Proc. Indian Acad. Sci. **A55** 1–4 (1962)

The infra-red absorption by diamond and its significance—Part I. Materials and methods

SIR C V RAMAN
Memoir No. 129 of the Raman Research Institute, Bangalore-6

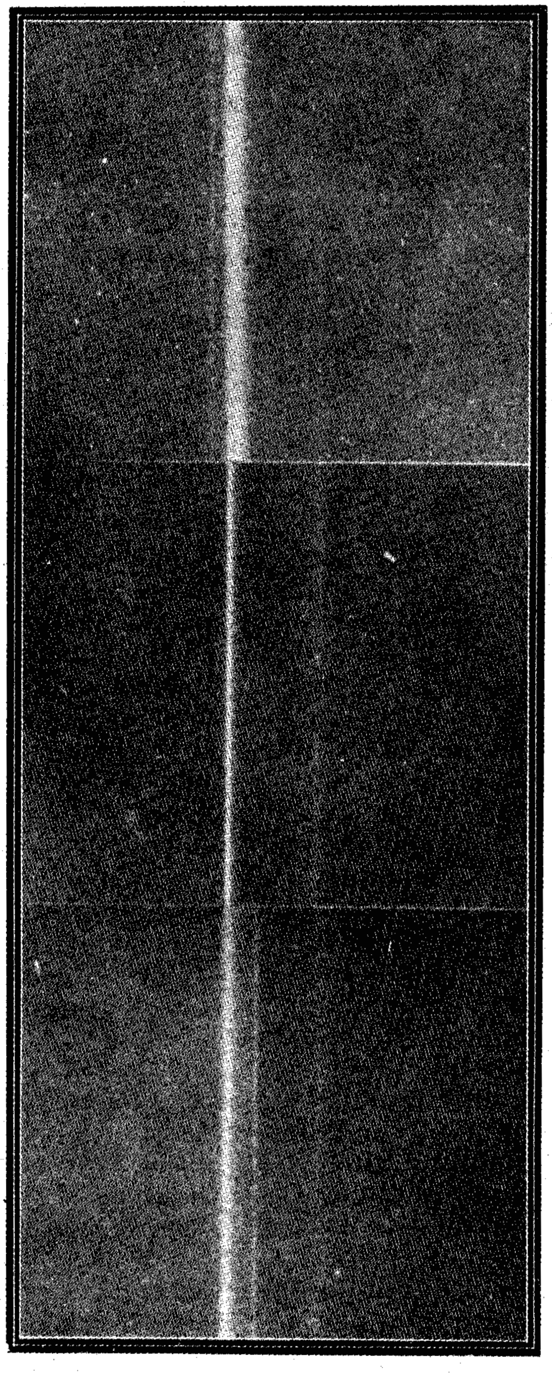
Received November 11, 1961

1. Introduction

Diamond is a material of extraordinary interest and importance. Both by reason of the simplicity of its structure and composition and by reason of the variety of techniques available for the investigation of its spectroscopic behaviour, the study of diamond offers a most promising approach to the elucidation of the fundamental aspects of crystal physics. Questions such as the following need an answer. What is the nature of the atomic vibration spectrum of a crystalline solid and how is it related to its structure? Why does the passage of light through a crystal result in its diffusion with a change of frequency? In what circumstances and in what manner does the absorption of infra-red radiation occur in its passage through a crystal? How are the spectroscopic properties of a crystal related to its thermal energy content? Answers to these and many other questions are furnished by the facts which emerge from a study of the spectroscopic behaviour of diamond.

A remarkable property of diamond is that even selected material of the highest quality shows an astonishing variation of behaviour in certain respects, including especially its transparency to ultra-violet light and to infra-red radiation. Specially noteworthy also are the enormous variations observed in the intensity and spectral character of the visible luminescence exhibited by diamond under ultra-violet illumination. The explanation of these and other variations and the correlations which exist between them is an important part of the field of research presented by diamond and adds greatly to the interest of the subject. But in recognising this, one should not overlook the importance of finding answers to the fundamental questions which arise in respect of all diamonds. Indeed, not unless the more general questions have been satisfactorily answered can we hope to give the correct replies to the question why particular diamonds differ amongst themselves.

The morphology, structure and properties of diamond have interested the writer and have been the subject of numerous investigations and published



(a)

(b)

(c)

Figure 1. For explanation, see text.

Plate X

reports by him and his collaborators in earlier years. To enable these studies to be undertaken, specimens were acquired from time to time and the collection thus built up now includes some hundreds of diamonds of varied origins and of diverse forms and qualities. Crystals of diamond in their natural forms as found near Panna in Central India and from the South African mines form the most attractive items in the collection. But by far the most useful specimens included in the collection are the flat polished plates, one hundred in number, which are of diverse thicknesses and sizes and exhibit varied types of behaviour. There is no more convenient form of diamond for examining its optical properties than a flat polished plate, especially if its faces have a known crystallographic orientation, as is frequently the case for the plates in the writer's collection. It is obvious that for a real understanding of the problems presented by diamond, it is necessary to study such an extensive range of material and to examine the individual diamonds in detail in respect of diverse properties, and then to compare and correlate the results thus obtained. One of the most surprising facts about diamond is the existence of the correlations which come into evidence in an extremely striking and convincing fashion in such studies. That they must be recognised and need to be explained is obvious. But more important still is the fact that they point the way to a real understanding of the nature and properties of diamond.

2. Methods of study

It had long been the desire of the writer personally to study the infra-red behaviour of the entire collection of plates of diamond in his collection. But only recently however has the acquisition for this Institute of a Leitz recording infra-red spectrophotometer provided with both NaCl and KBr optics enabled this project to be seriously undertaken. The region of wavelengths between 1 μ and 15 μ can be traversed with the NaCl optics and between 13 μ and 24 μ with the KBr optics. With the spectrograph properly adjusted and worked, it becomes almost a routine operation to record the percentage transmission curves in these ranges. A special point of importance which has to be attended to is the most appropriate speed of operation. To get out the records quickly, one might be tempted to tend to run the spectrograph at the maximum permissible speed. But experience shows that, especially with the plates of smaller area, this is an erroneous procedure to follow. The best records are those in which the recording apparatus is set at slow speed as the maximum of detail and the highest definition are then obtained. Merely to record the percentage transmission curves of a large number of plates can serve no useful purpose unless one also examines each individual plate by other methods of study which can throw some light on the nature of the material under investigation. Of such methods there are several. But we shall here mention only three techniques which involve the minimum of labour and at the same time are highly revealing. The first is the examination of the transparency of the material in the ultra-violet region of the spectrum. The second is the absence or presence of birefringence. The third is the visible luminescence of the diamond under ultra-violet illumination and especially the variations of the intensity and the colour of such luminescence.

A simple method of examination for ultra-violet transparency is to place the plate of diamond on a sheet of uranium-tinted glass which fluoresces strongly under ultra-violet illumination. A convenient source of such illumination is that commonly used for examining the luminescence of minerals, viz., a mercury vapour lamp in a tube of fused quartz, enclosed in a metal case one side of which is open but is covered by a filter which cuts off the visible light but allows the ultra-violet radiation of the lamp to pass through. When the lamp is held over the diamond, its transparency or lack of transparency is immediately revealed by the appearance presented by the glass plate as viewed either from above or from below. The area covered by the diamond appears dark if it is opaque and bright if it is transparent. While this simple technique suffices for a qualitative examination of the ultra-violet transparency of diamond, it is desirable to use the $\lambda 2536 \cdot 5$ resonance radiation of the mercury arc isolated by a quartz monochromator for more critical studies in which it is sought to observe and photograph the variations, if any, which the plate of diamond exhibits in respect of its ultraviolet transparency over its entire area. We shall in a later part of this memoir return to the results obtained in this manner.

Examination of a diamond plate for the presence or absence of birefringence is a very simple matter. The diamond is placed on a strain-free glass plate and viewed through a pair of crossed polaroid sheets against a brilliant source of white light. Even the faintest birefringence becomes visible in these circumstances. The nature and character of the birefringence, if any, that is present can be determined by examination through a magnifier of appropriately chosen power.

The technique for observing the luminescence of the diamond is equally simple. The plate of diamond is placed on a sheet of black glass and a beam of sunlight filtered through a sheet of black glass which transmits only the ultra-violet part of the solar spectrum is focussed on it. The presence or absence of luminescence and its colour and intensity, if present, then become evident to observation. The use of filtered sunlight in the experiment ensures that the illumination of the diamond is of adequate intensity, so that a feeble luminescence is not mistakenly regarded as indicating the absence of luminescence. It is by no means generally the case that luminescence when present has the same intensity or colour over the entire area of the plate. It is possible, of course, to record the luminescence patterns of the diamond in such cases photographically on a colour film. It is sufficient, however, to photograph the luminescent diamond on ordinary film through appropriately chosen colour filters so as to exhibit these variations. We shall return in a later part of the memoir to this aspect of the subject.

3. Summary

The author's collection of diamonds includes one hundred polished plates of diverse thicknesses and sizes and exhibiting a varied behaviour. This form of diamond is exceptionally well suited for critical studies of the optical properties of diamond. The importance in the study and interpretation of the infra-red absorption by diamond of a parallel investigation of other properties is indicated. Of particular importance are three of them, viz., ultra-violet transparency, birefringence and luminescence. Simple and convenient methods for studying them are described.