

The Perfection of Quartz and Other Crystals and Its Relation to Surface Treatment

R. M. BOZORTH AND F. E. HAWORTH, *Bell Telephone Laboratories, New York*

(Received April 9, 1934)

The perfection of various crystals has been determined by using an x-ray double crystal spectrometer. The materials examined were quartz, Rochelle salt, fluorite, tourmaline, pyrites, barite, rocksalt, gypsum, and the metallic crystals aluminum, iron, nickel, tungsten, and permalloy (65 percent nickel). The results indicate that quartz is a "perfect" crystal and that specimens of Rochelle salt, fluorite and possibly tourmaline and pyrites, might be found which could be so classed. The others tested are definitely in the "imperfect" class, the widths of the rocking curves at half-maximum lying between 100 and

1500 seconds of arc. The effect of surface treatment on perfection, as determined by x-rays, was examined for quartz by grinding with carborundum of two different sizes and by etching for different lengths of time. The surface of the permalloy crystal was also investigated by etching to different depths. As a result of the tests here reported, etched quartz crystals are suggested as suitable for use in the double crystal spectrometer on account of their high resolving power which is about twice that of calcite.

INTRODUCTION

IT was found in the course of some earlier work that x-ray reflections from single crystals of quartz were unusually sharp, and it seemed of interest to determine more accurately the perfection of these crystals by the use of a double crystal spectrometer. Since other kinds of crystals were available in sufficient size, and since the perfection of very few crystals have been reported in the literature, a variety of other specimens was also examined. In addition to some well-known minerals, specimens of several metallic crystals were measured, including a single crystal of an alloy. These metal crystals were of particular interest because electron diffraction experiments had been made on some of these same specimens by L. H. Germer.¹

It soon appeared that the treatment of the surface, known to be important in the case of the non-metallic crystals, was especially important for the softer metallic crystals. Accordingly, experiments were made on the treatment of the surface of one of the metallic crystals as well as on several specimens of quartz.

METHOD OF MEASUREMENT

The crystals were measured on a double crystal spectrometer, usually in the (1, -1) position. The first crystal (crystal *A*) was set to

reflect with maximum intensity the $K\alpha$ -radiation from molybdenum. The second crystal (crystal *B*) was mounted on a holder with one axis in the plane of the crystal surface and perpendicular to the x-ray beam. This holder also turns about a second axis perpendicular to the first and also lying in the plane of the crystal surface. Motion around the latter axis, for azimuthal adjustment, could be read directly to 6 seconds on a tangent screw head. Motion about the former axis, important for the final rocking curves, was read directly on the head of a screw pressing on a lever arm. The screw head was 25 cm in circumference, one complete revolution of the head causing a rotation of *B* through 100 seconds. The distance between the two crystals was 15 cm. The position of the axis of crystal *B* was adjusted, with the crystal surface always parallel to the beam reflected from crystal *A*, until the intensity of the beam was cut to one-half.

The intensity of the twice reflected beam was measured by an ionization chamber containing methyl bromide, in connection with an amplifier and a Moll galvanometer. The current from the ionization chamber passed through a resistance of 10^{11} ohms connected between the grid and filament of the "electrometer tube" of the amplifier, so that the deflection of the galvanometer was proportional to the x-ray intensity. The galvanometer had a full period of less than a

¹ L. H. Germer, *Phys. Rev.* **44**, 1012 (1933).

second and readings were made in three or four seconds after movement of the crystal.

Crystal *B* was adjusted in azimuth until the rocking curve was narrowest. Actually this position was found by making an azimuthal adjustment and noting the deflection of the galvanometer at the peak of the rocking curve. A curve was plotted showing the relation between azimuthal settings and these maximum galvanometer deflections, and the final azimuthal setting made for which this curve was a maximum.

No absolute measurements were made of reflection angle or intensity of reflection.

MATERIALS

The single crystals examined were as follows:

Quartz

(1a) Brazilian quartz, cut and ground with 100 mesh carborundum parallel to a (11·0) plane (perpendicular to a natural prism face), within 10 minutes of arc.

(1b) Same as (a) except a different specimen.

(2) Quartz similar to (1) but in addition etched 40 hours at 30°C in 48 percent hydrofluoric acid solution, to give a smooth surface free from surface irregularities and strains due to cutting and grinding. Two specimens.

(3) Quartz similar to (1) but ground with 600 mesh carborundum.

(4) Quartz similar to (1), except cut and ground with 100 mesh carborundum parallel to a (10·0) plane (the natural prism face).

(5) Quartz similar to (4), but etched 100 hours. Two specimens.

(6) Quartz similar to (4), but given successive etches ranging from 20 seconds to 20 hours, measurement being made between etches.

(7) Quartz similar to (4), except ground with 600 mesh carborundum.

(8) Quartz similar to (7), but given successive etches ranging from 20 seconds to 20 hours.

Other non-metallic crystals

(9) Rochelle salt, cut and ground parallel to a (100) plane, and lightly etched with water.

(10) Rocksalt, cleaved parallel to a (100) plane.

(11) Calcite, cleaved parallel to a (100) plane.

(12) Gypsum, cleaved parallel to a (010) plane.

(13) Fluorite, cleaved parallel to a (111) plane.

(14) Fluorite, natural (100) face.

(15) Barite, natural (001) face.

(16) Iron pyrites, natural (210) face.

(17) Same as (16), but etched in hot concentrated nitric acid.

(18) Tourmaline,² ground and polished parallel to a (10·0) plane.

Metallic crystals

(19) Iron, grown and annealed in hydrogen, surface inclined slightly to a (100) plane.

(20) Iron, ground and polished parallel to a (100) plane to within 15 minutes of arc, and then etched in dilute acid.

(21) Nickel, ground and polished parallel to a (111) plane, and etched in dilute acid.

(22) Aluminum, ground and polished parallel to a (100) plane, and etched in dilute acid.

(23) Tungsten, ground and polished parallel to a (110) plane, and etched in alkaline potassium ferricyanide.

(24) Permalloy, 65 percent nickel, ground and polished parallel to a (100) plane, and annealed in hydrogen at 1400°C for two hours.

(25) Same as (24), but given successive etches totaling 60 minutes, in a mixture of concentrated hydrochloric and nitric acids.

RESULTS WITH ETCHED QUARTZ CRYSTALS, AND COMPARISON WITH THEORY

The rocking curve widths at half-maximum, for several pairs of crystals, are shown in Table I.^{2a}

According to Darwin's theory³ of reflection from a perfect crystal, total reflection of x-rays polarized so that the electric vector is parallel to the plane of incidence occurs over an angular range

$$\Delta\theta = 2nFZ^{-1}\lambda^2e^2(\text{ctn } 2\theta)/(\pi mc^2) \quad (1)$$

where n is the number of extranuclear electrons per cm³, Z the number of extranuclear electrons in the unit of structure on the basis of which the structure factor F is calculated, and the other symbols have their usual significance. For two crystals in the parallel position, S. K. Allison⁴ has shown that following Darwin's theory the width of the rocking curve at half-maximum is

$$W = 1.40\Delta\theta \quad (2)$$

² The hexagonal unit cell of this specimen was determined from three reflection photographs from faces mutually perpendicular: $c = 7.05\text{Å}$, $a = 15.78\text{Å}$. See also C. Kulaszewski, *Abh. d. Sachs. Akad. d. Wiss. (M.-P. Kl. 3)* **38**, 81 (1921).

^{2a} Rocking curves for the natural faces of quartz and some other crystals have been taken by Sakisaka, *Jap. J. Physics* **4**, 171 (1927) and **12**, 189 (1930), the narrowest for quartz being 14'' wide at half-maximum. The effect of grinding the surface was also investigated, but no etching experiments were reported. More recently, Richtmyer, Barnes and Manning, *Phys. Rev.* **44**, 311 (1933) have determined the effect of etching the surfaces of calcite crystals and have found considerable narrowing of the rocking curves for small angles of reflection.

³ C. G. Darwin, *Phil. Mag.* (6) **27**, 675 (1914).

⁴ S. K. Allison, *Phys. Rev.* **41**, 1 (1932).

when absorption by the crystal is neglected, and that when absorption is allowed for by Prins's⁵ method, the relation is usually not much changed. When the incident rays are unpolarized the width of the region of total reflection is unchanged, but there is some change in the amount of reflection at angles for which the reflection is not perfect. The width of the rocking curve for unpolarized incident rays may then be expected to lie between the two limits corresponding to polarizations parallel and perpendicular to the plane of incidence. Substituting in Eq. (2) the mean of these two values of $\Delta\theta$, the width of the rocking curve at half-maximum is given by

$$W = 0.45nFZ^{-1}\lambda^2e^2 \operatorname{ctn} \theta / (mc^2) \quad (3)$$

an equation which should be correct within a few percent when the values of θ are as small as they are in the experiments described here.

The width given by Eq. (3) is about three-fourths of that calculated by earlier methods, according to which the theoretical effective width of the once-reflected ray, $4/3$ of the $\Delta\theta$ of Eq. (1), was multiplied by $2^{1/2}$ to obtain W .

The width calculated by this equation can be compared with that experimentally determined for the etched quartz crystals (2). The structure factor, however, is not accurately known so we calculate FZ^{-1} from Eq. (3) using the observed value of W , and obtain the result

$$FZ^{-1} = 0.36.$$

This may be compared with the value of FZ^{-1} calculated for the case in which the centers of all of the atoms lie on (11·0) planes and the atoms have the scattering powers⁶ appropriate for the value of $\sin \theta/\lambda$ of our experiment. The FZ^{-1} so obtained is 0.72, just twice that calculated from the rocking curve. A powder photograph of quartz indicates that the structure factor for this plane has neither an exceptionally large nor exceptionally small value. The structure factor calculated from the structure proposed by Gibbs⁷ is small, but little significance can be attached to this because the parameters are not sufficiently well determined. A similar calculation was made

for the second order reflection from (11·0), for which $W = 1.7$ seconds. Using Eq. (3) we obtain $FZ^{-1} = 0.41$, whereas the maximum value for a silicon and two oxygen atoms⁶ at this angle and wave-length is 0.44. The corresponding figures for reflections from (10·0) ($W = 11$ seconds) are 0.9 and 0.87. Thus the results of the application of Eq. (3) show that quartz is a perfect crystal as nearly as can be determined with our present knowledge of the structure factors.

A determination of percent reflection was made for first order reflection from (11·0). When the (11·0) planes of the two crystals (2) were parallel, the intensity of the beam reflected from crystal *B* was 40 percent of that reflected from crystal *A*. This is lower than the 80 percent reflection predicted by Darwin's theory⁴ and may be compared with the 60 percent observed⁴ for calcite for this wave-length and with the 35 percent observed for calcite for a wave-length of $0.2A$.

The use of quartz crystals cut parallel to the (11·0) planes has some advantage over calcite in a double crystal spectrometer. The rocking curve width is half that for calcite and the reflection angle is slightly greater, the resolving power of quartz being consequently 2.5 times that of calcite in the first order. With a beam of x-rays of given intensity incident upon the first crystal and with the crystals exactly parallel, the intensity of the twice reflected beam is less for quartz than for calcite, largely on account of the greater resolving power of the quartz.

QUARTZ WITH GROUND SURFACES

As shown in Table I, quartz finished with 100 mesh carborundum gives a rocking curve 36 seconds wide at half-maximum. Since the rocking curves for etched crystals are much narrower, it was important to know how much of the ground surface had to be etched away before the narrower rocking curve could be obtained. To test this point, crystals (6) (ground with 100 carborundum) and crystal (8) (600 carborundum) were prepared, and their rocking curves measured after various times of etch in 48 percent hydrofluoric acid at 30°C. In these experiments crystal *A* of the spectrometer,

⁵ J. A. Prins, *Zeits. f. Physik* **63**, 477 (1930).

⁶ L. Pauling and J. Sherman, *Zeits. f. Krist.* **81**, 1 (1932).

⁷ R. E. Gibbs, *Proc. Roy. Soc. London* **A110**, 443 (1926).

specimen (5), was one that had been etched a long time, and crystal *B* was the one under test. The results are shown in Fig. 1. From other experiments it is known that the thickness of quartz etched away from each surface under these conditions is about 0.005 mm/hr.⁸ for specimen (6) and 0.001 mm/hr. for (8), so that the rocking curve width has decreased to one-half of its original width when a layer less than 200Å in thickness (as measured) has been removed from the surface of the crystal. It is rather surprising that the imperfections due to grinding are confined to such a thin layer.

Crystals with ground surfaces were also used in another series of experiments. In each instance both crystals of the spectrometer were cut to (10·0) planes and used in the parallel position, but the surfaces were treated differently. The combinations used and the results obtained are shown in Table I. Besides showing that the angular distortion of the surface is greater after grinding with coarser carborundum, a result to be expected, the data indicate also that the width of the rocking curve for a combination of two "imperfect" surfaces is more nearly equal to the *sum* than to the root mean square of the

TABLE I. *Rocking curve widths at half-maximum.*

No. of Quartz Specimen		Surface of crystal B	Order $n_A, -n_B$	θ	<i>W</i> sec.
Crystal A	Crystal B				
(Reflection from (11·0) planes)					
(2)	(2)	Etched	1	8° 20'	2.6
(2)	(2)	"	2	16° 51'	1.7
(2)	(1a)	Ground ^a	1	8° 20'	28 ^b
(2)	(1b)	"	1	8° 20'	52
(1a)	(1b)	"	1	8° 20'	88
(2)	(3)	Ground ^c	1	8° 20'	13
(Reflection from (10·0) planes)					
(5)	(5)	Etched	1	4° 48'	11
(5)	(5)	"	2	9° 38'	3.8
(5)	(4)	Ground ^a	2	9° 38'	36 ^d
(5)	(7)	Ground ^c	2	9° 38'	24 ^e
(4)	(7)	"	2	9° 38'	61

^a Ground with 100 mesh carborundum.

^b Several specimens similarly prepared gave rocking curve widths (at half-maximum) from 28 to 52 seconds.

^c Ground with 600 mesh carborundum.

^d Several specimens similarly prepared gave rocking curve widths (at half-maximum) from 29 to 59 seconds.

^e Several specimens similarly prepared gave rocking curve widths (at half-maximum) from 13 to 49 seconds.

⁸ As measured between a plane surface and one 2 mm in diameter, both optically perfect.

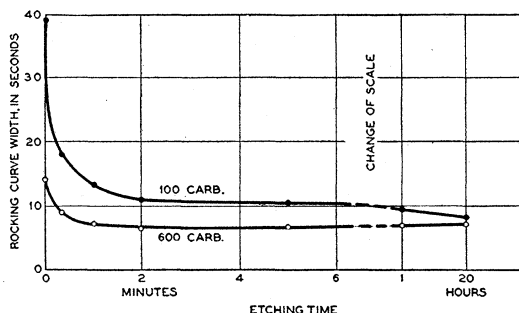


FIG. 1. Effect of etching on the rocking curve width at half-maximum, for (10·0) surfaces of quartz originally ground with 100 or 600 carborundum. Reflections are in the second order.

rocking curve widths of each surface when paired with a perfect crystal. This latter result is in approximate accord with the suggestion of Hoyt⁹ that the form of the rocking curve is best expressed by the equation

$$y = a(1 + b^2x^2)^{-1},$$

and is definitely contradictory to the assumption frequently made that the curve follows the Gaussian error function. The predicted width of the rocking curve for the two ground crystals (1a) and (1b) used in combination is 77 seconds by Hoyt's formula,¹⁰ 88 seconds by experiment and only 59 seconds by the Gaussian error formula. In crystals (4) and (7) the corresponding values are 59, 61 and 44 seconds, respectively.

OTHER NON-METALLIC CRYSTALS

The widths of the rocking curves of the other non-metallic crystals are shown in Table II. In most of these experiments the first crystal of the spectrometer was the etched quartz specimen (2), one of the pair for which the rocking curve width was 2.6 seconds. In other experiments, when preliminary work indicated a wide rocking curve, the ground crystal (3) was used as crystal *A* to increase the intensity of the reflected x-ray beam. Since the Bragg angles θ are never the same for the first and second crystals of the spectrometer, in order to obtain the angular deviation due to the second crystal alone a correction to the observed widths of Table II may

⁹ A. Hoyt, Phys. Rev. **40**, 477 (1932).

¹⁰ As worked out by S. W. Barnes and L. D. Palmer, Phys. Rev. **43**, 1050 (1933).

be applied according to the usual equation¹¹

$$W^2 = W_A^2 + W_B^2 + D^2 W_\lambda^2.$$

In our case¹² this reduces to

$$W^2 = W_A^2 + W_B^2 + 8400(\tan \theta_A - \tan \theta_B)^2$$

where W_A and W_B refer to the widths in seconds at half-maximum of the functions (now assumed Gaussian) representing reflection from crystal A and from crystal B , and θ_A and θ_B are the Bragg angles for these reflections. In almost all cases listed in Table II, however, this correction is negligible, the greatest correction being for Rochelle salt where it amounts to 1.4 seconds or about 25 percent.

TABLE II. *Widths of rocking curves.*

Crystal B	hkl	θ_B	W sec.
(Crystal A = quartz (2), (11·0), etched, $\theta_A = 8^\circ 20'$)			
Rochelle salt (9)	100	$6^\circ 53'$	5.2
Rocksalt (10)	100	$7^\circ 15'$	400
Calcite (11)	100	$6^\circ 43'$	7.8
Fluorite (13)	111	$6^\circ 28'$	17
Fluorite (14)	100	$14^\circ 52'$	66
Barite (15)	001	$11^\circ 29'$	250
Tourmaline (18)	10·0	$13^\circ 29'$	27
Pyrites (16)	210	$8^\circ 27'$	44
(Crystal A = quartz (3), (11·0) ground 600 mesh, $\theta_A = 8^\circ 20'$)			
Pyrites (17)	210	$8^\circ 27'$	56
Gypsum (12)	010	$2^\circ 41'$	42

The materials listed in Table II show great variations in perfection, the rocking curve widths varying by a factor of almost 300. Rocksalt has been known for many years to be decidedly imperfect, and some quantitative measurements have been reported for this material,¹³ for barite,¹⁴ and for Rochelle salt.¹⁴ The results for Rochelle salt reported previously are qualitatively confirmed here. Assuming for the moment

¹¹ M. Schwarzschild, Phys. Rev. **32**, 162 (1928); see also S. K. Allison and J. H. Williams, Phys. Rev. **35**, 1476 (1930) for discussion.

¹² With $W_\lambda = 0.29$ X.U., the wave-length width of the $K\alpha_1$ line according to S. K. Allison, Phys. Rev. **44**, 63 (1933).

¹³ W. L. Bragg, R. W. James and C. H. Bosanquet, Phil. Mag. (6) **42**, 1 (1921); B. Davis and W. M. Stempel, Phys. Rev. **19**, 504 (1922); P. Kirkpatrick and P. A. Ross, Phys. Rev. **43**, 596 (1933); W. L. Bragg, C. G. Darwin and R. W. James, Phil. Mag. (7) **1**, 897 (1926), discuss the perfection of fluorite, barite and calcite as determined by the integrated intensity of reflection.

¹⁴ Kirkpatrick and Ross, reference 13.

that this crystal was perfect, we calculated the structure factor from Eq. (3) and found FZ^{-1} to be 0.88. Since this is much too high to be consistent with the scattering powers of these atoms in planes of this spacing, even if arranged in the most favorable way, we may conclude that this specimen of Rochelle salt is not a perfect crystal. On the other hand, the small width indicates that perfect crystals might be grown. The data for some of the other substances, such as fluorite and tourmaline, indicate that perfect specimens of these may also exist.

METALLIC CRYSTALS

The results on the single crystals of Al, Fe, Ni and W, given in Table III, show that they are unquestionably "imperfect" crystals. The most

TABLE III. *Rocking curve widths for metallic single crystals.*

Crystal B	hkl	θ_B	W sec.
(Crystal A = quartz (3), (11·0) ground 600 mesh, $\theta_A = 8^\circ 20'$)			
Iron (20)	100	$14^\circ 28'$	840 ^a
Nickel (21)	111	$10^\circ 8'$	1500
Aluminum (22)	100	$10^\circ 8'$	1500
Tungsten (23)	110	$9^\circ 9'$	360
(Crystal A = quartz (1), (11·0) ground 100 mesh, $\theta = 8^\circ 20'$)			
Permalloy (24)	100	$11^\circ 27'$	660
Permalloy (25)	100	$11^\circ 27'$	132

^a Using two crystals of iron similar to iron (19), a rocking curve was obtained for which W was 480 seconds.

complete experiments were performed on a single crystal of permalloy, containing approximately 65 percent Ni and 35 percent Fe. This crystal was made in the following way: Eight hundred grams of technically pure iron and nickel were heated to 1400°C in an alundum boat in an atmosphere of carefully purified moist hydrogen and maintained at that temperature for 16 hours. The material was then melted and after about two hours was allowed to cool through the melting point at the rate of 10°C/hr. It was then cooled to room temperature in two hours. About half of the piece so prepared was a single crystal from which a slab about 6 mm thick was cut parallel to a (100) plane, using a revolving metal disk fed with 100 mesh wet carborundum. This surface, about 2 cm² in area, was finally polished with No. 0000 emery paper and

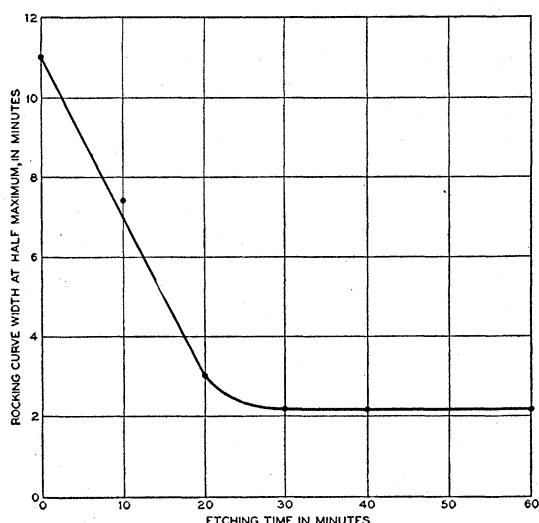


FIG. 2. Effect of etching on the rocking curve width at half-maximum, for first order reflection from the (100) surface of a single crystal of permalloy containing 65 percent nickel. The first crystal was quartz (11·0), first order reflection from a ground surface.

the slab annealed for two hours at 1400°C in hydrogen. The rocking curve for this surface was 11 minutes wide at half-maximum, as shown in Table II. The specimen was then etched repeatedly in strong acid (equal parts conc. HCl and conc. HNO₃), rocking curves being taken between etchings. The time for each etch was 10 minutes, about 0.1 mm being removed during this time. Fig. 2 shows that the width decreases as the surface is etched and it is not until about 0.3 mm has been etched away that the narrowest rocking curve is obtained. The final width, 2.2 minutes, is apparently characteristic of the in-

terior of this crystal. These results indicate that the atomic planes of metallic single crystals are easily disturbed, and in this sense are in accord with many other observations which have been made since the technique for growing metallic single crystals has been developed. The results also indicate that metallic crystals are imperfect, even when prepared from pure materials under the best conditions so far known.

The single crystals of iron (20), nickel (21), and tungsten (23) were the same specimens as those used by Germer¹ in his experiments on electron diffraction. His measurements showed that some of the crystal planes were inclined as much as 1 degree to the average position of the planes. By combining the x-ray with the electron diffraction data, it may be concluded, as already pointed out by Germer, that parts of the surface of these crystals are inclined considerably more than are the internal mosaic blocks to the mean position of the planes. The results obtained with the crystal of permalloy emphasize the conclusion that the misalignment observed by Germer is the direct result of the method of preparation of the surfaces which he examined.

ACKNOWLEDGMENTS

We wish to express our indebtedness to Mr. P. P. Cioffi for the preparation of the single crystal of permalloy, to Dr. L. H. Germer for the loan of most of the other metallic crystals, to Professor Bergen Davis for the minerals (except quartz and tourmaline), and to the Brush Laboratories for the Rochelle salt crystal.