X-Ray Studies of Surface Layers of Crystals

By ELIZABETH J. ARMSTRONG

1. Introduction

WHEN a crystalline substance is sawed, ground, lapped or polished, the crystal structure adjacent to the worked surface is distorted and ruptured. Since the selective diffraction of X-rays by a crystal is a result of the orderly arrangement of the planes of atoms of the crystal, disturbance of this arrangement is detectable by X-ray diffraction.

Research on aging of quartz oscillator plates seems to indicate that changes which are accelerated by high humidity take place in this disturbed material resulting in changes in the frequeny and activity[1] of the crystal plate. A knowledge of the nature and extent of this disturbed layer is essential to an understanding of the changes that are taking place in it and may contribute to the improvement of the quality of crystal plates, apart from the problem of aging.

The purpose of this paper is to present a review of X-ray techniques that have been or may be useful tools for the examination of the nature of the surface layers of crystals. Each technique is also discussed from the standpoint of the kind of evidence which it seem best suited to bring to light. Familiarity with the general principles of X-ray diffraction as outlined in this Journal, volume xxii, number 3, pages 293 and 297, is assumed.

It has long been known that the nature of the surface preparation of a crystalline substance affects the intensity of the reflected X-rays. As early as 1913, about a year after the first X-ray diffraction experiments with crystals, de Broglié and Lindemann[2] noticed that the spots in Laue photographs of certain crystals were inhomogeneous and suggested the interpretation that the darker parts of the spots might result from disturbed material. A. H. Compton[3], using a double crystal spectrometer in 1917, found that the reflection from a ground surface of a calcite crystal was three times that from a cleavage face.

[1] One plate is said to have greater activity than another similar plate if its amplitude of oscillation is greater when the two are tested under identical conditions. The activity of a plate is reduced by friction with its mountings or with particles on its surface, either of quartz or of a foreign material.

[2] de Broglié, M. and Lindemann, F.-A., *"Sur les Phénomènes Optiques Présentés par les Rayons de Röntgen Rencontrant des Milieux Cristallins, Comptes Rendus,* 156 (1913), pp. 1461–1463.

[3] Compton, A. H., *"The Reflection Coefficient of Monochromatic X-Rays from Rock Salt and Calcite," Phys. Rev.,* 10 (1917), pp. 95–96.

The explanation of the higher intensity of reflection from the disturbed surface lies in the fact that the rays of the incident X-ray beam, collimated by a pair of slits, are not perfectly parallel, but diverge, meeting the crystal plate at various angles, whose range, depending on the geometry of the slits, is usually about 15 to 25 minutes of arc. If the surface regiln of the crystal plate is undisturbed only a very small part of the incident beam will meet the crystal at the Bragg angle for X-ray reflection. If, however, some of the quartz has been disturbed it will have a variety of orientations with respect to the main crystal structure and the various disturbed bits of quartz will be at the Bragg angle for the various divergent rays of the incident X-ray beam. In this way more of the incident beam is reflected by a disturbed crystal surface than by an undisturbed crystal surface. The disturbed material measured by this technique differs in orientation from that of the main plate by not more than a few minutes so that even this disturbed material uses only a small sector of the divergent incident beam. Surface particles misoriented by larger angles are not numerous enough to reflect X-rays into the ionization chamber with measurable intensity.

An alternative interpretation of the higher intensity of reflection from the disturbed material should be mentioned although it has little practical significance. Consideration of the Bragg equation, $n\lambda = 2d \sin \theta$, will show that a range of d values would make it possible for a range of θ values to satisfy the equation. If, therefore, there were some variability in the spacing, d, between the atomic planes from which the X-rays were being reflected, reflection would take place over a corresponding range of angles of incidence.[4] Such variability in d spacing would be a result of lattice distortion. It would generally be accompanied by misorientation and therefore its consideration as a phenomenon distinct from misorientation becomes rather academic. The disturbance will therefore be spoken of as misorientation although it probably also involves small changes in d spacing.

Measurable lattice distortion can be produced by other means than surface working. The reflection-intensity of an etched plate is increased three or four times if the plate is strained by bending during the reflection of the X-ray beam. When the pressure on the plate is released the reflection-intensity resumes its former value. The distortion produced by unequal pressures on the plate results in the heterogeneity of orientation which makes possible the use of a larger part of the incident beam, resulting in higher reflection-intensity. When lapped plates are similarly deformed the increase in reflection-intensity is less since some heterogeneity of orientation already exists. As would be expected, the effect of the deformation is progressively less with

[4] Consideration of the known compressibility and tensile strength of quartz indicates that the maximum change in d spacing which could be obtained would be of the order of 0.1%. For small values of θ the change in θ for this d change would also be 0.1%, increasing, with larger θ values to about 0.2% at $\theta = 70°$.

increasing grain size of the abrasive with which the surface of the plate was lapped.

2.1 The Single Crystal Spectrometer

The single crystal spectrometer is used for X-ray measurement of the orientation of quartz oscillator plates. In this instrument slit-collimated X-rays are reflected from a crystal into an ionization chamber and the relative intensity of the reflected X-rays is read from a meter showing the

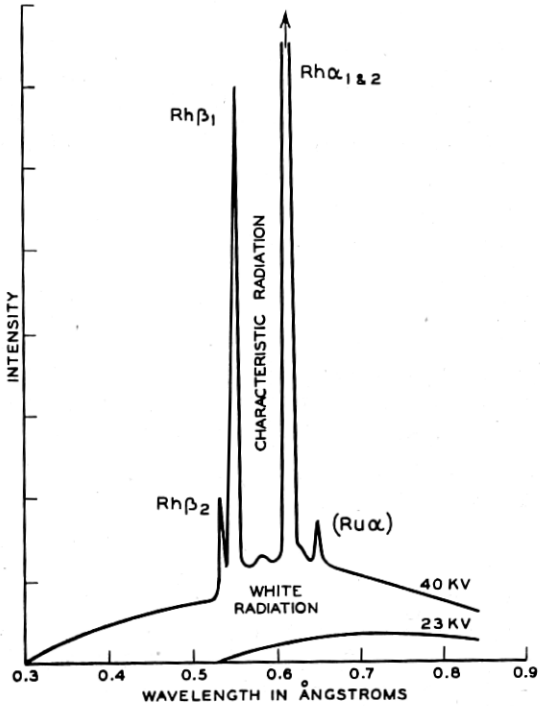

Fig. 1.—X-Ray spectra from a rhodium target at 23 and 40 kilovolts. Ruthenium impurity present. (Adapted from *Siegbahn, Spectroscopy of X-Rays*).

amplified current resulting from the ionization of the gas in the chamber by the X-rays. Since the reflected white radiation is too weak to cause a measurable amount of ionization, only the reflected characteristic radiation is measured by the ionization chamber. For most purposes a copper-target tube is used and the β radiation (comparable to Rh_β of Fig. 1) is eliminated by a selective filter so that only the α radiation is used, the X-rays thus being essentially "monochromatic".

Three different techniques for examining surface layers of crystals with the single crystal spectrometer will be described. Two of these employ

photographic films or plates in addition to the ionization chamber for measuring the reflected rays.

2.2 Reflection-Intensity Measurements on the Single Crystal Spectrometer with the Ionization Chamber (Fig. 2)

Working with the single-crystal spectrometer, Bragg, James and Bosanquet[5] found the reflection-intensity from a ground face of rock salt two to four times that from a cleavage face. Dickinson and Goodhue[6] found the reflection-intensity from ground faces of sodium chlorate and sodium

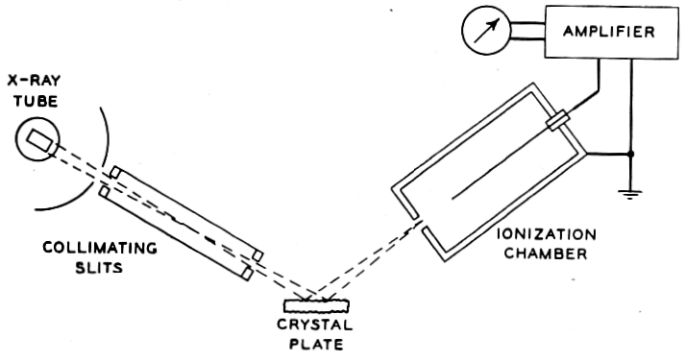

Fig. 2.—Single crystal spectrometer

bromate twice that from the natural face. Sakisaka[7] found the reflection-intensity from a quartz plate lapped with #30 carborundum $2\frac{1}{4}$ times that from a plate lapped with very fine emery, which, in turn, was twice that from an etched plate. Recent measurements by the writer have shown that the reflection-intensity of an etched surface increases with progressive lapping and that of a ground surface decreases with progressive etching as shown in Fig. 3. In these figures the reflection-intensity is given in terms of the ratio of the intensity from the test plate to that from a standard plate of the same cut, etched 20 minutes following fine lapping. The initial rate of increase of intensity-ratio with lapping or decrease with etching is very high.

This technique would be most useful in sample-testing groups of plates to check whether they had been inadequately etched or whether any lapping at all had occurred after etching. (In either case the plate would be subject to

[5] Bragg, W. L.; James, R. W. and Bosanquet, C. H.; "The Intensity of Reflexion of X-Rays by Rock Salt," Part I. *Phil. Mag.* 41 (1921) pp. 309–337; Part II, *Phil. Mag.* 42 (1921) pp. 1–17.

[6] Dickinson, R. G. and Goodhue, E. A.; "The Crystal Structure of Sodium Chlorate and Sodium Bromate," *Jour. Amer. Chem. Soc.* 43 (1921) pp. 2045–2055.

[7] Sakisaka, Y.; "The Effects of the Surface Conditions on the Intensity of Reflexion of X-Rays by Quartz," *Japanese Jour. Phys.* 4 (1927) pp. 171–181.

aging.) Although a plate lapped with 180 carborundum can be easily distinguished from one lapped with 303½ emery by a comparison of intensity ratios, plates lapped with nearly similar abrasives cannot be distinguished with certainty, except on a statistical basis.

That the disturbed material measured by this technique differs in orientation from that of the main plate by less than a few minutes is shown by the fact that the range of incident angles over which ionization-detectable X-ray reflection takes place from a lapped crystal plate is the same within the

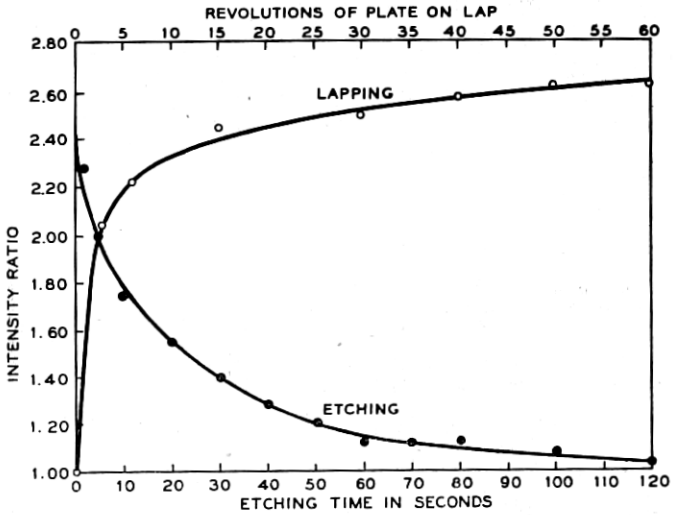

Fig. 3.—Effect on reflection-intensity produced by lapping on etched plate with 303½ emery and soap solution and by etching the lapped plate with 48% hydrofluoric acid at 25°C.

limits of error of measurement as that for reflection from an etched crystal plate.

2.3 Photographic Measurement of Angular Misorientation with the Single Crystal Spectrometer

A technique which does indicate quartz misoriented by more than a few minutes has been devised by Dr. C. J. Davisson. Although the X-rays reflected from this material are too weak to produce a measurable current in the ionization chamber, they will darken a photographic plate or film if adequate exposure time is allowed. The principles of this technique are illustrated in Fig. 4 and some of the resulting photographs are shown in Figs. 5 and 6.

The plate to be measured is placed at the Bragg angle to the incident X-rays as determined by preliminary measurement of the maximum ionization

current produced in the ionization chamber which is at twice the Bragg angle to the incident beam. A film in a paper envelope is then placed before the ionization chamber in a holder which permits a small portion of it to be exposed at a time. A brief (5 or 10-second) exposure is then made with the crystal plate in this "zero position",[8] (see Figs. 4 and 5), recording the strong characteristic radiation reflected from the main crystal plate. At the same

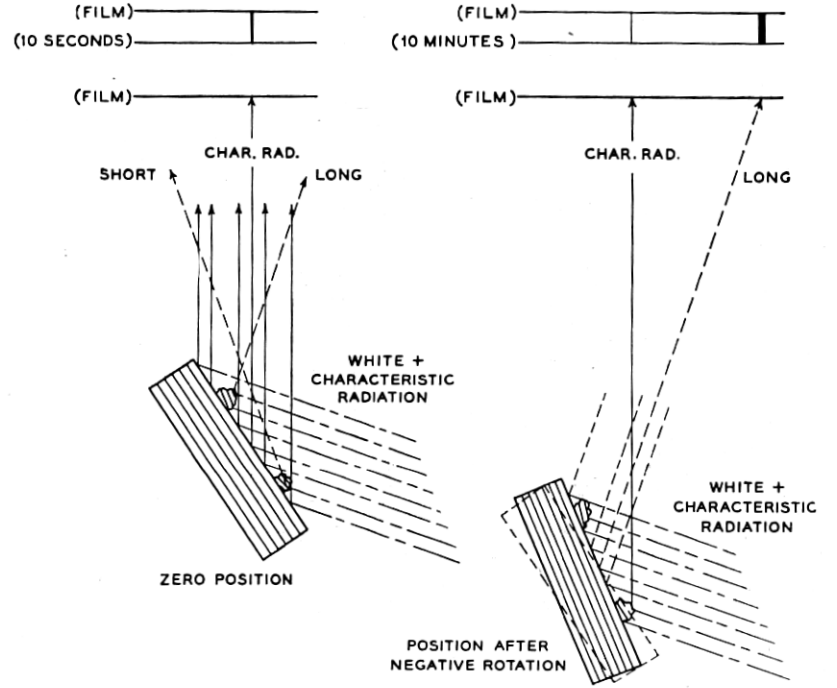

Fig. 4.—Spectrometer photography of misoriented crystalline material

time the weak white radiation is being reflected from the disturbed material, but this radiation is relatively so weak and the disturbed material of such

[8] To check the correctness of the "zero" setting, a "rocking" exposure is taken, during which the plate is rocked through the Bragg angle. The upper half of the beam should be shielded for the "zero" exposure and the lower half for the "rocking" exposure so that the film need not be moved between the two exposures. In the "rocking" exposure the beam is reflected during only a fraction of the exposure time and because the exposure is so brief only the reflection of the strongest part of the incident beam (the part that is going to produce the reflections in later exposures) is recorded. In the "zero" exposure the crystal plate may have been set so as to reflect the divergent, weaker rays of the beam which may differ in direction from the strong part of the beam by as much as 15 minutes. The terms "stronger" and "weaker" do not refer here to characteristic and white radiation, but to parts of the beam that have more or fewer X-rays due to the geometry of the collimating system with relation to the target.

relatively small volume that the reflection does not noticeably darken the photographic film in five seconds. Successive ten-minute exposures are then taken with the crystal plate turned at successively greater angles from the zero position. At any given angle the disturbed quartz that has thus been brought into the proper position to reflect the characteristic radiation does so, producing a center line on the film whose intensity is roughly proportional to

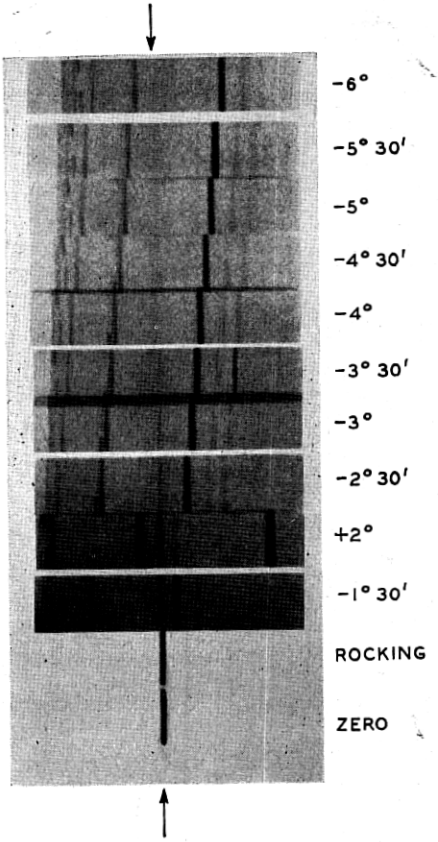

Fig. 5.—Spectrometer photograph of BT quartz plate lapped with 303½ emery

the volume of quartz misoriented to this angle. Various wave-lengths of the white radiation will satisfy the Bragg equations for various atomic planes of the main plate at each angular position and will be reflected to other positions on the film. Although the incident white radiation is relatively weak the reflected beams are strong enough to darken the film in ten minutes because rays reflected from the main plate are reflected by a much greater

volume of quartz than are rays reflected from the disturbed layer. The strongest of these "white" reflections from the main plate is that from the set of atomic planes most nearly parallel to the surface of the plate, the planes that reflected the characteristic radiation in the zero position.

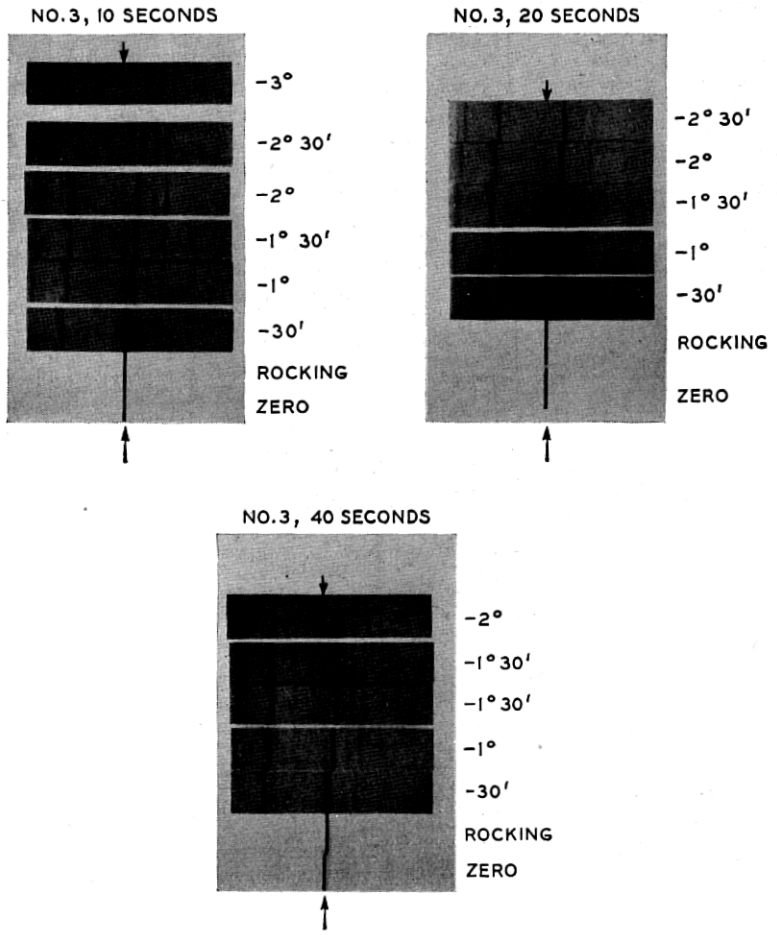

Fig. 6.—Spectrometer photographs showing effect of etching a 303½ emery-lapped BT quartz plate with 48% hydrofluoric acid

In Fig. 5, the central line (indicated by the arrow) resulting from the characteristic radiation reflecting from the disturbed quartz, is distinctly present through the 4° exposure but not in higher-angle exposures, indicating that in the 303½ emery-lapped surface from which the X-rays were reflected there was not enough quartz misaligned by more than 4° to reflect a beam that

would visibly affect a photographic film during a ten-minute exposure. The dark line that moves to the right as the negative angular rotation increases results from the reflection of progressively longer wave-lengths from the quartz of the main plate. The three series of exposures in Fig. 6 show the progressive removal of the disturbed quartz by etching with 48% hydrofluoric acid. After ten seconds' etching the line from the disturbed material does not show distinctly beyond the 1° 30′ position; after 20 seconds' etching it is distinct only through the 1° 00′ position and after 40 seconds it can only be seen distinctly at the 30′ position. If the film had been exposed for a longer time at each position the line from the disturbed material at each angle would have persisted with longer etching. With the arbitrarily

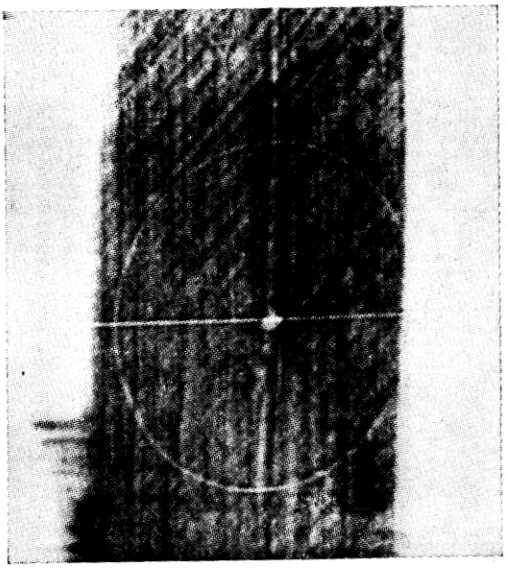

Fig. 7.—Photograph produced by reflection of a broad X-ray beam from the (100) cleavage face of a rock salt crystal (Berg)

chosen ten-minute exposures a line from material misoriented by 45′ disappears after about 25 seconds' etching with 48% hydrofluoric acid, but the disappearance of the 30′ line occurs only after 70 seconds' etching, which removes an amount of quartz equivalent in weight to a layer about four-tenths of a micron thick on each surface.

With this technique we are measuring the more grossly misoriented surface material, material that is probably not continuous with the quartz of the main plate. This is evident from the fact that a piece of quartz would have to have a length-thickness ratio of 26 to 1 to take a 3° deflection without breaking and the microscopic evidence does not indicate the presence of any such long, thin pieces of quartz attached to the plate.

Although about a half-minute's etching with 48% hydrofluoric acid removes all quartz misoriented by more than 45′, quartz misoriented by a smaller angle than this is not entirely removed by more than an hour's etching, as indicated by photographs taken with X-rays passing through the plate, a technique to be described later in this paper. The ionization chamber and amplifier are not sensitive enough to register the reflection from the small amount of this material left after two minutes' etching.

The disappearance of the more widely misoriented material in the earlier stages of etching may mean either that this material is preferentially removed or that there is uniform removal of all the misoriented material with the consequent disappearance of that which is smallest in amount. Geiger-Müller counter measurements of the intensity-distribution of the reflections from the misaligned material at various angles at the various stages of etching would indicate which of the two alternatives is true. These measurements are being made by Davisson and Haworth, but are not yet complete.

2.4 Photography of the Disturbed Surface with a Broad X-Ray Beam

A second photographic method with the single-crystal spectrometer, used by Berg in 1931[9], Gogoberidze in 1940[10], and others involves the reflection of a broad monochromatic beam from an appreciable area of the crystal surface (placed at the Bragg Angle, θ) onto a photographic plate or film placed parallel to the crystal face. The different reflection-intensities from the variously disturbed parts of the surface of the crystal plate darken the film differently, giving a map-like picture of the distribution of different degrees of disturbance over the surface of the plate. One picture produced in this way by Berg is reproduced in Fig. 7. The thin white cross and circle are reference marks scratched on the surface of the rock-salt crystal, the lines being parallel to the cube edges. The two sets of sub-parallel streaks are the traces of dodecahedral {101} planes and "show that the crystal structure in these places differed from the ideal lattice". They are interpreted as slip planes (störebenen) in the crystal. C. S. Barrett[11] has recently refined this technique and broadened its application to the study of a wide variety of metallurgical problems.

The application of this technique to the study of quartz surfaces might provide useful information on disturbance distribution which is not furnished by the other techniques.

[9] Berg, Wolfgang, "Über eine röntenographische Methode zur Untersuchung von Gitterstörungen an Kristallen," *Naturwissenschaften* 19 (1931), pp. 391–396.

[10] Gogoberidze, D. B., "Investigation of Surface Structure of Crystals by Means of Reflection of a Monochromatic X-Ray Beam, *Jour. Exptl. Physics, U.S.S.R.* 10 (1940) p. 96 (in Russian).

[11] C. S. Barrett; "A New Microscopy and Its Potentialities," *Metals Technology*, April, 1945.

3.1 The Double Crystal Spectrometer

In the double crystal spectrometer (Fig. 8), X-rays reflected from a crystal plate are again reflected from a second crystal plate into the ionization chamber. Their intensity is indicated by a meter showing the amplified ionization current, as in the case of the single crystal spectrometer. The divergent white rays from the collimating slits are reflected from crystal plate A as shown in Fig. 8: those of longer wave-length at higher angles and those of shorter wave-length at lower angles in accordance with Bragg's law. If

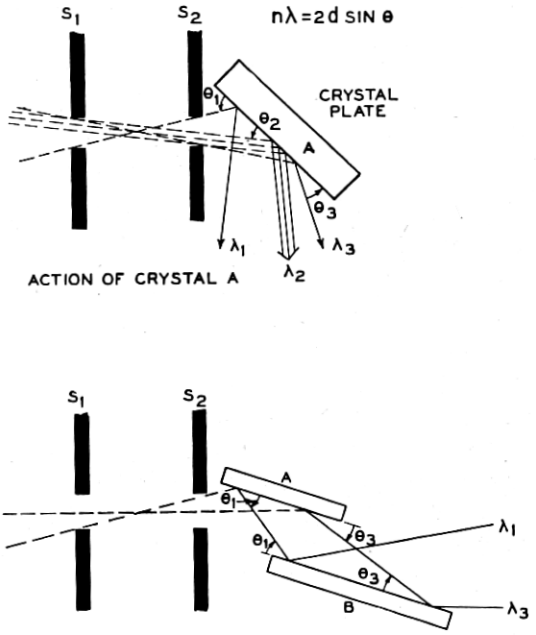

Fig. 8.—Double crystal spectrometer, parallel position. S_1 and S_2 are collimating slits

crystal plates A and B are placed so that similar sets of atomic planes in the two plates are parallel, the same rays that were reflected from plate A will also reflect from plate B as shown in Fig. 9 since each ray will meet this plate at the particular angle, θ, which will satisfy Bragg's law for that wave-length for the atomic planes in question.

If plate B is rotated a few seconds away from this position, however, and if the crystal is perfect, the conditions for reflection are destroyed for all rays so that no X-rays enter the ionization chamber. However, a plate with a surface layer of misoriented crystal material will still reflect when thus

rotated because the misoriented particles will be brought into the reflecting position as the main plate is turned away from it. The farther the main plate is turned from the reflecting position, the weaker will be the reflected radiation because less quartz will be misoriented to this angle. In this respect the double crystal spectrometer technique is similar to C. J. Davisson's photographic technique, but is measuring much smaller angular rotation and higher reflection-intensity. A curve of the variation of reflection-intensity with angular rotation of the B crystal plate for two differently finished crystal plates measured by Davis and Stempel[12] is shown in Fig. 9

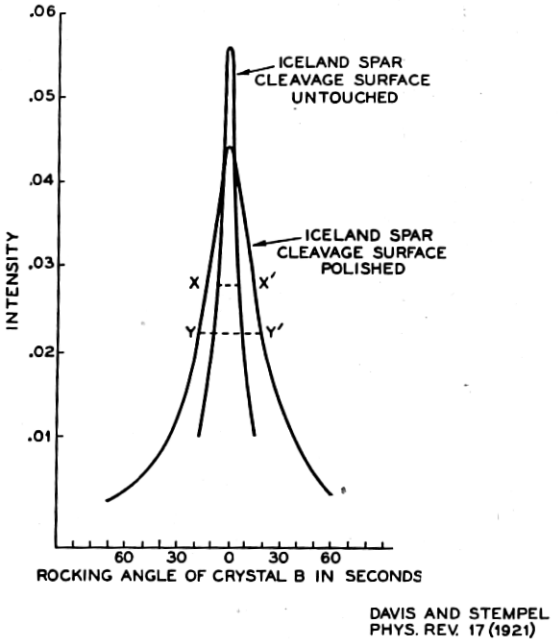

Fig. 9.—Double crystal spectrometer rocking curves

The higher reflection-intensity at the "zero angle" and the very rapid decrease of intensity as the plate is turned away from this position show that the untouched surface is less disturbed. The lower reflection-intensity at the "zero angle" and the less rapid decrease of intensity as the plate is turned away from this position show the polished surface to be more disturbed. The width of such "rocking" curves at half-maximum (as x–x′ and Y-Y′ in Fig. 9) has often been taken as a measure of perfection of the reflec-

[12] Davis, B. and Stempel, W. M., "An Experimental Study of the Reflection of X-Rays from Calcite," *Phys. Rev.* 17 (1921) pp. 608–623.

ting crystal. Bozorth and Haworth[13] made such measurements for variously prepared surfaces of quartz and found that the rocking-curve width at half-maximum was least for etched plates, the smallest width measured being 1.7 seconds. The greatest rocking-curve width measured was 88 seconds for which both crystal plates (A and B, Fig. 8) were lapped with 100-mesh carborundum. Bozorth and Haworth also showed that the rocking-curve width decreased very rapidly in the initial stages of etching

With this technique we are measuring the angular frequency distribution of the disturbed material that was detected with the intensity-ratio measure-measurements with the single crystal spectrometer. Thus, with the rocking curve, we show the intensity for each angle of incidence separately, but with the single crystal spectrometer we measure the intensity for a relatively wide range of angles of incidence at one measurement, which is the integrated intensity under the double crystal spectrometer rocking curve.

None of this small-angle disturbance is detectable by the Davisson photographic technique because at small angles the reflected rays are too close to those from the main plate and become confused with them on the film. Conversely, none of the material detected by the Davisson photographic technique is detectable by this technique because the intensity of the reflected rays from large-angle disturbance is not great enough to produce a measurable current in the ionization chamber.

Together, these various measurements indicate a relatively large amount of quartz misoriented by less than a minute and a smaller amount of quartz misoriented by larger angles up to three or four degrees.

The use of a photographic film in place of the ionization chamber in the double crystal spectrometer would presumably permit the precise measurement of the smaller amount of material misoriented by more than that now measured with this instrument, as in the Davisson technique with the single crystal spectrometer. This has not, to the writer's knowledge, been done.

4.1 The Transmission Laue Camera

In the transmission Laue camera (see Fig. 10) a beam comprising a large range of wave-lengths is passed through a stationary plate. Various sets of atomic planes in the crystal, each with a different interplanar spacing, d, making a variety of angles, θ, with the incident beam, reflect whatever wave-lengths of radiation in the incident beam satisfy the Bragg equation, $n\lambda = 2d \sin \theta$, and the reflected beams are recorded photographically. Figure 11 shows films resulting from one-hour exposures. As in the case of the single-crystal spectrometer, the slit-collimated beam comprises non-parallel rays,

[13] Bozorth, R. M. and Haworth, F. E., "The Perfection of Quartz and Other Crystals and Its Relation to Surface Treatment," *Phys. Rev.* 45 (1934) p. 821–826; *Bell Telephone System Technical Publications Monograph* B-801.

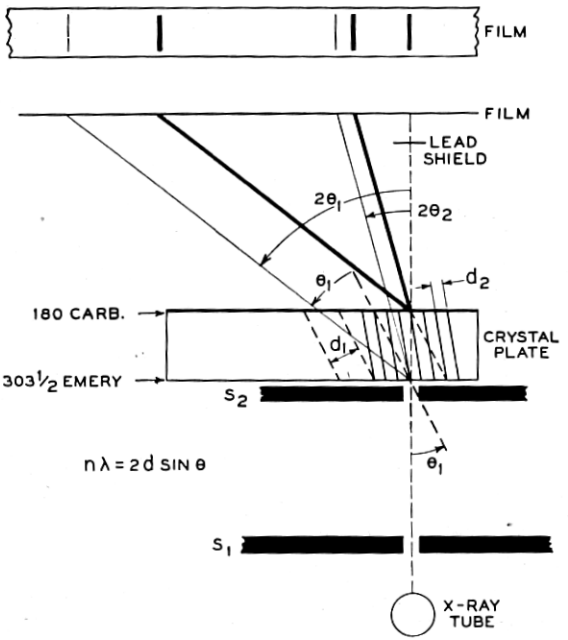

Fig. 10.—Section of transmission Laue camera. S_1 and S_2 are collimating slits

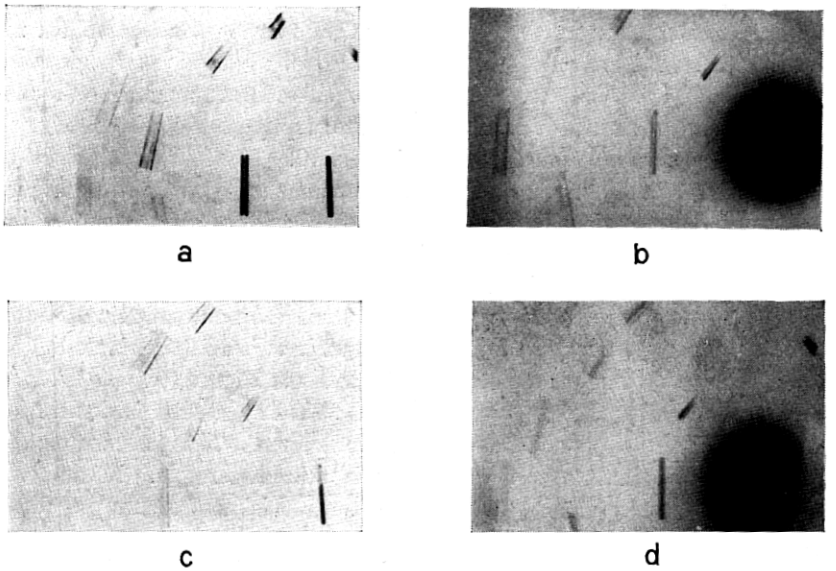

Fig. 11.—Transmission Laue photographs of a 4 mm.-thick BT quartz plate. (a) Face nearer film lapped with 180 carborundum. Other face lapped with 303½ emery. (b) Same as a, after 47 hours' etching. (c) Same as a, but through a different part of the plate. Plate rotated 180° in its own plane. (d) Same as c, after 20 minutes' etching.

but in this case exposures are long enough to record the "white" radiation reflected from both the small-angle disturbed and undisturbed material. If reflections from material misoriented by more than a few minutes were recorded on the film the lines from the reflected X-rays would be broader than they are.

In the undisturbed material there is one wave length from a ray traveling in a given direction that will satisfy the Bragg equation for a given set of atomic planes. Most of these "usable" X-rays are reflected by the first thin layer of undisturbed crystal they meet and therefore very little reflection of X-rays of this wave-length from this ray takes place from deeper layers of the undisturbed crystalline material. This removal of the reflectable X-rays by the first thin layer of undisturbed crystal is known as "primary extinction".

In the disturbed surface layer, on the other hand, regions of dissimilar orientation are superposed. In this case a ray traveling in a given direction will have X-rays of one wave-length subtracted from it by the first crystalline material of a particular orientation it meets in accordance with the Bragg equation; then, beneath this, crystalline material at a different orientation will subtract from it X-rays of a different wave-length and so on so that from each ray a broader range of wave-lengths is diffracted by the disturbed material than by the undisturbed, resulting in a stronger reflected beam from the disturbed material. Since the lapped surfaces of the crystal plate give a stronger reflected beam than the undisturbed interior of the plate, the reflection of the slit collimated beam from each set of atomic planes appears on the film as a pair of lines. The density of these lines is related to the disturbance and their width is related to the depth of the disturbed surface layer, as shown diagrammatically in Fig. 10. The four photographs in Fig. 11 were taken in this way, all through the same BT quartz plate. Figure 11a shows the reflections from the various atomic planes of the 4 mm.-thick BT-cut quartz plate, lapped on one side with coarse abrasive (180 carborundum) and on the other with fine abrasive (№ 303½ emery). As shown in Fig. 10, the coarsely lapped surface was toward the photographic film and therefore the line closer to the line from the direct beam (the single line in the lower right corner) is the stronger of the two. Figure 11b was taken in the same way after the plate had been etched in 48% hydrofluoric acid for 47 hours. The acid was renewed every few hours. The presence of disturbed material near the two surfaces is still discernible. Micrometer measurements after etching indicated that the thickness of the plate had been reduced by 0.14 mm.

Such a measurement is from the peaks of the rugged etched surface on one side of the plate to the peaks on the other side: over most of the plate the etching had proceeded to a greater depth than the .07 mm. indicated by the

micrometer measurements. Since the disturbance is still discernible it appears that its depth in this plate was greater than .07 mm.

With the discovery that the disturbed material may be more than 70 microns thick, it becomes apparent that great care must be taken to remove the disturbance produced by all previous lapping and sawing prior to measurement of disturbance produced by a particular lapping technique. This may require more than 48 hours' etching with 48% hydrofluoric acid which will produce a rugged surface. An alternative procedure is to use a natural crystal which has never been cut or worked. Since the natural faces of some crystals do show disturbance, preliminary tests should be made with the various techniques for detecting the presence of any disturbed material. A transmission Laue photograph of a small quartz crystal from Herkimer County, N. Y., taken by C. J. Davisson, showed no disturbed material. If a natural face of such a crystal were lapped under carefully controlled conditions and the resulting disturbance measured by the various techniques, a reliable picture of the disturbance produced by that lapping procedure would be obtained.

In many of these photographs some darkening occurs between the two lines that mark the outer surfaces of the plate. In most cases it appears as well-defined streaks, as in 11c, but may be irregular, as in 11a. Such streaks appear to be due to disturbed zones within the quartz plate whose disturbance is related to the growth history of the crystal. Where they adjoin the disturbed surface layer they may be responsible for erroneous measurements of the misorientation and depth of the surface layer.

Photograph 11c was taken prior to any etching, like 11a, but through a different part of the plate and shows different internal imperfections. Photograph 11d was taken through the same part of the plate after only 20 minutes' etching and shows very little surface disturbance. To get a picture of the distribution of the surface disturbance and internal imperfections of a plate a series of exposures should be taken with the plate translated a short distance relative to the beam between each exposure.

Measurements of the depth of the disturbed layer have given widely different results with different techniques. The Laue photographs just described indicate the depth to be more than .07 mm. or 70 microns in some cases, even with a 303½ emery finish.[14] This is in accord with the 0.1 mm. depth assigned by Y. Sakisaka on the basis of two sets of measurements made by him with two widely different techniques.[15] This value is also in

[14] Since adequate precautions for the removal of all previous disturbance were not taken, this value may be erroneous.

[15] Sakisaka, Y., "The Effects of the Surface Conditions on the Intensity of Reflexion of X-rays by Quartz, *Japanese Journal of Physics* 4 (1927) p. 171–181.

Sakisaka, Y., "Reflexion of Monochromatic X-rays from Some Crystals," *Proc. Phys.-Math. Soc. of Japan*, Ser. III, v. 12 (1930), p. 189–202.

accord with the measurements on the double crystal spectrometer made by Bozorth and Haworth who show that after 20 hours' etching with 48% hydrofluoric acid at 30° C. the rocking-curve width of a plate originally lapped with 100-mesh carborundum was still measurably greater than that of a plate originally lapped with 600-mesh carborundum.[13]

The measurements that have given half a micron for the depth of the disturbed layer have been made with techniques incapable of showing part of the disturbed material. The reflection-intensity measurements made with

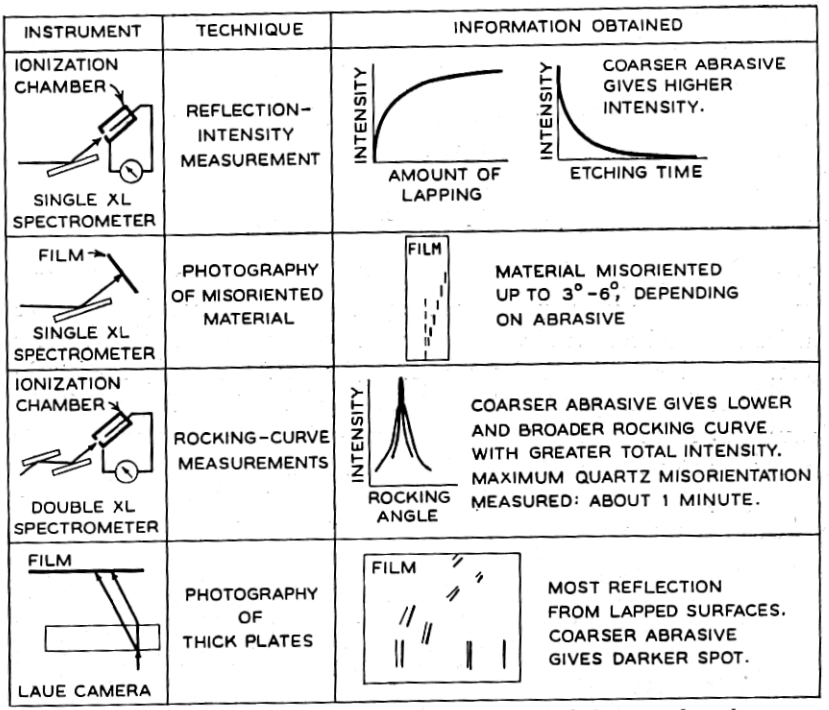

Fig. 12.—Diagrammatic summary of instruments, techniques, and results

the single crystal spectrometer can only show the material present in large enough amount to cause measurable ionization in the ionization chamber. The Davisson photographs with the single crystal spectrometer cannot show material misaligned by less than 15 minutes. Any photographic technique which is capable of measuring material misoriented by a few seconds has shown a disturbed layer much thicker than half a micron at any worked surface of quartz crystal.

Figure 12 is a diagrammatic summary of the various techniques that have been described. Table 1 summarizes the present knowledge concerning the

TABLE I

SUMMARY OF INFORMATION CONCERNING THE NATURE OF THE DISTURBED SURFACE MATERIAL OF QUARTZ PLATES

Description of the disturbed material	Method of detection
Randomly oriented powder on the surface, removable by scrubbing	Electron diffraction photography only
Material misoriented from approximately 45′ to approximately 4½°, removable by about 30 seconds' etching with 48% hydrofluoric acid. Not removable by scrubbing. About ½ micron thick.	Photography with the single crystal spectrometer
Material misoriented from 0° to 45′, in some cases requiring more than 47 hours' etching with 48% hydrofluoric acid for removal. Not removable by scrubbing. May be 50–100 microns thick.	Reflection intensity measurements with the single crystal spectrometer. Rocking-curve width measurements with the double-crystal spectrometer. Laue photography of thick crystal plates.

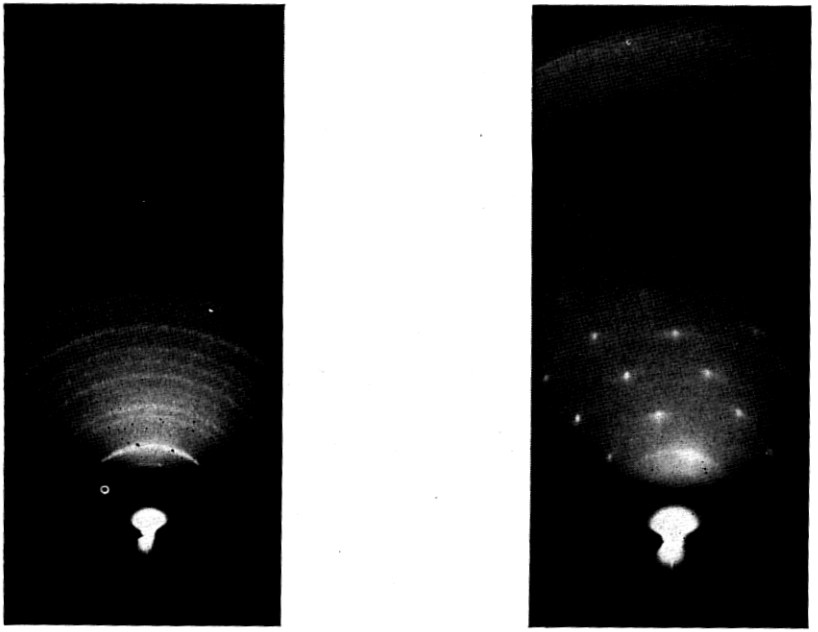

Fig. 13.—Electron diffraction photographs of a BT quartz plate taken with a 50 kv. electron beam (C. J. Davisson)

disturbed layer of worked surfaces of quartz, indicating the technique through which the information was obtained in each case. In order that this table shall be complete the electron diffraction work of C. J. Davisson

must be included although it does not properly belong in a paper on X-ray techniques. Dr. Davisson took an electron diffraction photograph of a quartz plate that had been lapped with 303½ emery, water rinsed, and air dried. The plate was then scrubbed vigorously with soap and water and toothbrush and a second photograph was taken. The two photographs are reproduced in Fig. 13. The first shows a series of continuous rings indicating the presence of a large number of small particles of quartz with random orientation. In the second photograph, these rings have disappeared and there remain only arc-segments associated with spots. The spots are the "reflections" from undisturbed quartz. The arcs represent quartz rotated through a small range of angles from this position, the misoriented material indicated by the Davisson photographs with the single crystal spectrometer. These electron diffraction photographs show that a lapped plate has randomly oriented quartz on its surface which may be removed by scrubbing and quartz with limited misorientation which is not removed by scrubbing. No X-ray technique has shown the existence of the randomly oriented material.

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