure.

Most of the critical points in the phonon spectra occur at points of high symmetry in the Brillouin zone. Indeed Phillips (1959) has shown that for lattices based on the face-centred cubic structure (which includes diamond, rocksalt and zinc blende) critical points must occur on all phonon branches at the symmetry points Γ, X, L and W (we use here the notation of Bouckaert *et al.* 1936). This holds for both the single- and the two-phonon branches. The remaining critical points can occur on lines or planes of symmetry or at general points in the zone. As mentioned above, the structure of the observed Raman spectrum is influenced by the frequency dependence of the interactions involved as well as by the frequency dependence of the two-phonon density of states. The interactions are unlikely to have a frequency dependence sufficiently rapid to introduce additional discontinuities in slope of the type occurring in the density of states. However, where second-order Raman scattering accompanied by creation of a particular phonon pair, corresponding to a critical point in the two-phonon spectrum, is a forbidden process, the effect of the discontinuous change of slope in the density of states is quenched, and the measured spectrum should show no discontinuity. It is thus important to have selection rules at particular $\mathbf{k}$-vectors for the pairs of phonon branches which can contribute to the second-order Raman effect.

The selection rules are simplest to calculate for the second-order line spectrum, where both phonons have effectively zero wave vector, and for the part of the second-order continuum due to $\mathbf{k}=0$ phonons. The requisite group theory has been given by Bhagavantam and Venkatarayudu (1939). There is a slight distinction between a case where the two phonons belong to the same branch, and the two-phonon state is an *overtone*, and where they belong to different branches, and the two-phonon state is a *combination*. For combination states the Raman transition is allowed if the Kronecker product of the irreducible representations of the two phonons contains irreducible representations in common with the polarizability tensor. For overtone states, the symmetrized Kronecker square of the phonon irreducible representation must be formed to determine the selection rule. As explained in the previous section, the second-order scattering gives rise to a line if both phonons are active in first-order scattering, otherwise it forms part of the continuum. Several general rules follow in an obvious way for the second-order line spectrum. In a crystal possessing inversion symmetry, only odd-parity states can be electric-dipole active and only even states can be Raman active. The $\mathbf{k}=0$ phonons have a well defined parity and thus no first- or second-order Raman line can possibly also occur in the crystal's absorption spectrum, and a rule of mutual exclusion applies. Also, the symmetrized Kronecker square of every $\mathbf{k}=0$ irreducible representation contains the identity representation, and a component of the polarizability tensor always transforms by the identity representation. The overtones of all $\mathbf{k}=0$ phonons are therefore Raman active.

Selection rules for the second-order continuous spectrum due to phonons with non-zero wave vector are in principle calculated in exactly the same way as outlined above. However, the phonon wave vector $\mathbf{k}$ now ranges over the entire Brillouin zone and in calculating the selection rules it is necessary to form Kronecker products and symmetrized Kronecker squares of space-group irreducible representations corresponding to all $\mathbf{k}$-vectors. General methods for this type of calculation have been developed by Birman (1962). Although the mechanics of the calculation are basically the same as for $\mathbf{k}=0$ phonons, the actual manipulations are more complex due to the higher dimensionality of the representations involved and the fact that more than one group of $\mathbf{k}$ enters. Even in crystals possessing inversion symmetry, the phonons having non-zero wave vector do not in general have a well-defined parity and the rule of mutual exclusion breaks down. It can however be shown that the two-phonon overtone at a general wave vector is Raman active. Detailed selection rules for second-order Raman scattering have been tabulated for the diamond and zinc blende structures by Birman (1963), for diamond by Loudon and Johnson (1964) and for the rocksalt structure by Burstein *et al.* (1964).

The selection rule calculation also provides information about the state of polarization of the scattered radiation in the second-order Raman effect. Consider for example scattering from a cubic crystal with the experimental geometry of fig. 6 for $\phi=0$, and unpolarized incident light. The pair of phonons which collaborate to produce the second-order scattering generate a Kronecker square or product representation, whose reduction contains a sum of $\mathbf{k}=0$ representations. For Raman activity this sum must contain one of the $\mathbf{k}=0$ irreducible representations listed in the table. The A and E representations are associated with zero depolarization ρ and the F representation with non-zero ρ. The second-order Raman-scattered light thus has ρ non-zero or zero according as the sum of $\mathbf{k}=0$ representations does or does not contain F. Values of ρ for particular phonon pairs have been tabulated by Loudon and Johnson (1964) for diamond, and by Burstein *et al.* (1964) for rocksalt. Birman (1963) has tabulated depolarizations for scattering by powdered crystals of diamond and zinc blende structure. These depolarizations for the second-order continuum are difficult to measure experimentally since the scattering at a particular frequency is usually due to several different pairs of phonons from a variety of branches and having a variety of **k**-vectors.

Armed with a critical-point analysis and a set of selection rules, one is in a position to understand and interpret the second-order Raman spectrum. This type of interpretation has not so far been fully carried out, although the corresponding analysis for the infra-red absorption spectra of diamond-structure semiconductors has been successfully completed. For the Raman effect, some tentative interpretations of features in the measured spectra in terms of pairs of phonons at critical points have been given by Loudon and Johnson (1964) for diamond and by Burstein *et al.* (1964) for some of the rocksalt-structure alkali halides. The power of critical-point interpretations will increase as lattice dynamics calculations and Raman spectrum measurements improve.

At this point mention must be made of the method of Raman spectra interpretation used by Raman himself (see Raman 1956 a for a recent exposition). In Raman's theory, the linear dimension of the unit cell is taken to be twice that assumed by other workers. This leads to a unit cell having eight times the normal volume, and hence a Brillouin zone having one-eighth the volume usually derived. The resulting total dimensionality of phonon branches at $\mathbf{k}=0$ is now $6\times 8=48$ for lattices of diamond or rocksalt symmetry. In the usually accepted Brillouin zone, six of these phonon branches are at Γ, 18 are at the three X points and 24 are at the four L points. In Raman's theory it is further assumed that only $\mathbf{k}=0$ phonons and their overtones and combinations can produce scattering. In the theory used by other workers, this is tantamount to assuming that only phonon pairs at Γ, X and L can contribute to second-order Raman scattering. Since important critical points usually occur at Γ, X and L, Raman's assumption may sometimes be a good one and he and his co-workers have met with some success in interpreting features of the second-order spectra. In diamond, Raman's 48 $\mathbf{k}=0$ phonon modes have nine distinct frequencies (including one zero-frequency acoustic branch). Using Raman's approach, Venkatarayudu (1954) has shown that the rule of mutual exclusion breaks down for second-order Raman scattering by the phonons which are at symmetry point X in the usual picture. This is in agreement with selection rules given by Birman (1963). The Raman theory predicts a second-order spectrum consisting of a limited number of discrete lines, rather than the continuous and line spectra predicted by the Born theory outlined above. Raman's views have not received any substantial acceptance outside India.

3.3. *Experimental Results*

3.3.1. *Diamond*

Apart from the alkali halides, diamond is the only crystal for which a fairly complete measurement of the second-order Raman spectrum has been made, although there are some fragmentary results for other crystals. Second-order spectra have been published by Krishnan (1946 b, 1947 b) and the interpretation of the observed features has been the subject of much discussion. In the work of Smith (1948), already mentioned, the distribution of intensity in the second-order Raman spectrum of diamond was interpreted in terms of a weighted density of two-phonon states. Her calculation was challenged by Krishnan (1948), who regarded the entire second-order spectrum as being composed of discrete lines, and who presented a rival interpretation in terms of Raman's theory of lattice dynamics. This theory of the second-order spectrum has been further elaborated by Raman (1956 b). More recently Loudon and Johnson (1964) have given selection rules for the second-order Raman effect in diamond and have compared the positions of features in the spectrum with the phonon frequencies at critical points deduced from absorption measurements by Hardy and Smith (1961) (see also the absorption measurements by Raman 1962). The phonon frequencies in diamond are not well established and any critical-point interpretation of the Raman spectrum can only be tentative. There is also room for improvement in the experimental results. Part of the second-order spectrum is obscured by one of the subsidiary mercury vapour lamp emission lines, which is scattered in the crystal without change of frequency. This difficulty could perhaps be avoided by the use of a laser source instead of the mercury lamp. For use in theoretical interpretations, the results of second-order Raman experiments are best presented as plots of scattered intensity against frequency, instead of direct plots of micro-photometer traces. Some of Krishnan's original measurements have been replotted on an intensity scale by Narayanan (1951).

A second-order Raman line occurs in diamond at twice the frequency shift of the first-order line. The elementary process which gives rise to the second-order line is illustrated in fig. 7, and the scattering efficiency can be calculated by sixth-order perturbation theory using an extension of the method of § 2.2 for the first-order scattering efficiency. The second-order scattering efficiency S_2 is not simply equal to the square of the first-order scattering efficiency S_1 (the same quantity as S given by (31)) because the photon which is present in the intermediate state of fig. 7 is a virtual one and there is no energy conservation in this state. The result of a calculation of the second-order scattering efficiency S_2, assuming the same geometry as in eqns. (29) and (31) is:

$$\frac{S_2}{S_1} = \frac{S_1}{Ld\Omega}\frac{V\epsilon\omega_{\mathrm{i}}^2}{9\pi^2c^2} f\left(\frac{\omega_{\mathrm{i}}}{\omega_{\mathrm{g}}}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (72)$$

where ω_{g} is the frequency of the forbidden electronic energy gap and all the other symbols are as previously defined. The function f has a complicated dependence on $\omega_{\mathrm{i}}/\omega_{\mathrm{g}}$ and has an order of magnitude 10^{-2} for the experimental situation in diamond. The dependence of S_2 on the crystal volume, already discussed in § 3.1, is evident in (72). An experimental value for the ratio S_2/S_1 has been measured by Krishnan and Narayanan

(1950) to be 1/270. They do not state all the dimensions of their diamond crystal, but their numerical result appears to be roughly consistent with the theoretical estimates of $S_1/Ld\Omega$ given earlier.

3.3.2. *Alkali halides*

Both the NaCl and CsCl alkali halide structures have two atoms in the unit cell and optic modes of negative parity at zero wave vector. They therefore have no first-order Raman effect and no second-order line spectrum. However, many of the alkali halides give a strong second-order continuous Raman spectrum. Among the NaCl-structure alkali halides, the second-order spectra of LiCl, NaCl, NaBr, NaI, KCl, KBr, KI and RbBr have been measured, and MgO can also be included in this group since it has the same structure. Among the CsCl-structure alkali halides, CsBr and CsI have been measured. References to the more recent of these measurements are listed in a separate group at the end of the article. The references for some of the older measurements can be found in the review article by Menzies (1953).

The first theoretical interpretation of a second-order Raman spectrum was made by Born and Bradburn (1947) using the measurements on NaCl by Krishnan (1945). A better measurement of the NaCl second-order Raman spectrum was subsequently made by Welch *et al.* (1949). Burstein *et al.* (1964) have given selection rules for second-order Raman scattering by pairs of critical-point phonons in the NaCl lattice and have shown that nearly all the observed features in the spectrum of Welch *et al.* can be accounted for as sums or differences of four characteristic phonon frequencies. By comparison with a lattice dynamics calculation for NaCl by Hardy and Karo (1960) it appears that the four important critical-point phonons are those at the symmetry point X. Raman (1961) has interpreted the NaCl spectrum in terms of his own theory of lattice dynamics.

The phonon frequencies in NaI and KBr have been measured by neutron spectroscopy for the important symmetry directions by Woods *et al.*, (1963). Burstein *et al.* (1964) have shown that the majority of the features in the Raman spectra of these two crystals can be accounted for by combinations of phonon frequencies at symmetry points in the Brillouin zone given by the neutron scattering measurements.

Complete interpretations of the Raman spectra of the alkali halides must await sufficiently accurate lattice dynamics calculations or sufficiently detailed neutron spectroscopy measurements for full critical-point analyses to be carried through, following the lines indicated in § 3.2.

§ 4. RAMAN SCATTERING OTHER THAN BY PHONONS

Raman scattering from crystals is normally associated with the creation or destruction of phonons, and the article has so far been exclusively concerned with this type of scattering. However, other types of crystal excitation can in principle produce Raman scattering. In this section we review the proposals which have been made for Raman scattering experiments involving four different types of crystal transition; only the first one has so far been observed experimentally.

4.1. *Electronic States*

Elliott and Loudon (1963) have proposed Raman scattering from paramagnetic ions in crystals as a useful method for determining the low-lying ionic energy levels, and Hougen and Singh (1963, 1964) have observed this type of Raman scattering from Pr^{3+} ions in $PrCl_3$. Electronic Raman scattering had previously been observed in the X-ray region by Das Gupta (1959, 1962). The scattering efficiency for a process in which an ion is excited from an initial state with energy E_i to a final state with energy E_f is easily derived from the theory of Heitler (1954) for atomic Raman scattering to be:

$$S=\frac{N}{V}\,\frac{e^4\omega_\mathrm{s}L\,d\Omega}{m^4\omega_\mathrm{i}c^4}\left|\sum_j\left\{\frac{\mathbf{e}_\mathrm{i}\cdot\mathbf{p}_{ij}\mathbf{e}_\mathrm{s}\cdot\mathbf{p}_{j\mathrm{f}}}{E_j-E_\mathrm{i}-\hbar\omega_\mathrm{i}}+\frac{\mathbf{e}_\mathrm{s}\cdot\mathbf{p}_{ij}\mathbf{e}_\mathrm{i}\cdot\mathbf{p}_{j\mathrm{f}}}{E_j-E_\mathrm{i}+\hbar\omega_\mathrm{s}}\right\}\right|^2. \quad . \qquad (73)$$

Here N/V is the number of paramagnetic ions per unit volume, and the remaining symbols all have their previously defined meanings. The summation j runs over all electronic intermediate states.

Numerical estimates on the basis of (73) indicate that, depending on the matrix elements and the positions of the excited intermediate states, the efficiency for electronic Raman scattering can be as large or larger than that for the lattice vibration Raman effect. This is the result for concentrated crystals where the paramagnetic ion under study is a normal constituent of the lattice so that $N/V \sim 10^{22}/\mathrm{cm}^3$. For dilute crystals, where the paramagnetic ion is present as an impurity, the scattering efficiency is correspondingly smaller, although as Hougen and Singh point out, the sharpening of the electronic levels as the paramagnetic ions are diluted offsets the reduction in the integrated scattering intensity to some extent.

The selection rules and angular dependence of the electronic Raman scattering depend only on the symmetries of the initial and final states, and the results of the table can be used for electronic states. For ions which are situated at a lattice point having inversion symmetry, Raman scattering measures the energy separations between two states having the same parity (the lower state will normally be the ground state). In the rare-earth ions the initial and final states arise from the $4f^n$ configuration and the most important intermediate states will be of opposite parity and are expected to be from the $4f^{n-1}5d$ configuration. It is not clear from the work of Hougen and Singh to what extent this type of Raman effect experiment can supplement the knowledge of rare-earth energy levels obtained from the more conventional absorption and fluorescence measurements.

4.2. *Spin Waves*

Two different mechanisms for Raman scattering by spin waves have been proposed. Bass and Kaganov (1960) have treated the process where the spin system of a ferromagnet is coupled directly to the radiation field by the magnetic-dipole interaction. Consider a cubic crystal with incident radiation parallel to the direction of saturation magnetization M_S which is taken to be the z axis. The scattering mechanism depends on the fact that the x and y components of the magnetization are linear in the spin-wave creation and destruction operators, whereas the z-component includes quadratic terms in the operators (see for example Van Kranendonk and Van Vleck 1958, eqn. (11)). The Raman effect for spin-wave creation proceeds as follows. 1. An incident photon, interacting only with the x and y components of the magnetization, is destroyed and an intermediate spin-wave quantum is created. 2. A scattered photon is created, via its interaction with the z-component of the magnetization, accompanied by destruction of the intermediate spin wave and creation of the final spin-wave quantum. Obviously the scattered radiation must make a finite angle ψ with the z-axis in order to be non-vanishing. The scattering efficiency for this process is:

$$S=\frac{(g\beta)^3 M_S \epsilon^2 \omega_i \omega_S (n_0+1) L\, d\Omega \sin^2\psi}{2\hbar^2 c^4}, \quad . \quad . \quad . \quad . \quad (74)$$

where g is the g-factor of the spins, β is the Bohr magneton and n_0 is now the spin-wave population. The spin-wave dispersion curve is essentially flat with frequency ω_0 at the wave vectors of interest, and $\omega_S=\omega_i-\omega_0$. For the anti-Stokes component of the scattering n_0+1 is replaced by n_0, and $\omega_S=\omega_i+\omega_0$.

Bass and Kaganov propose a scattering experiment using incident radiation of wavelength 1 mm, which leads to a typical right-angle scattering efficiency per unit length per unit solid angle of about $10^{-19}(n_0+1)$. This is very small, but the experiment might be feasible in the microwave region where powerful sources are available. It is not clear what advantages the experiment would have over an ordinary ferromagnetic resonance experiment (ω_0 typically corresponds to a wavelength of order 1 cm).

Elliott and Loudon (1963) have pointed out that the existence of spin–orbit interaction in magnetic crystals leads to a mechanism for Raman scattering from spin waves. Consider a crystal containing magnetic ions whose ground states have quenched angular momentum, and spin S. The spin waves are made up from spin transitions on individual atoms, and a spin wave can be excited by a photon-scattering process of the type described by eqn. (73) where i and f now refer to the $S_z=S$ and $S_z=S-1$ states of the ground multiplet of a single atom. In order to achieve a change in spin component as a result of two successive electric-dipole transitions it is necessary to have a mixing of spin and orbital states either in the ground state or in one of the intermediate excited states j, and this results in an extra factor of order $\lambda/(E_j-E_i)$ (spin–orbit splitting/configuration splitting) in the matrix element of eqn. (73). The estimated scattering efficiency for optical radiation is about 10^{-5} to 10^{-6}, but would be comparable with that resulting from Bass and Kaganov's mechanism if microwave radiation were used.

At small wave vectors the spin-wave frequency ω_0 in an anti-ferromagnet is given by $\hbar\omega_0 \approx (2JK)^{1/2}$, where J is the exchange energy and K is the anisotropy energy. For some anti-ferromagnets this corresponds to a wavenumber in the range 10–100 cm^{-1} where ordinary absorption measurements are difficult. Raman shifts of this magnitude can however be measured without too much difficulty at optical frequencies. Some ferrimagnets have 'optical' spin-wave branches with frequencies of the same order which should also be accessible to this type of measurement. The selection rules for the symmetry types of spin wave which can cause Raman scattering are discussed by Elliott and Loudon. The method could not be used for ferromagnetic spin waves, as the shifts would be too small to detect easily at optical frequencies.

4.3. *Superconductors*

Superconducting crystals possess a forbidden energy gap in their electronic spectra when they are cooled below the transition temperature. The breadth of the forbidden gap is typically in the range 10–30 cm^{-1} and it gives rise to an absorption edge which can be studied by far infra-red spectroscopy (Richards and Tinkham 1960). The gap can in principle also be detected and measured by a Raman scattering experiment, the scattered light occurring in a continuous distribution with Raman shifts greater than or equal to the gap frequency. The skin effect allows the incident light to penetrate only a very small distance into the superconductor (of order 10^{-5} cm) and the Raman frequencies must be sought in the light which is scattered from the specimen surface. This greatly reduces the scattered intensity available for detection and Khaikin and Bykov (1956) have made an unsuccessful attempt to measure Raman-scattered light from a superconducting lead film. The theory of this type of scattering has subsequently been worked out by Abrikosov and Fal'kovskii (1961), who estimate a scattering efficiency of order 10^{-13} or smaller for the process. The detection of this small fraction of the incident light intensity at optical frequencies represents a formidable experimental problem and a sensitivity at least 10^5 times that of Khaikin and Bykov would be required.

4.4. *Plasmons*

The Raman scattering of incident radiation by plasmons has been treated theoretically by Sobel'man and Feinberg (1958), but no experiments have been reported. Plasmons normally have frequencies well above the optical range and the frequency of the exciting radiation must be even higher than the plasma frequency. The experiment has the advantage that plasma modes which are inactive in direct absorption of radiation could be detected by their Raman effect.

§ 5. RECENT DEVELOPMENTS

5.1. *Use of Lasers as Raman Sources*

Raman scattering from lattice vibrations is a weak effect and a powerful sharp-line source of radiation is required in order that its detection should be feasible. Most experiments have used mercury vapour lamp sources whose strongest line occurs at a wave number 39420 cm^{-1}, and with three moderately strong lines two orders of magnitude less intense at wave numbers 24 710, 22 950 and 18 310 cm^{-1}. If the incident and scattered radiation is not to be absorbed in a crystal due to the excitation of electronic transitions across the forbidden energy gap, then the gap must be wider than about 2·3 ev, and preferably wider than about 5 ev so that the strongest of the mercury lines can be used ($1\ \mathrm{ev} = 8066\ \mathrm{cm}^{-1}$). Thus a wide range of crystals has been excluded from study by Raman effect experiments. In particular, there have been no Raman effect measurements of lattice vibration frequencies in semi-conducting crystals.

These experimental restrictions are likely to be relaxed by use of the optical and near infra-red masers (lasers) recently developed. These are powerful single-line sources which emit radiation either in very intense short pulses, or continuously with a smaller intensity comparable to that of the three moderately intense mercury lines. The pulse repetition frequency of the former variety of laser may be quite high, e.g. 1000 times per second. The scattered intensity in the Raman effect is proportional to the incident intensity, and since the spectrum is usually recorded photographically, the only requirement on the source is that its output integrated over a convenient exposure time should be sufficiently large. The high intensity of the low repetition frequency pulsed laser may thus be offset by the short pulse duration, and high peak power is not necessarily an advantage for a Raman source (see however the following section). Continuous wave and high repetition frequency pulsed lasers may prove to be the more useful Raman sources. Using a pulsed source, photoelectric detection of the scattered light using a cut-out on the detector between pulses seems to be a promising technique. This type of detection has been previously used by Valentin (1957) who employed a pulsed mercury lamp as his Raman source. The laser possesses the advantage as a Raman source that its emission spectrum may consist of a single line or at worst a very small number of lines. In contrast, the mercury vapour lamp has a large number of emission lines, so that the Raman scattered light originating from an intense mercury line is often partly obscured by light originating from a weaker line scattered without change of frequency. This is the case for example in the second-order Raman spectrum of diamond (Krishnan 1964 b).

Lasers have so far been used mainly as sources for the Raman spectroscopy of liquids. Porto and Wood (1962) have used a pulsed ruby laser source in this way, and more recently Kogelnik and Porto (1963) have employed a helium–neon laser. In unpublished work, some observations of the Raman spectra of ruby and CaF_2 have been made using laser sources. It seems likely that the Raman spectra of many crystals will be measured for the first time in the next few years as the technology and availability of lasers are improved.

5.2. *Stimulated Raman Effect*

In the ordinary Raman effect, the scattered radiation is emitted *spontaneously* in directions distributed anisotropically over the complete 4π solid angle. Thus in calculating the time constant for Raman scattering in eqn. (30), the number of scattered photons at frequency ω_s in the initial state of the system was set equal to zero. The intensity of the scattered beam in the ordinary Raman effect is small, having characteristically 10^{-6} or 10^{-7} times the intensity of the incident beam. Observations are normally made at right angles to the incident beam to exclude from the spectrograph as much as possible of the radiation at frequency ω_i.

If the incident light beam is made sufficiently intense, scattered photons may be produced sufficiently fast for the number n_s of photons in the crystal having frequency ω_s and specified direction to become significant. This may be allowed for in the theory, and leads to the result that the expression for $1/\tau$ is multiplied by an extra factor (n_s+1). The unit term corresponds to the original spontaneous scattering, while the term proportional to n_s corresponds to a stimulated emission of scattered photons. Stimulated Raman scattering requires intense incident radiation and has been observed only with the use of high-power pulsed ruby laser sources. The first observation was made by Woodbury and Ng (1962) in Raman scattering from nitrobenzene, and most of the subsequent experiments have been on liquids. However, Eckhardt *et al.* (1963) have observed stimulated Raman scattering from crystals of diamond, calcite and α-sulphur, and other crystals will doubtless show the effect. Chiao and Stoicheff (1964) have made more detailed measurements on calcite.

Stimulated Raman effect experiments have been carried out either with the scattering sample inside the optical cavity of the laser or with the sample outside the cavity and the laser beam focused to increase its photon density. In the former case, the scattered radiation builds up coherently in the cavity, the most favourable direction for $\mathbf{k}_s$ being perpendicular to the end mirrors of the cavity so that the scattered beam can be successively amplified by feedback effects as it re-passes through the Raman sample. Using a focused laser beam, no feedback occurs and the stimulated Raman photons can in principle be emitted from the crystal in all directions consistent with symmetry requirements. However, only the part of the sample which is illuminated by the laser is effective in producing and amplifying the radiation at frequency ω_s. The focused laser beam is very narrow, and its path length in the Raman sample is generally arranged to be as long as possible. The greatest intensity of scattered radiation is produced in those directions where the path length of the scattered photons through the effective part of the crystal is greatest. Thus even when the Raman sample is outside the laser cavity, the majority of stimulated scattered radiation emerges from the sample in, or close to, the forward direction. The scattering efficiency in a typical stimulated Raman effect experiment is much higher than in the ordinary or spontaneous Raman effect, and values as high as 10^{-1} for the ratio of scattered to incident intensity have been reported. The high intensity of the Raman beam makes possible its spectroscopic resolution from the laser beam, even though their directions are the same.

The first suggestion for a stimulated Raman effect experiment in the optical region using a crystal scatterer was made by Zeiger and Tannenwald (1963). They considered the case of stimulated Raman scattering from electronic states of impurity ions in crystals. The corresponding spontaneous scattering experiment has been treated in § 4.1. Let us consider the theory of the experiment for the case where the scattering crystal is inside the laser cavity and where the scattered radiation builds up in a single mode of the cavity having an angular frequency width which is small compared to the width 2Γ of the Raman line observed in spontaneous scattering. In addition to the extra factor $(n_{\mathrm{s}}+1)$ in the scattering probability per unit time, the sum over scattered photons whose wave vector direction lies within a solid angle $d\Omega$ must be replaced by the contribution of the single cavity mode excited. Assuming that the cavity mode has a frequency equal to that of the centre of the Lorentzian Raman line, then the strength of the scattering into the mode is proportional to $1/\Gamma$. The result of the calculation of Zeiger and Tannenwald (1963) for the stimulated part of the scattering probability per unit time can be written:

$$\frac{1}{\tau_{\mathrm{stim}}}=\left(\frac{S}{L\,d\Omega}\right)\frac{8\pi^2c^4}{\omega_{\mathrm{s}}^2\Gamma\epsilon^2}\frac{n_{\mathrm{i}}n_{\mathrm{s}}}{V}, \qquad (75)$$

where S is given by (73). If the z-coordinate is measured parallel to the axis of the laser cavity, the equations describing the attenuation of the flux ρ_{i} of incident photons and the growth of the flux ρ_{s} of scattered photons are:

$$-\frac{d\rho_{\mathrm{i}}}{dz}=\frac{d\rho_{\mathrm{s}}}{dz}=\frac{\rho_{\mathrm{i}}\rho_{\mathrm{s}}V}{\lambda c}, \qquad (76)$$

where

$$\rho_{\mathrm{i}}=\frac{n_{\mathrm{i}}c}{V\epsilon^{1/2}},\quad \rho_{\mathrm{s}}=\frac{n_{\mathrm{s}}c}{V\epsilon^{1/2}},\quad \frac{n_{\mathrm{i}}n_{\mathrm{s}}}{\lambda}=\frac{\epsilon}{c\tau_{\mathrm{stim}}}. \qquad (77)$$

If the front face of the crystal is at $z=0$ and ρ_{i}^0 and ρ_{s}^0 are the values of ρ_{i} and ρ_{s} at this point, then the solution of (76) for ρ_{s} is:

$$\rho_{\mathrm{s}}=\rho_{\mathrm{s}}^0\left(1+\frac{\rho_{\mathrm{i}}^0 zV}{c\lambda}\right)+\mathrm{O}(z^2). \qquad (78)$$

If L is the length of the crystal and R_{s} is an effective reflection coefficient which takes account of all losses from the radiation at frequency ω_s, then the criterion for the stimulated Raman effect to occur is

$$\frac{\rho_i^0 VL}{c\lambda} > 1 - R_s. \qquad (79)$$

Zeiger and Tannenwald (1963) have evaluated this criterion for various impurities in a range of host lattices and find that the production of stimulated Raman radiation in this type of experiment should be feasible. No successful experiments have however been reported.

The analogous calculation for stimulated Raman scattering from lattice vibrations has been carried out by Loudon (1963 a). Consider for example a diamond crystal in the same scattering geometry as described above. If a principal axis of the crystal coincides with the z-axis, then the stimulated part of the scattering probability per unit time is:

$$\frac{1}{\tau_{\mathrm{stim}}} = \frac{2\pi^2 e^4 n_i n_s}{\hbar^3 m^4 d^2 M \epsilon^2 \Gamma \omega_s^2 \omega_0} [|R_{xy}^z|^2 + |R_{yx}^z|^2]. \qquad (80)$$

The scattered radiation is thus unpolarized for unpolarized incident radiation, and the phonons produced have longitudinal polarization. There is no proportionality to the phonon population function n_0 in the above equation because of a cancellation between the Raman process and its inverse. Comparison with the equation analogous to (31) for the case of forward Raman scattering ($\psi = 0$ in fig. 5) shows that (75) holds also for the case of stimulated Raman scattering from lattice vibrations, except that the quantity S refers to the corresponding spontaneous experiment at a low temperature where n_0 is negligible. Equations (76) to (79) also apply to scattering by lattice vibrations. Eckhardt *et al.* (1963) have observed stimulated Raman scattering from diamond. They see a strong Stokes line and a weaker line at twice the normal Stokes shift. This second line is caused by stimulated Raman scattering excited by the Stokes radiation. An anti-Stokes line was also observed in these experiments.

Stimulated Raman scattering from lattice vibrations in piezo-electric crystals can be treated in the same way. For the zinc blende lattice, reference to fig. 1 shows that it is not possible to satisfy the wave vector conservation requirement (27) for forward scattering from transverse phonons (this may no longer be true when photon dispersion due to the electronic states is taken into account). However, it is possible to have Raman scattering from the longitudinal phonons even when $\mathbf{k}_i$ and $\mathbf{k}_s$ point in the same direction. When the unpolarized incident light is propagated parallel to the principal z-axis of the crystal, the stimulated scattering probability per unit time is given by (75), but with S replaced by the S_l of (52) for $n_l = 0$ (the equality of R_{xy}^z and R_{yx}^z has been used at this point). There have been no experimental observations of stimulated Raman scattering from zinc blende structure crystals.

The theory of stimulated Raman scattering from lattice vibrations in uniaxial crystals has been considered by Loudon (1963 a). Both the incident and scattered radiation can have either ordinary or extraordinary polarization, leading to a variety of ways in which the wave vector conservation requirement (27) can be satisfied. The dependence of phonon and photon frequencies on crystal orientation leads to the possibility of obtaining stimulated radiation at a range of frequencies ω_S as the crystal is rotated. The phonons produced in this type of experiment would lie in general on the parts of the dispersion curves in figs. 2 and 3 where the crystal excitation is partly electromagnetic and partly mechanical in character. There is some confusion in this region between the processes of stimulated Raman effect and optical parametric amplification, and a consideration of the theory would lead us somewhat outside the scope of the article. The interplay between the Raman effect and parametric amplification has been considered theoretically by Butcher *et al.* (1964).

REFERENCES

ABRIKOSOV, A. A., and FAL'KOVSKII, L. A., 1961, *Soviet Phys.—JETP*, **13,** 179.

BASS, F. G., and KAGANOV, M. I., 1960, *Soviet Phys.—JETP*, **37**(10), 986.

BHAGAVANTAM, S., 1953, *Proc. Indian Acad. Sci.* A, **37,** 350.

BHAGAVANTAM, S., and VENKATARAYUDU, T., 1939, *Proc. Indian Acad. Sci.* A, **9,** 224.

BIR, G. L., and PIKUS, G. E., 1961, *Soviet Phys.—Solid State*, **2,** 2039.

BIRMAN, J. L., 1959, *Phys. Rev.*, **115,** 1493 ; 1962, *Ibid.*, **127,** 1093 ; 1963, *Ibid.*, **131,** 1489.

BLOUNT, E. I., 1963, *Solid State Physics*, **13,** 305.

BORN, M., and BRADBURN, M., 1947, *Proc. roy. Soc.* A, **188,** 161.

BORN, M., and HUANG, K., 1954, *Dynamical Theory of Crystal Lattices* (Oxford : Clarendon Press).

BOUCKAERT, L. P., SMOLUCHOWSKI, R., and WIGNER, E., 1936, *Phys. Rev.*, **50,** 58.

BRILLOUIN, L., 1922, *Ann. Phys., Paris*, **17,** 88.

BURSTEIN, E., JOHNSON, F. A., and LOUDON, R., 1964, *Phys. Rev.* (to be published).

BUTCHER, P. N., LOUDON, R., and MCLEAN, T. P., 1964, *Proc. phys. Soc. Lond.* (to be published).

BUTCHER, P. N., and MCLEAN, T. P., 1963, *Lasers and Applications*, Edited by W. S. C. Chang (Ohio State University Press), p. 173.

CHANDRASEKHARAN, V., 1963, *Z. Phys.*, **175,** 63.

CHIAO, R., and STOICHEFF, B. P., 1964, *Phys. Rev. Letters*, **12,** 290.

COCHRAN, W., and COWLEY, R. A., 1962, *J. Phys. Chem. Solids*, **23,** 447.

COUTURE-MATHIEU, L., KETELAAR, J. A. A., VEDDER, W., and FAHRENFORT, J., 1952 a, *Physica*, **18,** 762 ; 1952 b, *J. chem. Phys.*, **20,** 1492.

COWLEY, R. A., 1962, *Phys. Rev. Letters*, **9,** 159.

DARWIN, C. G., 1934, *Proc. roy. Soc.* A, **146,** 17.

DAS GUPTA, K., 1959, *Phys. Rev. Letters*, **3,** 38 ; 1962, *Phys. Rev.*, **128,** 2181.

DAYAL, B., 1950, *Proc. Indian Acad. Sci.* A, **32,** 304.

ECKHARDT, G., BORTFELD, D. P., and GELLER, M., 1963, *Appl. Phys. Letters*, **3,** 137.

EHRENREICH, H., 1957, *J. Phys. Chem. Solids*, **2,** 131.

ELLIOTT, R. J., and LOUDON, R., 1963, *Physics Letters*, **3,** 189.

GRECHKO, L. G., and OVANDER, L. N., 1962, *Soviet Phys.—Solid State*, **4,** 112.

HAAS, C., 1956, *Spectrochim. Acta*, **8,** 19.

HAAS, C., and HORNIG, D. F., 1957, *J. chem. Phys.*, **26,** 707.

HARDY, J. R., and KARO, A. M., 1960, *Phil. Mag.*, **5,** 859.

HARDY, J. R., and SMITH, S. D., 1961, *Phil. Mag.*, **6,** 1163.

HEINE, V., 1960, *Group Theory in Quantum Mechanics* (Oxford : Pergamon Press).

HEITLER, W., 1954, *The Quantum Theory of Radiation* (Oxford : Clarendon Press).

HERZBERG, G., 1945, *Infra-red and Raman Spectra of Polyatomic Molecules* (New York : D. Van Nostrand).

HOUGEN, J. T., and SINGH, S., 1963, *Phys. Rev. Letters*, **10,** 406.

HUANG, K., 1951, *Proc. roy. Soc.* A, **208,** 352.

KETELAAR, J. A. A., HAAS, C., and FAHRENFORT, J., 1954, *Physica*, **20,** 1259.

KHAIKIN, M. S., and BYKOV, V. P., 1956, *Soviet Phys.—JETP*, **3,** 119.

KLEINMAN, D. A., and SPITZER, W. G., 1962, *Phys. Rev.*, **125,** 16.

KOGELNIK, H., and PORTO, S. P. S., 1963, *J. opt. Soc. Amer.*, **53,** 1446.

KONDILENKO, I. I., KOROTKOV, P. A., and STRIZHEVSKII, V. L., 1960, *Optics and Spectroscopy*, **9,** 13.

KONDILENKO, I. I., and STRIZHEVSKII, V. L., 1961, *Optics and Spectroscopy*, **11,** 137.

KRISHNAN, R. S., 1948, *Proc. Indian Acad. Sci.* A, **28,** 307.

LAX, M., and BURSTEIN, E., 1955, *Phys. Rev.*, **97,** 39.

LOUDON, R., 1963 a, *Proc. phys. Soc., Lond.*, **82,** 393 ; 1963 b, *Proc. roy. Soc.* A, **275,** 218.

LOUDON, R., and JOHNSON, F. A., 1964, *Proc. roy. Soc.* A, **281,** 274.

LYDDANE, R. H., SACHS, R. G., and TELLER, E., 1941, *Phys. Rev.*, **59,** 673.

MARADUDIN, A. A., 1962, *Phys. Stat. Sol.*, **2,** 1493.

MARADUDIN, A. A., and FEIN, A. E., 1962, *Phys. Rev.*, **128,** 2589.

MARADUDIN, A. A., FEIN, A. E., and VINEYARD, G. H., 1962, *Phys. Stat. Sol.*, **2,** 1479.

MARADUDIN, A. A., MONTROLL, E. W., and WEISS, G. H., 1963, *Solid State Physics*, Supplement 3, *Theory of Lattice Dynamics in the Harmonic Approximation* (New York : Academic Press).

MATHIEU, J. P., 1945, *Spectre de Vibration et Symétrie des Molécules et des Cristaux* (Paris : Hermann) ; 1956, *Phys. Soc. Year Book*, p. 23 ; 1962, *Proceedings of the Conference on Optics and Spectroscopy at all Wavelengths*, p. 476.

MENZIES, A. C., 1953, *Rep. Prog. Phys.*, **16,** 83.

MERTEN, L., 1960, *Z. Naturf.* A, **15,** 47 ; 1962, *Ibid.*, **17,** 65.

MITRA, S. S., 1962, *Solid State Physics*, **13,** 1.

NARAYANAN, P. S., 1951, *Proc. Indian Acad. Sci.* A, **34,** 1.

NOZIÈRES, P., and PINES, D., 1958, *Phys. Rev.*, **109,** 762.

NYE, J. F., 1957, *Physical Properties of Crystals* (Oxford : Clarendon Press).

OVANDER, L. N., 1960, *Optics and Spectroscopy*, **9,** 302 ; 1962 a, *Ibid.*, **12,** 405 ; 1962 b, *Soviet Phys.—Solid State*, **3,** 1737 ; 1962 c, *Ibid.*, **4,** 1081 ; 1962 d, *Ibid.*, **4,** 1078.

PEIERLS, R. E., 1955, *Quantum Theory of Solids* (Oxford : Clarendon Press).

PHILLIPS, J. C., 1956, *Phys. Rev.*, **104,** 1263 ; 1959, *Ibid.*, **113,** 149.

PORTO, S. P. S., and WOOD, D. L., 1962, *J. opt. Soc. Amer.*, **52,** 251.

POULET, H., 1952, *C.R. Acad. Sci., Paris*, **234,** 2185 ; 1954, *Ibid.*, **238,** 70 ; 1955, *Ann. Phys., Paris*, **10,** 908.

RAMAN, C. V., 1956 a, *Proc. Indian Acad. Sci.* A, **43,** 327 ; 1956 b, *Ibid.* **44,** 99 ; 1961, *Ibid.*, **54,** 253 ; 1962, *Ibid.*, **55,** 1.

RICHARDS, P. L., and TINKHAM, M., 1960, *Phys. Rev.*, **119,** 575.

SAKSENA, B. D., 1940, *Proc. Indian Acad. Sci.*, A, **11,** 229.

SMITH, H. M. J., 1948, *Phil. Trans.* A, **241,** 105.

Sobel'man, I. I., and Feinberg, E. L., 1958, *Soviet Phys.—JETP*, **34**,(7), 339.

Spitzer, W. G., and Kleinman, D. A., 1961, *Phys. Rev.*, **121**, 1324.

Spitzer, W. G., Kleinman, D. A., and Frosch, C. J., 1959, *Phys. Rev.*, **113**, 133.

Spitzer, W. G., Kleinman, D. A., and Walsh, D., 1959, *Phys. Rev.*, **113**, 127.

Strizhevskii, V. L., 1962, *Soviet. Phys.—Solid State*, **3**, 2141.

Theimer, O., 1951, *Proc. phys. Soc., Lond*, A, **64**, 1012 ; 1952, *Ibid.*, **65**, 38 ; 1953, *Acta Phys. Austr.* **7**, 216 ; 1955, *J. Phys. Radium*, **16**, 493 ; 1956, *Canad. J., Phys.*, **34**, 312.

Valentin, F., 1957, *C.R. Acad. Sci., Paris*, **244**, 1915.

Van Hove, L., 1953, *Phys, Rev.*, **89**, 1189.

Van Kranendonk, J., and Van Vleck, J. H., 1958, *Rev. mod. Phys.*, **30**, 1.

Venkatarayudu, T., 1954, *J. chem. Phys.*, **22**, 1269.

Viswanathan, K. S., 1963, *Canad. J. Phys.*, **41**, 423.

Whitfield, G. D., 1961, *Phys. Rev.*, **121**, 720.

Wilson, E. B., Decius, J. C., and Cross, P. C., 1955, *Molecular Vibrations* (New York : McGraw-Hill Book Co.).

Wood, D. L., and Kaiser, W., 1962, *Phys. Rev.*, **126**, 2079.

Woodbury, E. J., and Ng, W. K., 1962, *Proc. Inst. Radio Engrs, N.Y.*, **50**, 2367.

Woods, A. D. B., Brockhouse, B. N., Cowley, R. A., and Cochran, W., 1963, *Phys. Rev.*, **131**, 1025.

Zeiger, H. J., and Tannenwald, P. E., 1963, Paper presented at the Third International Symposium on Quantum Electrodynamics, Paris.

First-order Lattice Vibration Raman Experiments

Ananthanarayanan, V., 1960, *Z. Phys.*, **159**, 51.
$NaClO_3$
1962, *Z. Phys.*, **167**, 39.
CaF_2

Bazhulin, P. A., Mysasnikova, T. P., and Rakov, A. V., 1964, *Soviet Phys.—Solid State*, **5**, 1299.
Ferro-electrics (e.g. NH_4HSO_4)

Bobovich, Ya. S., 1962, *Optics and Spectroscopy*, **13**, 254.
Ba_2TiO_4

Bobovich, Ya. S., and Tulub, T. P., 1959, *Optics and Spectroscopy*, **6**, 362 ; 1960, *Ibid.*, **9**, 392.
SiO_2, CaF_2, $Al._2O_3$, etc. (temperature dependence)

Bobovich, Ya. S., and Bursian, E. V., 1961, *Optics and Spectroscopy*, **11**, 69.
$BaTiO_3$

Brahms, S., and Mathieu, J. P., 1960, *C.R. Acad. Sci., Paris*, **251**, 938.
$HgCl_2$

Couture-mathieu, L., and Mathieu, J. P., 1953, *C. R. Acad. Sci., Paris*, **236**, 371.
ZnS (Zinc blende)

Couture-Mathieu, L., Poulet, H., and Mathieu, J. P., 1952, *C.R. Acad. Sci., Paris*, **234**, 1761.
$NaClO_3$ and $NaBrO_3$

Flubacher, P., Leadbetter, A. J., Morrison, J. A., and Stoicheff, B. P., 1959, *J. phys. Chem. Solids*, **12**, 53.
Vitreous silica (first order Raman and Brillouin)

Geiger, W., and Kulp, M., 1960, *J. Phys. Chem. Solids*, **12**, 341.
Quartz glass (Brillouin scattering)

Gross, E., 1930, *Nature, Lond.*, **126**, 201.
Quartz (Brillouin scattering)

Hadni, A., Henry, C., Mathieu, J. P., and Poulet, H., 1961, *C.R. Acad. Sci., Paris,* **252,** 1585.
Hg_2Cl_2
Hougen, J. T., and Singh, S., 1964, *Proc. roy. Soc.* A, **277,** 193.
$PrCl_3$ and $LaCl_3$ (electronic and vibrational)
Ikegami, S., 1964, *J. phys. Soc., Japan,* **19,** 46.
$BaTiO_3$
Krishnamurti, D., 1954, *Proc. Indian Acad. Sci.* A, **40,** 211.
Diamond
1956, *Proc. Indian Acad. Sci.* A, **43,** 210.
$MgCO_3$
1957, *Proc. Indian Acad. Sci.* A, **46,** 183.
$CaCO_3$ (calcite)
1958. *Proc. Indian Acad. Sci.* A, **47,** 276.
SiO_2 (quartz)
1962, *Proc. Indian Acad. Sci.* A, **55,** 290.
TiO_2 (rutile)
Krishnan, R. S., 1946 a, *Proc. Indian Acad. Sci.,* **24,** 45.
Diamond (temperature dependence)
1947 a, *Nature, Lond,* **159,** 740 ; 1947 b, *Proc. Indian Acad. Sci.,* **26,** 399.
Diamond (Brillouin scattering)
1953, *Proc. Indian Acad. Sci.* A, **37,** 377.
Fused quartz (first-order Raman and Brillouin)
1955, *Proc. Indian Acad. Sci.* A, **41,** 91.
Brillouin scattering (see § 2.7.2)
Krishnan, T. S., 1956, *Proc. Indian Acad. Sci.* A, **44,** 96.
$SrCO_3$
Krishnan, R. S., and Narayanan, P. S., 1963, *Indian J. pure appl. Phys.,* **1,** 196.
BaF_2
Mathieu, J. P., and Couture-Mathieu, L., 1952 a, *J. Phys. Radium,* **13,** 271.
$ClO_4Li \cdot 3H_2O$
1952 b, *C.R. Acad. Sci., Paris,* **234,** 1961.
SiO_2 (quartz)
1953, *J. Chim. Phys.,* **50,** 573.
$CuCl_2$
Mathieu, J. P., Couture, L., and Poulet, H., 1955, *J. Phys. Radium,* **16,** 781.
K_2SO_4 and Li_2SO_4
Mathieu, J. P., and Poulet, H., 1957, *C.R. Acad. Sci., Paris,* **244,** 2794.
SiC (carborundum)
Mathieu, J. P., Poulet, H., and Klee, W., 1963, *Copenhagen Lattice Dynamics Conf. Abstracts,* p. 55.
ZnS (wurtzite)
Mathieu, J. P., Poulet, H., and Tramer, A., 1960, *Z. Elektrochem.,* **64,** 699.
CuCl
Moszynska, B., 1963, *C.R. Acad. Sci., Paris,* **256,** 1261.
$SnBr_4$, $SnCl_4$ and $TiCl_4$
Narayanan, P. S., 1953, *Proc. Indian Acad. Sci.* A, **37,** 411.
TiO_2 (rutile)
Narayanan, P. S., and Vedam, K., 1961, *Z. Phys.,* **163,** 158.
$SrTiO_3$
Narayanaswamy, P. K., 1947, *Proc. Indian Acad. Sci.* A, **26,** 511, 521.
Calcite and quartz (temperature dependence)

Nedungadi, T. M. K., 1940, *Proc. Indian Acad. Sci.*, **11,** 86.

Quartz (temperature dependence)

Pershina, E. V., and Raskin, Sh. Sh., 1962, *Optics and Spectroscopy*, **13,** 272.

$AlCl_3$ and $AlBr_3$

Poulet, H., and Mathieu, J. P., 1956, *J. Phys. Radium*, **17,** 472.

$BeSO_4 . 4H_2O$ and $NH_4H_2PO_4$

Reding, F. P., and Hornig, D. F., 1954, *J. chem. Phys.*, **22,** 1926.

NH_3 and ND_3

Richman, I., 1964, *Phys. Rev.*, **133,** A1364.

SrF_2 and BaF_2

Richman, I., Satten, R. A., and Wong, E. Y., 1963, *J. chem. Phys.*, **39,** 1833.

$LaCl_3$ and $LaBr_3$

Scrocco, M., and Mathieu, J. P., 1958, *Ann. Phys., Paris*, **3,** 463.

$PbSO_4$

Srinivasan, R., 1953, *Proc. Indian Acad. Sci.* A, **37,** 405.

AlF_2SiO_4 (topaz)

Stekhanov, A. I., 1955, *C.R. Acad. Sci., U.S.S.R.*, **100,** 685.

Gypsum

1957, *Optika i Spektrosk.*, **3,** 143.

$CaCO_3$ (calcite) and $BaSO_4$

Stekhanov, A. I., and Chisler, E. V., 1962, *Soviet Phys.—Solid State*, **3,** 2549.

SiO_2, $CaCO_3$ and CaF_2 (temperature dependence)

Stekhanov, A. I., and Gabrichidze, Z. A., 1963, *Soviet Phys.—Solid State*, **5,** 972.

Rochelle salt

Tramer, A., 1959 a, *C.R. Acad. Sci., Paris*, **248,** 3546 ; 1959 b, *Ibid.*, **249,** 2531.

$NaNO_2$

Weil, A., and Mathieu, J. P., 1954, *C.R. Acad. Sci., Paris*, **238,** 2510.

Mg and Zn perchlorates

Zubov, V. G., and Osipova, L. P., 1961, *Soviet Phys.—Crystallography*, **6,** 330.

Quartz

1962, *Soviet Phys.—Doklady*, **7,** 525.

Quartz (neutron irradiated)

Zubov, V. G., Osipova, L. P., and Firsova, M. M., 1962, *Soviet Phys.—Crystallography*, **6,** 623.

Quartz (electric field applied)

Second-order Raman Experiments

Khambátá, S. J., 1956, *Proc. phys. Soc., Lond.* A, **69,** 426.

MgO

Krishnamurthy, N., and Krishnan, R. S., 1963, *Indian J. pure appl. Phys.*, **1,** 239.

CsI

Krishnan, R. S., 1945, *Nature, Lond.*, **156,** 267.

NaCl

1946 b, *Proc. Indian Acad. Sci.*, **24,** 25.

Diamond

Krishnan, R. S., and Krishnamurthy, N., 1963, *Z. Phys.*, **175,** 440.

NaI

Krishnan, R. S., and Narayanan, P. S., 1949, *Nature, Lond.*, **163,** 570.

KBr

1950, *Proc. Indian Acad. Sci.* A, **32,** 352.

Diamond

Krishnan, R. S., and Narayanan, P.S., 1957, *J. Indian Inst. Sci.* A, **39,** 85.

KI

Narayanan, P. S., 1955, *Proc. Indian Acad. Sci.* A, **42,** 303.

CsBr

Raman, C. V., 1963, *Proc. Indian Acad. Sci.* A, **57,** 1.

KBr

Stekhanov, A. I., and Eliashberg, M. B., 1961 a, *Optics and Spectroscopy*, **10,** 174 ;
1961 b, *Soviet Phys.—Solid State*, **2,** 2096.

KBr and KBr–KCl mixed crystals

Stekhanov, A. I., Gabrichidze, Z. A., and Eliashberg, M. B., 1961, *Soviet Phys.—Solid State*, **3,** 964.

KI

Stekhanov, A. I., and Korol'kov, A. P., 1963, *Soviet Phys.—Solid State*, **4,** 2311.

CsBr

Stekhanov, A. I., Korol'kov, A. P., and Eliashberg, M. B., 1962, *Soviet Phys.—Solid State*, **4,** 945.

LiCl

Welsh, H. L., Crawford, M. F., and Staple, W. J., 1949, *Nature, Lond.*, **164,** 737.

NaCl

Recent Publications

The following list of publications, with descriptions of their contents, brings the references up to date at the time of proof-reading (end of October 1964).

Axe, J. D., 1964, *Phys. Rev.*, **136,** A42.
Develops method for approximate numerical evaluation of eqn. (73), § 4.1, and compares the theoretical predictions with the results of Hougen and Singh (1963, 1964).

Chiao, R. Y., Townes, C. H., and Stoicheff, B. P., 1964, *Phys. Rev. Letters*, **12,** 592.
Measurements of *stimulated* Brillouin scattering from quartz and sapphire using a ruby laser source (cf. §§ 2.7 and 5.2).

Cowley, R. A., 1964, *Proc. phys. Soc., Lond.*, **84,** 281.
Contains shell-model theory of Raman scattering, with numerical calculations of the second-order spectra of NaI and KBr.

Hobden, M. V., and Russell, J. P., 1964, *Phys. Letters* (to be published).
First and second-order Raman spectra of GaP using a He–Ne laser as the source. This is the first published crystalline Raman spectrum using a laser source (cf. § 5.1).

Kleinman, D. A., 1964, *Phys. Rev.*, **134,** A423.
It is shown that a measurement of the Raman spectrum of the F-centre could provide important new information about the centre.

Kondilenko, I. I., Verlan, E. M., Korotkov, P. A., and Strizhevskii, V. L., 1963, *Soviet Phys.—Solid State*, **5,** 1158.
Contains theory of the variation of Raman intensity with scattering angle for uniaxial crystals, and a comparison with experiments on the 466 cm^{-1} vibration of quartz (cf. §§ 2.3. and 2.4).

Lubchenko, A. F., and Pavlik, B. M., 1963, *Soviet Phys.—Solid State*, **5,** 1246.
Theory of Raman and Rayleigh scattering from impurity molecules in crystals.

POULET, H., and MATHIEU, J. P., 1964 a, *C.R. Acad. Sci., Paris,* **258,** 2043 ; 1964 b, *Ann. Phys., Paris* (to be published).

The Raman frequencies of CdS excited by the green and yellow Hg lines are tabulated and interpreted.

RUSSELL, J. P., 1964, *Proc. phys. Soc., Lond.* (to be published).

First and second-order Raman spectra of CaF_2 excited by a He–Ne laser (cf. § 2.6.3).

STRIZHEVSKII, V. L., 1963, *Soviet Phys.—Solid State,* **5,** 1099.

Discusses a polarizability-theory approximation for the Raman scattering tensor in crystals (cf. § 2.2).

WARRIER, A. V. R., and KRISHNAN, R. S., 1964, *Naturwissenschaften,* **51,** 8.

First-order Raman shift of SrF_2 measured to be 285 cm^{-1} (cf. § 2.6.3).