THERMAL SCATTERING OF LIGHT IN BIREFRINGENT CRYSTALS

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THE existence of a genuine diffusion of light in a crystal was first recognised by Sir C. V. Raman.[1] The phenomenon arises from thermal agitation and may, therefore, be called thermal scattering. In Brillouin's theory,[2] the effect is ascribed to a "coherent reflection" of the light waves by the periodic stratifications produced by elastic waves of thermal origin in the crystal. The moving elastic waves would give rise to spectral shifts in the diffused light, which are in the nature of a Doppler effect. Since 1930, several investigators including Mandelstam, Landsberg and Leontowitsch,[3] Tamm,[4] Mueller,[5] Gross,[6] Bhatia and Krishnan,[7] and Kastler[8] have considered the theory of thermal scattering in crystals and the Doppler shifts occurring in them. The picture that is generally accepted at present is that in a crystal, whether birefringent or not, only three pairs of Doppler components occur, due respectively to the three types of elastic waves which are propagated with different velocities in any given direction. However, none of the authors have specifically considered the effect of birefrigence on the Doppler shifts. When this is examined in detail, the remarkable result emerges that there are, *in general*, not three but *twelve* Doppler components which can occur for a *birefringent* crystal. A short discussion of these new results is given below.

The expression for the magnitude of the shifts can easily be derived either on the basis of the quantum ideas or of the classical wave theory and the results are the same in either case. The Doppler shifts of the components of the scattered light depend on the velocity of the elastic wave as well as on the velocities of the incident and of the scattered light waves. Inside a birefringent crystal the incident light wave (i) divides itself into two waves which, in general, travel with different velocities and are polarised in mutually perpendicular planes. Similarly, the scattered wave (s) can travel with either of the velocities corresponding to the two states of polarisation of the wave. Let n_i (and n_s) be either of the two refractive indices of the crystal for the direction of incidence (and of scattering) and let λ be the wavelength of the incident light in vacuum. Then the conditions for coherence of phase of the scattering by the different volume elements lying on a particular stratification are (a) that the stratification should be normal to the plane of scattering and (b) that it should make angles θ_i and θ_s with the direction of incidence and that of scattering, such that

$$n_i \cos \theta_i = n_s \cos \theta_s \quad (1)$$

$$\theta_i + \theta_s = \theta , \quad (2)$$

where θ is the angle of scattering.

Further, the condition for the coherence of phase by volume elements lying on successive stratifications is:

$$\lambda_e = \frac{\lambda}{\sqrt{n_i^2 + n_s^2 - 2n_i n_s \cos \theta}} \quad (3)$$

where λ_e is the wave-length of the elastic wave.

The Doppler frequency shifts $\Delta \nu$ of the components of the scattered radiation are the same as the frequency of the appropriate elastic waves, and are given by:

$$\frac{\Delta \nu}{\nu} = \pm \frac{v_e}{c} \sqrt{n_i^2 + n_s^2 - 2n_i n_s \cos \theta} , \quad (4)$$

where c is the velocity of light in vacuum and v_e is the velocity of the elastic wave giving rise to scattering.

The characteristics of the scattered radiation may be analysed using the four fundamental equations (1) to (4)! Since n_i and n_s can each take two values, there would be four pairs of values for (n_i, n_s) in equation (4) and consequently four values for λ_e and θ_i (and θ_s). Further, for a given direction of elastic wave normal, there are three types of elastic waves, each of which has a different velocity v_e. Thus, from equation (4), it is seen that there must, in general, be $3 \times 2 \times 2 = 12$ values for the frequency shifts ($\Delta \nu$). Therefore, the light scattered by a *birefringent* crystal, like calcite, must consist of *12 pairs of Doppler shifted components*. The possibility of such a large number of components has not been previously envisaged.

Equations (1) to (4) are symmetrical with respect to the suffixes i and s. Consequently, if the direction of incidence and that of scattering are interchanged, the frequency shifts of the components would remain unaltered.

For a given direction of incidence and of scattering, the two polarised incident light waves may be designated A and B and the two polarised scattered waves P and Q. Since either incident wave A or B can, in general, give rise to either of the scattered waves P or Q, the scattered radiation consists of four "species" P_A, Q_A, P_B and Q , each with a distinctive polarisation character. Each species will consist of 3 pairs of Doppler components due to the three elastic waves. By the use of a proper polarising device, such as a double image prism, in the incident path to separate A and B and another in the scattered path to separate P and Q one can independently study the four species of the scattered radiation.

In certain circumstances, it is possible that for some of the four species, $\cos\theta > n_i/n_s$ or n_s/n_i. Then the wave front of the elastic wave responsible for the scattering lies outside the internal angle between the directions of the incident and scattered wave normals. In such cases, the process of scattering must be regarded appropriately as "coherent refraction" of light wave by elastic waves.

If we consider scattering in the exact forward direction ($\theta = 0$), then the shifts for two Doppler components, say P_A and Q_B are zero, but the shifts for Q_A and P_B components are finite, but equal to each other. We thus have the strange result of a refraction without change of direction, but with change of frequency. In calcite, the magnitude of the shift is as large as $0\cdot22$ cm.$^{-1}$ when light of wavelength λ 2537 is incident perpendicular to the optic axis.

In the case of a single refracting medium $n_i = n_s = n$ and therefore, equation (4) reduces to the familiar expression

$$\frac{\Delta\nu}{\nu} = \pm\frac{2v_e}{c}\, n \sin\frac{\theta}{2}. \qquad (5)$$

Then all the four species have the same shifts and there can only be 3 pairs of Doppler components. The effective elastic wave front always bisects the internal angle between the incident and scattered directions and the scattering process may therefore always be regarded as "specular reflection". Further when $\theta \to 0$ $\Delta\nu \to 0$ and therefore, in the forward scattering the frequency shifts are vanishingly small.

To give an idea of the differences in the Doppler shifts for the four species, the calculated values of the frequency shifts are given below for backward scattering along the normal to the cleavage face of calcite for λ 2537 excitation. They are in cm.$^{-1}$ P_A—3·31, 1·43, 1·24; Q_B — 3·06, 1·32, 1·15 ; P_B — 3·19, 1·38, 1·19 ; Q_A — 3 19, 1 38, 1·19. The differences are well within the limits of measurement and some experiments have been made which support these ideas. The full details are, however, reserved for another communication.

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1950 NOBEL AWARDS FOR CHEMISTRY AND MEDICINE

THE Nobel Prize for Chemistry has been awarded this year jointly to the German organic chemists, Prof. Otto Diels and Prof. Kurt Alder. They were the co-discoverers in 1929 of the well-known reaction, which has since been called the Diels-Alder Reaction. The reaction consists in the addition of compounds containing a conjugated system of double bonds quantitatively to compounds containing groupings like CH : CH·CO to form cyclic compounds. Both Diels and Alder have continued to develop and apply this technique of "Diene Synthesis" to various problems during the last two decades. These studies have played a large part in the preparation of synthetic rubber. Diels is also the author of a well-known text-book of Organic Chemistry in German, which has since been translated into many other languages.

The Nobel Prize for Medicine has been awarded jointly to Drs. Philip S. Hench and Edward C. Kendall, of the Mayo Clinic, Rochester, Minnesota, and to Prof. Tadeus Reichstein, of the University of Basle, Switzerland. This recognizes not only the recent outstanding work (first published last year) on the treatment of rheumatoid arthritis with cortisone and A.C.T.H., but Dr. Kendall's earlier important contributions to biochemistry—the first crystalline preparation of thyroxine in 1914, the first synthesis of glutathione in 1929, and numerous chemical studies of the adrenal cortical hormones—and also Dr. Reichstein's fundamental chemical work on the steroids of the cortex which led him to the original discovery of cortisone, in 1937, and of desoxycoricosterone acetate, as well as his successful synthesis of vitamin C in 1933.