RAMAN EFFECT IN RELATION TO CRYSTAL STRUCTURE

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I. Introduction

IT is now widely recognised that a study of the Raman effect furnishes a convenient and powerful method of solving several problems of physical and chemical interest. During the past ten years, its applications have been varied and numerous as may be seen from the very large number of original communications that have appeared from time to time. Amongst the major fields of investigation thus opened up, mention may be made of the structure of molecules, nature of interatomic forces, electrolytic dissociation, formation of molecule complexes, etc. Numerous as have been its successes in the above fields, there is little doubt that this discovery is capable of yielding much more and that it has not yet been made use of to the fullest extent to which it is possible. In this connection it is of interest to recall the following remarks of Lord Rutherford.[1] 'The Raman

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[1] *Proc. Roy. Soc.*, 1931, (A), **130**, 259.

effect must rank among the best three or four discoveries in experimental physics of the last decade. It has proved, and will prove, an instrument of *great power in the study of the theory of solids."* This latter aspect is of special importance in connection with the physics of the solid state but has not yet been the subject of any intensive investigation. The comparative ease with which experimental data may be collected in liquids has resulted in the accumulation of a wealth of information relating to this branch but the advance has not been so marked in the case of solids. The experimental difficulties arising out of the fact that it is not easy to get large and transparent solid lumps have been the chief obstacles in the latter case. Special methods have nevertheless been devised and some progress has been made even with crystals.

No systematic attempt has however so far been made to correlate the meagre results that are available with the known crystalline properties. Results of great complexity are usually obtained with crystals and their interpretation has hitherto been merely empirical. A proper study of the normal modes of oscillation of a crystal with special reference to the selection rules in Raman effect and infra-red absorption is likely to throw considerable light on a variety of detail such as the appearance of several additional component lines in crystals, the origin of low frequency Raman bands in certain solids, the relationship of such bands to the wings in the corresponding liquids, the variations which the Raman spectrum undergoes as we pass from one crystalline modification to another, the dependence of the characteristics of Raman lines on the direction and manner of excitation and many other similar problems.

Apart from throwing light on such details, these studies may confidently be expected to bring into evidence the connection between Raman effect and certain other physical properties of crystals. The Raman spectrum results may be broadly divided into three branches, namely, those relating to (i) the fine structure of the Rayleigh lines, (ii) Raman lines due to the oscillations of the lattice groups as a whole and (iii) Raman lines due to internal oscillations of the atoms within the groups themselves. Results in respect of the first item are closely connected with the elastic properties of the crystal. On the other hand, the symmetry of the crystal and the disposition of the atoms and molecules in the lattice will determine the appearance or otherwise of Raman lines corresponding to specific normal modes coming under the second and the third items. It may be mentioned here that when a group of ions or molecules, each of which is characterised by a certain degree of symmetry are built into a crystal lattice having a lower degree of symmetry, some of the degenerate normal modes may be expected to split up. Thus the results

in respect of the lattice and the internal oscillations are very intimately connected with crystal structure.   Next in importance is the subject of specific heat of solids.   A complete analysis of the normal modes of oscillation of a crystal and a verification of the same with the help of Raman and infra-red absorption spectra is obviously of great help in evaluating its specific heat. Among the other fields which have a bearing on this branch of investigation, mention may be made of the anisotropic properties of crystals in respect of refraction, magnetic susceptibility, thermal expansion, etc.   The effect of temperature on the positions and sharpness of Raman lines, particularly those coming under the category of lattice oscillations, is of special interest as it is likely to throw light on the nature of the crystalline forces and how they are released with increasing temperature.   The gradual transition of these bands into the continuous wing usually encountered with in the molten state is intimately connected with the mechanism of melting.   Thus practically all the important physical properties of a crystal are brought into the discussion when we attempt to explain the phenomenon of light scattering in crystals.

Brester,[2] Dennison[3] and others have studied the normal modes of some symmetrical systems by employing certain special methods.   Wigner[4] has recently shown that the application of group theory to a study of the molecular oscillations greatly facilitates the work.   Other investigators such as Tisza,[5] Wilson,[6] Placzek[7] and Rosenthal and Murphy[8] have subsequently made important contributions to the subject.   In the present investigation, an account of this theory is given in a form that is applicable to crystals.   The question of selection rules has been examined in detail and a section dealing with the same is included.   The methods have been applied to a few simple cases of crystals and the results are discussed with special reference to Raman effect with a view to illustrate the more important points.[9]

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[2] *Kristallsymmetrie und Reststrahlen, Diss. Utrecht*, 1923 ; *Z. f. Phys.*, 1924, **24**, 324.

[3] *Rev. Mod. Phys.*, 1931, **3**, 280.

[4] *Göttinger Nachrichten*, 1930, 133.

[5] *Z. f. Phys.*, 1933, **82**, 48.

[6] *Phys. Rev.*, 1934, **45**, 706.

[7] *Handbuch Der Radiologie*, 1934, **2**, 205.

[8] *Rev. Mod. Phys.*, 1936, **8**, 317.

[9] A comprehensive account of the theory formally applicable to crystals is purposely included with a view to make the paper self-contained. A similar treatment in a form that is applicable to molecules has already been published by Tisza and by Rosenthal and Murphy. Attempts have been made to draw physical analogies wherever possible. The more important conclusions are given in italics and a reader who is interested only in the application of the group theoretical methods will find these statements useful.

II. *Groups and Group Characters*

Rosenthal and Murphy have given an excellent exposition of the subject in the paper already referred to and a detailed description need not be attempted here. Some of the theorems which have to be used in the following sections may be enunciated.

All the symmetry operations of a crystal lattice furnish a typical illustration of the elements of a group. If G is any abstract group and H is a group of linear substitutions and if to every element A of G there corresponds an element A′ of H such that the product of two elements A and B of G corresponds to the product of the two corresponding elements A′, B′ of H, then the group of matrices H is called a representation of G.

The character of a group element is the same in equivalent representations.

A group of homogeneous linear substitutions is spoken of as *reducible*, if it is possible to find a set of linear functions of the variables $(X_1, X_2, .., X_n)$ less in number than the variables such that they are transformed among themselves by every operation of the group. If it is not possible to find such a set of linear functions of the variables, the group of substitutions is said to be *irreducible*. A reducible group of homogeneous linear substitutions is called completely reducible when it is possible to choose the variables in such a way that (i) they fall into sets, each set of variables being transformed among themselves by every operation of the group while (ii) the group in each set is irreducible.

III. *Normal Modes of Oscillation of a Crystal Lattice*

1. *Normal Modes and Irreducible Representations.*—We will now regard all the equivalent points of the lattice as having the same motion at a given instant of time. Accordingly, we need describe the position of only one set of non-equivalent points for completely specifying the motion of the whole lattice. Let there be n non-equivalent points in a crystal lattice. The position of the atoms may be described by giving the $3n$ cartesian co-ordinates $x_1, y_1, z_1, .., x_n, y_n, z_n$ and they may be taken to correspond to zero values for the equilibrium position. For oscillations of small amplitudes, the potential and kinetic energies may be expressed as general quadratic functions of the co-ordinates. These may be simultaneously reduced to the canonical form

$$2\,V = \Sigma\,\lambda_i\,Q_i{}^2; \quad 2T = \Sigma\,\dot{Q}_i{}^2$$

with the help of suitable linear transformation of co-ordinates. $Q_1, Q_2, .., Q_{3n}$ are called the normal co-ordinates and the corresponding normal frequencies are given by the equations $4\pi^2\,\nu_k{}^2 = \lambda_k$. The normal co-ordinate gives the mode of oscillation. Thus, if

$$Q_k = \Sigma_l\,a_{kl}\,x_l + \Sigma_m\,b_{km}\,y_m + \Sigma_n\,c_{kn}\,z_n$$

is the expression for the normal co-ordinate Q_k in terms of the $3n$ cartesian co-ordinates of the n non-equivalent points, the amplitude of oscillation of the lth atom in the x direction is given by the coefficient of x_l, namely a_{kl}. The configuration of the lattice may now be denoted by Q_k. If we perform a symmetry operation R on the lattice, we get a new configuration which we denote by RQ_k. If by means of the operation R the kth atom goes over into the lth atom, we shall suppose that the lth atom remains in its own neighbourhood but gets the motion of the kth atom. By doing this for every atom we keep all the atoms in the neighbourhood of their original equilibrium positions and obtain a configuration of the lattice which is geometrically identical with RQ_k. If we denote this new configuration by $\bar{R}Q_k$, $\bar{R}Q_k$ evidently represents a normal co-ordinate having the same frequency ν_k because the relative configuration of the atoms is not altered. If $\bar{R}Q_k$ is distinct from Q_k we obtain two distinct modes of oscillation having the same frequency ν_k. Such a case will not arise for non-degenerate modes of oscillation. Now if R runs through all the symmetry operations of the group G we get all the normal modes of oscillation belonging to the same frequency. But all these modes of oscillation may not be linearly independent.

Let Q_1, Q_2, .., Q_f be a set of linearly independent normal co-ordinates having the frequency ν_k. Then every other normal mode of oscillation with the frequency ν can be obtained as a superposition of these f normal modes of oscillations. The oscillation ν_k is therefore f-fold degenerate. Similarly we obtain the normal co-ordinates of different frequencies. Now the normal co-ordinates belonging to a definite frequency define an irreducible representation of the group G. For if Q_1, Q_2, .., Q_f are a set of normal co-ordinates with a certain frequency ν, the co-ordinates Q_1, Q_2, .., Q_f combine among themselves by the application of a symmetry operation and we cannot find linear combinations of Q_1, Q_2, .., Q_f smaller in number than f which combine among themselves by symmetry operations. Thus, if

$$\bar{R}\, Q_1 = a_{11}\, Q_1 \ldots\ldots\ldots + a_{1f}\, Q_f$$
$$\bar{R}\, Q_2 = a_{21}\, Q_1 \ldots\ldots\ldots + a_{2f}\, Q_f$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\bar{R}\, Q_f = a_{f1}\, Q_1 \ldots\ldots\ldots + a_{ff}\, Q_f$$

then $R \rightarrow \bar{R} \rightarrow$ the matrix (a_{ij})

and the correspondence also defines a representation of the group G. *Thus a set of normal co-ordinates of a definite frequency define an irreducible representation.*

2. *Determination of the Number of Normal Modes that belong to a given Irreducible Representation.*—We divide the $3n$ normal co-ordinates into