THE DIFFRACTION OF X-RAYS BY DIAMOND: PART III

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1. INTRODUCTION

IN the first part of the present memoir, it was shown from theoretical considerations of a very general nature that when X-radiations traverse a crystal, their passage could result in exciting vibrational transitions in the energy levels of the crystal and as a consequence of such excitation lead to a reflection of the incident X-rays by the lattice planes of the crystal with a change of frequency. The theory indicated it as an essential condition for such a process to occur that the vibrational transitions in question are effective as absorbers of infra-red radiation of the appropriate frequency. The phenomenon here envisaged is quantum-mechanical in its nature; in other words, vibrational transitions would be excited and would be accompanied by X-ray reflections of altered frequency even when the frequency of the vibrations is so high that they would not be thermally excited to any appreciable extent. However, considerations of a purely classical nature assist in elucidating the nature of the phenomenon and in deducing its observable features. The infra-red activity of a vibrational mode in a crystal arises because it involves a periodic displacement of the electronic clouds in the crystal with the same frequency; such a displacement would result in an oscillation of the stratifications of electron density which reflect the X-rays traversing the crystal and hence also to dynamic reflections of altered frequency.

Perhaps the most striking feature of the theory expounded in Part I is the connection which it indicates between the behaviour of a crystal in X-ray diffraction and the activity of the modes of its internal vibration in the absorption of infra-red radiation. The particular case of diamond is of special interest in this connection. For, as was shown in Part II of the memoir, theoretical considerations indicate that diamonds should be forthcoming in forms which differ in the inner symmetry of their electronic configuration and hence also in their infra-red behaviour. The detailed discussion showed that the diamonds of which the inner symmetry is octahedral would *not* exhibit dynamic X-ray reflections, whereas those diamonds of which the

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symmetry is tetrahedral would exhibit such reflections. In other words, the case of diamond enables us to put the relation between X-ray diffraction and infra-red activity to a direct experimental test. Further, it was also shown in Part II of the memoir that in the case of diamond, we are concerned with three modes of vibration which are respectively parallel to the three cubic axes of crystal and hence variously inclined to the lattice-spacings in it. As a result, the dynamic reflections by these spacings differ both in their number and in their geometric configuration in a highly characteristic fashion. Thus, the application of the general theory to the particular case of diamond furnishes us with abundant material for comparison with the facts of experiment.

2. THE TETRAHEDRAL AND OCTAHEDRAL FORMS OF DIAMOND

Three diamonds employed in the present investigation are represented in Plate I. The first is a cleavage plate parallel to the (111) spacings of the crystal. The second is a flat tabular crystal in its natural form as a hexagonal plate with faces parallel to the (111) planes. The third is a thin facetted plate of diamond with its faces nearly parallel to the (111) planes. All three diamonds are perfectly colourless, without any visible cracks or inclusions in their interior and obviously of the highest quality. Nevertheless, the first two diamonds differ enormously in their physical behaviour from the third, as is apparent from a comparison of the photographs reproduced in the Plate. We proceed to explain how these photographs were obtained.

The photographs on the left-hand side were recorded by placing the diamond against a fluorescent screen. (This was a slab of lithium fluoride crystal impregnated with a little uranium oxide.) The $\lambda 2537$ radiation from a water cooled magnet-controlled mercury arc in quartz was isolated by a a monochromator and allowed to fall on the diamond and then on the LiF-UO$_2$ screen placed behind it, and the fluorescence excited in the latter was photographed from the rear. The photographs on the right-hand side of the Plate were obtained in a very simple manner. The diamond was placed between two crossed polaroids and photographed as seen through them against a bright source of light. It is seen from the photographs reproduced in Plate I that *the cleavage plate and the tabular crystal are both perfectly opaque to the $\lambda 2537$ radiations of the mercury arc and that they exhibit not a trace of birefringence, in other words that they are truly and perfectly isotropic crystals.* On the other hand, *the thin facetted plate is completely transparent to the $\lambda 2537$ radiations of the mercury arc, but it exhibits a feeble but nevertheless readily observable birefringence pattern with definite geometric features related in their orientation to the structure of the crystal.*

Diamond is, in effect, a giant macro-molecule of carbon. Hence a specimen of it which exhibits no detectable birefringence, in other words, is optically homogeneous, may, *prima facie*, be expected to make a close approach to the ideal state of crystal perfection. *Per contra*, a specimen of diamond—which exhibits over its entire area, a geometric pattern of birefringence however feeble it may be in intensity—must necessarily be regarded as very remote from such ideality. A striking confirmation of the correctness of these remarks is furnished by the results of a simple experimental test in which the diamonds figured in Plate I were used as X-ray spectrometers to resolve the $K\alpha_1$ and $K\alpha_2$ radiations from a copper target. The X-ray beam from the target diverged through a fine slit and fell on the diamond in an appropriate setting placed at a distance of 5 cm. from the slit. The surface reflection of the X-rays by the (111) planes of the crystal was recorded on a photographic film held at a distance of about 100 cm. The spectrograms recorded with the flat tabular diamond and by the facetted plate are reproduced as Fig. 1 (*a*) and 1 (*b*) respectively in Plate II. A very great difference between the two diamonds in regard to the degree of their crystal perfection is indicated by the difference in the two spectrograms. But the actual difference is even greater. For, the width of the $K\alpha_1$ and $K\alpha_2$ lines as recorded in Fig. 1 (*a*) in Plate II represents the natural spectral widths of these radiations and is therefore not a true measure of the crystal perfection of the tabular diamond. To obtain a true measure of that perfection, it is necessary to adopt a spectrographic technique in which two crystals of diamond are employed. The results of that technique are depicted in the series of spectrograms reproduced as Fig. 2 (*a*), (*b*), (*c*) and (*d*) of Plate II and in Figs. 1 (*a*), (*b*) and (*c*) of Plate X. We shall revert to the details of the technique and the significance of the results obtained with it in a subsequent section of the present paper.

Studies on the infra-red absorption spectra of diamond have established the fact that diamonds which are completely transparent to the λ 2537 radiations of the mercury arc in the ultra-violet are also completely transparent to infra-red radiations over the entire range of the characteristic frequencies of vibration of the structure of diamond ranging from 1332 cm.$^{-1}$ downwards to longer wavelengths. *Per contra*, the diamonds which are opaque to the λ 2537 radiations also exhibit a marked absorption over that entire range of infra-red wavelengths. It is thereby established that diamonds of the former kind possess an inner electronic configuration which has the full or octahedral symmetry of the cubic system, whereas the diamonds of the latter kind possess an electronic configuration which possesses the lower or tetrahedral symmetry of that system. The remarkable fact that diamonds with

a lower degree of symmetry are highly perfect crystals, while those with a higher degree of symmetry are highly imperfect receives a natural explanation on the basis of the theory of the structure of diamond expounded in Part II of the memoir. As there explained, the tetrahedral diamonds are those in which each dextro-carbon atom is linked to four lævo-carbon atoms and likewise each lævo-carbon atom is linked to four dextro-carbon atoms. *There is thus no physical difference between the two sub-species Td I and Td II* of the tetrahedral class of diamonds but only an interchange in the description of the two lattices which constitute the structure. On the other hand, the octahedral type of diamonds consists entirely of dextro-carbon atoms or entirely of lævo-carbon atoms; *the two sub-species Oh I and Oh II are therefore physically different*. These circumstances are clearly favourable for the Td diamonds exhibiting a high degree of homogeneity and for the Oh diamonds to be markedly heterogeneous in their texture. But there is another and a deeper consideration which has also to be borne in mind. When a dextro-carbon atom is linked to a lævo-carbon or *vice versa*, the two electrons shared between them describe their orbits about the valence direction in the same sense. On the other hand, when a dextro-carbon atom combines with a dextro-carbon atom or a lævo-carbon atom with a lævo-carbon atom, the shared electrons describe their orbits about the common valence direction in opposite senses. It would seem that a homogeneous structure extending through large volumes would be more likely to appear in the former case than in the latter.

It is appropriate at this stage to remark that it is the perfect diamonds belonging to the tetrahedral class that exhibit the phenomena of dynamic reflection of X-rays, while it is the imperfect diamonds of the octahedral type that do not show those phenomena. This is in agreement with the indications of the theory developed in Part II of the memoir. But it is necessary to demonstrate that the failure of the octahedral diamonds to exhibit dynamic reflections is not ascribable to their imperfection of structure, but is a consequence of their inactivity in infra-red absorption. We shall revert to this presently.

3. Dynamic X-Ray Reflections and Crystal Symmetry

Figure 1 in Plate III is a Laue photograph of a cleavage plate of diamond whose faces are parallel to the (111) planes of the crystal. The crystal was set exactly normal to a fine pencil of X-rays from a copper target. The picture shows perfect trigonal symmetry not only with regard to the ordinary or Laue reflections but equally also with regard to the dynamic reflections appearing in the vicinity of the hexagonal corners of the print adjacent to

the intense (111) Laue spots. Figure 2 in Plate III is a similar photograph taken in similar circumstances with a crystal of diamond which exhibits twinning of the spinel type. It will be seen that this pattern exhibits hexagonal symmetry in all its features, including especially the dynamic reflections which are seen at all the six corners of the hexagonal print. The fact clearly evident from Figs. 1 and 2 in Plate III that the dynamic X-ray reflections of diamond exhibit the symmetry of the crystal in the same manner and to the same extent as the static reflections is obviously of the highest significance. Taken in conjunction with the circumstance that the diamonds which exhibit the dynamic reflections are perfect and indeed—as will appear presently—are ideal crystals, it demonstrates the correctness of the view expressed by the author in the original publication of the year 1940 that these phenomena exhibited by diamond are fundamental in their nature and of the highest importance in relation to the theory of X-ray diffraction in crystals.

As already remarked earlier, the fact that the dynamic reflections are not manifested by the diamonds of octahedral symmetry is a confirmation of the theoretical ideas set out in Part I of the memoir. But the circumstance that these diamonds are imperfect tends to create some doubt in the matter. Very frequently, indeed, diamonds of this class give distorted Laue patterns. Hence a critical observer might be disposed to infer that it is this imperfection rather than the inactivity in infra-red absorption which is responsible for the non-appearance of the dynamic reflections. To dispel such an impression, it is necessary to investigate the matter with carefully selected material. The intensity of the birefringence exhibited by these diamonds is a measure of the imperfections in their structure. It is therefore desirable to select a specimen in which such birefringence is of extremely low intensity. The specimen illustrated in Figs. 3 (*a*) and 3 (*b*) in Plate I was found to be the best available in this respect. Even so, the mosaicity of its structure exhibits itself in a notable enhancement of the intensity of the Laue spots in its diffraction patterns. Such enhancement is particularly striking in the case of spots that are only feebly recorded with diamonds of the tetrahedral class. Even such a weak effect as the diffuse X-ray scattering due to thermal agitation is recorded with greatly enhanced intensity by this specimen. But there is no observable distortion of the Laue spots, and had the dynamic reflections been present, they would have been very striking features in the recorded patterns. Actually, not a trace of them is observable in Figs. 1 (*b*) and 1 (*d*) in Plate VIII which were recorded with this diamond in appropriate settings. For the sake of comparison, the patterns recorded with the tetrahedral diamond in identical settings are reproduced as Fig. 1 (*a*) and 1 (*c*) side by side with them in the same Plate VIII.

4. OBSERVABLE FEATURES OF THE DYNAMIC REFLECTIONS

The following special points are worthy of mention:

I.   As the dynamic reflections by diamond are a consequence of the excitation by the incident X-rays of an infra-red vibration of high frequency, variations of temperature within wide limits should be entirely without effect either on the intensity or the sharpness of these reflections.

II. As a result of the crystal perfection of diamond, the ordinary reflections of monochromatic X-rays would demand a very precise setting of the crystal for their observation, on either side of which they would disappear completely. The dynamic reflections would coincide with the static reflections at the correct setting, but would not disappear when the setting is altered. Their intensity would however fall off rapidly as the crystal is moved away from the correct setting in their direction.

III. The dynamics of the excited vibration in diamond demands that the phase-waves which determine the direction in which the dynamic reflections appear are precisely normal to one or another of the cubic axes of the crystal. As a consequence, the reflections would be very sharply defined, being indeed in this respect almost comparable with the static reflections.

IV. By making observations of the directions in which the dynamic reflections appear, it is possible to determine the orientation of the phase-waves. The most suitable arrangement for such determination is to place the crystal so that one of the cubic axes lies in the plane of incidence of the X-rays on the (111) planes, and then to alter the setting in such manner that the plane of incidence does not change. The geometric law of dynamic reflection takes a very simple form in this case and a precise measurement of the orientation of the phase-waves becomes possible.

The various special features referred to above were all fully established by the observations made by the author and his collaborators in the months following the original publication of April 1940. Detailed reports of those studies appeared in the *Proceedings of the Indian Academy of Sciences* in the years 1940 and 1941. It would be superfluous here to traverse the same ground or to comment on the literature of a controversial nature published from other laboratories on the subject then and subsequently. To

make the present memoir complete, however, a series of photographs showing the dynamic reflections by the (111) planes, (220) planes, (311) planes and (400) planes of diamond in various settings are reproduced as Plates IV, V, VI, VII, VIII and IX accompanying the present paper. A comparison of the features noticed in this series of photographs with the theoretical diagrams given in Part II of the memoir will show how complete the agreement is between fact and theory.

5. Spectral Analysis of X-Ray Diffraction

We now return to a detailed description of the technique which enables a spectroscopic analysis to be made of the X-ray diffraction phenomena exhibited by diamond. The general nature of this technique to which a brief reference was made earlier will be evident from Fig. 1, text. A powerful source of X-rays from a copper target passes first through a wide slit and then
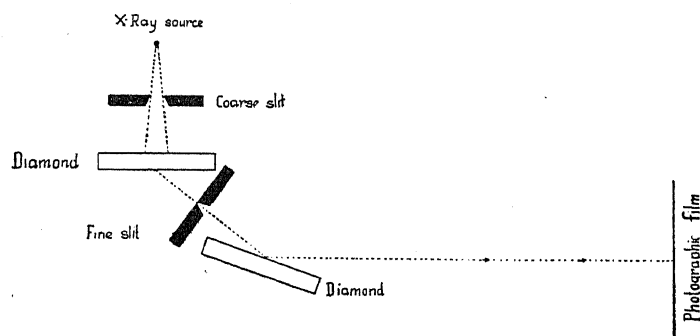
Fig. 1 (Text)

through the diamond under study. The rays *internally* diffracted by the (111) planes of this diamond are restricted by a fine slit through which they pass before they are incident on the surface of a second perfect diamond which functions as a spectrometer. The rays reflected *externally* by the second diamond are received and recorded on a photographic film placed at a distance of 100 cm. The actual technique consists in rotating the first diamond in steps through very small angles over a total range of a few minutes of arc. What is actually recorded on the photographic film is the spectrum of X-radiation in the narrow range between the $K\alpha_1$ and $K\alpha_2$ lines and perhaps a little more on either side of them.

The nature of the results obtained will be evident from a scrutiny of the series of spectrograms reproduced as Figs. 2 (*a*), (*b*), (*c*) and (*d*) in Plate II and the three others which appear as Fig. 1 (*a*), (*b*) and (*c*) in Plate X. The latter three have been enlarged so as to be readily comparable with the single

crystal spectrogram appearing as Fig. 1 (a) in Plate II. The most significant
feature of the series of spectrograms is the appearance of an extremely sharp
line which drifts in its position as the diamond is rotated. The spectral
width of this sharp line is not more than about a tenth of the natural width
of the $K\alpha_1$ or the $K\alpha_2$ radiations. It represents the super-monochromatic
radiation manufactured by the first diamond from the incident white radia-
tion by Laue reflections at the (111) stratifications. Its extreme sharpness
reflects the extraordinary perfection of the diamond.

It will be seen that the relative intensities of the $K\alpha_1$ and $K\alpha_2$ lines differ
enormously in the different spectrograms. That they persist over the whole
range of settings of the diamond clearly shows that they represent the dynamic
reflections of the $K\alpha_1$ and the $K\alpha_2$ radiations by the (111) planes of the first
diamond. The static reflections of those radiations are recorded only at
the precise settings at which those reflections are possible.

6. ACKNOWLEDGEMENT

The Laue patterns reproduced in Plates III, IV, V, VI, VII, VIII and IX,
as well as the single crystal and double crystal X-ray spectra reproduced in
Plates II and X accompanying this memoir were recorded in the X-ray Labo-
ratory of the Raman Research Institute by the Assistant Director of the
Institute, Professor A. Jayaraman, for whose valuable co-operation in the
research the author of this memoir is greatly indebted. The gift to the Insti-
tute of a rotating target X-ray set by Sri Purushottamdas Thakurdas made
the work possible.

7. SUMMARY

Studies on the crystal perfection of diamond by single-crystal and the
double-crystal X-ray spectroscopic methods demonstrate that the non-birefrin-
gent diamonds which are infra-red active and possess only tetrahedral sym-
metry in their electronic configuration are extraordinarily perfect and are
indeed ideal diamonds. It is these diamonds that exhibit the phenomena
of dynamic reflection of X-rays. The detailed studies of the phenomena
show that the experimental facts of the subject are completely in agreement
with the results of the theory expounded in the first two parts of the memoir.
The non-appearance of the dynamic X-ray reflections with the diamonds
which have an octahedral symmetry of electronic configuration is shown
to be consequential on these diamonds being inactive in the absorption of
infra-red radiation.
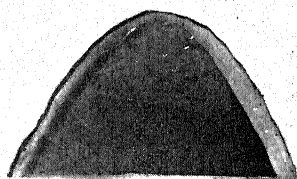
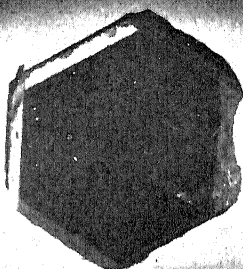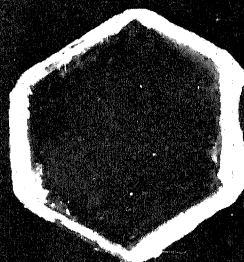FIG. 1 (a)   (b)
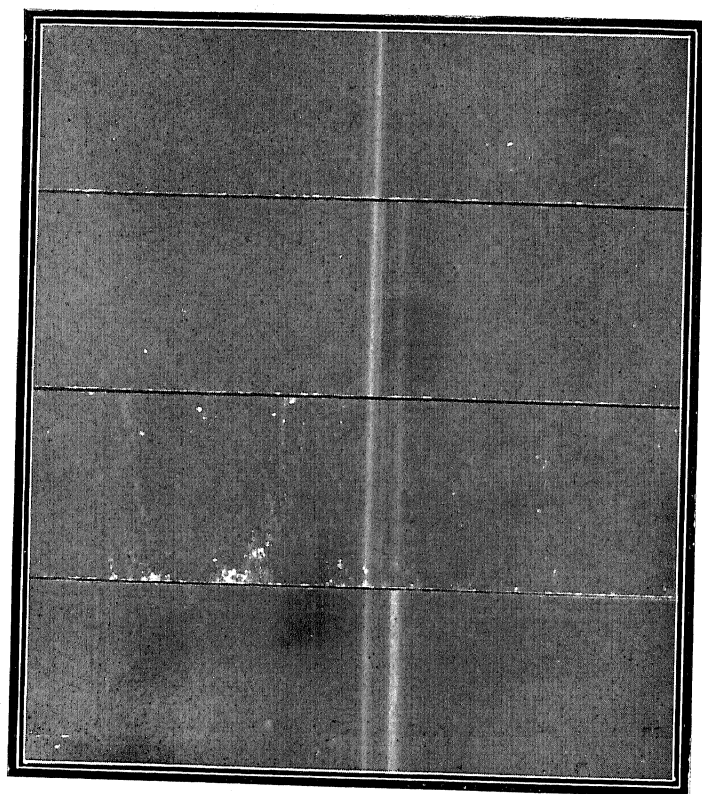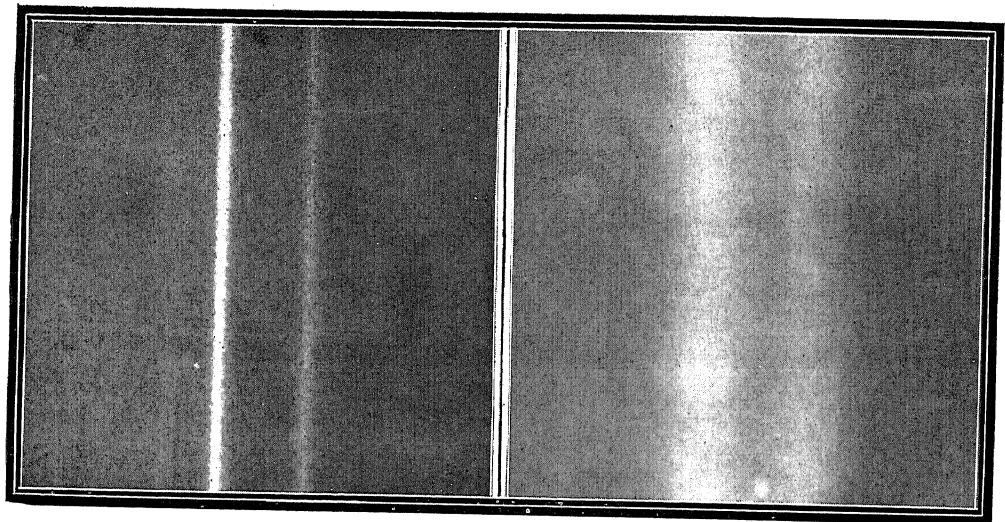
FIG. 2 (a)   (b)
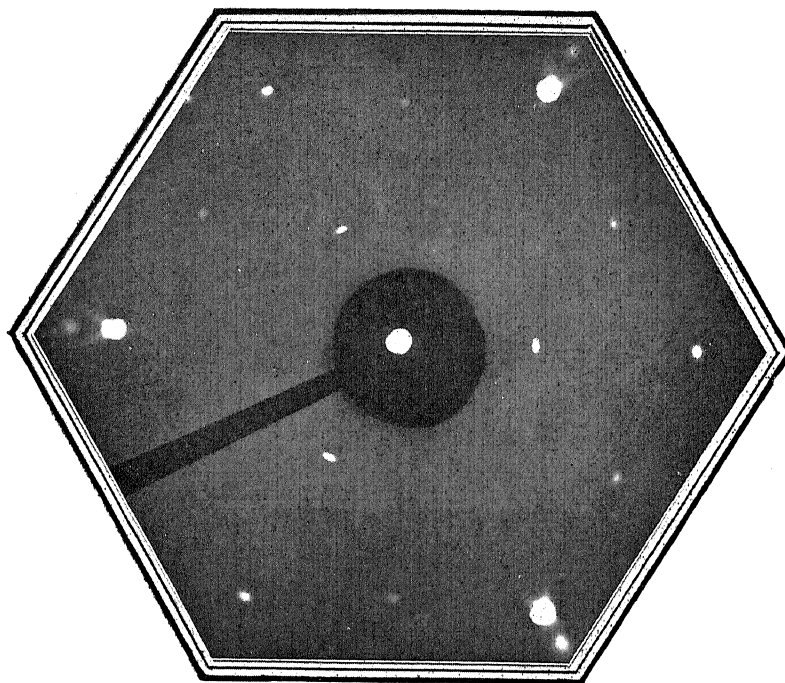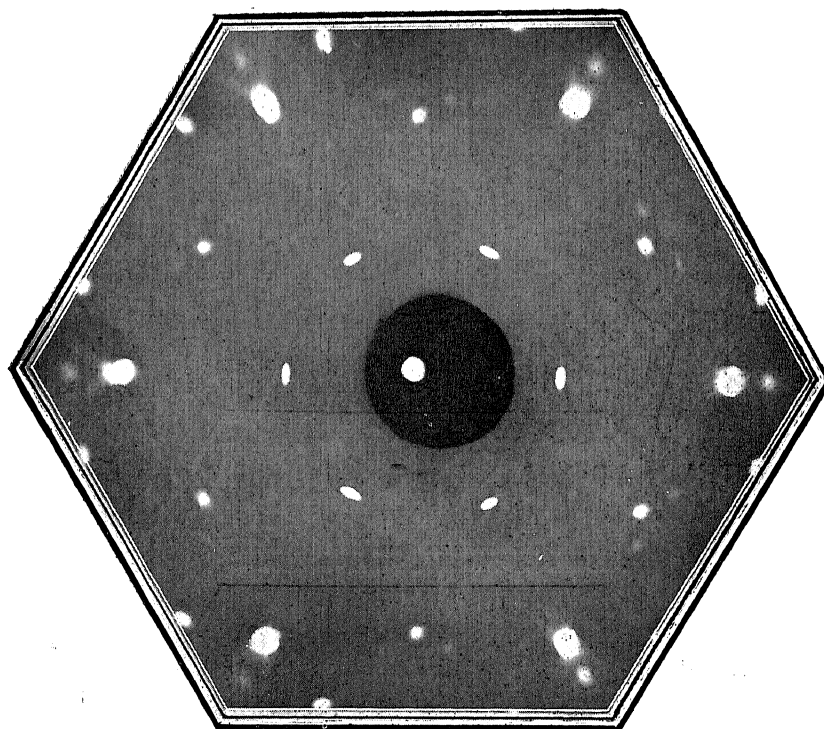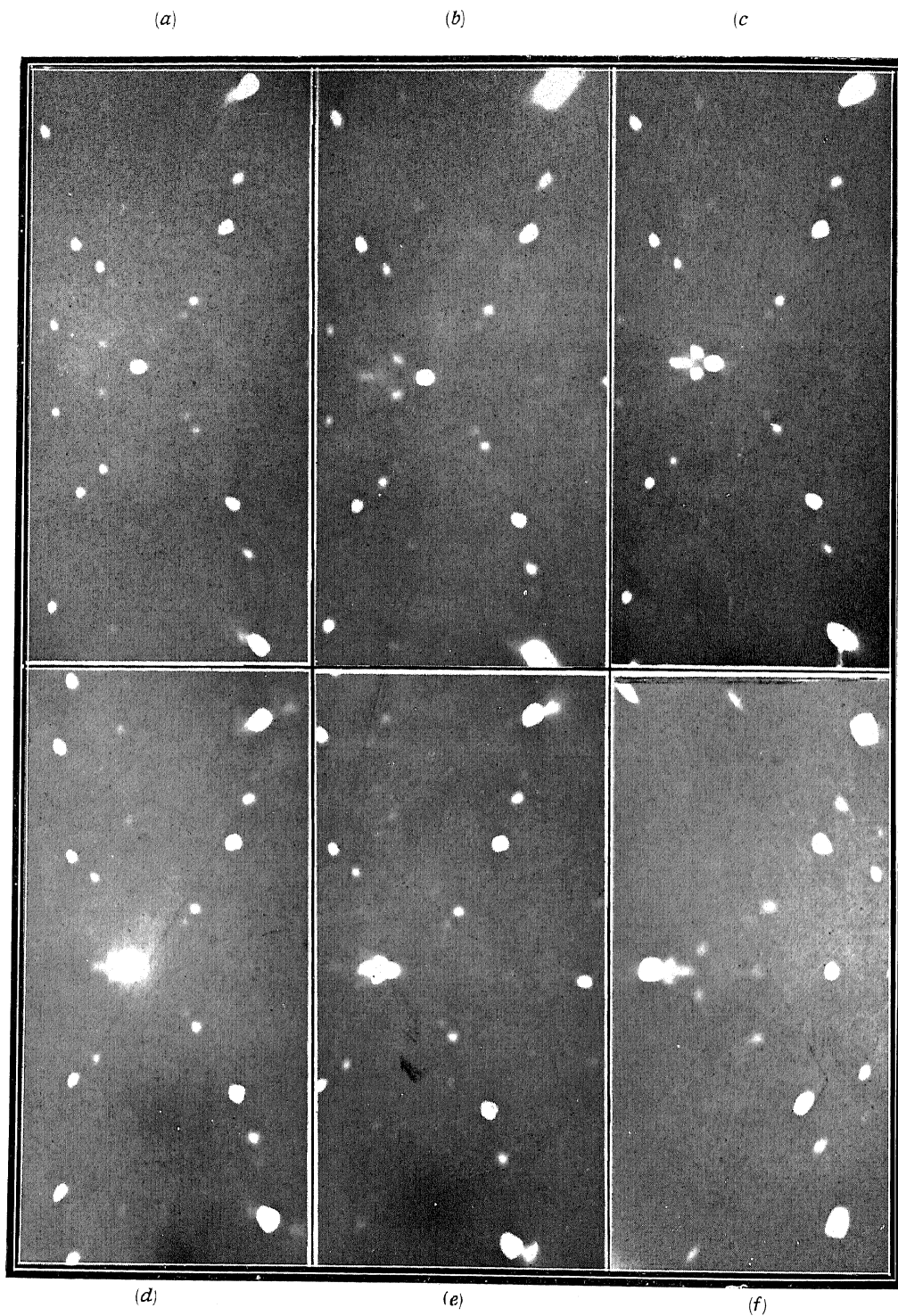
FIG. 3 (a)   (b)

FIG. 1 (a)   FIG. 1 (b)

FIG. 2

Fig. 1

Fig. 2

(a)   (b)   (c

(d)   (e)   (f)

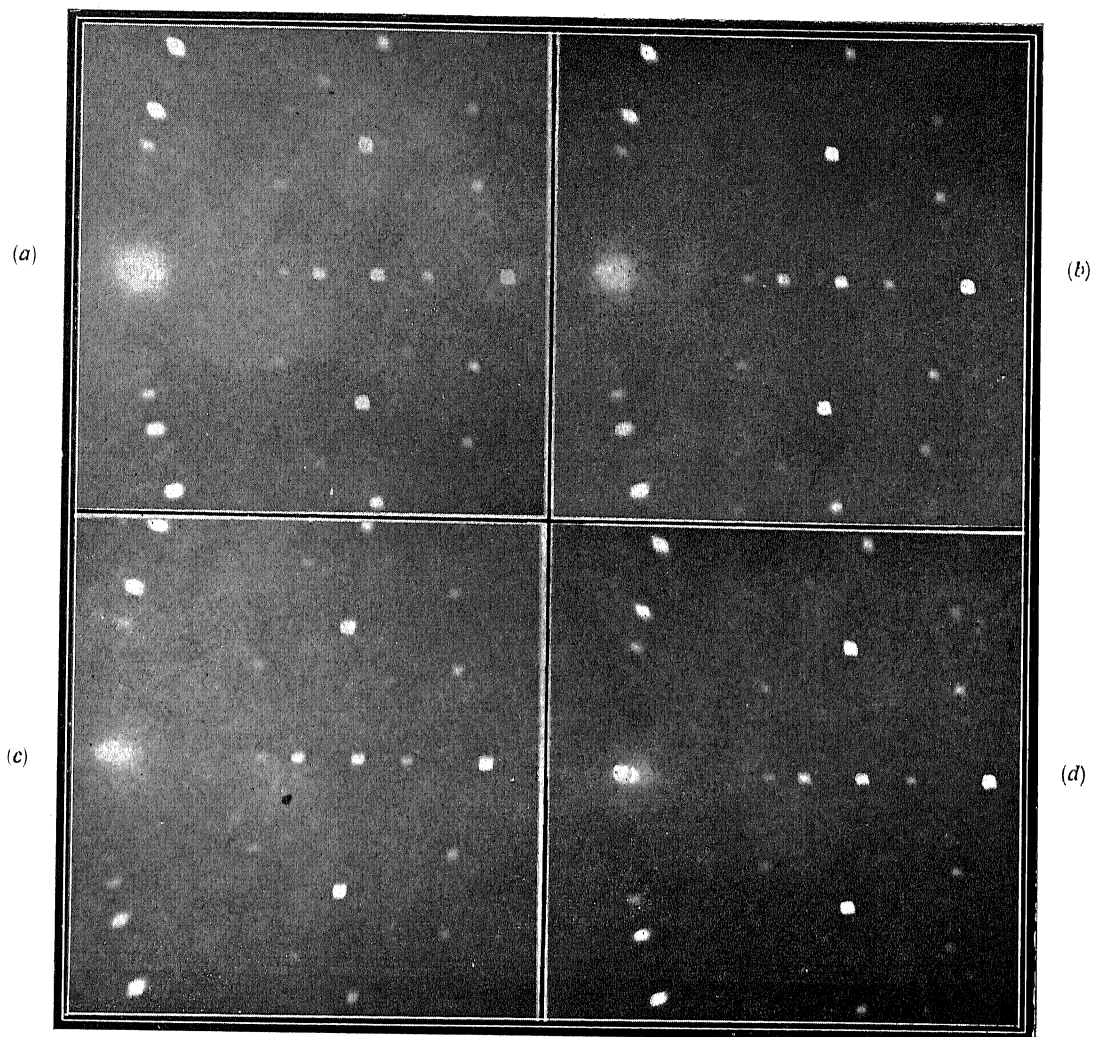FIG. 1. Exhibiting the dynamic reflections by the (111) planes at various settings.
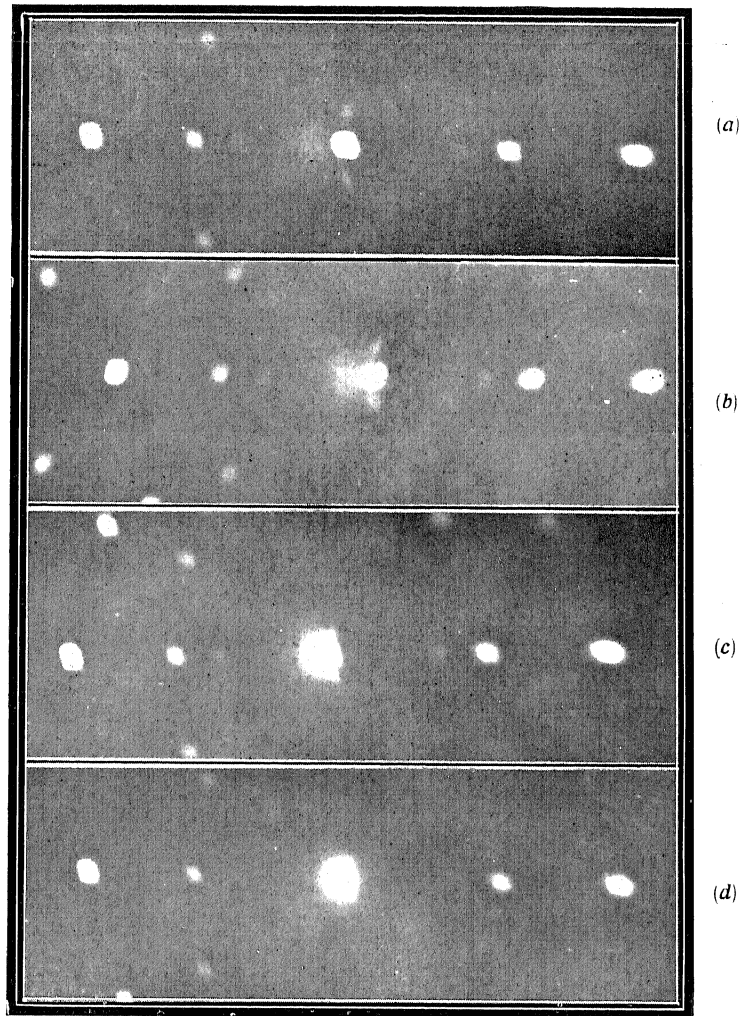
FIG. 1. Exhibiting the dynamic reflections by the (220) planes at various settings.

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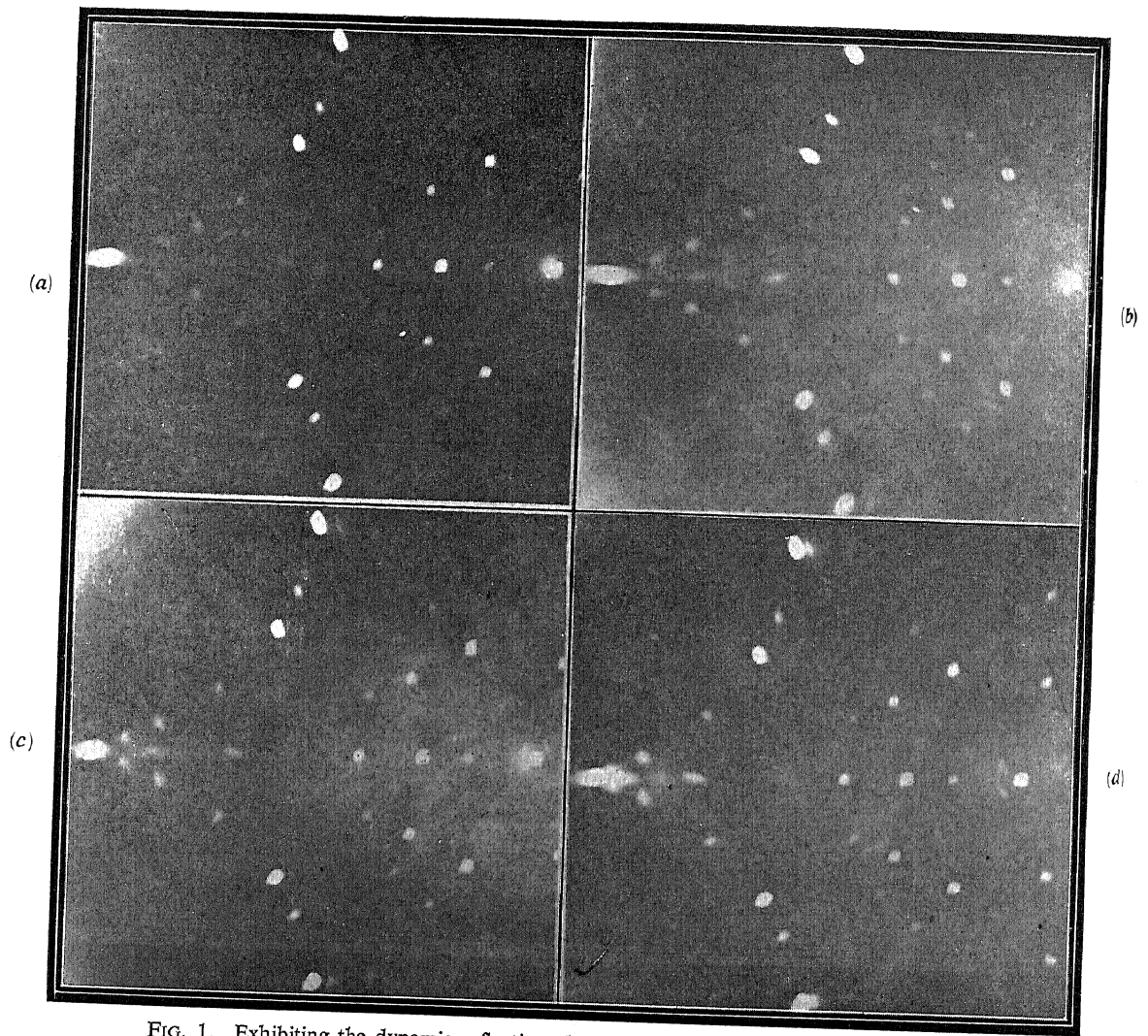
FIG. 1. Exhibiting the dynamic reflections by the (111) planes at the left and by the (113) planes at the right.

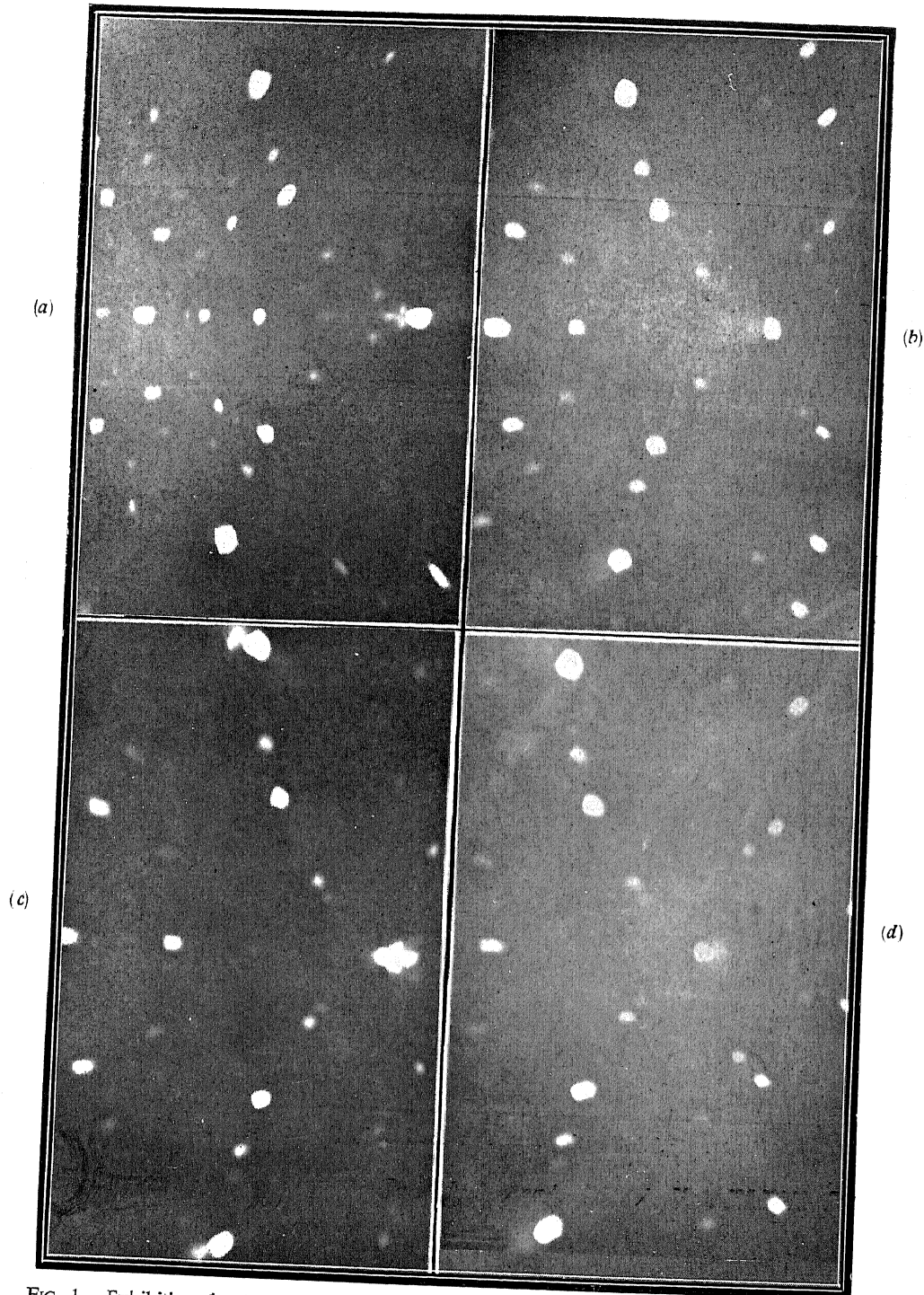FIG. 1. Exhibiting the dynamic reflections by the (400) planes at the left.

FIG. 1. Exhibiting the dynamic reflections by the (111) planes of tetrahedral diamond on the left and their absence with octahedral diamond on the right.
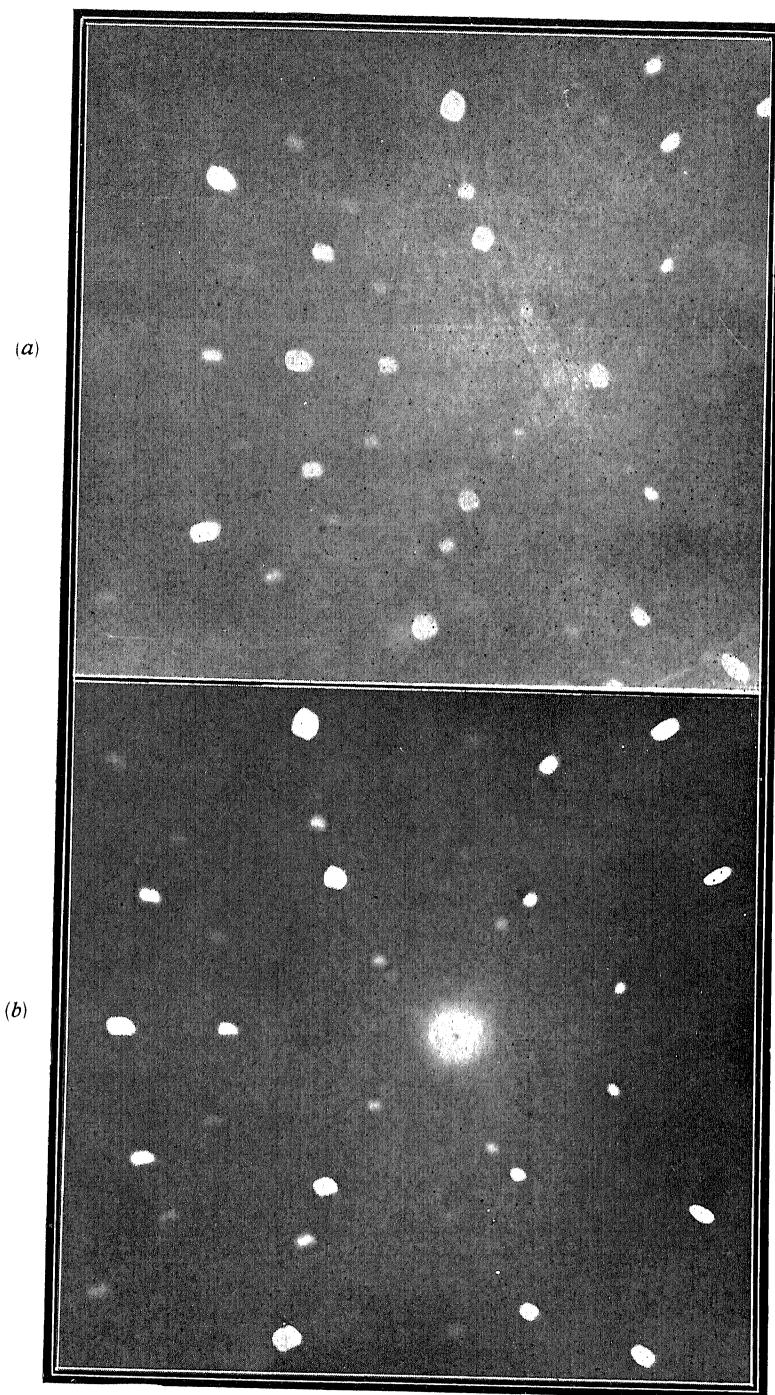
FIG. 1. Laue patterns of octahedral diamond showing intense reflection by the (111) planes at different settings.
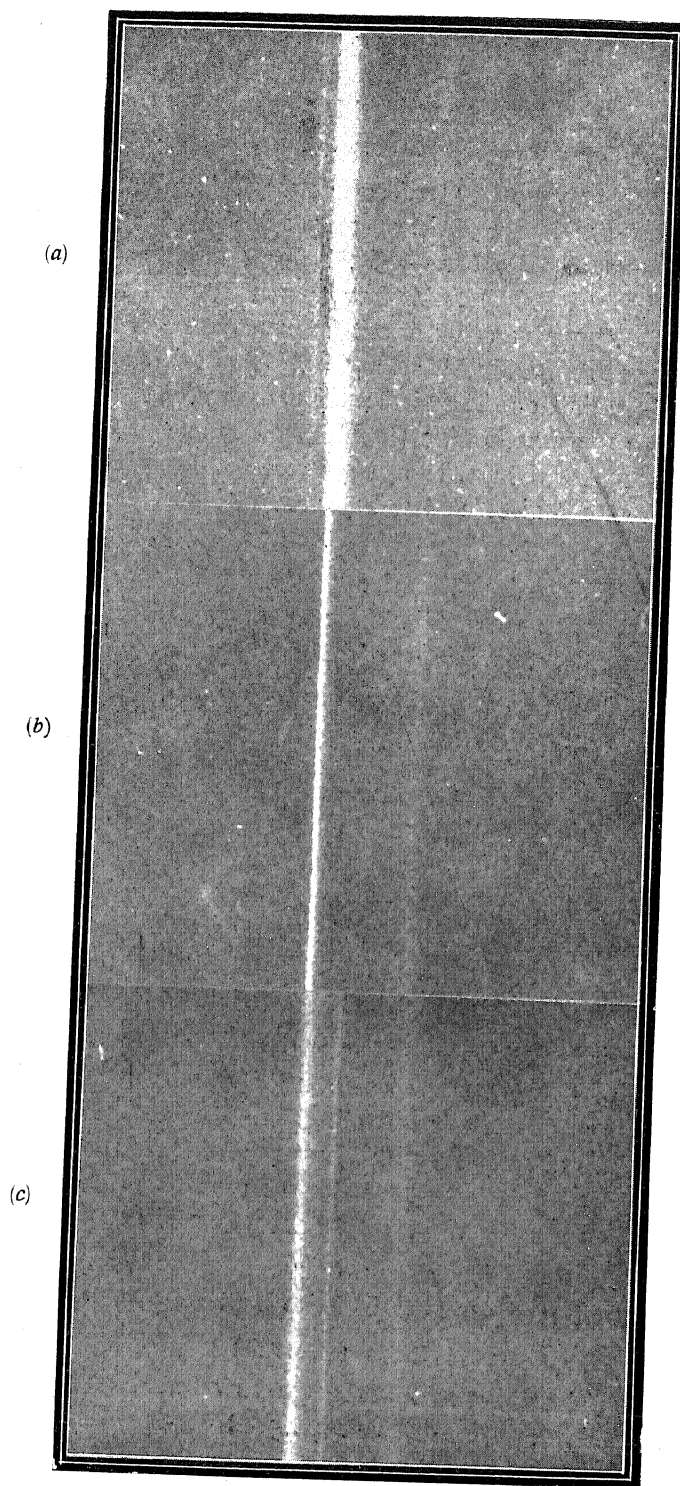
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(a)

(b)

(c)

FIG. 1. For explanation, see text.