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X-RAY REFLECTION FROM INHOMOGENEOUSLY STRAINED QUARTZ

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ABSTRACT

Laue spots from quartz crystals undergoing piezo-electric vibrations are found to have a fine structure. The nature of this structure is such as to indicate that the increase of reflecting power of a given crystallographic plane varies greatly from point to point in the crystal, while at a given point in the crystal the reflecting power of different planes is increased in different amounts with a resultant intensity distribution unlike that obtained from a rough-ground surface of the crystal. It is proposed that these effects are due to the existence of strain gradients in the crystal, distributed at random in the rough-ground surface but in definite directions in the case of a vibrating crystal. This view is substantiated by some static tests on inhomogeneously strained crystals. Some specimens of quartz with imperfect interior regions are found to have random strain gradients. The effect on reflected intensity may be accounted for on the basis of a reduction of extinction. The phenomenon is used in the study of modes of vibration of quartz plates.

IT IS well known that the ability of a crystal to reflect x-rays is influenced by the degree of perfection of the crystal. This is explained by assuming the presence of an extinction of the x-ray beam superimposed upon the ordinary absorption of the beam.[1] Extinction is of two types, primary and secondary. Considering a crystal to be a mosaic of perfect crystallites, the relation of each type to the structure of the crystal lattice may be stated thus: primary extinction arises within the perfect crystallites and is reduced by a reduction of the size of these (provided they are not already smaller than about 10^{-4} cm); secondary extinction depends upon the parallelism of the blocks and is reduced when this is reduced.

Many investigators[2,3,4,5,6,7] have noted that grinding or polishing the surfaces of various crystals greatly increases their reflecting power as would be expected if this treatment reduced perfection and consequently extinction in the crystal.

Fox and Carr,[8] looking for a change in the sharpness of Laue reflections

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[1] cf. C. G. Darwin, Phil. Mag. **43**, 800 (1922); W. L. Bragg, C. G. Darwin, R. W. James, Phil. Mag. **1**, 897 (1926).

[2] A. H. Compton, Phys. Rev. **10**, 95 (1917).

[3] W. L. Bragg, R. W. James, and C. H. Bosanquet, Phil. Mag. **41**, 309 (1921); **42**, 1 (1921).

[4] R. G. Dickenson and E. A. Goodhue, J. Am. Chem. Soc. **43**, 2045 (1921).

[5] B. Davis and W. M. Stempel, Phys. Rev. **17**, 608 (1921); **19**, 504 (1922).

[6] E. Wagner and H. Kurlenkampff, Ann. d. Physik **68**, 369 (1922).

[7] Y. Sakisaka, Jap. Jour. Phys. **4**, 171 (1927); Proc. Phys.-Math. Soc. of Japan, Ser. III, **12**, 189 (1930).

[8] G. W. Fox and P. H. Carr, Phys. Rev. **37**, 1622 (1931).

from a quartz plate put into piezoelectric oscillation, found instead a large change in intensity of the Laue spots. Langer[9] suggested that the phenomenon could be explained by a tilting of the mosaic blocks during oscillation of the crystal—a theory based on the reduction of secondary extinction as a result of the tilting. Explanations were independently advanced by Nishikawa, Sakisaka, and Sumoto,[10] and by Barrett[11] on the basis of a reduction of extinction due to inhomogeneous strains in the crystal, and Laue photographs were published showing that the interior of the crystal becomes highly reflecting during oscillation[12] in the same way that the surfaces become highly reflecting when ground. That static inhomogeneous strains within the elastic limit could thus affect the reflecting power of quartz and certain other crystals was demonstrated by Nishikawa, Sakisaka and Sumoto,[13] who also showed that homogeneous strains had little or no effect.

The failure of Fox and Cork[14] to observe changes in intensity of oscillating quartz using reflection from the surface of a quartz plate in a Bragg spectrometer was probably due to the existence of an imperfect surface layer which was the seat of practically all the reflected energy in their experiment, a layer in which extinction had already been reduced to a minimum by the preparation of their crystal.[15]

Experimental Method and Results

When the Laue method is used with a sufficiently well-defined primary beam, the Laue spots are elongated images of the slit, each portion of the spot being formed by rays reflected from a corresponding region within the crystal. Contrary to results of previous observers who did not attend carefully to the parallelism of the beam, the spots from a vibrating quartz crystal are not uniformly dark, but generally display a fine structure. Laue photographs of the same part of a crystal in both vibrating and rest conditions showed that this fine structure is not similar to that produced by permanent flaws in the crystal which sometimes become evident by this method. Nor is it caused by the ground or polished surface of the crystals: the different type of structure seen in the spots from non-oscillating ground or polished crystals as well as the added length of exposure time necessary to form a pattern of non-oscillating crystals proves this. Peculiarities of x-ray focal spot or slits could not have caused the fine structure, nor could the presence of characteristic radiation in the primary beam. The origin of the fine structure was

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[9] R. M. Langer, Phys. Rev. **38**, 573 (1931).

[10] S. Nishikawa, Y. Sakisaka, and I. Sumoto, Phys. Rev. **38**, 1078 (1931).

[11] C. S. Barrett, Phys. Rev. **38**, 832 (1931).

[12] Here, and wherever hereafter the term "oscillating" occurs in this paper, the reader will understand that the word "vibrating" is intended. The former term is so completely established in electrical usage that it is adopted in this paper, even at the risk of confusion with its ordinary implication to those familiar with x-ray spectrographs.

[13] S. Nishikawa, Y. Sakisaka and I. Sumoto, Phys. Rev. **38**, 1078 (1931); Y. Sakisaka and I. Sumoto, Proc. Phys.-Math. Soc. of Japan, Ser. III, **13**, 211 (1931).

[14] G. W. Fox and J. M. Cork, Phys. Rev. **38**, 1420 (1931).

[15] C. S. Barrett and C. E. Howe, Phys. Rev. **38**, 2290 (1931).

found to shift with the crystal when the crystal was shifted and to disappear when the crystal ceased vibrating. There appears no room for doubt that the fine structure represents a variation of reflecting power from point to point in the crystal resulting from the processes of vibration.

To facilitate the investigation, pin-hole slit systems were constructed whereby several beams from a single x-ray tube could be made to strike adjacent portions of the same crystal and produce simultaneously several Laue patterns on the same film. With a suitable distance from crystal to film each pattern could be obtained free from confusion with the others.

Another device to aid in the rapid production of suitable Laue patterns brought into use the focussing property of rays reflected through a crystal plate, illustrated in Fig. 1. A narrow diverging beam from a point source penetrates a crystal standing perpendicular to the beam at a distance from the source. In passing through the crystal these diverging rays are reflected from atomic planes throughout their path in the crystal. Those reflected from the front of the crystal will be brought to a focus at a certain point in space, those from the back of the crystal will focus at another point, and similar focussing will occur for reflections originating at any given depth in the crystal. The layer at a distance r from the source will reflect rays to a focus on a sphere of radius $r/2$ tangent to this layer. From Fig. 1 it will be seen that a photographic plate at the distance $r \cos^2 2\theta$ from this layer will receive the focussed rays reflected from crystallographic planes inclined $\theta°$ to the beam. If $r \cos^2 2\theta$ is large compared with the cross-section of the beam and the thickness of the crystal, the film will be approximately in focus for all layers of the crystal and for a considerable range of θ. The radial distribution of intensity in the Laue spot will then represent the distribution of reflecting power in the different layers of the crystal, as it does in the simple case of a narrow bundle of parallel rays. A point source of x-rays not being available, rays were used leaving a flat target at an angle of 4°, which gave effectively a line source. With the target face horizontal, satisfactory focussing occurred for reflections occurring in or near a vertical plane. Other reflections lacked detail and were disregarded. It was necessary, of course, to limit the cross-section of the primary beam until no important loss of detail in the spots resulted from either the averaging over the crystal surface or the cross fire in the horizontal direction.

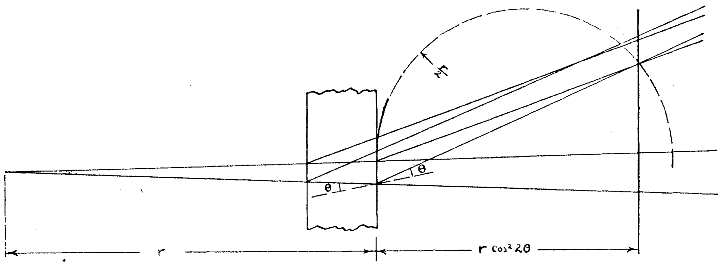

Fig. 1.

Fig. 2 shows a portion of a Laue pattern from an x-cut (0° or Curie cut)[16] quartz crystal of dimensions $l_x=4.0$ mm, $l_y=20.78$ mm, $l_z=26.40$ mm, where l_x and l_z are measured parallel to the electric and optic axes respectively, and l_y perpendicular to both these. The crystal was cut and polished with an accuracy of about 45′ with respect to the optic axis and 15′ with respect to the electric axis. It was oscillating piezoelectrically at a calculated frequency of about 715 kilocycles (the so-called x-oscillation).[17] The spots in this pattern are grouped by threes corresponding to the three pin-hole slits (each $0.02'' \times 0.02'' \times 1\frac{3}{4}''$) diverging from a common point at the focal spot of the tube with an angular separation of 1° between adjacent slits. The portion of the pattern reproduced is one in which focussing is satisfactory—space prohibits printing the whole pattern on a scale sufficiently large to show the fine structure of the spots.

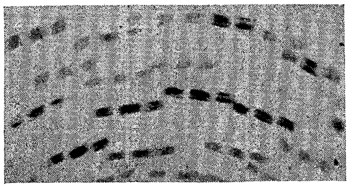

Fig. 2. Laue spots from an x-oscillating x-cut quartz plate.

It will be seen at once from Fig. 2 that the reflecting power of the interior of the oscillating crystal is not uniform. Since the fine structure of the spots differs among the three spots of a triplet it follows that a given crystallographic plane varies in reflecting power from point to point inside the crystal. Furthermore, corresponding members of triplets (for example, the middle spots) differ in structure showing that at certain points in the crystal the reflecting power of some planes is increased much more than that of others.

Similar Laue patterns with multiple slits of 3, 4 and 5 holes were taken of four different x-oscillating x-cut crystals in all, yet less than 10 percent of the stronger spots showed a uniform darkening and in general there was no similarity between the fine structure of any but adjacent spots.

An attempt was made to trace the reflecting power distribution throughout the interior of the x-cut crystal described above, by making a series of 96 Laue patterns with the primary beam penetrating the crystal at 96 different places. This crystal was mounted between x-face electrodes in the holder shown in Fig. 3. A bakelite framework fastened to a mechanical stage from a microscope supported the crystal and permitted it to be shifted parallel to itself at will. Two pieces of thin aluminum sheet served as electrodes, one moving with the crystal and the other fixed to the heavy brass plate of the

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[16] For the method used in the preparation of crystals at the Naval Research Laboratory and the associated nomenclature, cf. Proc. Inst. Radio Eng. **18**, 2128 (1930).

[17] The circuit used was of the type used by Fox and Carr (reference 8), the plate voltage 420, the R. F. tank-circuit current 900 m.a., the rays were from a molybdenum x-ray tube at 30000 volts a.c.

holder. A hole in the brass plate allowed the passage of the direct and reflected rays.

With the crystal, triple slits, and circuit constants mentioned above, enough exposures were made to examine about half the volume of the crystal, the beam in each case entering the crystal approximately parallel to the x-axis. Prints were made of each film and the spots formed by reflection from the same strongly reflecting plane were cut out of each print. These individual spots, each representing the reflecting power of the same plane along a line through the crystal parallel to the x-axis, were assembled in correct relative positions on a plot (Fig. 4). The rectangle in Fig. 4 represents on an enlarged scale the surface of the crystal normal to the x-axis and containing the Y and Z axes as indicated. The left edge of each spot exhibits the reflecting power for the given plane at the front face of the crystal, the right edge does the same for the back surface and intermediate points for corresponding interior points in the crystal.

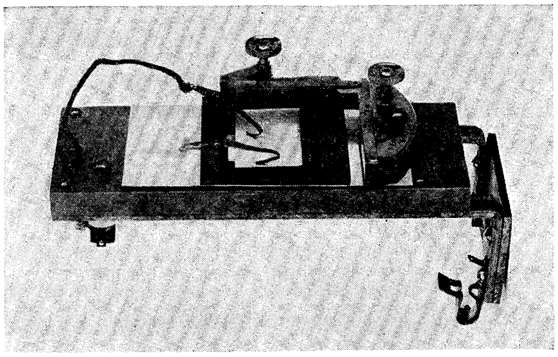

Fig. 3. Crystal holder.

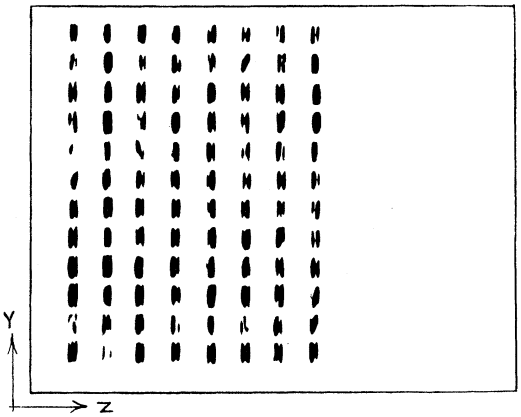

Fig. 4. Plot of reflecting power in an x-oscillating x-cut quartz crystal.

The complex distribution of the reflecting power in this vibrating crystal is at once obvious from the plot. The photographs were not taken closely enough together to enable one to trace continuously, from one spot to its neighbors, the streaks of high and low intensity. Regardless of how the reflecting power is related to the mechanical distortions, Fig. 4 testifies to an exceedingly complex mode of vibration. We were not surprised to find evidence of the same complexity by dusting lycopodium powder on the edges and surface of the crystal while oscillating: no simple or completely reproducible powder pattern resulted on any face. The nodes and loops were apparently even less regularly distributed than the complicated ones recently recorded by Wright and Stuart[18] by lycopodium powder methods. These observations confirm their conclusion that the frequency of a mode of this nature cannot be a simple function of Young's modulus in the direction of the thickness and the thickness dimension. The crystal fractured while the powder patterns were being investigated.

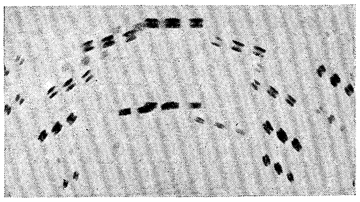

Fig. 5. Laue spots from an oscillating y-cut quartz crystal.

Laue patterns of oscillating y-cut (30°) crystals appear, in general, to be much simpler. A majority of the spots from four different specimens was merely simple doublets. A portion of one pattern containing only doublets is reproduced in Fig. 5. (This crystal had the dimensions $l_x=28$ mm, $l_y=4$ mm, $l_z=26$ mm, and was oscillating at a calculated frequency of about 560 kilocycles.) The exposures to produce patterns from oscillating crystals were so much shorter than those required for non-oscillating crystals that no registration of the non-oscillating pattern could have occurred in Fig. 5. The doublets there are, therefore, not due to reflection from the ground surfaces. In fact, their appearance is quite different from non-oscillating crystal patterns taken with the same apparatus: Fig. 5 shows the intensely reflecting region to extend to a depth of over a millimeter beneath each face, while the effect of grinding extends down only about 1/10 mm below the surface.[19]

It can be said that in general the enhancement of the reflecting power of

[18] R. B. Wright and D. M. Stuart, Bur. of Standards, Jour. of Research **7**, 519 (1931).

[19] Null results were obtained with the so-called y-oscillation of an x-cut crystal ($l_x=6.8$, $l_y=20.2$, $l_z=25.7$, 131 kilocycles calculated frequency) which showed a simple lycopodium powder pattern. The spots were of the same type and approximate intensity whether the crystal was oscillating or not. Several positions on the crystal were investigated, and the primary beam was tried at 30° to the x-axis as well as parallel to it, each case with the same result. It may be that the amplitude of the oscillations was insufficient (R. F. tank-circuit current 60 m.a., plate voltage 400) or that the very simplicity of the mode of vibration is to account for this.

various planes is essentially different when it results from grinding than from piezoelectric vibrations. If this were not so every spot in Fig. 3 would be identical in structure, as is always the case with a non-oscillating crystal with ground surfaces[20] and as is the case with some specimens of quartz having internal flaws or imperfect regions which came under our observation. The reduction of extinction in oscillating crystals is not the isotropic phenomenon that it appears to be in the ground surface of a crystal or in imperfect crystals. An interpretation in terms of the inhomogeneous strains that must be the cause of reduced extinction is that imperfection of the type produced by grinding results from a random orientation of strain gradients, while imperfection produced by vibration results from non-random direction of strain gradients.

Quantitative intensity measurements are not available to show whether or not this accurately describes the situation, but the following qualitative experiment is evidence for it. Laue photographs were taken of a quartz crystal with ground surfaces subjected to inhomogeneous static strain as shown in Fig. 6. Forces were applied to bend the quartz bar into a cylinder with the optic axis vertical, parallel to the axis of the cylinder, (perpendicular to the paper in Fig. 6) and the primary beam was directed radially. Under these conditions spots on the Laue pattern above and below the central spot remained doublets resembling those in the unstrained crystal, but spots to the right and left of the central spot increased in intensity and became uniformly darkened. These observations were confirmed with quartz slabs of differing dimensions, and with the plane of the x-ray tube target rotated 90° from the position indicated in Fig. 6 (this in order to eliminate confusion due to the shape of the focal spot).

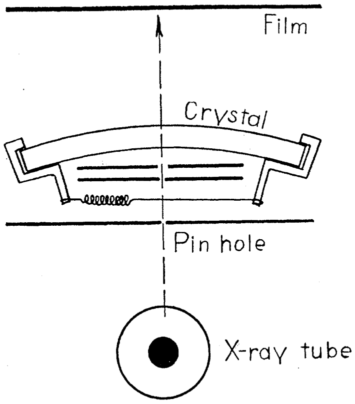

Fig. 6. Apparatus for diffraction from an inhomogeneously strained crystal.

Along the path of the beam in the interior of the quartz, this inhomogeneous strain should produce a maximum *variation* in atomic plane spacing and orientation for those reflecting planes standing approximately parallel

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[20] cf. C. S. Barrett, reference 11, Fig. 1; Y. Sakisaka and I. Sumoto, reference 13, Fig. 1.

to the axis of bending and a minimum variation of interplanar spacing for those approximately perpendicular thereto. Extinction, dependent upon the variation, along the path of the ray, of interplanar spacing and angle of incidence of rays upon the planes, should accordingly be reduced for the planes approximately axial and practically unaltered for the others. The observed intensities were in agreement with this view.

DISCUSSION

It cannot be doubted that the warping of quartz during vibration reduces extinction and causes increased reflection, but whether it is primary or secondary extinction that is involved is not so definite.

Suppose, in the first place, that *secondary* extinction is important for unstrained quartz. Could vibrations reduce this appreciably? The angular width of a monochromatic beam reflected from unstrained quartz was determined by Sakisaka[7] to be 45″ (width at half maximum intensity); estimating the variation in tilt of planes in a vibrating crystal from measurements of surface motion by Osterberg,[21] we find a distribution of the same order of magnitude. It appears, then, that secondary extinction would be reduced if present, for it would be unaltered only if the reflected line were much wider than the superimposed broadening due to the vibrations. The uneven distribution of extinction among the different reflecting planes, as reported in this paper,might be explained on the basis of secondary extinction simply by postulating a suitable distribution function for the orientation or for the interplanar distance of the reflecting planes along the path of the primary beam. This distribution function would be dependent upon the direction and magnitude of the strain gradients in the crystal.

It is by no means certain that the above supposition is correct; Sakisaka[7] in fact, concluded that only *primary* extinction was important in quartz. His conclusion was based on ionization measurements of reflected intensities, and was confirmed by his observations of the shape of the reflected line and the thickness of the reflecting layer of quartz as a function of the coarseness of grinding. He visualized quartz as a mozaic of rather large perfect crystallites in which primary extinction was large, with a scattering from parallelism between different crystallites sufficient to make secondary extinction negligible. More recently in a note by Nishikawa, Sakisaka and Sumoto[13] the statement is made that both primary and secondary extinction is large in quartz. No reason is given for this departure from the conclusions of the earlier experimental data; it does not appear to be justified.

To explain the present results on the basis of primary extinction requires simply that the distorting effect of strains extend into the perfect regions that are the seat of primary extinction. Whether the crystal is a mosaic of blocks with abrupt transitions between them, or a continuous but slightly warped lattice, it would be expected that stresses would reduce primary extinction. To deny this possibility would be equivalent to postulating that the crystal is a mosaic of blocks so loosely welded together that the perfection of the

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[21] H. Osterberg, Proc. Nat. Acad. Sci. **15**, 802 (1929).

lattice of each block is unaffected by shifting or tilting the neighboring blocks, which seems unlikely. With the size of the perfect regions as the determining factor for primary extinction, it becomes necessary to postulate a temporary reduction in size under stress, followed by a return to normal with the removal of stress. A reduction in effective size of the perfect part of the lattice need not require a fracture or a permanent deformation; it should only be necessary to introduce strains great enough to destroy coherence in the diffraction from different portions of the normally perfect crystalline unit. If the applied stresses deform the individual perfect blocks of the lattice so that their effective size is larger in one direction than in another, they might produce the anisotropic character of the reflecting power reported in this paper.

The points to be emphasized are that inhomgeneous strains may deform a crystal, normally of high perfection, in such a way that certain lattice planes lose their near perfect spacing and parallelism, while others do not. On the other hand homogeneous strains do not destroy the perfection of any lattice planes. X-ray reflections are influenced by this perfection of planes (and not by the perfection of atomic distribution on a plane) and thus contain evidence of the condition of inhomogeneous strain in the lattice.

This x-ray method of observing distortions in materials contrasts sharply with the photo-elastic method; here the strain gradient at a point is measured, while photo-elastically one observes the strain itself but is unable to observe it as a function of depth below the surface. The numerous methods that have been used to observe modes of vibration in quartz resonators and oscillators —air currents, powder patterns, observation of surface motion, crossed Nicol prisms, air ionization patterns—all yield data of different type than this.

The authors are indebted to the personnel of the Radio Division of this Laboratory for its assistance and interest in this work.

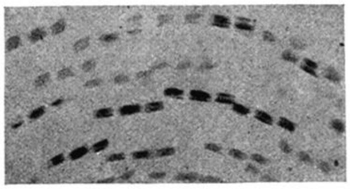
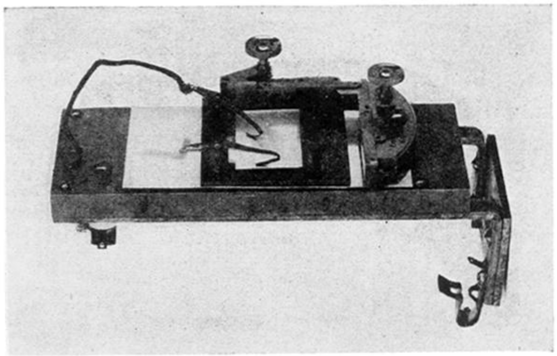


Fig. 2. Laue spots from an x-oscillating x-cut quartz plate.



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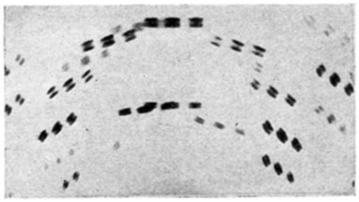

Fig. 5. Laue spots from an oscillating *y*-cut quartz crystal.