THE SCATTERING OF LIGHT IN CRYSTALS AND THE NATURE OF THEIR VIBRATION SPECTRA

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1. Introduction

IN an essay[1] by the present writer published in February 1922, it was remarked that transparent crystals, such as ice and quartz, when traversed by an intense beam of white light, exhibit an observable blue opalescence due to the diffusion of the incident radiations by the thermally induced fluctuations of density and refractive index in the medium. Six years later,[2] the use of monochromatic light and of spectral analysis in such studies revealed that in the radiations scattered by crystals, there are large and readily observable shifts of frequency. The field of investigation opened up in 1922 was thus vastly enlarged by the discovery of 1928. Since that time, many investigations have been made and much valuable knowledge gathered regarding the scattering of light in crystals and the accompanying changes of frequency.

In any attempt to connect the physical properties of crystals with their ultimate structure, we inevitably come up against the following questions. What is the nature of their vibration spectra, and how are the modes and frequencies of vibration of the atoms in a crystal related to its structure? The answers to these questions are of fundamental importance to the physics of the solid state. The study of the spectral shifts observed in light scattering is the most powerful method available to us for obtaining information concerning these issues. It is the purpose of the present paper to show that a consideration of the facts ascertained by such studies enables us to reach definite conclusions regarding the questions raised above.

2. The Two Types of Light Scattering in Crystals

Spectroscopic studies have shown that the scattering of light in crystals is of two distinct species which differ fundamentally in their observable characters and which correspond respectively to the two phenomena whose existence was recognised in 1922 and in 1928. The first type of light-scattering is an effect primarily of thermal origin: the frequency shifts in it vary with the angle of scattering and are so small that they can only be

61

measured with the most powerful instrumental aids at our disposal. Quantitative studies of this type of scattering have shown that it arises from the presence in the crystal of sound-wave patterns of thermal origin which diffract the light-waves traversing it. In other words, the light-scattering of the first kind is a macroscopic phenomenon which can be explained in purely classical fashion. The second type of light-scattering differs from the first in the magnitude of the frequency shifts which are much larger and correspond to wave-lengths in the infra-red spectrum. From this and the fact that similar effects are also observed with other states of molecular aggregation, viz., gases, liquids and amorphous solids, we infer that the second type of light-scattering, unlike the first, is a molecular phenomenon which is explicable only on quantum-mechanical principles. This conclusion is confirmed by many other facts of observation and especially by the results of comparative studies made with materials in diverse states of molecular aggregation. Such studies enable us to understand how the state of aggregation influences the observed phenomena and assist us in reaching a correct interpretation of the effects observed with crystals.

3. The Elastic Vibrations of Crystalline Solids

The spectral shifts of frequency observed in the scattering of light by gases are of three distinct species and of widely different orders of magnitude which we associate respectively with the three possible kinds of movement of a free molecule, viz., translation, rotation and vibration. Likewise, in the case of crystals, we shall be justified in assuming that the two types of light-scattering actually observed are associated respectively with the two possible kinds of movement of the lattice cells of a crystal, viz., translations and internal vibrations. The translatory movements have no pre-determined frequency of their own, whereas the internal vibrations may clearly be expected to possess characteristic frequencies fixed by the structure of the crystal, viz., by the masses and positions of the atoms and the strength of the interatomic forces. It is thus evident that the two classes of movement differ fundamentally in their nature and they have therefore to be considered separately.

The translatory movements of the lattice cells may properly be identified with the displacements of the volume-elements in the crystal contemplated in the classical theory of elastic wave-propagation in solids. The whole of that theory is based on the assumption that a solid may be subdivided into volume elements small enough to justify their being treated as single particles for the evaluation of their kinetic energy and yet large enough for the potential energy of deformation to be evaluated on the same basis as

for a solid of macroscopic dimensions. The assumption is a justifiable approximation, provided the wave-length of the elastic vibration is large compared with the lattice spacings of the crystal and its frequency is small in comparison with the characteristic frequencies of its structure. But as we go down in the scale of wave-lengths or go up in the scale of frequencies, we would inevitably reach and pass the limits beyond which these are no longer valid assumptions. It follows that the ideas and methods of the classical theory of elasticity are limited in their application to the movements in the lower ranges of frequency where the elastic displacements may properly be identified with translatory movements of the lattice cells of the crystal, and only infinitesimal alterations in the interatomic distances are involved. The situation is entirely different in the second class of movements, *viz.*, the internal vibrations of the lattice cells which we now proceed to consider.

4. The Characteristic Vibrations of Crystal Structures

The vibrations of a free polyatomic molecule and the internal vibrations in the lattice cells of a crystal differ in so far as that in the latter case, the interactions between each unit of the structure and those surrounding it have to be considered. The results of such interaction can be foreseen by considering the simple example of two pendulums of equal length suspended from a common support. The yielding of the support and the consequent coupling of the pendulums results in the system having two different periods of oscillation instead of one; the oscillations of the two pendulums have equal amplitudes in both cases, but their phases are the same in one case and opposite in the other. In a paper published eight years ago in these *Proceedings*,[3] the writer gave a formal proof of the following theorem which is the generalised three-dimensional analogue of the theory of coupled oscillators. *In the normal modes of vibration of the structure of a crystal, equivalent atoms in adjacent cells have the same amplitude of vibration, while their phases are either the same or else opposite in successive cells of the lattice along each of its three axes.* An easy verification of this theorem is furnished by considering the effect of giving the crystal a unit displacement along any one of the three axes of the lattice. Such displacement brings the atoms in a cell into the positions previously occupied by the equivalent atoms in an adjacent cell: since the normal mode is a characteristic property of the crystal structure, we should expect it to remain unaltered following the unit translation, and it is readily seen that this is so in all the cases covered by the theorem and *in no others*. In other words, the theorem provides us with a means of completely enumerating the possible normal modes of vibration of the structure of the crystal.

Since the phases of the vibration of equivalent atoms in adjacent cells may be either the same or opposite along each of the three axes of the lattice structure, we have $2 \times 2 \times 2$ or 8 distinct situations regarding the relative phases of the vibrations in a unit cell and in those surrounding it. Thus, when we proceed to write down the $3p$ equations of motion of the p atoms in a unit cell, taking into account the interactions with the atoms in surrounding cells, we have to consider 8 different sets of $3p$ equations, each of which contains $3p$ variables. Accordingly, we obtain $24p$ solutions in all. This total number may be subdivided as follows: $(3p - 3)$ solutions represent normal modes of vibration in which the phases are the same in adjacent cells of the structure; $21p$ solutions represent normal modes in which the phases of vibration are opposite in adjacent cells along one, two or all three of the axes of the lattice; and finally a residue of 3 solutions which represents the three excluded translations. An element of volume whose dimensions are twice as large and whose content is therefore 8 times as great as for a unit cell of the crystal, would contain $8p$ atoms whose total degrees of freedom would number $24p$. The $(24p - 3)$ normal modes of vibration indicated by the theory may therefore be regarded as the modes of internal vibration of the atoms included in this 8-cell unit, and the 3 excluded solutions as the three translations of such unit.

5. THE NATURE OF THE VIBRATION SPECTRUM

The results of the two preceding sections may be summed up by the statement that the character of the vibration spectrum is totally different in the two regions of it arising respectively from the translations and vibrations of the lattice cells of the crystal. The translatory movements give us a continuous spectrum of elastic vibrations lying in the lower range of frequencies, while the vibratory movements give us a line-spectrum which is characteristic for the crystal and appears in the upper or infra-red range of frequencies. The total degrees of freedom of atomic movement in the crystal are divided between the two species of vibration in the proportion of $(24p - 3):3$. Thus, even in crystals with the simplest structures for which $p = 1$, only one-eighth of the total degrees of freedom appears as vibrations of the elastic solid type. For crystals with more complex structures for which $p = 2$ or 3 or any larger number, the proportion is correspondingly smaller and the vast majority of the degrees of freedom appear as the characteristic modes of vibration of the crystal structure.

The foregoing results enable us without further explanation to understand the phenomena exhibited by crystals in light-scattering. It is known that the frequency shifts exhibited by crystals appear, in general, as sharply

defined lines. They evidently owe their origin to the activity in light-scattering of one or more of the $(3p - 3)$ characteristic modes of vibration in which the phase is the same in adjacent cells: the remaining $21p$ modes are necessarily inactive, since their vibrations alternate in phase along one or more of the axes of the lattice. The number of frequency shifts actually observed in any case may be fewer than $(3p - 3)$. For, as a consequence of the symmetry properties of the crystal, some of the $(3p - 3)$ modes may have the same frequency and the number of distinct frequencies would thereby be reduced. Again, some of the $(3p - 3)$ modes might be inactive by reason of their being of an antisymmetric type.

The continuous spectrum of elastic vibrations would necessarily be inactive in light-scattering, since the phase alternates in successive cells of the stationary wave-pattern. An exception, however, arises when the separation between the nodal planes of the pattern is so related to the wavelength of the light traversing the crystal and the angle of incidence on the nodal planes that there is a coherent reflection of the incident light waves by the elastic wave pattern. Such a reflection would exhibit frequency shifts, both positive and negative, the magnitude of which depends on the angle of scattering, as is actually observed.

6. OVERTONES AND COMBINATIONS

The so-called second-order spectra of light-scattering are very feeble and can only be recorded under intense excitation. They appear when the amplitudes of atomic vibration in any particular mode or modes are finite in comparison with the interatomic distances. For, in such a case, the anharmonicity of the optical polarisability would result in the scattered radiations including spectral components whose frequency shifts are overtones and summations of the vibration frequencies of the modes under consideration.

It is evident that the thermally excited vibrations of the elastic solid type would be incapable of giving any observable second-order effects. For, the energy of any such vibration having a specified frequency would be distributed over the volume of the crystal and the amplitudes of vibration could, therefore, only be infinitesimal. The interatomic displacements associated with the translatory movements would be of a still smaller order of magnitude. Hence, the local variations in optical polarisability associated with the elastic vibration of any particular frequency would be excessively small, and since they vary in phase from point to point within the crystal, their external effects would cancel out completely. In other

words, the elastic vibrations of all frequencies are inactive in light-scattering not merely in the first approximation, but absolutely, except in the particular case of a coherent reflection already referred to. Even in this case, there could be a first-order effect but none of higher order.

The situation is altogether different in the case of the characteristic vibrations whose frequencies lie in the infra-red range. The excitation of these vibrations is a quantum-mechanical effect, and the energy of excitation would necessarily be localised in the element of volume under consideration, viz., a group of lattice cells whose linear dimensions are of the same order of magnitude as the range of the intermolecular forces. A quantum of vibrational energy when distributed over such a small volume would result in atomic movements of finite amplitudes and hence, as the result of optical anharmonicity, give rise to scattered radiations with overtones or summational frequency-shifts.

The second-order spectra arising in the manner explained could include overtones and summations of the frequencies of all the $(24p - 3)$ modes and not merely of those modes which are active in the first order. The $21p$ modes which are inactive in the first approximation may thus become accessible to observation, though only as overtones or summations. The second-order spectrum of light-scattering would necessarily be a line spectrum. But as the overtones and summations would be numerous, it would be a crowded spectrum, and further crowding up may arise from subsidiary effects, such as a splitting up of individual overtones or summations into several distinct components as the result of mechanical anharmonicity and removal of degeneracy. We cannot, therefore, expect the line character of the second-order spectrum to be quite so obvious to inspection in all cases as with the spectrum of the first order.

7. The Theoretical Conclusions

We may now sum up the conclusions reached in the preceding sections.

I. The frequencies of characteristic vibration of the structure of a crystal constitute a line spectrum. This is accompanied by a continuous spectrum of elastic vibrations in the lower ranges of frequency. Only 3 out of every $24p$ degrees of freedom appear in the latter.

II. The $(3p - 3)$ characteristic modes in which the phase of the vibration is the same in adjoining cells of the structure may appear as frequency shifts in light-scattering: the $21p$ modes in which the phase alternates along one, two or all the three axes of the lattice are inactive,

III. Overtones and summations of the frequencies of all the $(24p - 3)$ modes are, however, allowed as frequency shifts in light-scattering.

IV. The continuous spectrum of elastic vibrations is inactive in light-scattering except in the particular case of a coherent reflection of the light-waves by the elastic wave-patterns. Overtones and summations of their frequencies are totally forbidden.

8. Some Illustrative Examples

(i) *Diamond* (Fig. 5 in Plate V and Figs. 6 and 7 in Plate VI).—The simplicity of the structure of diamond and its cubic symmetry enable its characteristic modes of vibration to be completely described and their frequencies to be evaluated by a rigorous procedure. The $(24p-3)$ or 45 modes possible give only 8 distinct frequencies. Expressed in wave-numbers, they are, 1332 (3), 1250 (8), 1232 (6), 1149 (4), 1088 (6), 1008 (4), 752 (6) and 620 (8), the numbers enclosed in brackets being their respective degeneracies. The first or triply degenerate mode represents an oscillation having the same phase in adjacent cells of the lattice, while the others are modes in which the motion alternates in phase in successive cells. The three elastic constants of diamond can also be computed theoretically from the same set of force-constants as the characteristic vibration-frequencies and used to evaluate the distribution of frequency in the continuous spectrum of elastic vibrations. Thus, all the data necessary are forthcoming for an independent calculation of the specific heats of diamond. A satisfactory agreement is found between the calculated and observed elastic constants, as also between the calculated and observed specific heats over the whole range of temperature for which data are available.

That diamond exhibits a single sharp and intense line with a frequency shift of 1332 cm.$^{-1}$ in light-scattering was discovered by C. Ramaswamy in the year 1930. More recent investigations by R. S. Krishnan revealed the second-order spectrum with all the features predicted by the theory. Like-wise, it was shown by him that the continuous spectrum of elastic vibrations is completely inactive in light-scattering except in the particular case of a coherent reflection of the incident light-waves by the elastic wave-pattern.

The case of diamond thus affords a complete quantitative verification of the theoretical conclusions set forth above. The reader is referred to recent papers by P. S. Narayanan[4] and D. Krishnamurti[5, 6] in these *Proceedings* for further details of the case and for literature citations.

(ii) α-*Quartz* [Figs. 8 (*a*) to (*d*) in Plate VII].—The three atoms of silicon and six of oxygen in each unit cell of the structure of quartz give us

$(3p - 3)$ or 24 modes of vibration having identical phases in adjoining cells. The trigonal symmetry reduces this number to 16 distinct frequencies and renders 4 of them inactive in light-scattering. Thus, only 12 frequency shifts are to be expected in the first-order spectrum. This is the number actually recorded in moderately exposed spectrograms, provided two rather close doublets actually observed are counted as single lines. If all the $(24p - 3)$ or 213 fundamental frequencies of vibration of the structure could give octaves and summations with observable intensity, the second-order spectrum would obviously be very complex and difficult to decipher. Actually, by giving exposures about a hundred times greater than that necessary to record the first-order spectrum, R. S. Krishnan[7] obtained spectrograms which revealed 29 frequency shifts of the second-order. Only 17 of these could be explained as octaves and summations of the $(3p - 3)$ modes, and the remaining 12 therefore presumably represent the strongest amongst the numerous others which are theoretically possible.

(iii) *Calcite and Aragonite* [Fig. 9 (*a*) and (*b*) in Plate VII].—Since there are two $CaCO_3$ groups in each unit cell of the calcite structure, the $(3p - 3)$ characteristic modes of vibration in which the phase is the same in adjacent cell number 27 in all. The trigonal symmetry of the crystal reduces the number of distinct frequencies to 18, of which no less than 13 are inactive in light-scattering, leaving us with only 5 distinct frequency shifts to be expected in the first-order spectrum. Exposures about 500 times more prolonged than that sufficient to exhibit the first-order frequency shifts enabled R. S. Krishnan[8] to record 11 additional frequency shifts which could all be explained as overtones and combinations of the $(3p - 3)$ characteristic frequencies of the structure.

Likewise, in the case of aragonite, R. S. Krishnan[9] obtained spectrograms exhibiting 25 frequency-shifts, 19 of which were fundamental frequencies and 6 belonged to the second-order spectrum.

(iv) *Barytes and Gypsum* [Fig. 10 (*a*), (*b*), (*c*), (*d*) in Plate VIII].— Strongly exposed spectrograms obtained with a large clear block of barytes and a high-speed instrument enabled R. S. Krishnan[10] to record no fewer than 39 frequency shifts with this crystal. 20 of these which were sufficiently intense to appear on spectrograms obtained with a much slower instrument were interpreted as first-order frequencies, and the remaining 19 (with one exception) as octaves and summations of them.

Likewise, in the case of gypsum,[11] 34 frequency shifts were recorded of which 29 were identified as belobging to the first-order spectrum and 5 as octaves and summational frequencies.

(v) *The Alkali Halides* [Fig. 11 (a) and (b) in Plate VIII].—By reason of the cubic symmetry of the structure of rock-salt, the $(24p - 3)$ or 45 possible modes of its vibration give only 9 distinct frequencies. As each metallic ion is surrounded symmetrically by six halogen ions and *vice-versa*, the triply-degenerate oscillation of the two sets of atoms against each other is inactive and there is, therefore, no first-order spectrum of light-scattering. The total number of octaves and summations which could appear in the second-order spectrum is 45, and since the fundamental frequencies are themselves degenerate in different degrees, mechanical anharmonicity would result in the splitting up of the summational frequencies into several distinct components. Hence, the second-order spectrum of the alkali halides would necessarily be rather complex, and the difficulty of exhibiting its discreteness or line-character would be enhanced by the fact that the entire spectrum falls within a range of 350 wave-numbers in the case of rock-salt and of 300 wave-numbers in the case of potassium bromide. Even so, the fact that some of the lines are much more intense than the rest, *e.g.*, 235 cm.$^{-1}$ in the case of rock-salt, makes the true nature of the spectrum evident to inspection, and it becomes even clearer when the spectrograms recorded by R. S. Krishnan[12] with instruments of lower and higher dispersing powers are compared with each other.

9. Descriptive Notes on the Spectrograms

The majority of the spectrograms illustrating this paper were obtained by Dr. R. S. Krishnan in the investigations already referred to. A few are by other authors (T. M. K. Nedungadi, P. S. Narayanan, M. M. Patel, V. M. Padmanabhan and Roop Kishore). All except those in Plate III were obtained with the intense excitation provided by the $\lambda 2537$ radiations of a water-cooled magnet-controlled mercury arc in quartz. The spectrograms have been reproduced as negatives for the sake of clarity.

Plate III, Figs. 1 *and* 2.—The spectrograms of naphthalene (crystal), benzophenone (both as liquid and as crystal) and of methyl methacrylate (glass) appearing in these figures illustrate the close similarity of the spectroscopic behaviour of liquids, amorphous solids and crystals in the region of higher frequencies. In all these cases, the larger frequency shifts are seen as sharp lines.

Plate IV, Figs. 3 *and* 4.—This series of six spectrograms illustrates the sharpness of the spectral shifts given with crystals and the increase in their number with increasing complexity of crystal structure. Fluorite gives only one frequency shift, while alumina gives 7, beryllium silicate 25, topaz 32,

Rochelle-salt 49, and cane-sugar 63 distinct frequency shifts. The mercury lines have been marked off with the symbol λ in the spectrograms to distinguish them from the frequency shifts given by the crystal.

Plate V, Fig. 5 and Plate VI, Figs. 6 and 7.—These illustrate the case of diamond. The development of a second-order spectrum in the region of frequency shifts between 2666 and 2176 with increasing exposures and its absence in the region of the elastic wave-spectrum even in heavily exposed spectrograms will be seen from Fig. 5 (*a*), (*b*) and (*c*). The microphotometer record in Fig. 6 and the high-resolution spectrograms in Fig. 7 exhibit very clearly the sharp lines with frequency shifts 2666, 2440–70 and 2176 which are the octaves of the fundamental frequencies 1332, 1232 and 1088 respectively.

Plate VII, Fig. 8.—This series of four spectrograms illustrates the development of the second-order spectrum of quartz with increasing exposures.

Plate VII, Figs. 9 (a) and (b).—These illustrate respectively the spectra of aragonite and calcite which are seen to be strikingly different. Some of the sharply defined lines appearing in the second-order spectrum of calcite are marked in Fig. 9 (*b*).

Plate VIII, Fig. 10 (c) and (d) illustrate strongly exposed spectra of barytes. Its second-order spectrum is clearly seen in both figures, but better in the more heavily exposed spectrogram.

Plate VIII, Figs. 11 (a) and (b).—Note the sharply-defined line with a frequency shift 235 seen in the second-order spectrum of rock-salt and the intense line with the frequency shift 126 in that of potassium bromide.

10. SUMMARY

The facts of light-scattering in crystals are reviewed and the nature of the atomic movements and the character of their vibration spectra in the different frequency regions are deduced therefrom. Whereas the movements based on the translations of the lattice cells result in elastic wave motions in the solid with a continuous frequency spectrum, the modes based on their internal vibrations are localised and have monochromatic frequencies analogous to those of polyatomic molecules. The total degrees of atomic freedom are shared between the latter and the former in the ratio $(24p - 3):3$. The frequency shifts ordinarily observed in light-scattering arise from the group of $(3p - 3)$ modes in which the phase of the vibration is the same in adjacent cells of the lattice. But these as well as the $21p$ additional modes in which the phase alternates along the axes can give rise to shifts which are overtones and summations of their fundamental frequencies.
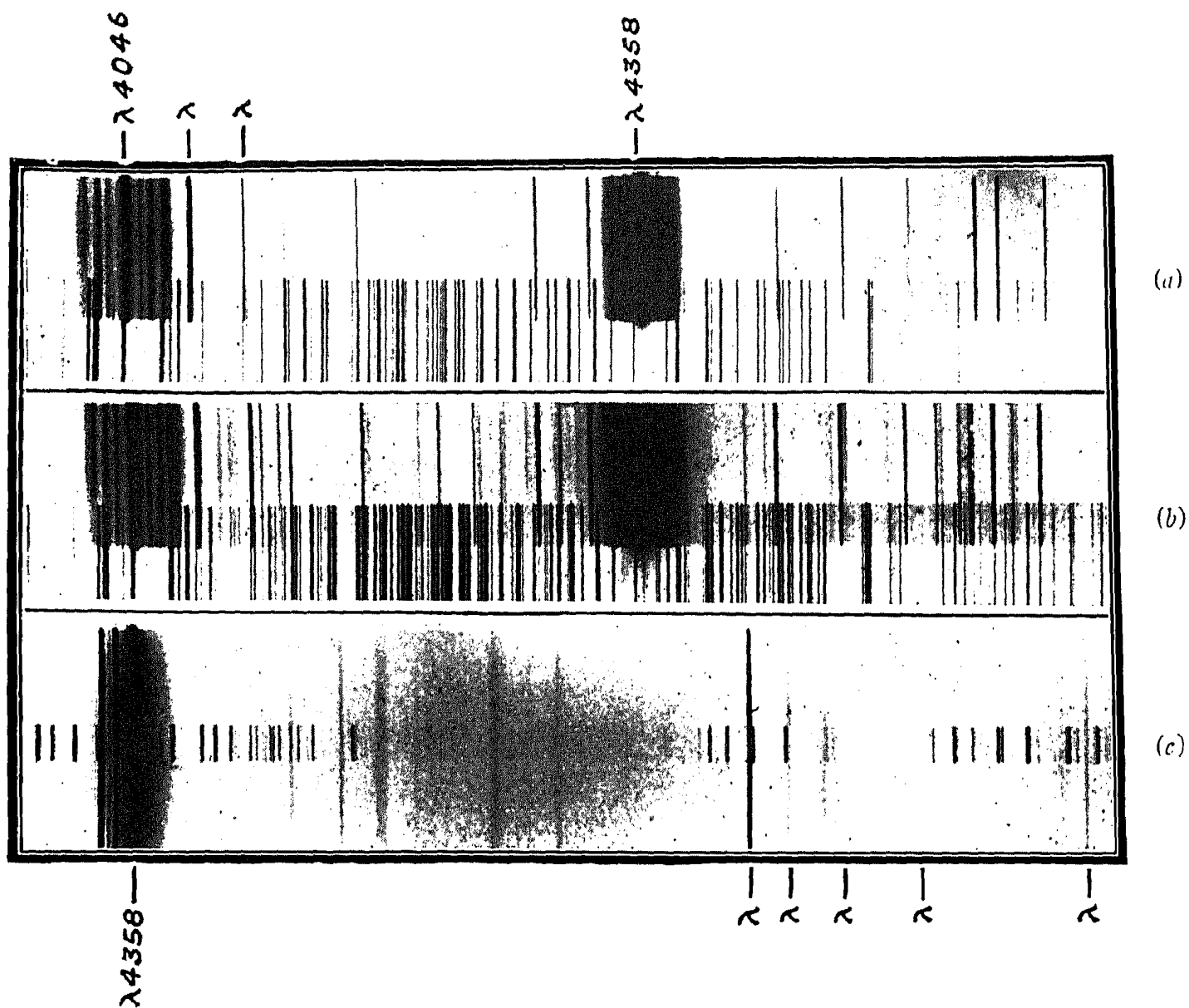
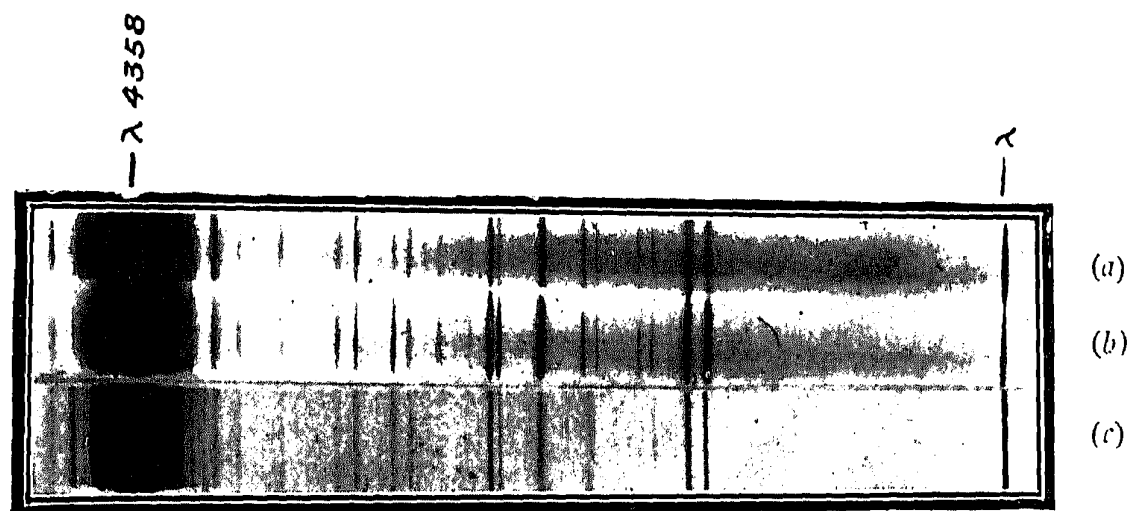Fɪɢ. 1.   (*a*) and (*b*): Naphthalene Crystals.   (*c*): Methyl Methacrylate Glass

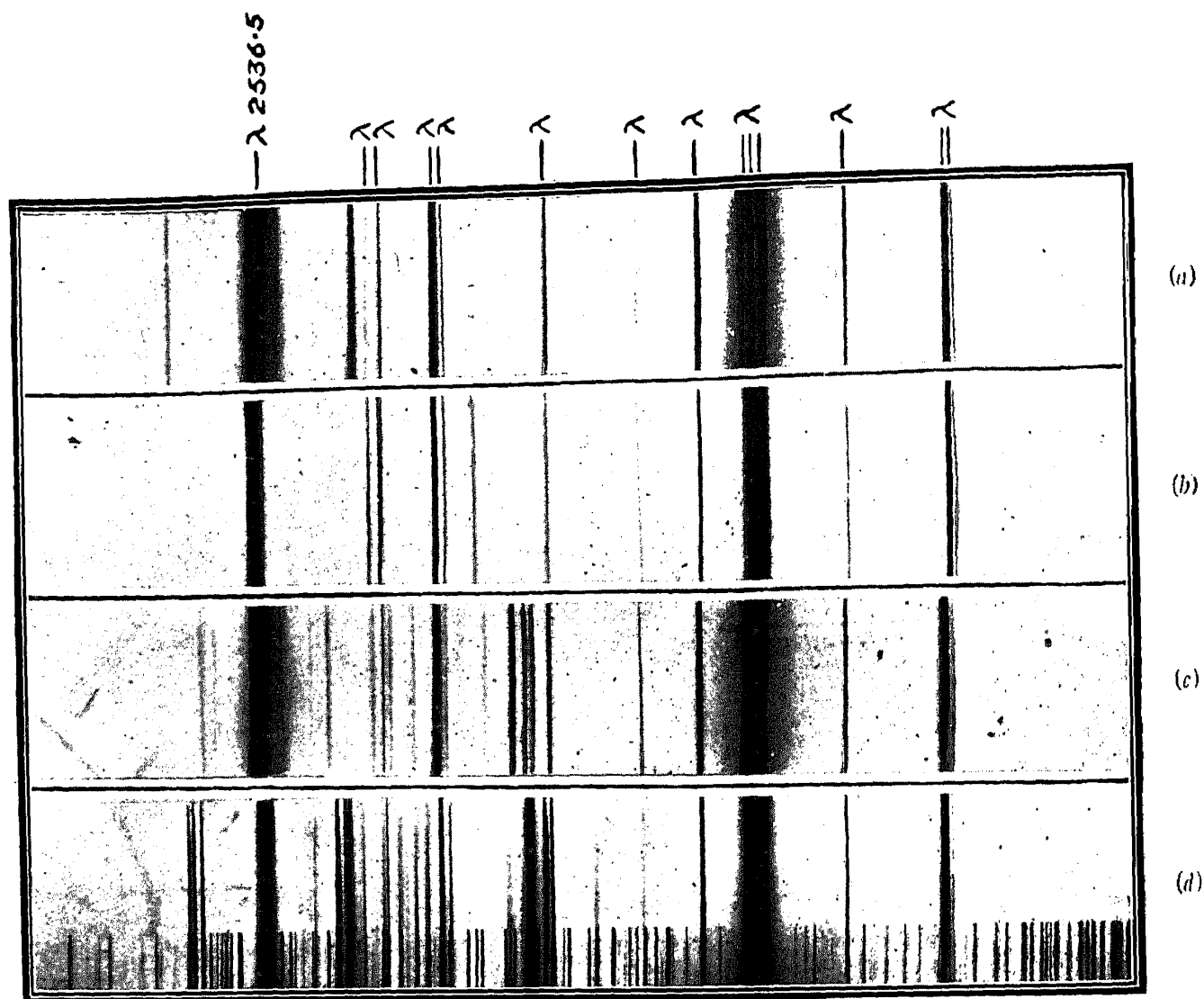Fɪɢ. 2.   (*a*) and (*b*): Benzophenone Liquid.   (*c*): Benzophenone Crystal

Sir C. V. Raman

Proc. Ind. Acad. Sci., A, vol XXXIV, Pl. IV

FIG. 3. (a) Fluorite. (b) Alumina. (c) Beryllium Silicate. (d) Topaz.
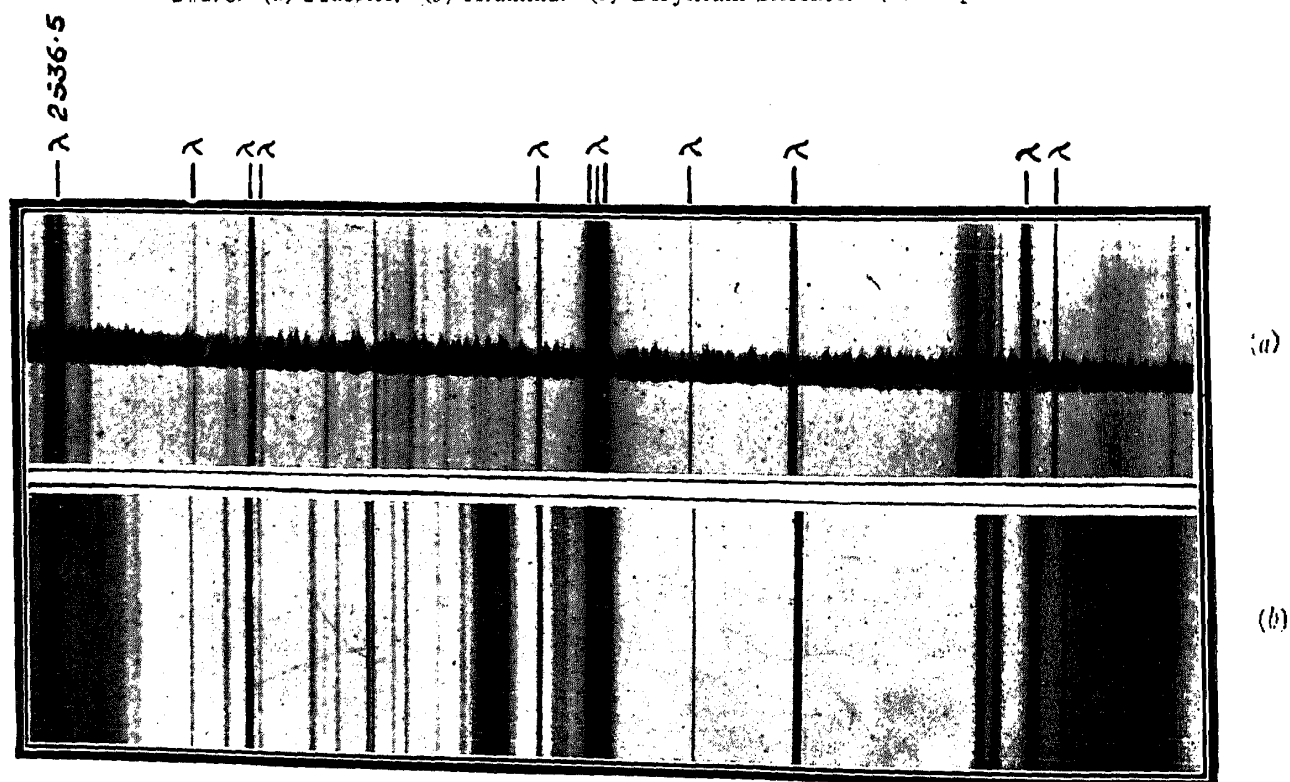
FIG. 4. (a) Cane-Sugar. (b) Rochelle Salt.

$-\lambda 2536\ 5$

$- 1332$
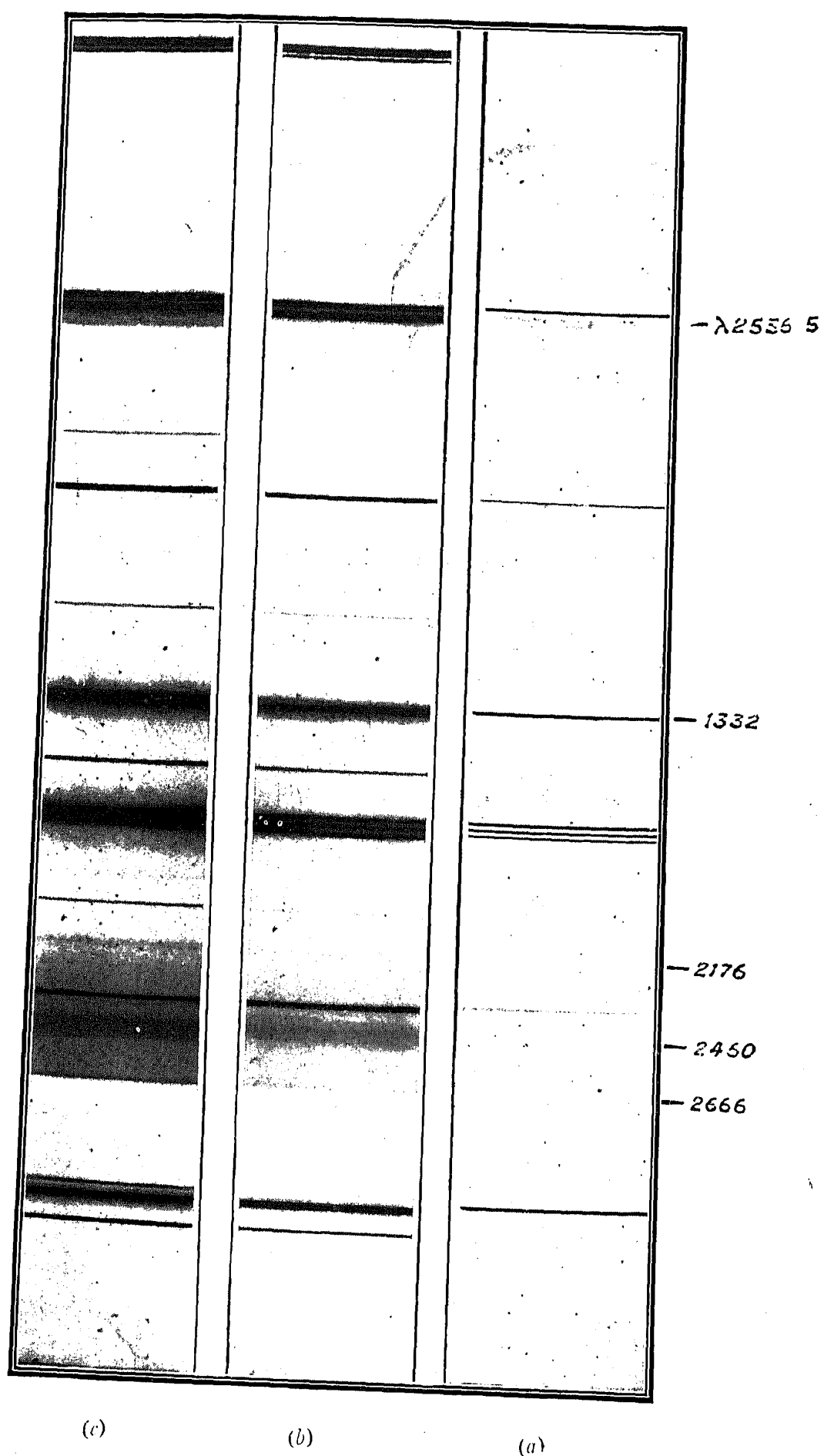
$- 2176$

$- 2450$

$- 2666$

(c)   (b)   (a)

FIG. 5. Diamond (iMedum Spectrograph) (a), (b), (c) with increasing exposures
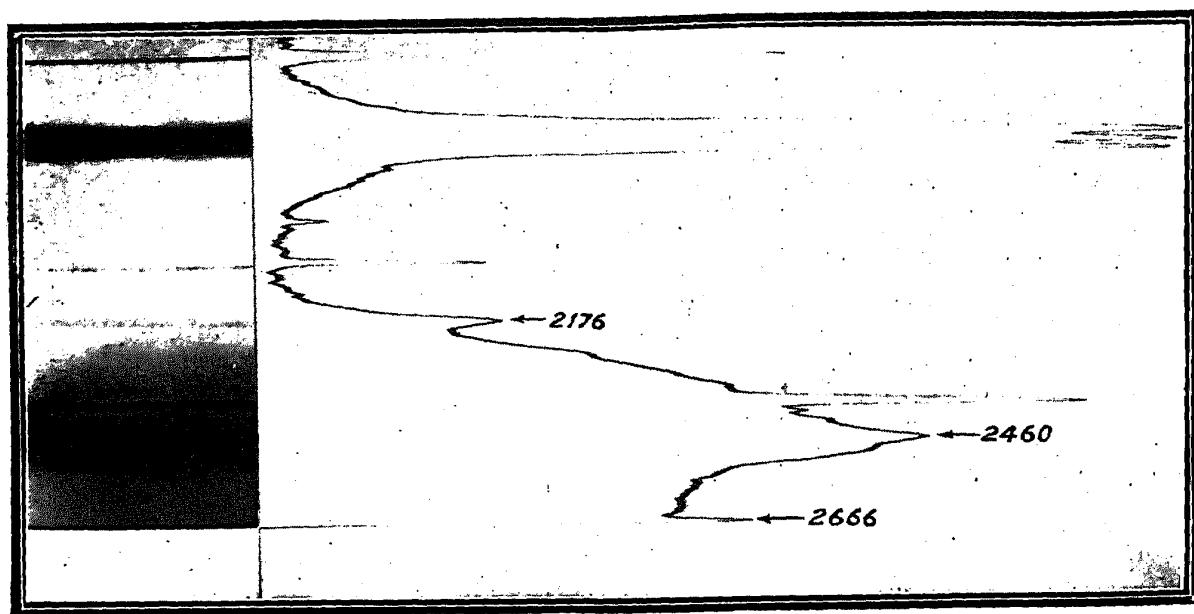
FIG. 6.   Diamond (Medium Spectrograph)

(d)   (c)   (b)   (a)
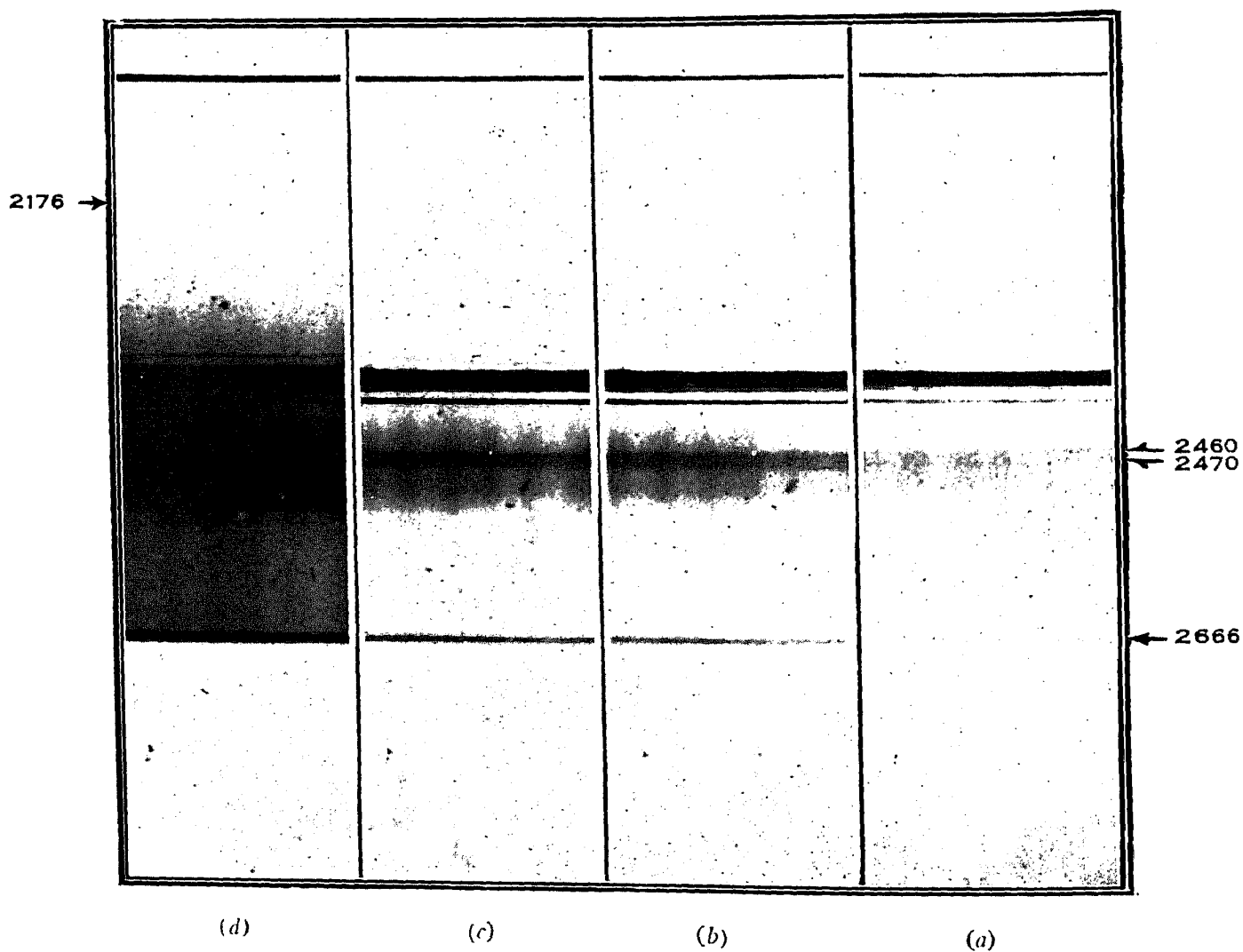
FIG. 7.   Diamond (Large Spectrograph) (a), (b), (c), (d) with increasing exposures
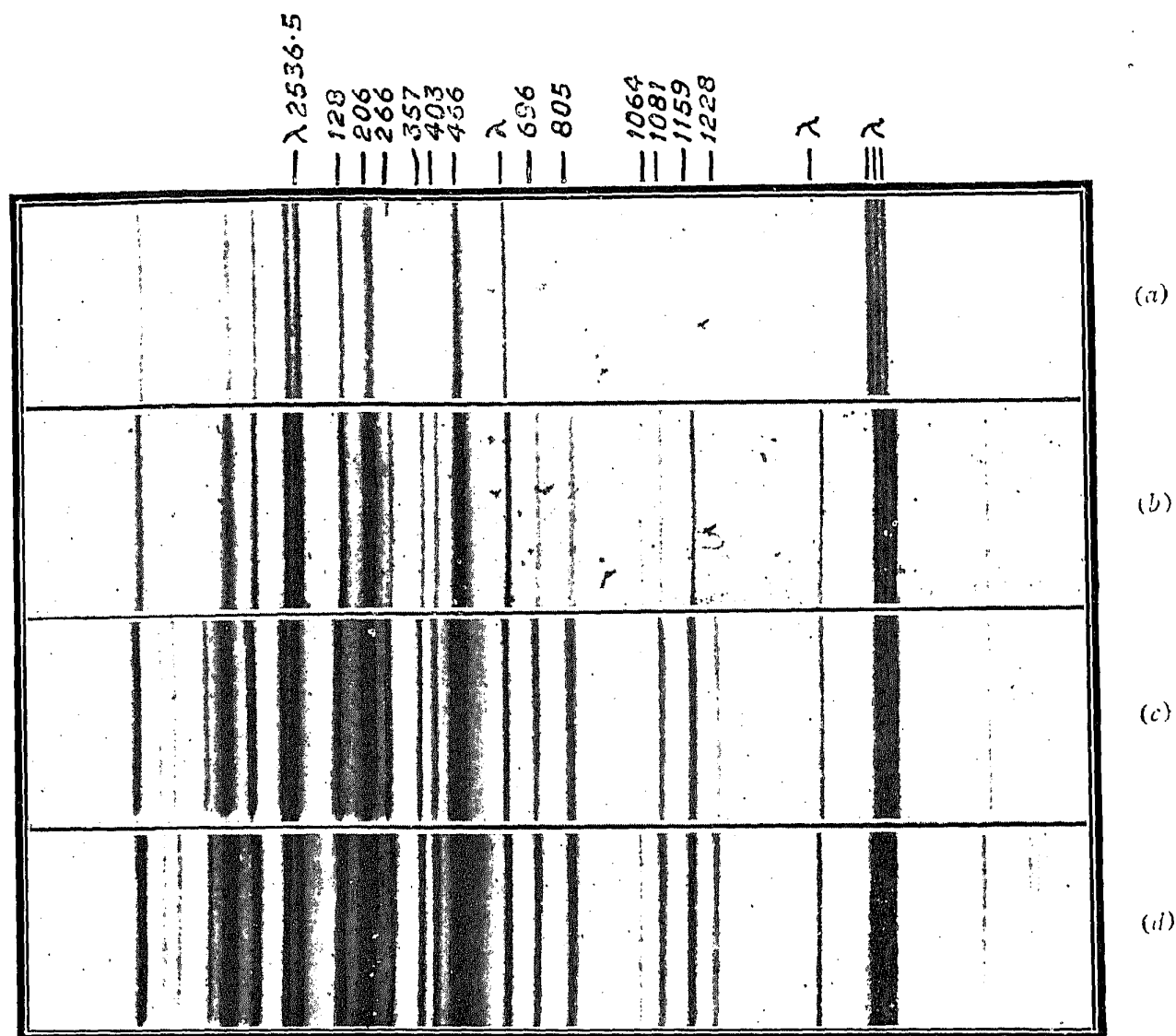
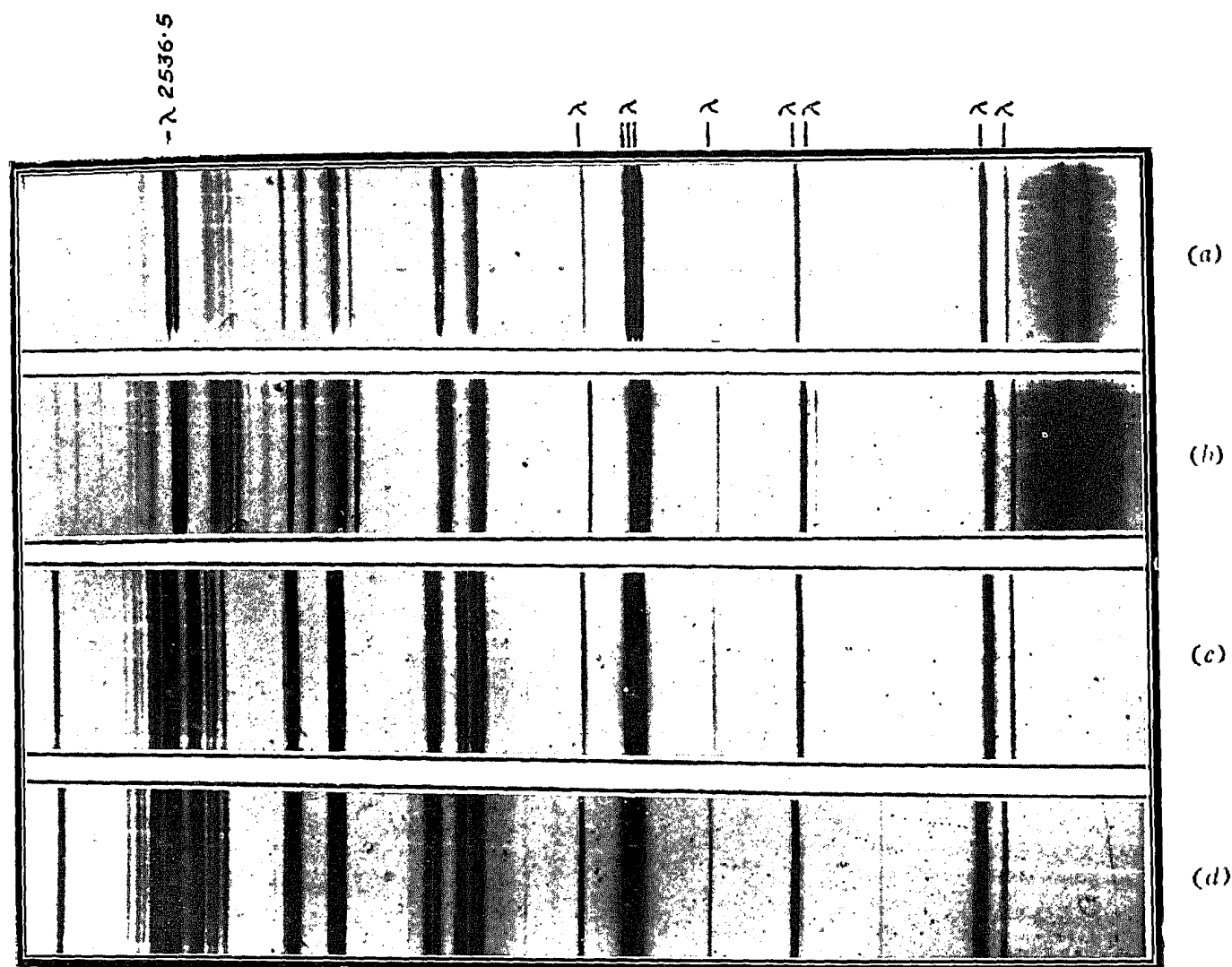FIG. 8. Quartz: a), (b), (c), (d) with increasing exposures
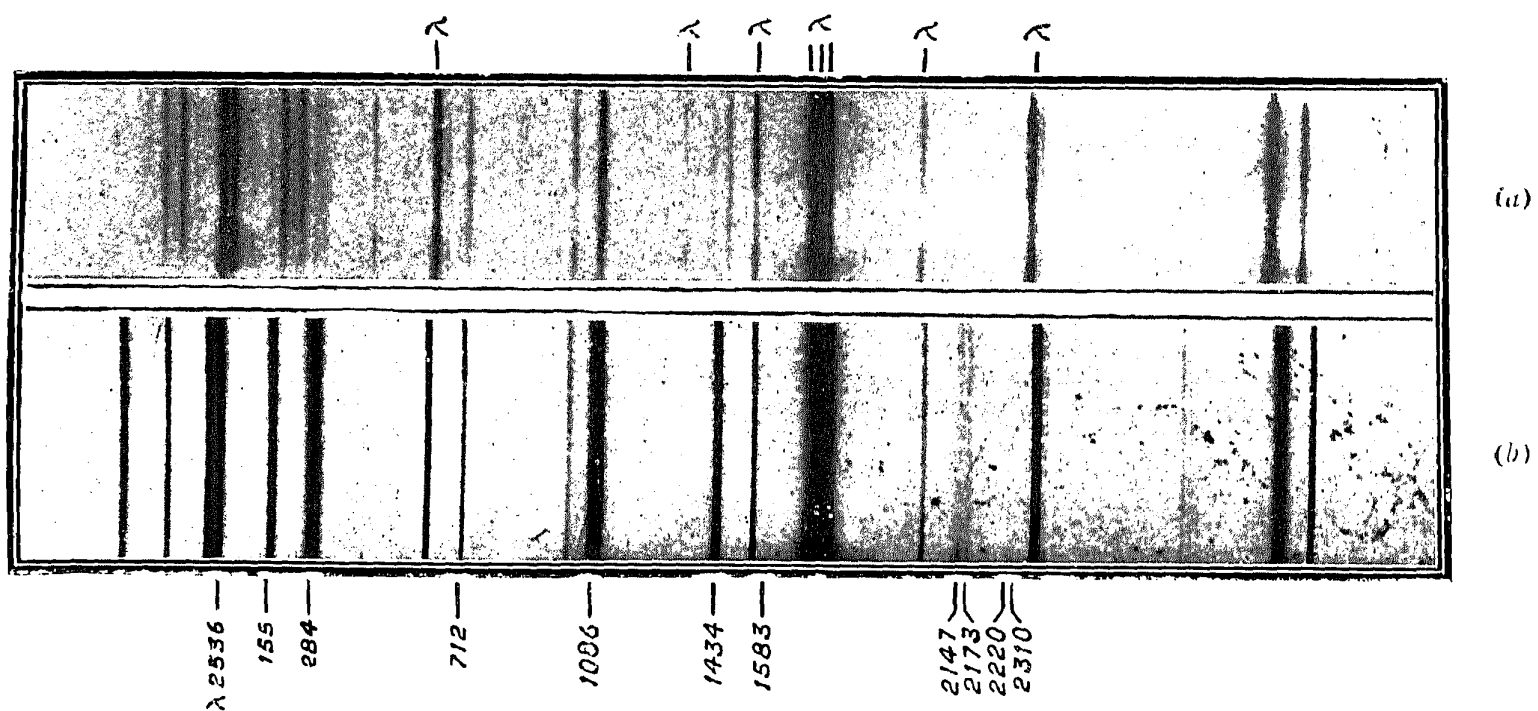
FIG. 9. (a), Aragonite. (b) Calcite

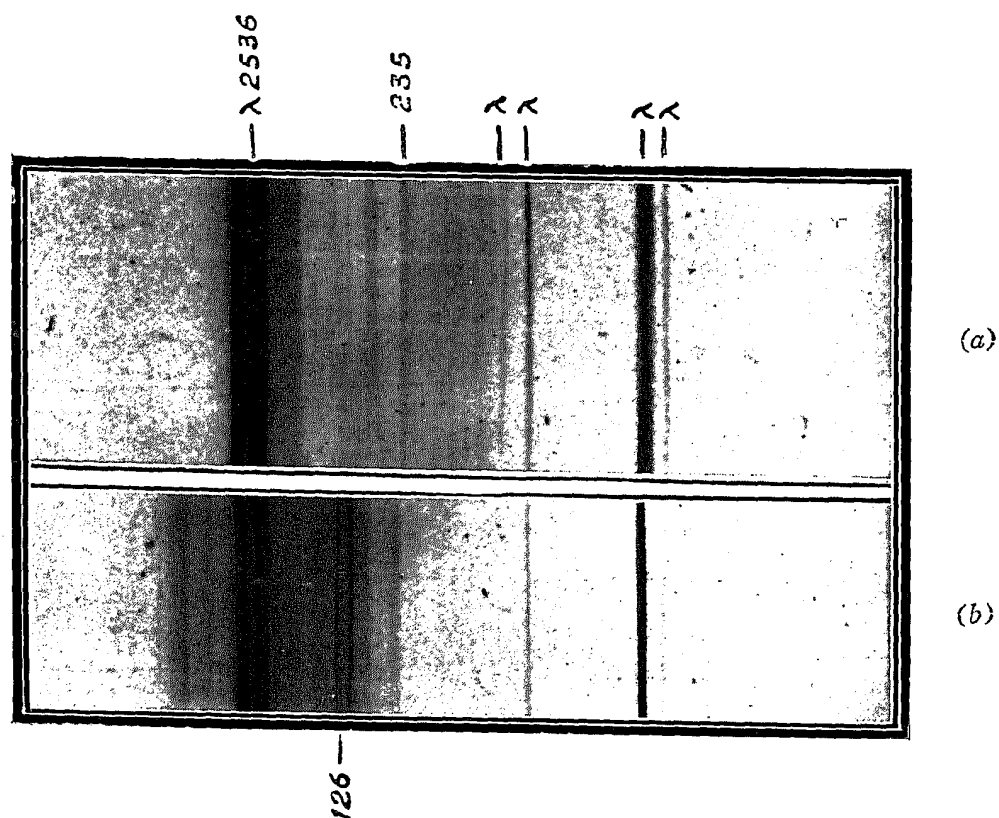Fɪɢ. 10.　(*a*) and (*b*) Gypsum, (*c*) and (*d*) Barytes, with two different exposures in each case

Fɪɢ. 11.　(*a*) Rock-salt; (*b*) Potassium Bromide

The localisation of the internal vibrations permits of these overtones and summations appearing as frequency shifts with observable intensity. On the other hand, the continuous spectrum of elastic vibrations is completely inactive in light-scattering, apart from the particular case of a coherent reflection of the light waves by the elastic wave pattern.

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7. Krishnan, R. S.   ..   *Ibid.*, 1945, **22**, 329.

8. ——————   ..   *Ibid.*, 1945, **22**, 182.

9. ——————   ..   *Ibid.*, 1950, **31**, 435.

10. ——————   ..   *Ibid.*, 1946, **23**, 288.

11. ——————   ..   *Ibid.*, 1945, **22**, 274.

12. ——————   ..   *Ibid.*, 1947, **26**, 419.