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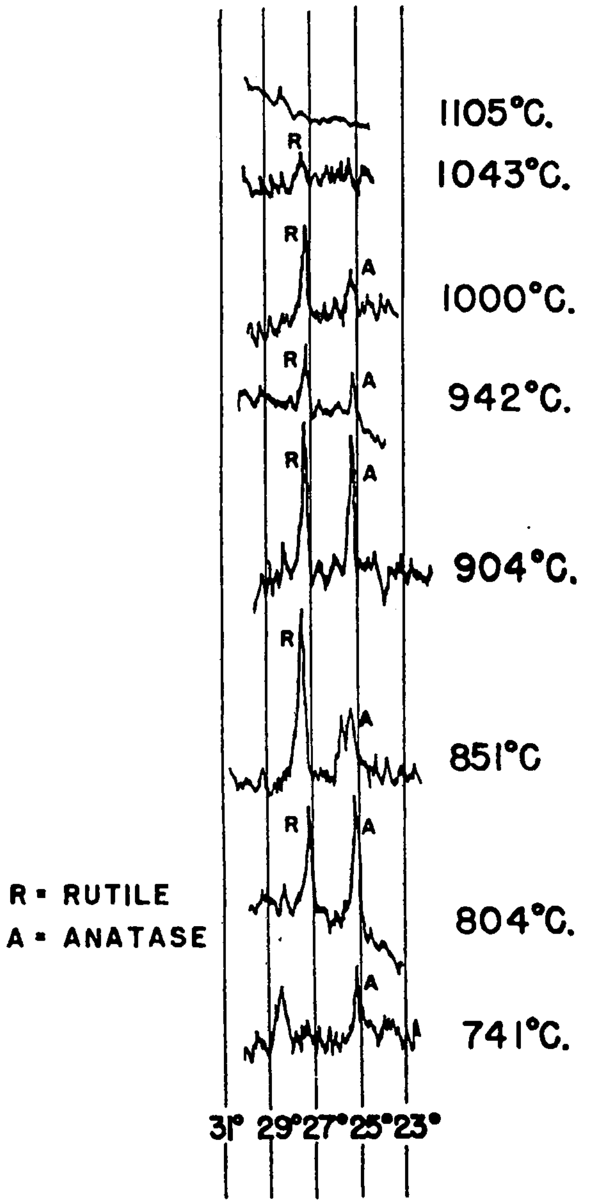

FIG. 1. Portion of X-ray diffractometer patterns of a titania-opacified enamel frit at various temperatures.

was present, but no rutile. At 804°C the curve shows that both rutile and anatase were present (some anatase was transformed to rutile between the temperatures 741° and 804°C). The anatase peak was higher than the same peak at 741°C; therefore, more anatase crystals were developed at 804° than at 741°C. At 851°C a maximum number of rutile crystals was developed in the specimen. As the temperature increased, the rutile crystals were dissolving and the number of crystals had become less and less. At 1105°C all rutile crystals were dissolved. The evidence of this was shown by the relative height of the rutile peak as the temperature increased to 1105°C. For the same reason, the anatase peak indicated that a maximum number of anatase crystals had developed at 904°C and the crystals had completely dissolved at 1043°C. The short peak of the anatase at 851°C was probably caused by some impurity in the anatase crystals.

TIN BOO YEE

TITANIUM DIOXIDE CRYSTALLOGRAPHY. See Perfection of Crystalline Structures.

TOOTH MINERAL CRYSTALLOGRAPHY. See Bone and Tooth "Mineral".

TOPOGRAPHY, X-RAY DIFFRACTION

Principles. In numerous solid-state researches it is necessary to investigate inhomogeneities of crystalline material. This is most directly achieved by preparing topographs which depict point-by-point the variations of particular characteristics of the specimen. Such topographs are of value whether it is the distribution of inhomogeneities themselves that is being studied, or whether the presence of inhomogeneities is of interest merely because of their influence on some other property of the material. Topographs may be taken that show, for example, the distribution of optical absorption or optical fluorescence in a specimen. Absorption and fluorescence topographs may be obtained in the X-ray spectrum as well: the former are the essential bases of the highly developed techniques of radiography and microradiography, the latter were pioneered by von Hamós^{14} for elemental analysis and find modern expression in scanning X-ray emission microanalyzers.^{10} In addition, X-rays provide a highly sensitive probe of specimen properties through crystal diffraction. The wide variety of X-ray diffraction topographic methods developed in recent years, and some of their applications, will be discussed in this article. Essentially, the two properties that X-ray diffraction topographs can reveal are local variations in crystal lattice perfection, and local variations in lattice orientation. An idea of the sensitivity obtainable in the first case is given by considering that, under properly chosen diffraction conditions, the X-ray reflecting power of a small volume of ideally mosaic crystal may exceed that of a similar volume of perfect crystal by two orders of magnitude. Hence point-by-point variations of X-ray reflecting power are most sensitive indicators of departures from perfect lattice regularity. In the second case, sensitivity to changes of lattice orientation can be raised to a level such that a bending of the crystal to a radius of more than a mile can be detected.

The first diffraction topographs were prepared by Berg^{3,4} who pointed out the geometrical differences between forming the image of a crystal surface by optical specular reflection and by Bragg reflection of characteristic X-rays. Thus, in the arrangements shown in plan in Fig. 1, all light rays diverging from the point source, *S*, in Fig. 1(a) and falling on the crystal, *C*, between the limiting rays 1 and 2 can contribute to forming an optical image of the surface of *C* on the film, *F*. On the other hand, if an image of the whole surface of *C* is to be obtained by monochromatic X-rays reflected from it under the Bragg condition then the incident rays 1, 2 and 3 must all

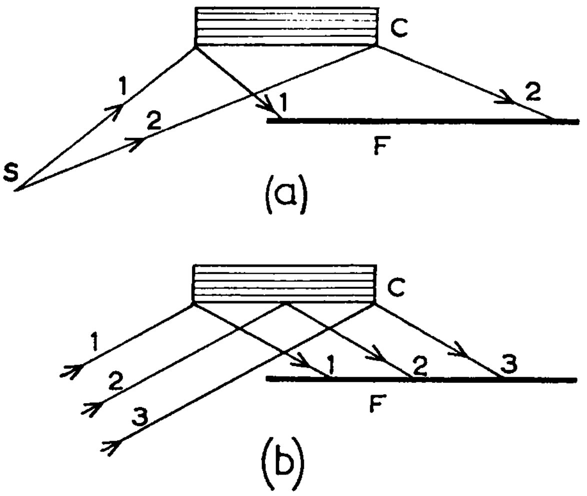

FIG. 1. Imaging of surface of crystal C by (a) continuous radiation and (b) Bragg-reflected characteristic radiation.

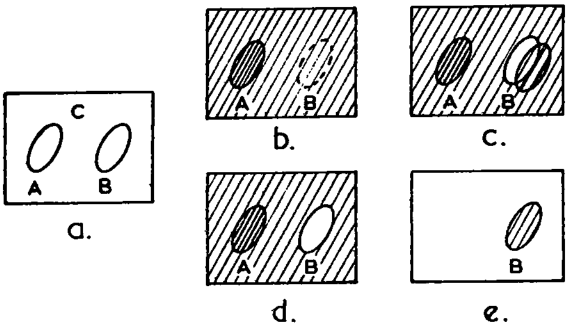

FIG. 2. (a) Crystal surface (C) with imperfect region (A) and misoriented region (B). Continuous radiation topographs with $D' \ll D$ in (b) and $D' \sim D$ in (c). Characteristic radiation topographs, (d) main reflection, (e) B only reflecting.

make the same angle with *C*, as in Fig. 1(b). Thus they must either come from different points of an extended source, or from a small source so far away that 1, 2 and 3 are effectively parallel. Berg used an extended source of W Lα radiation and studied reflections from cleavage planes of rock salt. It is clearly desirable to form an undistorted image of the crystal. With reflection from crystal surfaces this may be largely achieved by simply placing the photographic film or plate parallel to the specimen surface. However, there will be some magnification in a direction perpendicular to the figure in the case of Fig. 1(b), depending upon the ratio of distance from source to specimen, D, to the distance from specimen to film, D'. This magnification is $(D + D')/D$. When imaging takes place as in Fig. 1(a) there is a magnification in the plane of the figure as well, with a similar dependence on D and D'. If continuous (white) radiation is used instead of characteristic radiation imaging exactly analogous to the optical case of Fig. 1(a) can be obtained, the image being simply an extended Laue spot. Then, if the emission of the source varies little in intensity between the upper and lower wavelength limits represented by a given order of reflection of rays 1 and 2, respectively, and no absorption edges of specimen or film fall in this range, an undistorted uniformly reflecting crystal, *C*, will give a uniform patch of darkening on *F*.

Whether continuous or characteristic radiations are used provides the main basis for classifying topographic techniques, for they produce different topographic imaging effects, with different dependence upon D'/D, in response to variations of lattice orientation in the specimen. Consider an idealized situation represented by Fig. 2. Suppose the surface of the crystal *C* (Fig. 2(a)) has a patch, *A*, more imperfect than the surrounding crystal and a patch, *B*, which is misorientated relative to its surrounds. On a continuous-radiation reflection topograph obtained according to Fig. 1(a) the image would appear as in Fig. 2(b) with $D' \ll D$, and as in Fig. 2(c) with D' relatively larger. (The change in size of image with increase of D' is neglected.) In both Figs. 2(b) and 2(c) the imperfect patch, *A*, manifests itself by enhanced reflecting power, but the misorientation of *B* only becomes measurable when D' is large enough to show the deviation of rays diffracted by *B* relative to those diffracted by adjacent regions. On the other hand, using characteristic radiation, and a good degree of collimation of the incident beam, *B* will not reflect at all when its surrounds reflect, (Fig. 2(d)) but it can be brought into reflection by varying the glancing angle of incidence upon *C*, reflection from the rest of the crystal then vanishing (Fig. 2(e)). Apart from changes in magnification in one direction, the general appearance of the topograph is not sensitive to changes of D' in the characteristic-radiation case. Misorientations in any direction may be determined by measuring the amount and direction of image displacement in the continuous-radiation case, but this is only feasible if the misoriented region is sharply bounded. With characteristic radiation the component of misorientation in the plane containing incident and diffracted beams only is measured by rotating the crystal about the normal to this plane, and a succession of topographs must be taken to cover the reflecting range unless an appropriate counter recording technique is used. However, the precision now obtainable is high, and can be better than 1 sec. of arc, depending upon the method of collimation of the incident characteristic radiation. The continuous-radiation method has the advantage that with a single, stationary, noncritical setting of the specimen, an image of its whole surface may be obtained, and, in fact, several reflected Laue-images may be received on the same film, with various degrees of distortion. On the other hand, in contrast to the idealization of Fig. 2, local variations of reflecting power are usually associated with local tilts and bends of the crystal lattice, and hence the interpretation of the intensity distribution on a continuous-radiation topograph is often difficult, even if a set of topographs at various D' values is taken. For directness of interpretation, for high intensity and resolution, characteristic-radiation topographs are preferable in serious studies of lattice imperfections.

Topographic methods may be further classified according to whether the diffracted rays are reflected from the specimen surface or transmitted through it. Clearly, the transmission arrangement demands that the specimen be sufficiently thin that absorption losses are not intolerable. However, using radiation such as AgKα (λ = 0.56A) light elements may be examined in transmission with thicknesses of the order of a millimeter, and only the heaviest elements must be thinned to less than 10 microns. It is arguable that in the transmission method the potentialities of X-ray diffraction topographs are best realized, for they then provide a general, nondestructive method for examining the interior structures of crystals of such a thickness that their interior state adequately represents conditions in the bulk material. Transmission methods present the complication that the primary beam, also transmitted through the specimen, must not be allowed to fall upon the emulsion and obscure the diffracted beam. Thus interposition of slits passing only the diffracted beam, and restriction of width of the primary beam, are necessary if the distance D' is to be kept small. An exception to this situation occurs with thick specimens when anomalous transmission, the Borrmann effect, is utilized (see below).

With characteristic radiation it is desirable to register only the Kα_1 diffracted rays, unless D' can be kept down to about 1 mm, in order to avoid loss of resolution due to superimposition of Kα_1 and Kα_2 images. This requires good collimation of the incident beam, which is also a necessity if misorientations are to be measured sensitively. Such collimation can be achieved by use of a fine-focus X-ray tube, a narrow slit close to the specimen, and a large value of D; but then some means for scanning the specimen with the beam must be used if large specimen areas are to be examined. Alternatively, a wide parallel incident beam may be produced by prior reflection at a monochromator crystal. The type examples of these techniques and some other variants of the topographic method will now be described in outline.

Typical Experimental Arrangements. ***Continuous Radiation, Reflection Specimen.*** The method of Schulz[29] employs the geometry of Fig. 1(a) in conjunction with a microfocus tube as source. With an X-ray tube focus of projected size about 3 × 30 microns topographs of good resolution can be obtained with D' relatively large, and making $D \sim D'$ gives a reasonable combination of angular and topographic resolution. If standard double-coated X-ray film is used then it is advisable to place the film normal to the Laue diffracted rays of chief interest: distortion of the image is not very serious since diffracted beams making relatively large angles (~45°) with the specimen surface are used. Coyle *et al.*[11] have discussed the geometrical basis for interpreting topograph images formed by this method.

Continuous Radiation, Transmission Specimen. This is one of the earliest topographic methods and was developed quite thoroughly by Ramachandran[26] for the study of plates of diamonds up to 1 cm^2 in area, using reflecting planes fairly steeply inclined to the surface of the plate. Ramachandran plotted graphically the relative angular settings of specimen and film needed to give an undistorted image for various values of D/D'. He used $D/D' = 12$, so his arrangement had the characteristics of Fig. 2(b) and his topographs were hence sensitive to variations in lattice perfection but not to misorientations.

Characteristic Radiation, Stationary Reflection Specimen. The refined experiments of Barrett[1] set the standard with this particular technique. The basic arrangement is simply that of Fig. 1(b), as used by Berg, but Barrett achieved excellent topographic resolution by keeping D' not greater than 1 mm and recording on high resolution spectroscopic plates. Use of such thin emulsions has the advantage that the diffracted beam may fall on them obliquely without serious loss of resolution. Barrett also found that the best reflection topographs were obtained using soft radiations such as Cr Kα to Cu Kα. The technique, now known as the Berg-Barrett method, was further developed by Newkirk[23] who established it as one of the leading methods of studying individual dislocations by X-ray diffraction topography. Newkirk made a special effort to reduce D' to ~0.1 mm by choosing radiation and reflecting plane so that the incident beam made a small angle with the specimen surface and the diffracted beam left it nearly normally: the emulsion could then be placed almost parallel to the specimen surface, and very close to it.

Characteristic Radiation, Moving Reflection Specimen. Various methods have been devised to obtain Bragg reflections of characteristic rays from an extended crystal surface without using an extended X-ray source. N. Wooster and W. A. Wooster[33] bathed the crystal in a divergent beam of radiation and rocked it and the film together so that all points of the specimen surface had a chance to reflect at the Bragg angle. In this way the conditions of a continuous-radiation reflection topograph are approached and the method is more sensitive to variations in lattice perfection than orientation. An alternative arrangement, capable of high angular resolution, was described by Merlini and Guinier.[22] The reflection specimen and the film, mounted parallel to the specimen surface, were together translated in a direction perpendicular to a narrow beam so that the whole specimen surface was scanned. Another arrangement, allowing diffracted rays to fall normally on the film so that a thick emulsion could be used, yet giving an undistorted image of the crystal surface, was used by Lang.[19] In this method, shown schematically in Fig. 3, a well-collimated incident beam is used and the film, F, is stationary. The crystal whose surface is to be imaged is translated back and forth during the exposure between the positions AB and $A'B'$. The direction of translation is selected so that the width of image $A''B''$ is equal to the width of the face, AB. Since D' cannot be made small in this method, D must be large and/or a very fine X-ray tube focus used to give good topographic resolution. The incident beam must also be kept narrow at the specimen.

These two conditions ensure good angular resolution as well.

Characteristic Radiation, Stationary Transmission Specimen. The method of "section topographs" (Lang,[20]) is shown in Fig. 4. A narrow beam of penetrating characteristic radiation is reflected by lattice planes normal, or nearly normal to the surface of the specimen, *C*, and the diffracted beams fall normally on the emulsion, *F*. Diffraction conditions may be chosen so that a region of imperfection, *I*, within the crystal gives a local intensification, *I'*, in the image *A'B'* of the crystal section *AB* cut by the incident beam. The crystal and film may be together moved stepwise, preferably in a direction parallel to the specimen surface, and the distribution of imperfections in the specimen interior deduced from the series of section topographs so obtained. With this technique, diffraction images of individual dislocations were first recorded.

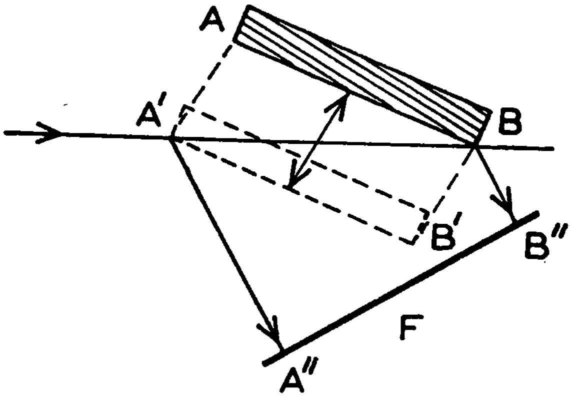

Fig. 3. Arrangement for Bragg reflection, moving reflection specimen.

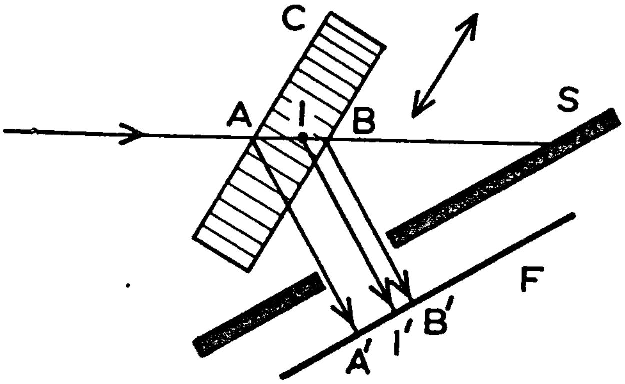

Fig. 4. Arrangements for "section topographs" and "projection topographs".

Characteristic Radiation, Moving Transmission Specimen. Provided the crystal is not too thick and the density of imperfect regions within it not too large, a more direct display of the distribution of imperfections is obtained by the method of "projection topographs."[21] The arrangement is as shown in Fig. 4 with the specimen and emulsion being traversed back and forth together in the direction of the double arrow during the exposure. A stationary slit, *S*, allows only the diffracted beam to fall on the emulsion. The image produced can be regarded as a superimposition of many section topographs, and is a projection along the diffracted-beam direction of the imperfection content of the whole of the specimen. Information on the depth within the specimen of a particular imperfection can often be deduced from the form of its diffraction image, but is usually obtained by taking a stereo-pair of projection topographs. This consists of a pair of reflections *hkl* and $\bar{h}\bar{k}\bar{l}$. The topographs, suitably magnified, may be studied in a conventional stereoviewer, or they may be examined directly through twin microscopes. An example of such a stereopair is shown in Fig. 5, the pair being formed from the 111 and $\bar{1}\bar{1}\bar{1}$ reflections of a natural diamond octahedron. Fig. 6 explains the geometry. The flecks of enhanced dif-

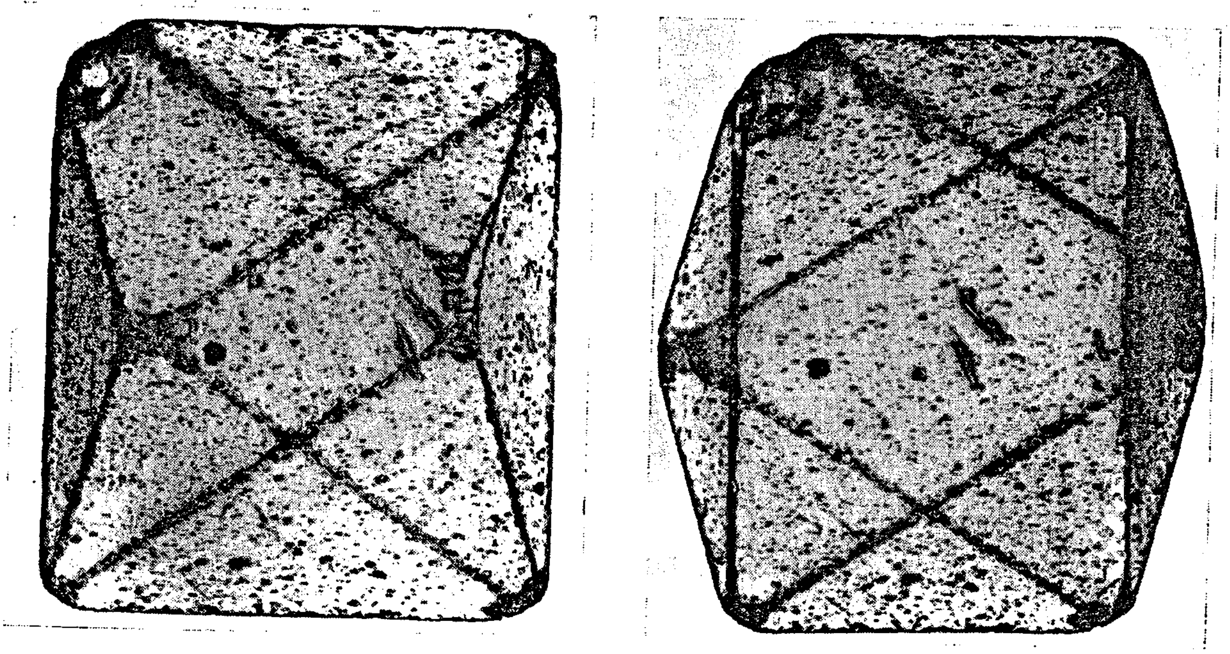

Fig. 5. Stereo-pair of projection topographs of a diamond.

fracting power come mainly from surface damage, such as scratches and ring cracks. Damage is especially heavy along the octahedron edges. The interior of the stone is remarkably free from imperfections, the most noticeable being a small imperfect included diamond which gives a strong reflection.

Incident Beam Monochromatized. Consider the arrangement of Fig. 7. Characteristic radiation from the X-ray tube focus, S, is reflected by a highly perfect monochromator crystal, M, before impinging on the specimen crystal, C. Thus a broad incident beam is obtained in which each wavelength may have a divergence in the plane of the figure of only a few seconds of arc, the angular range of reflection of the perfect crystal M. Misorientations in C can then be measured with great sensitivity by taking a series of topographs with the angular setting of C changing in small steps so that differently oriented parts of it are in turn brought into the Bragg reflecting position and produce blackening on the emulsion, F. The topographs indicate differences in reflecting power of less sensitivity since the divergence of the beam incident upon the specimen will not be large enough to permit imperfect regions in C to give their complete integrated reflection. If the Bragg angles are the same for the reflections from M and C then the dispersionless property of the "parallel" double-crystal spectrometer arrangement is obtained. The angular range over which C reflects will then contain no broadening due to the finite range of wavelengths in the characteristic radiation used. By using an asymmetric reflection from M, as shown in Fig. 7, the beam incident on C can be made wider than the width of the source S and a correspondingly wider specimen surface examined. This arrangement was used by Bond and Andrus.[5] The method has been developed by Bonse and Kappler[7] and Bonse,[6] who have used it for studying the lattice distortions around individual dislocations. The angular resolution can be enhanced by making use of the reduction in angular range of reflection which can occur in asymmetric reflection from perfect crystals.[27, 28]

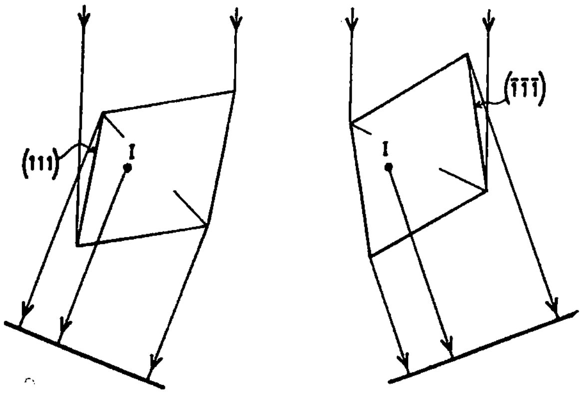

FIG. 6. Settings of diamond octahedron for 111 and $\bar{1}\bar{1}\bar{1}$ stereo-pair of projection topographs. Strongly diffracting inclusion at I.

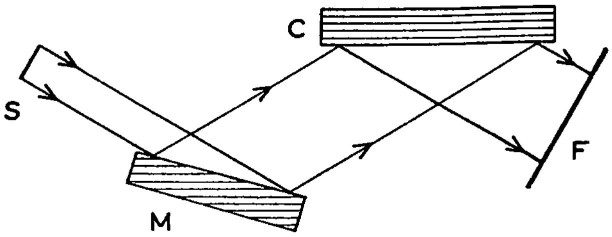

FIG. 7. Arrangement with monochromatization of incident beam.

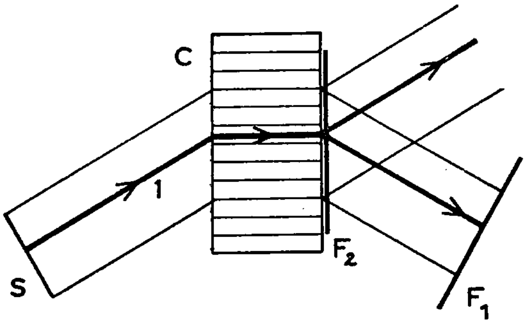

FIG. 8. Arrangements using anomalous transmission.

Specimen Anomalously Transmitting. If the transmission specimen is a highly perfect single crystal, and the product of its thickness, t, and the usual X-ray absorption coefficient, μ, is such that μt is more than a few units, then it is found that for rays satisfying the Bragg condition both primary beam and diffracted beam undergo anomalously low absorption. This effect was discovered by Borrmann[8, 9] (A brief account of its underlying diffraction theory is given by Webb.[32]) For highly perfect specimens with $\mu t \geqslant 10$, say, practically only those rays satisfying the Bragg condition exactly are transmitted through the crystal, and they travel through the crystal in a stream closely parallel to the Bragg planes. In Fig. 8, C represents such a thick, perfect crystal and Bragg reflection is occurring at planes normal to the faces of the specimen. The path of a typical Bragg reflected ray, 1, is as shown. If an extended source, S, is used then a film placed in the diffracted beam at F_1 registers a topograph formed by the anomalously transmitted diffracted rays. This is the arrangement of Barth and Hosemann.[2] Rays of any wavelength satisfying the Bragg condition travel parallel to the reflecting planes within the crystal but outside the crystal their directions correspond to their appropriate Bragg angle with the reflecting planes. Since the source, S, subtends a relatively large angle at the specimen both the $K\alpha_1$ and $K\alpha_2$ radiations, and possibly the $K\beta$ lines as well, can satisfy the Bragg conditions. Hence multiple images of the crystal will appear on the film placed at F_1. This difficulty due to polychromacity can be avoided by placing the emulsion at F_2 in close contact with the exit surface of the crystal. Upon leaving a given point on the exit surface both primary and diffracted rays, of any wavelength satisfying the Bragg condition, will form an image on the same point of the emulsion. Such an arrangement has been used by Gerold and Meier[13] and gives better topographic resolution than the arrangement of Barth and Hosemann.