

Absolute X-Ray Reflectivities of Single Crystals of Calcite, Rocksalt, Rochelle Salt and Barite

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With a two-crystal spectrometer absolute x-ray reflectivity measurements have been performed upon four different crystals. In the case of a large calcite crystal of uniform appearance, considered a good spectrometer crystal, with $K\alpha$ radiation of silver it is found that the theoretical values of percent reflection, integrated reflection, and rocking curve width calculated by Allison on the basis of the Darwin-Prins theory of reflection by a perfect absorbing crystal are not attained, the experimental and theoretical quantities being related by a factor not far from two in each case. Rocksalt crystals from a large exhibition specimen from Russia were found to be much more perfect in structure than any rocksalt specimens heretofore reported in the literature of x-ray spectrometry.

Rocksalt reflectivity data for Ag $K\alpha$ are given. Artificial Rochelle salt crystals are found to possess rocking curve widths as narrow as those of high-grade calcite, indicating a very uniform structure; at the same time the reflections are relatively weak. Rochelle salt reflectivity data for Ag $K\alpha$ are given. Percent reflection, rocking curve width and integrated reflection of barite were determined for eleven wave-lengths, and scattering factors were calculated. The variation of the scattering factor with wave-length in the neighborhood of the barium K limit is similar to the variation previously found by Wyckoff and by Glocker and Schäfer for lighter elements except that Wyckoff's maximum does not appear.

IN relatively few cases have the x-ray reflecting characteristics of crystals received the direct attention of investigators. Calcite has been rather adequately studied on account of its great interest as a spectrometer crystal. Existing data upon rocksalt may be traced partly to a similar interest and partly to the importance of this crystal as a standard reflector for use in the analyses of other crystals. In the performance of such analyses spectrometer observations of intensities of reflection have of course been made on many crystals, but while these observations have been sufficient for their ends they are often of diminished permanent value in themselves either because of the slight attention paid to absolute as contrasted with relative values, or because the reflection data themselves do not attain publication. Since the integrated reflection is the only reflection characteristic of use to the crystal analyzer, his work at best provides no information about the angular distribution of reflecting power, nor can this characteristic be deduced in the general case from a knowledge of the crystal structure, however complete.

The reflectivity observations presented below were obtained with a two-crystal spectrometer

which has been previously described.¹ The x-ray tube, a dismantlable type with changeable targets, was operated on constant potential direct current and continuously evacuated by a strong pumping system. The reflectivity determinations discussed below were all conducted according to a uniform procedure which in its general aspects is familiar through the writings of Davis,² Allison³ and others. Having selected the crystal to be examined, an entirely similar one in material, perfection, and treatment was mounted in the A position. The Seemann slit of the A crystal was adjusted to an opening of about half a millimeter. A narrow self-centering slit was mounted on the B crystal table, the crystal and its Seemann slit being absent, and the A crystal was adjusted in its holding device by screws provided for the purpose until radiation reflected from it was received centrally through the slit on the B table. This condition was sometimes observed by using the spectrometer ion chamber, but the adjustment

¹ P. A. Ross, R.S.I. 3, 253 (1932).

² B. Davis and W. M. Stempel, Phys. Rev. 17, 608 (1921); 19, 504 (1922). B. Davis and H. M. Terrill, Phil. Mag. 45, 463 (1923).

³ S. K. Allison and J. H. Williams, Phys. Rev. 35, 1476 (1930).

could be made more rapidly and quite as accurately by employing a fluoroscope. A vertical slit about a millimeter wide and a horizontal slit several millimeters high were installed between *A* and *B*, to limit the beam incident upon *B* to a roughly central area of the crystal. The adjusting slit was removed and the *B* crystal placed in the parallel position with its Seemann slit opened so wide as to be inoperative. The twice-reflected beam was found with the chamber, and adjustments, often laborious, to insure parallelism of the mean reflecting planes of the two crystals were carried out.

Parallel rocking curves were obtained by turning crystal *B*, step by step, through the reflecting position and observing the power of the twice-reflected beam at each step. Tube potentials were maintained at such values as to avoid the production of undesired high-order reflections. Before and/or after determining the rocking curve, crystal *B* was removed from its table and the power of the once-reflected beam observed.

From these data were derived, in the case of each crystal and wave-length, the integrated reflection *R*, the percent reflection *P*, and the half width *w* of the rocking curve at a height half way between the maximum and the level of the flat background.

CALCITE

The two similar pairs of crystals used are considered equal to the best spectrometer calcites in this laboratory. One pair, 1*A*-1*B*, has been polished on the reflecting surfaces while the other pair *U*₂-*T*₂, remains as split. First order reflec-

TABLE I. Reflection of *Ag Kα* by calcite.

	<i>w</i> (seconds)	<i>P</i>	$R \times 10^5$ (radians)
Polished surface (1 <i>A</i> -1 <i>B</i>)	20.5	30.0	9.63
Split surface (<i>U</i> ₂ - <i>T</i> ₂)	3.3	30.6	2.25
Perfect crystal (theoretical)	1.63	79	1.50

tion data for the *Kα* radiation of silver were obtained and are listed in the first two rows of Table I.

The theoretical values in the third row are those computed by S. K. Allison⁴ on the basis of

Darwin's theory of a perfect crystal as modified by Prins to take account of absorption. (The effect of the modification is very slight at this wave-length.) In common with most of the calcite crystals which have been studied heretofore the present data deviate from the predictions for perfect crystals in a sense which indicates some degree of mosaic structure. Evidently these crystals are similar in quality to Allison's pair designated II; they typify a high but not perfect grade of spectrometer calcite.

Perfect crystal predictions are of course not applicable to crystals which have been polished, whatever their former state of perfection. Polishing in this case had the usual effect of increasing the integrated reflection of the crystal at the expense of resolving power.

ROCKSALT

The rocksalt crystals used were from a fifty pound block of high quality, originating in Russia. The surfaces used were chosen from a large number of freshly cloven pieces by visual inspection and rough spectrometer examination. Not all of the pieces derived from this block were internally clear and superficially plane but the two specimens selected for use had the uniform appearance of fine calcite. Hence our rocksalt data, like those on calcite above, are not to be taken as representative of typical crystals of their kind but as pertaining to the best obtainable. Results for first-order reflection of the wave-length of silver *Kα* were as follows:

$$R = 18.2 \times 10^{-5}; \quad w = 87''; \quad P = 17.7.$$

The narrowness of the rocking curve shows the crystal to be very much more nearly perfect than any rocksalt crystal heretofore reported, though the width is still more than 50 times as great as the value for a perfect rocksalt crystal according to Darwin's⁵ treatment. The present value of 87'' may be compared with a value of 900'' obtained by Bragg, James and Bosanquet,⁶ with about the same wave-length and with the 300'' of Davis and Stempel.²

Though much of the early x-ray spectrographic work was done with rocksalt crystals, it is not

⁵ A. H. Compton, *X-Rays and Electrons*, (1926), p. 140.

⁶ Bragg, James and Bosanquet, *Phil. Mag.* **42**, 1 (1921).

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

highly regarded at the present time for such purposes, since advancing refinement in measurement has increased the demand for higher resolving powers. We think that the discovery of rocksalt crystals with resolving powers three and a half times as high as the previous best should do something to restore this crystal to favor in investigations where intensity rather than extreme resolution is the principal desideratum. While the resolution is by no means to be compared with that of good split calcite, the integrated reflection is eight times as great.

ROCHELLE SALT

The Rochelle salt surfaces used were adjacent portions of a large (001) face of an artificially-grown crystal from a laboratory supply house. The material is available in this way because of the interest in its piezoelectric properties. The face as received was a rectangle 17 cm long and 9 cm in breadth; it was sawed into three pieces, all large for spectrometer use.

Rochelle salt is a sodium-potassium tartrate with the formula $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. The structure, apparently, has not been determined. The grating space normal to the (001) planes was determined by observing with a single crystal the separation of the silver $K\alpha$ lines in the first and second orders and found to be 5.93Å. Reflectivity determinations were made for both first and

where n is the number of scattering units in unit volume, F is the structure amplitude corresponding to the same scattering unit, and the other symbols are of obvious interpretation. The only uncertainty in evaluating $\Delta\theta_0$ results from the uncertainty in F . Being in ignorance of the crystal structure, we can do no more than calculate an upper limit for F by adding the form factors⁷ of the constituent atoms of the chemical formula previously given. Such a calculation for the second order reflection leads to the value 101, which is the value that F would have for the second order reflection if temperature disturbances of the atomic positions did not occur and if the atoms were so located in the unit cell that they all scattered in phase. Of course neither of these conditions is fulfilled and consequently, on both counts, a lower value of F is to be expected, but we shall use the value 101 provisionally in Eq. (1), and obtain therefrom $\Delta\theta_0 = 11.5 \times 10^{-6} = 2.37''$. Allison⁸ shows that if the diffraction pattern of a single crystal is of the Darwin form the half width at half maximum of the parallel rocking curve should be $w = 0.60\Delta\theta_0$. The theoretical half width at half maximum under the assumption that $F = 101$ is therefore $0.60 \times 2.37 = 1.4''$, in striking coincidental agreement with the experimental value, 1.5''. This agreement may be taken as an indication that the approach of the crystal to perfection is comparable to the approach of F to the limiting value assumed. The low percent reflections do not, however, favor the presumption of a high state of perfection, but indicate that the narrow rocking curves result from a crystal structure permitting only a low degree of cooperation among the many atoms contributing to the scattering. It is perhaps unprofitable to speculate further upon this situation until some information about the crystal structure can be obtained. In spite of the low reflecting powers observed these gigantic and inexpensive crystals with resolving powers comparable to those of calcite should not be entirely overlooked as possible spectrometer material for certain applications.

TABLE II. Reflection of Ag $K\alpha$ by Rochelle salt.

Order of reflection	w (seconds)	P	$R \times 10^5$
First	3.5	6.3	0.25
Second	1.5	1	0.020

second order reflections of silver $K\alpha$ and the results are summarized in Table II.

These data are notable for the extreme narrowness of the rocking curves, resembling those of the best calcite, together with the very low percent reflections and integrated reflections. According to Darwin's⁵ theory of reflection by perfect crystals the angular region of perfect reflection, a quantity closely related to the width of the rocking curve, is given by

$$\Delta\theta_0 = nF\lambda^2 e^2 \cot \theta / \pi mc^2, \quad (1)$$

⁷ R. W. James and G. W. Brindley, *Phil. Mag.* **12**, 81 (1931).

⁸ S. K. Allison, *Phys. Rev.* **38**, 203 (1931).

BARITE

Natural crystals of barite (BaSO_4) from Felsoebanya, Hungary, with cleavage faces 3 by 4 cm were mounted on the spectrometer in such a way as to utilize face reflections from the (001) planes. The length of the unit cell normal to these planes is given by Wyckoff⁹ as 7.17Å. If this value be taken as d in Bragg's equation, it is found that no first order reflections occur, because of the complete interference of identical planes of half the above separation. The first reflection observed is therefore in the second order, and all barite reflections hereinafter discussed are properly specified by (002).

The principal point of interest in connection with this crystal concerns the K limit of the barium constituent which comes within the available x-ray range. As it was desirable to select wave-lengths within this range with entire freedom, the continuous spectra of tungsten and platinum were used as sources. The rocking curves obtained were not all as symmetrical as those obtained with good crystals such as calcite but bear more resemblance to the curves of rock-salt of average quality. On a few occasions singular excrescences appeared on the sides or feet of the curves, which could be traced to faulty areas on the crystal face and removed by installing horizontal slits or by moving the crystal. Table III presents the experimental results for the eleven wave-lengths investigated, together with data for one additional wave-length (0.71Å) taken from the work of James and Wood.¹⁰

TABLE III. Barite reflection data and structure factors.

$\lambda(\text{Å})$	w (min.)	P	R (rad.) $\times 10^5$	F'
0.260	11.5	0.47	2.46	118
0.295	7.0	0.50	1.54	99
0.306	8.0	0.6	2.34	
0.317	10	0.5	2.44	
0.330	5.3	1.6	6.56	
0.350	8	1.8	10.1	109.8
0.365	6.0	1.9	9.54	108.4
0.434	6.0	1.5	8.99	114.7
0.505	6	1.75	8.20	116.7
0.574	6.5	1.7	7.32	118.2
0.645	5.0	1.7	5.98	114.4
0.71			6.63	125

⁹ R. W. G. Wyckoff, *The Structure of Crystals* (1931), p. 289.

¹⁰ R. W. James and W. A. Wood, Proc. Roy. Soc. A109, 598 (1925).

Apparently there are no significant variations of the rocking curve width with wave-length, and the discussion to follow concerns the values of the integrated reflection. These are plotted in Fig. 1.

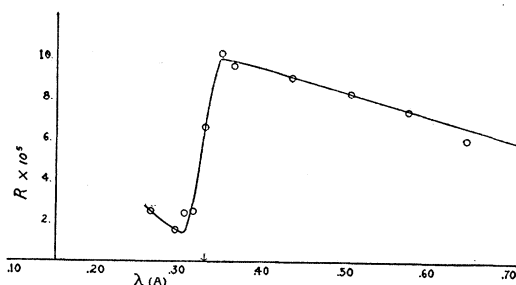


FIG. 1. Integrated (002) reflections of barite (BaSO_4). The last point, at the right is taken from James and Wood.¹⁰

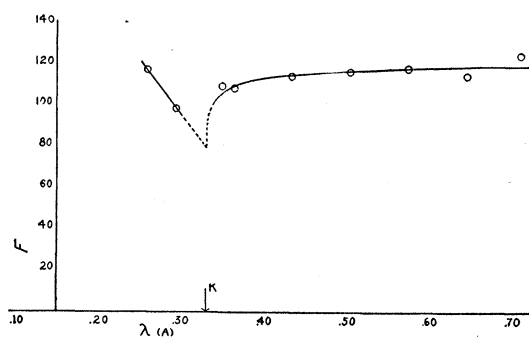


FIG. 2. Scattering factors of the barite unit cell (of four molecules) as derived from the integrated reflections of Fig. 1. (The three points of Fig. 1 nearest to the K limit do not permit the calculation of scattering factors because of uncertainty as to the appropriate absorption coefficients.)

The abrupt change which occurs at the wave-length of the barium K limit is most conspicuously displayed, though its full magnitude is not shown on account of the rounding effect of the finite wave band represented by each point. This break is chiefly caused by the change in absorption coefficient but a simple calculation shows that this change is insufficient to produce a discontinuity of the magnitude shown in the figure. A discontinuity in the scattering factor is indicated.

The last column of Table III and the curve of Fig. 2 exhibit the scattering factors of the unit cell, a group of four molecules, as computed by Darwin's¹¹ equation expressing the integrated

¹¹ R. W. G. Wyckoff, *The Structure of Crystals* (1931), p. 91.

reflection by imperfect crystals. This computation suffers from the usual uncertainties regarding the effects of extinction and of thermal agitation of the atoms, both of which effects have been ignored. Consequently on both counts we must expect the experimentally derived values of F to be too low, and this expectation is borne out by an independent calculation of the scattering factor of the unit cell, upon the basis of the independently known scattering factors of the constituent atoms and the structure of the barite crystal as determined by James and Wood.¹⁰ In such a calculation no account is taken of the special effect of absorption limits; so the calculated result is to be compared with Fig. 2 only at the longest wave-lengths, where, apparently, the effect of the limit is no longer manifested. This calculation yields unit cell scattering factors from 150 to 157, depending upon which of several available lists of atomic scattering factors is adopted. These values are clearly in excess of anything which the curve of Fig. 2 could attain to.

If we are to succeed in separating the scattering factors of barium from those of the rest of the crystal it is necessary to consider the cause of this discrepancy. It is not practicable to correct our scattering factors for the effects of thermal movements in this crystal but it is known that the correction would affect all ordinates of the curve of Fig. 2 proportionally and therefore leave the shape of the curve unchanged. Primary extinction would have a like effect, but secondary extinction would alter the curve shape. Strong secondary extinction effects are judged to be improbable, however, in a crystal with such strong ordinary absorption, since the extinction coefficient affects the integrated reflection only as an additive term to an absorption coefficient already large. James and Wood studied the similar crystalline sulphates of barium, strontium and lead and found discrepancies between theoretical and observed integrated reflections of the wave-length 0.710Å of just the kind encountered here. Had this difference been due to secondary extinc-

tion the discrepancy would presumably have been least in the strongly absorbent lead sulphate, whereas it was in fact greatest in this case. It seems correct to conclude that the shape of the curve representing the scattering factor of barium as a function of wave-length is as shown in Fig. 2, though the vertical scale of the plot is somewhat contracted and the constant scattering of the sulphur and oxygen atoms (about 55) has not been removed.

Variations of atomic scattering factors with wave-length, in the neighborhood of the K limits with the ratio $\sin \theta/\lambda$ held constant, have previously been measured by A. H. Armstrong¹² and by Wyckoff¹³ for nickel and copper, and by Glocker and Schäfer,¹⁴ and Bradley and Hope¹⁵ for iron. The present measurements, though performed on an element with twice as many scattering electrons, are in good agreement with the earlier work in disclosing a minimum in scattering power at or near the wave-length of the limit. Our results however do not show any maximum value of the scattering factor on the long wave-length side of the limit, such as Wyckoff¹⁶ described. In comparison with the predictions of the dispersion theory of Glocker and Schäfer our curve (Fig. 2) has the predicted general shape on the long wave-length side of the limit, but, like the experimental curve of Glocker and Schäfer, it rises too slowly on the side of shorter wave-lengths.

¹² A. H. Armstrong, Phys. Rev. **34**, 931 (1929).

¹³ R. W. G. Wyckoff, Phys. Rev. **36**, 1116 (1930).

¹⁴ R. Glocker and K. Schäfer, Zeits. f. Physik **73**, 289 (1931).

¹⁵ Bradley and Hope, Proc. Roy. Soc. **A136**, 272 (1932).

¹⁶ The evidence upon which this maximum is claimed is not considered strong. The curve of Fig. 3 (Phys. Rev. **36**, 1120 (1930)), showing the maximum, is not in agreement with the accompanying data of Table IV, sloping down at the right of the maximum three or four times as rapidly as the tabulated data would permit. This curve shows the values of the (200) reflection of nickel. Values of the (111) reflection given in Table IV and not plotted give no evidence of a maximum.