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Note on Thin Quartz Crystals as Used in the Cauchois Focusing X-Ray Spectrograph

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Doubled x-ray lines, produced by the Cauchois focusing spectrograph, have their origin as a result of double curvature of the crystal which causes defocusing of strong surface layer reflections. At the center of the lines shown in this paper, is a single portion, where the surface layer reflections are superimposed as a result of Cauchois exact focusing, showing that the surface layers share in the uniform strain of the crystal. Calculated separation of doubled lines, on the assumption of parallelism of surface layer reflections, shows poor agreement with the actual separations, adding support to the idea of the origin of the doubled lines as a result of crystal warping. The breaking of bent crystals is attributed to the presence of this double curvature. Broadened lines due to light etching are the result of poor resolving power of the thinned surface layers which still do the bulk of reflection.

INTRODUCTION

FINCH[1] first demonstrated that the surface layers of quartz (and other crystals), formed by grinding and polishing, are crystalline and integral with the body of the crystal. DuMond and Bollman[2] and D. L. Webster[3] have commented on the existence of doubled x-ray lines, observing that the two lines came from the two surfaces of the crystal. Watson[4] has observed doubled lines with the Cauchois spectrograph. Recently, a more detailed study[5] was made of these doubled lines. It is the purpose of the present paper to offer explanations for certain unexplained phenomena which exist in these studies[1–5] of crystals. They are: (1) Why are doubled lines, produced by the Cauchois focusing spectrograph, sometimes observed to be single lines at their center? (2) May we account for the separation of the doubled lines in terms of crystal thickness? (3) Why does light etching greatly broaden lines?

DISCUSSION

1. Doubled x-ray lines formed by the Cauchois spectrograph

In Fig. 1 is shown an enlargement (10×) of half of the length of the $K\alpha_{1,2}$ lines in a typical molybdenum K spectrum[6] taken with the Cauchois focusing spectrograph. In Fig. 1 the reader may assume that the missing half of the line is the mirror image of the half reproduced, the mirror being placed at right angles to the end of the single portion, to produce *a line doubled at the ends, and single at and near the center*. This is a new observation for which the following explanation is presented.

The fact that the line is single at the center, shows that Cauchois exact focusing exists for the center portion of the crystal: at the outside of the crystal the grating space of the crystal lattice is increased by tension; at the inside (next to the convex warping cylinder) the grating space is decreased by compression, the resulting alteration in Bragg angles being just exactly right for the two portions so that they will focus along with the radiation from the "zero strain surface" where the grating space is unaltered. Thus we have focusing from the thickness of the crystal, as well as along the arc of the crystal. Although the crystal has been ground and polished, *at the center of the line the reflections from the two disturbed surfaces are superimposed* (Cauchois exact focusing) *showing that the surface layers, at the center of the crystal at least, share in the uniform radial strain of the crystal.* This is in accord with the findings of Finch.[1]

We must now concern ourselves with the doubled ends of the x-ray line. Unmistakably, the two components of the doubled line are due to

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[1] G. I. Finch, Nature **138**, 1010 (1936); Science Progress (April, 1937).

[2] J. W. M. DuMond and V. L. Bollman, Phys. Rev. **50**, 524 (1936).

[3] Unpublished data.

[4] B. B. Watson, Rev. Sci. Inst. **8**, 480 (1937).

[5] F. R. Hirsh, Jr. and J. W. M. DuMond, Phys. Rev. **54**, 789 (1938).

[6] This is the same line whose photometric profile is shown in reference 5, Fig. 1.

the two disturbed surface layers of the crystal: this was clearly shown in reference 5. But why are not the two components exactly focused near the ends as at the center? The following explanation is offered. In bending an elastic quartz crystal between two rigid cylindrical surfaces, such as are employed in the Cauchois focusing spectrograph, the crystal does not assume a true cylindrical shape. The behavior of a simple elastic body such as rubber eraser will remind us that bending develops one curvature, while as a result of tension and lateral contraction on the outside of the eraser arc, and compression and lateral swelling on the inside arc, a second curvature develops at right angles to the primary curvature (see Fig. 2). The result of the curvature shown in the horizontal section of Fig. 2 is the curvature (shown exaggerated) in the vertical section of Fig. 2. As a consequence, the quartz crystal pulls back from the inside (convex) warping cylinder of the spectrograph at the top and bottom of the window aperture, while at the center the crystal should be roughly tangent to the convex warping cylinder and coincident with the focal circle. Thus the x-radiation from the top and bottom of the window comes to the photographic film on the focal circle "out of focus," being focused in front of the film and re-divergent at the film (see doubled ends of spectral lines in Fig. 1). The x-radiation from the horizontal central zone of the crystal at the window, where the crystal is approximately tangent to the convex warping cylinder, will be in quite sharp focus. (See single part of lines in Fig. 1.) (If, however, the crystal is not bent so as to be roughly tangent to the convex warping cylinder at the center of the window, we could not expect a single line at the center of the recording film. For a probable example of this see Fig. 3, reference 4. Here the warping cylinders must not have been tightened enough to bring the center zone of the crystal into tangency with the convex cylinder, i.e. coincident with the focal circle.)

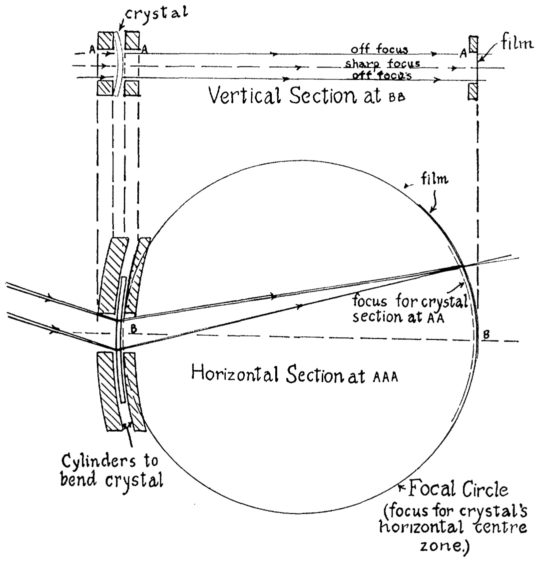

FIG. 2. Idealized sections of Cauchois spectrograph to demonstrate effects of double curvature of crystal.

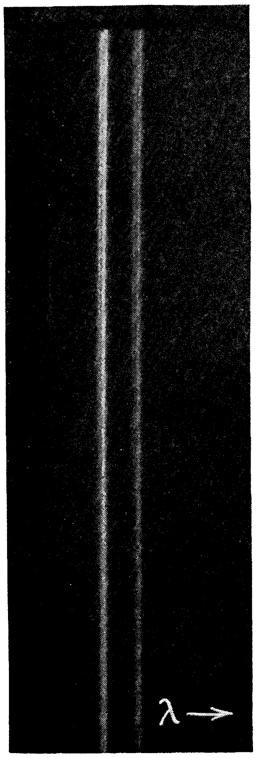

FIG. 1. Tenfold enlargement of half of the Mo $K\alpha_1$, α_2 lines secured in Cauchois spectrograph with thin quartz crystal. The lines are doubled near the ends, and in good focus (single) at center.

The beauty of this explanation of de-focusing of the two components (due to the disturbed surfaces) as a result of the double curvature of the crystal, is that the fact, discovered by Finch,[1] is not contradicted. The two surface layers are crystalline and integral with the crystal body as they share in the uniform crystal strain.

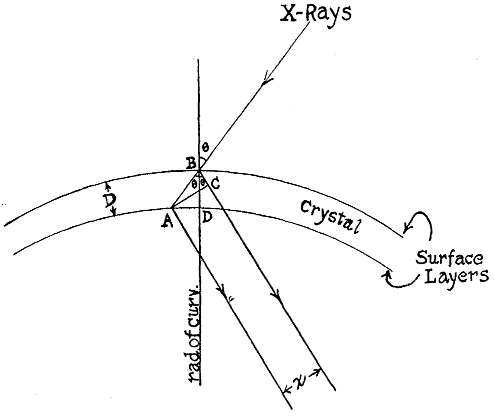

FIG. 3. Diagram to explain separation of doubled x-ray lines on assumptions of reference 5.

2. Separation of doubled lines in relation to crystal thickness

If we assume, as was done in reference 5, that the two surface reflections come from the two crystal surfaces parallel to each other, and that the two surface layers do not share in the uniform strain of the crystal, the linear separation of the two components of the doubled lines should be simply related to the thickness of the crystal. (Fig. 1 shows that such a simple relation does not hold.) However for the sake of argument, making the assumptions of reference 5, in Fig. 3, in triangle *ABD*, the side *AB* is equal to $D \sec \theta$. In triangle *ABC*

$$x/D \sec \theta = \cos (\pi - \pi/2 - 2\theta)$$

or the linear separation of the two components of the doubled line

$$x = D \sec \theta \cos (\pi/2 - 2\theta),$$
$$x = D \sec \theta \sin 2\theta$$

or

$$x = 2D \sin \theta,$$

where x is the distance between the two components of the doubled line, D is the perpendicular distance between the two surface layers on the quartz crystal, and θ is the Bragg angle of diffraction.

Taking Watson's[4] value of d for the basal planes of quartz as equal to 5.393A, and knowing that $n = 3$ for the first order of reflection by quartz, we have (using the Bragg relation):

$$\sin \theta = n\lambda/2d = (3 \times 0.7076)/(2 \times 5.393) = 0.1968, \text{ for MoK.}$$

Substituting in the expression for the double line separation, and knowing that the crystal used to obtain Fig. 1 was slightly under fifteen thousandths of an inch in thickness, we have:

$$x = 2 \times 2.54 \times 0.015 \times 0.1968 = 0.015 \text{ cm.}$$

With a comparator, on the original film of Fig. 1 the doubled lines were found to be separated by 0.009 cm about halfway from the single center portion to the end of the line where the doubling was clearest. When the observed separation, 0.009 cm, is compared with the separation calculated on the assumptions of reference 5 (0.015 cm), it seems clear that the reflection from the two crystal surfaces did not leave the crystal parallel to each other, but have been focused in front of the film and are now re-divergent, the position of actual focus depending on the second curvature of the crystal.

3. Breakage of crystals in holder due to secondary curvature

While working at the Cornell x-ray laboratory, the present author had considerable difficulty in bending calcite crystals without breakage, in a focusing spectrograph crystal holder. Much of this difficulty must have been due to the crushing effect of the warping cylinders on the doubly-curved crystal. Even quartz crystals show this tendency to fracture, which is easily explained by this view of the warped crystal shape. The calculation of the actual crystal shape will be a task of much interest.

4. Broadened lines caused by light etching of the crystal surface

Light etching will decrease the thickness of the disturbed surface layers which do the main amount of the x-ray reflection. Hence a very short (radially) imperfect grating is left. In Wood's *Physical Optics*[7] is this statement: "it to be specially noted that the resolving power of the grating does not depend on the closeness of the ruling, but merely on the number of lines." The radial grating of the disturbed surface layers of

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[7] R. W. Wood, *Physical Optics* (second edition, 1929), p. 216.

the bent quartz crystal, is thinned down by light etching until we have relatively few lines in our imperfect grating: the net result being that the doubled lines are un-resolved and even blurred (see Fig. 3(b), reference 5) by the scanty grating available.

ACKNOWLEDGMENTS

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The Fundamental Relation Between Lattice Constants and Density*

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Lattice constants have for many years been based on Siegbahn's crystal wave-lengths which are now known to be different from true wave-lengths. It is proposed that a unit called the "crystal angstrom" be defined as follows: 1 crystal angstrom $=1\text{A}_{\text{cr}}=10^3$ X units, and be used in crystal structure work where "crystal wave-lengths" are used. 1A_{cr} is not equal to 10^{-8} cm. To place the calculation of the density from lattice constant measurements on a sound and uniform basis it is proposed that the fundamental density equation be rewritten in the form $\rho=K(nM/V')$ where $n=$No. of atoms or molecules in the unit cell, $M=$atomic or molecular weight and $V'=$volume of the unit cell in crystal angstroms. The constant K is evaluated empirically from data on calcite and is found to be equal to $1.650_{23}\pm0.00015$ where 0.00015 is the calculated value of the standard deviation. This is the only value which is consistent with (1) the basis for the crystal wave-length scale adopted by Siegbahn, namely $d_{100}=3.02945$ $\text{A}_{\text{cr}}=3029.45$ X units at 18°C for the cleavage cell of calcite, and (2) the best available values for the atomic weight, density and rhombohedral angle of calcite. This value of K must be used in calculating densities from lattice constants if crystal wave-lengths are used. Density calculations are made for five metals and compared with directly measured densities. The error in the calculated density attributable to errors in lattice constant measurements is generally smaller than those due to the atomic weights and to K. For Al, Mg and Ni excellent agreement is obtained between the calculated and measured densities. For Cu and Ag there is marked disagreement but since the directly measured densities are far from concordant while the lattice constants of various investigators agree closely, it is concluded that the main source of the discrepancy lies in the directly measured values.

FOR many years, the scale of wave-lengths for x-rays proposed by Siegbahn and the relative wave-lengths tabulated by him have been the basis for the evaluation of lattice constants. Densities calculated from such lattice constant data have frequently not agreed well with directly measured densities and much speculation has arisen as to the reason for the disagreement. Fundamentally, the Siegbahn wave-length scale may be considered to be based on the measured density of calcite. This may be seen from the agreement between the calculated and measured calcite spacings which Siegbahn[1] himself discussed and considered as fortuitous. It seems unnecessary to enter into the detailed arguments at this point as to why calcite turns out to be the ultimate standard rather than sodium chloride. As far as density calculations are concerned we may state simply that if the value for Avogadro's number used by Siegbahn ($N=6.0594\times10^{23}$) had been used consistently in subsequent calculations of density from lattice constants based on the Siegbahn wave-length scale, the accuracy of densities would have been limited only by (1) the accuracy of the density and rhombohedral angle values of calcite used by Siegbahn, (2) the accuracy of the determinations of the lattice constants and (3) the relative accuracy of the molecular weight of calcite compared with that of

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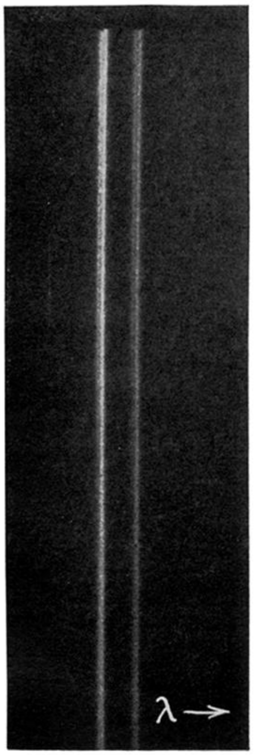
* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] M. Siegbahn, *Spectroskopic der Roentgenstrahlen* (Springer, Berlin, 2nd Ed., 1931).



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