THE RAMAN SPECTRA OF POLYCRYSTALLINE SOLIDS

By D. KRISHNAMURTI, F.A.Sc.

1. INTRODUCTION

CRYSTALLINE solids as found in nature or prepared artificially usually appear as polycrystalline masses, large and well-developed crystals being the exception rather than the rule. In the study of the Raman effect, it is often necessary to make use of such material. The internal reflections within the solid and the parasitic illumination resulting therefrom create difficulties in the successful recording of the spectra. These difficulties are enormously enhanced when, as is often the case with artificially prepared material, the solid appears in the form of very fine particles which are non-adherent or only loosely adherent to each other. The special techniques necessary to obtain any useful results with such material have been the subject of numerous investigations in the past, reference to which will be made later in the paper.

In the present author's studies on the Raman spectra of crystals, extensive use has been made by him of the $\lambda 2536 \cdot 5$ resonance radiation of the mercury arc and of the special technique originally proposed by Rasetti in that connection. It appeared to him therefore to be of interest to explore the possibility of using the same technique for satisfactorily recording the Raman spectra both of polycrystalline solids and of the finest crystal powders. The present paper is of a preliminary nature. It discusses the problems which arise in this connection and presents the results obtained in a few typical cases of interest.

2. A SURVEY OF THE PROBLEM

The theory of the propagation of light in polycrystalline media developed by C. V. Raman and K. S. Viswanathan (1955) and discussed by C. V. Raman (1957) with reference to the facts of observation provides an insight into the behaviour of these substances with regard also to the diffusion of light in them, since the properties in relation to transmission and diffusion of light are complementary to each other. The following points are germane to our discussion here on the nature and origin of the parasitic scattering and how

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best it can be minimized. When the sizes of the crystallites are large com-
pared with the wavelength of light and the birefringence of the solid is appre-
ciable, the effects arising may be considered from the standpoint of geometri-
cal optics as reflection and refraction of the incident light at the intercrystalline
boundaries. Since for a finite volume of the sample the total area of the
boundaries which scatter increases with diminishing particle size, the para-
sitic scattering of light would naturally be greater in the case of finer particles,
and a very small thickness of the medium suffices therefore to diffuse the
incident light totally in directions backward. However, as the size of the
crystallites diminishes further and becomes comparable to that of the wave-
length of light the effects arising have to be considered from the point of
view of wave-optics. In the case of a weakly birefringent solid the diminution
in the particle size at such a stage should result in a diminution in the scattering
and hence correspondingly increased transmission.

The foregoing remarks have a bearing on the case of fine crystal powders.
Since the intensity of the diffusion of light at the boundaries of the crystallites
depends on the refractive index of the substance with reference to the medium
surrounding it, the immersion of the powder sample in a medium of nearly
equal index should considerably reduce the parasitic scattering. The technique
of forming pellets of the substance diluted in a solid medium of nearly equal
index as is done for infra-red studies may also be effective in reducing the
parasitic scattering. Finally, the use of particles of colloidal dimensions
should also be helpful in such studies.

We shall, in the following, consider the effects arising from the parasitic
illumination and how the earlier investigators tried to minimize it. The
parasitic scattering besides causing an intense halation close to the exciting
line produces a general fog over the entire region of the photographic plate,
the latter effect arising from the multiple reflections of the light by the optics
within the spectrograph. In addition, the continuous spectrum that is
invariably present even in low pressure arcs is also recorded strongly. As a
result, not only does it become impossible to observe any Raman lines in the
vicinity of the exciting radiation, but also weak Raman lines of even high-
frequency shifts are masked by the general background of illumination.
Apart from all this, the imperfect transparency of the specimens themselves
(resulting from their polycrystalline nature) causes only a very small depth
of the substance to be effectively operative for observing the Raman scattering.

One of the important advances made in the study of the Raman spectra
of crystal powders is due to R. Ananthakrishnan (1937) who developed what
is known as the technique of complementary filters. A concentrated solution
of iodine in carbon tetrachloride was interposed in the path of the incident

radiation to absorb all the visible mercury lines excepting that at $\lambda\,4046$. The scattered light was filtered through a strong solution of sodium nitrite to absorb the exciting radiation $\lambda\,4046$. By this procedure he was able to obtain fairly clear spectra exhibiting the high-frequency Raman lines; however, since the absorption of the $NaNO_2$ solution extended over a finite region on either side of $\lambda\,4046$, the low-frequency lines could not be recorded. A similar technique was also developed by him for use with $\lambda\,4358$ excitation. Another technique used with success was due to Billroth, Kohlrausch and Reitz (1937) who constructed a special spectrograph consisting of two parts, each with a prism and two lenses and with a common slit between them. The light was incident on a plate on which was spread the crystal powder. This plate was set at such an angle so that its position was conjugate to the position of the photographic plate on which the lines were recorded. In effect, the lines of different wavelengths recorded on the photographic plate emanate from different corresponding points on the former plate on which the powder is deposited. By screening off the point on the plate from which the radiations $\lambda\,4358$ emanate, the overexposure arising due to this line was greatly reduced. Apart from such methods, absorption and interference filters have also been used to monochromatize the incident radiation and for removing the continuous background close to the exciting line. P. Krishnamurti (1930) used low-pressure arcs which had only a weak continuum and removed even this by a filter of didymium chloride solution. J. Brandmuller (1953) and M. C. Tobin (1959) have employed interference filters for monochromatizing the incident readiation, as also for suppressing the exciting radiation attendant with the Raman scattering.

Though with the aid of the above techniques it is possible to record the strong lines in the high-frequency region of the spectrum, the recording of the lattice frequencies which are of much interest in the case of studies on crystals is still a difficult problem. This is due to the fact that the absorption characteristics of all known filters extend over a finite range on either side of the exciting radiation that they are intended to suppress. On the other hand, the use of interference filters require that parallel light be employed, with the consequence that the scattered beam that can be brought to a focus on the slit of the spectrograph is of considerably reduced intensity. In addition, the low scattering power in the visible region of the spectrum coupled with the fact that only a small depth of the substance is effectively available for observation of the Raman scattering makes it very difficult to record weak Raman lines. It is in these respects that the technique of excitation of the Raman effect with the $\lambda\,2536\cdot5$ radiation, which we shall discuss in the following section, proves to be advantageous.

3. THE RASETTI TECHNIQUE

The details of this technique which have been fully described in an earlier paper by the author (1957) consist mainly of (i) the use of the intense $\lambda\, 2536 \cdot 5$ resonance radiation emitted by a water-cooled magnet-cotrolled quartz mercury arc and (ii) the suppression of the parasitic illumination of $\lambda\, 2536 \cdot 5$ radiation attendant with the Raman scattering by a filter of mercury vapour inside the spectrograph. The principal advantages in the technique arise from (i) the exceptional intensity of the exciting line compared to the neighbouring lines of the spectrum, (ii) the increased scattering power in the ultraviolet region of the spectrum and (iii) the successful elimination of the exciting radiation from the scattered light, thereby enabling the observation of the lattice lines appearing close to it. The power of the technique can be gauged by comparing the results of two studies by the author (1956, 1957) on magnesite and calcite. Whereas with the former and using the visible radiations of the mercury arc, only five lines could be observed with difficulty, in the latter no less than thirty-three frequency shifts could be clearly recorded. Apart from studies with single crystals, this technique has also been employed by the author (1959) to record the Raman spectra of several solid hydroxides, most of which were available either in the form of polycrystalline masses or as fine powders. It had been noticed that, though the strong Raman lines could be easily recorded, the continuous spectrum accompanying the exciting radiation impedes the observation of weaker Raman lines. Monochromatization of the incident beam, it is hoped, would help in the recording of the weaker lines also.

4. THE PRESENT STUDY: ITS RESULTS AND DISCUSSION

In the present study, we have considered two classes of substances, *viz.*, fine powders and compact polycrystalline solids. While in the former the crystallites are only loosely adherent to each other, in the latter the different microcrystalline domains of the substance are either linked together by atomic and intermolecular forces or held together by a cementing medium to form a compact solid. Besides the general interest attached to studies on the Raman spectra of such materials, there arise the important questions whether their Raman spectra would exhibit any variations depending on the size of the crystallites, and if so how small they have to be before such effects can be observed.

Calcite was chosen as a typical case for the exploratory studies on fine powders since its Raman spectrum is very well known. Two samples of $CaCO_3$ were used to record the spectra. One of them was the readily available commercial powder which contained aragonite as well. The method of

sedimentation was used both to obtain a powder of uniform particle size and also to remove the aragonite—which being denser than calcite settles at a fast rate. The other sample used was calcite precipitated in the cold by the addition of solutions of $CaCl_2$ and K_2CO_3. The powder was deposited thinly on the inside of a glass bulb which had two windows cut out for incident and scattered radiations. The spherical form of the bulb served to effectively utilize the exciting radiation by multiple reflections inside the container. The size of the particles of the powder used to record the spectrum was about $1\,\mu$ and was estimated under a high-power microscope. The spherical bulb was kept jammed against a water-cooled magnet-controlled quartz mercury arc intensely emitting the $\lambda\,2536\cdot5$ resonance radiation and the scattered light was focussed on the slit of the spectrograph by a quartz condenser.

Plate II accompanying this paper reproduces the microphotometer record of the Raman spectrum. The frequency shifts observed therein, viz., 1086, 282 and 155 cm.$^{-1}$ are fairly sharp and are identical with the frequency shifts recorded with large crystals of calcite. The spectrum does not exhibit any alteration either in the frequency shifts or their widths. Besides the above three lines, it should have been possible to record two other weaker lines at 712 and 1436 cm.$^{-1}$ but for the fact of the continuous spectrum of the arc masking them.

As typical cases of polycrystalline solids, we have chosen alabaster wherein the crystallites are randomly orientated, and fascicular or columnar gypsum consisting of crystallites in the form of rods (the b-axes of the crystallites being the axes of the rods) arranged parallel to each other. The X-ray diffraction pattern of the specimen of alabaster used in the present study had been reported earlier by C. V. Raman and A. Jayaraman (1954) and exhibits spotty rings indicating the random orientation of the crystallites in it, the particle sizes being of the order of $10\,\mu$. In the case of fascicular gypsum the rods though of minute dimensions are easily visible. The X-ray diffraction patterns recorded for it show that whereas the b-axes are all parallel to each other, the c and a axes exhibit a limited range of variation. Owing to the low birefringence of gypsum, both the specimens were translucent and their spectra could therefore be recorded without much difficulty. The spectrum of a single crystal of selenite in the form of a rectangular tablet was also recorded for comparison. The exciting radiation was incident on the broad face of the crystal and the scattering observed along an edge (perpendicular to the b-axis). In the case of fascicular gypsum the exciting radiation was incident parallel to the b-axis and the scattering observed perpendicular thereto.

Figures (*b*), (*c*) and (*d*) in Plate I accompanying this paper reproduce the Raman spectra of selenite, fascicular gypsum and alabaster recorded with adequate intensity. Figures (*a*) and (*e*) show the spectrum of the mercury arc for comparison. It is evident that the spectra recorded in the three cases exhibit no differences with regard to either the positions or the widths of the lattice and internal frequency shifts. The only noticeable feature is a variation in the relative intensities of the two intense water-bands ; this feature is a well-known orientational effect arising from the fact of the water molecules in gypsum being arranged in layers perpendicular to the *b*-axis (*vide, e.g.*, Roop Kishore, 1942). Finally, it should be remarked that with the same specimens it would have been impossible to obtain such clear spectra exhibiting the lattice lines with the visible radiations of the mercury arc as exciters of the Raman effect.

That no differences arise from the polycrystalline nature of the solids as well as from the finely divided form of the powders is consistent with the fact that the ranges of interatomic and intermolecular forces in crystals do not extend beyond a few lattice spacings. The individual crystallites in the polycrystalline samples and the fine powder used in the present study are still too large—each containing an enormous number of unit cells, of the order of 10^{10}. Since the number of lattice cells located well within the crystallites is large compared with that of the number of cells near the surface, no significant effects such as an alteration in the value of the frequency shifts, their intensities or widths can be expected to arise.

5. CONCLUDING REMARKS

The present studies have clearly shown that the Rasetti technique can be successfully employed to investigate the Raman spectra of polycrystalline masses and fine powders. However, particularly in the case of fine powders the continuous spectrum in the arc masks the weaker Raman lines. It is hoped that the parasitic illumination can be reduced considerably by the following techniques, *viz.*, (i) monochromatization of the incident beam, (ii) immersion of the powder in a liquid of nearly equal refractive index, (iii) by dilution of the sample in a substance of suitable refractive index and forming tablets of the substance under high pressure and (iv) use of powders of colloidal dimensions and dispersed as in method (ii) or (iii).

6. SUMMARY

The paper discusses the experimental techniques with regard to the recording of the Raman spectra of polycrystalline solids. The present studies on the typical cases of polycrystalline gypsum, and calcite in the form of a finely divided powder show that the Rasetti technique can be successfully employed to obtain clear spectra of such substances and also indicate the scope for further improvements in the techniques. It emerges that the polycrystalline nature of the gypsum and the finely divided form of the powder studied have no observable influence on their spectra.

7. REFERENCES

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