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Asymmetric X-ray Reflexion from Natural Quartz Crystals

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The variation of integrated intensity with the asymmetry of the reflexion has been determined for two natural quartz crystals. It is shown that the results are in agreement with the theoretical predictions of the dynamical theory; further it is shown that experimental measurement of structure amplitudes can be made from these experiments with a higher degree of accuracy than hitherto.

1. Introduction

Several recent publications (Evans, Hirsch & Kellar, 1948; Gay, Hirsch & Kellar, 1952) have been devoted to the examination of the variation of the intensity of X-ray reflexion with the degree of asymmetry of the reflexion. In particular, experimental and theoretical investigations of this variation have been made for abraded crystals (Gay *et al.*, 1952), i.e. crystals which can be considered to have a mosaic texture. The variation of the integrated reflexion with asymmetry of reflexion has recently been calculated by Hirsch & Ramachandran (1950) on the basis of the dynamical theory of X-ray reflexion (Ewald, 1924; Kohler, 1933). This paper describes experimental results obtained using natural quartz crystals; the texture of these crystals is probably intermediate between the theoretically perfect and mosaic states.

The experimental results obtained in the investigation of abraded crystals showed that a layer of non-reflecting material is present on the crystal surface; most of this layer consists of material which is misorientated from the main crystalline matrix. For the more asymmetric reflexions, the path length of the X-rays within the absorbing layer becomes great enough to reduce considerably the reflected X-ray intensity and modify the expected variation with asymmetry. The surfaces of the naturally occurring specimens used in the present experiments have been examined to find out if similar inhomogeneities are present, so that a true comparison of the experimental results with the theoretical calculations may be made. This comparison is important since the calculations are based on the dynamical theory of X-ray reflexion, of which there have been very few experimental tests.

In addition, it has become apparent that the experimental measurements can lead to an experimental determination of structure amplitudes, which, since it is independent of any assumptions about the texture of the material, is considerably more accurate than previous methods.

This paper, then, contains an account of the examination of the physical nature of the faces of the two natural quartz crystals used in the asymmetric reflexion measurements, together with the results of these measurements and their interpretation. It is shown that the predicted variation of integrated intensity is observed experimentally, and that measurements of the structure amplitudes for the $10\bar{1}1$ and $20\bar{2}2$ reflexions from these crystals can be made with high accuracy.

2. The physical nature of the crystal faces

Two natural crystals of quartz selected from the collection in the Department of Mineralogy and Petrology, Cambridge, were used in these experiments. The $(10\bar{1}0)$ faces of the crystals were examined by the back-reflexion and glancing-angle X-ray techniques used with the abraded crystal specimens. No evidence of material widely misorientated from the main crystalline matrix was found using either of these methods. It was not possible to use electron-diffraction methods for the examination of these large specimens.

More detailed examinations of one of these faces by interferometric methods (Tolansky, 1948) and the X-ray microbeam spectrometer (Thorp, 1951) have been made by T. Willis (Royal Holloway College, London) and J. S. Thorp respectively. The former method showed growth nuclei forming small pyramids and steps running parallel to the $(10\bar{1}0)$–$(10\bar{1}1)$ edge. The heights of the growth pyramids vary but none is greater than 2×10^{-4} cm.; the steps on the surface have heights less than $0{\cdot}2 \times 10^{-4}$ cm. Local variations in orientation of the surface up to 2 min. of arc are found. The micro-beam spectrometer technique confirmed the existence of the growth pyramids and showed the existence of small misorientations at the depth of penetration of the X-ray beams.

It can be concluded that although large misorientations, such as are found on abraded crystal surfaces, are not present on the surfaces of these quartz crystals, small misorientations do exist; protuberances in the form of growth pyramids and steps are also found.

3. Asymmetric X-ray reflexion from natural crystals

(*a*) *Experimental procedure*

Experiments were carried out to measure the intensity of the reflected X-ray beam as a function of the asymmetry of the reflexion. The degree of asymmetry of the X-ray reflexion may be simply defined in terms of the angle φ between the reflecting planes and the crystal surface; in this work, however, it is more convenient to define the asymmetry in terms of a variable $\beta = (1-R)/(1+R)$, where R, the concentrating ratio, is equal to the ratio of the widths of the reflected and incident beams. From the geometry of an asymmetric reflexion, $R = \sin(\theta-\varphi)/\sin(\theta+\varphi)$, where θ is the Bragg angle for the reflecting planes.

In the work on asymmetric reflexions from abraded crystals, it was shown that variation of the value of φ can be achieved by rotating a crystal wedge ground at some angle ω to the reflecting planes about the normal to these planes. It has been shown by Evans *et al.* (1948) that

$$\tan\varphi = \sin\psi\tan\omega\,, \tag{1}$$

where ψ is the angle of rotation of the wedge about the normal to the reflecting planes measured from the position of unit concentration ($\varphi = 0$, i.e. $\beta = 0$). Thus φ may be varied between the limits of $\pm\omega$, and if $\omega \geqq \theta$, then β can be varied between ± 1.

The two natural quartz crystals selected for examination were of simple habit showing prominent $\{10\bar{1}1\}$ and $\{10\bar{1}0\}$ forms. They were mounted with a $(10\bar{1}1)$ face normal to the axis of rotation, and the reflexion was taken from the $(\bar{1}010)$ face, so that the effective angle of the wedge used is $(10\bar{1}1) \mathbin{\hat{}} (10\bar{1}0) =$ 38° 13′. This ensures considerable variations in ψ for both the $10\bar{1}1$ and $20\bar{2}2$ reflexions which were examined; this is desirable since it ensures accurate measurements of the degree of asymmetry. Difficulties are encountered when the angle of the wedge is very much greater than the Bragg angle for the reflexion (e.g. in the case of the $10\bar{1}1$ reflexion from a calcite cleavage rhomb), since it is seen from the equation above that small changes in ψ then produce large changes in the asymmetry. The procedure for the determination of the position of unit concentration and the calibration of the dial angle (ψ) in terms of φ (or β) have been given elsewhere (see Gay & Hirsch, 1951).

The intensity measurements were carried out using the surface-layer Geiger counter spectrometer described in an earlier publication (Gay & Hirsch, 1951). At each value of β, values of the ratio of the total intensity in the reflected beam to the total intensity in the incident beam (I/I_0) were measured. It has been shown that relative measurements of integrated intensities can be obtained from a stationary crystal (Gay *et al.*, 1952). In the present work, it was required to place all the experimental measurements of I/I_0 on an absolute scale. This can be done if the integrated reflexion for one of them is known. A comparison of the value of I/I_0 for this measurement with the value of I/I_0 determined under the same experimental conditions for a crystal whose integrated reflexion is known, gives the proportionality factor by which all other values of I/I_0 must be scaled to give absolute values of integrated reflexion. The validity of this method has been demonstrated experimentally by Evans *et al.* (1948).

(*b*) *Experimental results*

The value of the specific reflexion, J (defined as the integrated reflexion per unit area of beam and directly proportional to I/I_0) is shown plotted as a function of β in Fig. 1. These typical curves were obtained for the $10\bar{1}1$ and $20\bar{2}2$ reflexions from the same crystal. The value of $J(0)$, i.e. the specific reflexion in the symmetric position ($\beta = 0$), has been scaled so that it is unity; all other points have been scaled accordingly.

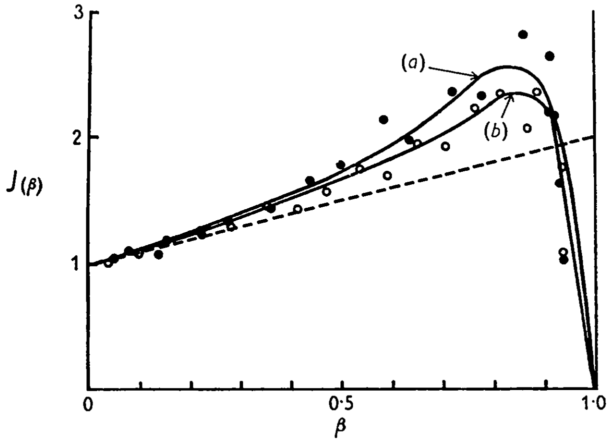

Fig. 1. Variation of $J(\beta)$ with β. The closed circles are experimental points for the $10\bar{1}1$ reflexion from quartz crystal B (θ = 13° 20′, Cu $K\alpha$ radiation); a smooth curve (*a*) has been drawn through the points, which have been scaled so that $J(0) = 1$. The open circles are experimental points for the $20\bar{2}2$ reflexion from the same crystal (θ = 27° 28′, Cu $K\alpha$ radiation); a smooth curve (*b*) has been drawn through the points, which have been scaled so that $J(0) = 1$. The broken line represents the expected variation for a mosaic crystal; this is also scaled so that $J_M(0) = 1$.

From the figures, it is seen that the characteristics of the curves are that they rise to a maximum and fall sharply to zero for the most asymmetric reflexions ($\beta \rightarrow 1$). The curves are similar in general shape to the curves of similar variables obtained for abraded crystals. However, for the mosaic crystals the peaks of the curves were always at heights less than twice the values of the corresponding symmetric reflexions. Indeed, the theoretical prediction for a mosaic crystal without an absorbing layer (shown in the figures) is that for $\beta = 1$, the value of the reflected intensity is only twice that for $\beta = 0$.

The decrease to zero is generally quite steep and occurs at high degrees of asymmetry; further the positions and heights of the peaks are different for the $10\bar{1}1$ and $20\bar{2}2$ reflexions from the same crystal.

All these features of the curves must be explained by any theoretical considerations, but it is clear that an interpretation based on the theory for mosaic crystals (Gay, 1951) is not possible. A discussion of the shapes of the curves is given in the following sections.

4. The theory of the intensity of asymmetric X-ray reflexions from perfect, absorbing crystals

A recent paper by Hirsch & Ramachandran (1950) has been devoted to an examination of the intensity of X-ray reflexion from perfect, absorbing crystals as a function of several variables, one of which included the asymmetry of the reflexion. It seems likely that a theoretical treatment of this kind is applicable to the natural quartz crystals. A brief presentation of the relevant results of the theoretical treatment is given below.

From the treatment of the dynamical theory adopted by Zachariasen (1945), it is found that the effects of asymmetry on the reflected intensity from perfect absorbing crystals can be most conveniently expressed in terms of the parameters g and k. These are defined by the expressions

$$g = \frac{-(1-b)}{4K\sqrt{|b|}} \cdot \frac{mc^2}{e^2\lambda N} \cdot \frac{\mu\sqrt{(1+k^2)}}{|F_H|} \tag{2}$$

and

$$k = F''_H/F'_H \, , \tag{3}$$

where

$F_H =$ structure amplitude of planes of index (hkl) $\equiv F'_H + iF''_H$,

$e =$ electronic charge,

$m =$ electronic mass,

$\mu =$ linear absorption coefficient,

$N =$ number of cells per cm.^{3},

$\lambda =$ wavelength of the X-rays *in vacuo*,

$K =$ polarisation factor ($K = 1$, for the normal component, $K = |\cos 2\theta|$ for the parallel component),

$b = -1/R$.

A number of reflexion curves for different values of the two parameters were calculated and integrated graphically. The results of these calculations were then used to discuss the variation of the integrated reflexion with the factors represented by g and k. In particular, the variation of the specific intensity with degree of asymmetry was determined.

The precise form of the variation of $J(\beta)/J_M(0)$ (= specific reflexion from a perfect crystal at asymmetry β/specific reflexion from a mosaic crystal in the symmetrical position) with β is shown in Fig. 2 of the publication by Hirsch & Ramachandran (1950). The curves are drawn for a number of values of $g(0)$; $g(0)$ is the value of g for the symmetric reflexion ($= -mc^2\mu/2Ke^2\lambda N|F_H|$). k was taken as zero since, unless the reflexion used is very weak or the incident wavelength is very close to a critical absorption edge, $|F''_H|$ is very small compared with $|F'_H|$. A particularly important feature of the curves is that when g is large, i.e. the reflexion is highly asymmetric, the value of the specific reflexion approaches asymptotically the value for a mosaic crystal.

Fig. 2 shows the theoretical curves which are scaled so that $J(0)/J_M(0)$ is unity. It is seen from the diagram that the increase in $J(\beta)$ as β varies from 0 to 1 is greater than twofold for all finite values of $g(0)$, and that the greater the ratio $J(1)/J(0)$ the smaller is the value of $g(0)$, i.e. the stronger the reflexion.

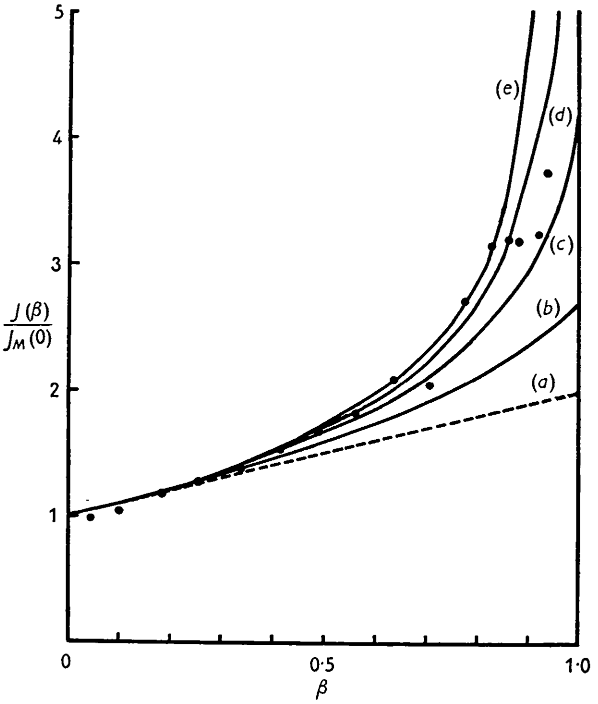

Fig. 2. The curves show the theoretical variation of $J(\beta)/J_M(0)$ with β, and have all been scaled to a common origin, unity, at $\beta = 0$. They represent (a) mosaic crystal, (b) $g(0) = 0{\cdot}5$, (c) $g(0) = 0{\cdot}2$, (d) $g(0) = 0{\cdot}1$, and (e) $g(0) = 0{\cdot}05$. The points are experimental points corrected for absorption within the layer and have been obtained for the $20\bar{2}2$ reflexion from quartz crystal B ($\theta = 27° \, 28'$, Cu $K\alpha$ radiation) after correction for a mean layer thickness ($\mu t = 0{\cdot}009$).

Two assumptions were made in the mathematical analysis. First, the reflexions considered are those of the 'Bragg' type, in which the reflected beam emerges from the same surface on which it is incident; this is the case in the present experiments. Further, it was assumed that the crystal possesses an inversion centre; this condition is not satisfied. However, in the calculations the terms F_H and $F_{\bar{H}}$ (which must be distinguished for a polar crystal) only occur in the product form, $F_H F_{\bar{H}}$; it can be shown that this product is equal to $|F_H|^2$ provided that we are not using a very weak reflexion nor workind near a critical absorption edge (Gay, 1951). Both these latter requirements are satisfied under the experimental conditions, and no modification of the theoretical treatment is necessary for the discussion of the experimental results here.

5. Interpretation of the experimental results

The experimental curves show increases in $J(\beta)$ as β varies from 0 to 1 similar to those predicted by the theory. However, the theoretical curves do not fall to zero as $\beta \to 1$. The fall in the experimental curves must be attributed to the presence of absorbing material on the surface of the crystal; the importance of the absorption increases as the reflexion becomes more asymmetric and the angle between the reflected beam and the crystal surface decreases. Since no heavily misorientated material is observed it is likely that absorption occurs in the projections on the surface (the growth pyramids and steps). In earlier work by Gay *et al.* (1952) a similar effect was found for a crystal of lithium fluoride when all the misorientated material had been etched away after grinding. It was seen that the effect of the projections may be treated by considering a layer of absorbing material on the surface of the crystal. This absorbing material is considered to be spread out over the surface of the crystal and condensed along the normal to it, so that the density at any point within the 'condensed' layer is equal to the density within the main crystalline matrix.

If it is assumed that the general shapes of the experimental curves are attributable to the modification of theoretical curves by the absorbing effect of the condensed layer, it is seen that the thickness of layer required to modify the theoretical curves so as to fit the experimental points is dependent on the value of $g(0)$ chosen. In the next section it is shown that upper and lower limits of μt ($t =$ thickness of the condensed layer) can be determined. If an average value of μt is taken, the experimental points can be corrected for the absorption within the projections; each experimental point is multiplied by the appropriate exponential factor $\exp[\mu t(1+R)/\sin(\theta-\varphi)]$ (see Gay *et al.*, 1952). One set of experimental points after the correction has been made is shown in Fig. 2.

After correction, the experimental points tend to follow the general trends of the theoretical curves. The points do not lie along a particular $g(0)$ curve; this would occur only if the effective texture were the same at all values of β, which is unlikely. Thus it can be concluded that the results are in qualitative agreement with the predictions of the theory, taking into account the absorbing effect of the projections on the surface.

In the next section, the method of estimating the thickness of the condensed layer is described, and it is shown how the limits of thickness found can be used to determine the limits of structure amplitudes for the $10\bar{1}1$ and $20\bar{2}2$ reflexions from quartz.

6. The determination of the thickness of the condensed layer

In the following, it is assumed that the thickness of the condensed layer on each crystal is the same for both the $10\bar{1}1$ and $20\bar{2}2$ reflexions. If the crystal were mosaic, the thickness of the layer could be estimated. Even with a perfect crystal, for reflexions for which $g(0)$ is large, i.e. weak reflexions, the crystal tends to behave as if it were mosaic, and the thickness of the layer can be determined. However, the $20\bar{2}2$ reflexion from quartz is still quite strong (see Table 1), so that estimates based on the assumption that the crystal is behaving as mosaic will provide only a lower limit to the layer thickness.

Table 1. *Values of the integrated reflexion in the symmetric position*

	J(0) (microradians)	
	$10\bar{1}1$	$20\bar{2}2$
Crystal *A*	117·6	16·8
Crystal *B*	166·0	18·5

An upper limit of the layer thickness may be found by assuming that the crystal is perfect. On this basis, a value of $g(0)$ may be calculated from the values of the integrated reflexions in the symmetric position. This value of $g(0)$ is a minimum, i.e. the corresponding curve of $J(\beta)\, v.\, \beta$ rises more sharply as β tends to 1 than do curves for less perfect crystals. Hence the thickness of layer which modifies the appropriate theoretical curve to give a good fit with the experimental points is a maximum value.

This method, when applied to the $20\bar{2}2$ reflexion, gives limits between which the values of μt must lie for both crystals.

A new estimate of the lower limit of thickness can be made by applying a similar technique to the appropriate $10\bar{1}1$ curves. For these curves, however, it is expected that the value of $g(0)$ is smaller and the lower limits are in general less than those found for the weaker $20\bar{2}2$ reflexion.

The value of the upper limit can be reduced in the following way. The experimental points on the $10\bar{1}1$ curves can be corrected for the appropriate upper limiting thickness derived from the $20\bar{2}2$ reflexion. The resultant corrected curves may then be regarded as upper limits below which the actual curves for the crystals must lie. Now it was pointed out earlier that for the more asymmetric reflexions the values of the specific reflexions become independent of texture. Thus the values of the specific reflexions at high degrees of asymmetry can be equated to $J_M(\beta)$ (the specific reflexion of a mosaic crystal with asymmetry

β); now $(1+\beta)J_M(0) = J_M(\beta)$, so that $J_M(0)$, and hence a value of $g(0)$, can be found. This value of $g(0)$ will be a minimum and it can be used to estimate the maximum thickness of the layer, as outlined above.

This procedure usually results in the reduction of the upper limit of the layer thickness. Further reductions can be made by correcting the $20\bar{2}2$ reflexions for the effect of the appropriate limiting thickness, and then following the procedure described in the previous paragraph for the $10\bar{1}1$ reflexion. Indeed, this technique may be applied to the $10\bar{1}1$ and $20\bar{2}2$ reflexions alternately until no further change in the upper limit is found. This stage is quickly reached. The final results for the two specimens are:

$$\begin{array}{ll} \text{Crystal } A & 0\cdot 005 < \mu t < 0\cdot 011\ , \\ \text{Crystal } B & 0\cdot 004 < \mu t < 0\cdot 015\ , \end{array}$$

from which the thicknesses of the condensed layers become:

$$\begin{array}{ll} \text{Crystal } A & 0\cdot 55\times 10^{-4}\ \text{cm.} < t < 1\cdot 20\times 10^{-4}\ \text{cm.}, \\ \text{Crystal } B & 0\cdot 44\times 10^{-4}\ \text{cm.} < t < 1\cdot 65\times 10^{-4}\ \text{cm.} \end{array}$$

In this way the limits of the layer thickness may be found to within a factor of three or four. It will be noticed that the condensed thickness is less than the maximum heights of the peaks of the growth pyramids determined from the interferometric measurements, as would be expected for a condensed layer.

7. The experimental determination of structure amplitudes

Previous methods for the determination of structure amplitudes have been based on the exact expressions derived by Darwin (1914, 1922) for the integrated intensity from ideally perfect and ideally mosaic crystals. Renninger (1934) selected two crystals which corresponded as far as could be seen to the perfect and mosaic ideal states. The integrated reflexion from each of these crystals was measured and the limits within which the structure amplitude must lie were calculated from the appropriate formulæ. Wooster & Macdonald (1948) attempted to extend this method by measuring the integrated reflexions for a number of crystals for two different radiations. Both these methods assumed ideal states of perfection or imperfection for the specimens; the results which are obtained are highly inaccurate for most specimens.

The present method is independent of any assumptions about the texture of the crystal, and depends on the fact that, for highly asymmetric reflexions, the value of the specific reflexion approaches that from an ideally mosaic crystal. First, however, it is interesting to evaluate the structure amplitudes on the basis of the two extreme states of perfection. Using the Darwin formulæ, the values of $F_{10\bar{1}1}$ and $F_{20\bar{2}2}$, obtained from the values of $J(0)$ given earlier for both crystals, are shown in Table 2.

Table 2. *Values of* $F_{10\bar{1}1}$ *and* $F_{20\bar{2}2}$ *calculated from the Darwin formulæ*

	$F_{10\bar{1}1}$		$F_{20\bar{2}2}$	
	Perfect	Mosaic	Perfect	Mosaic
Crystal *A*	110·1	21·7	34·6	12·9
Crystal *B*	156·0	25·8	38·2	13·5

Thus there is a wide range of uncertainty in the calculated F values.

In the preceding section, the limits of the thickness of the condensed layer were estimated. Each experimental curve can thus be corrected for the absorbing effect of the projections. For each experimental curve there will now be two corrected curves within which the actual curve must lie. Hence, by choosing the maximum and minimum possible values of $J(\beta)$ as β tends to 1, limits can be found within which $J_M(\beta)$ (and so J_M (0)) must lie. From the limits of $J_M(0)$, the limits of the structure amplitude may be calculated using the Darwin formula for a mosaic crystal. The results of these calculations are given in Table 3.

Table 3. *Limits of structure amplitudes*

Crystal *A*	$31\cdot 5 < F_{10\bar{1}1} < 38\cdot 9$;	$16\cdot 7 < F_{20\bar{2}2} < 19\cdot 5$
Crystal *B*	$33\cdot 9 < F_{10\bar{1}1} < 46\cdot 1$;	$15\cdot 6 < F_{20\bar{2}2} < 19\cdot 4$

Thus, from measurements on one crystal, structure amplitudes may be determined to an accuracy of ±10% without any assumptions about the crystalline texture. From Table 2, the accuracy using direct calculation from the Darwin formulæ is at best ±50%, and generally much worse. The accuracy may be further increased by combining the results for both crystals; then $33\cdot 9 < F_{10\bar{1}1} < 38\cdot 9$; $16\cdot 7 < F_{20\bar{2}2} < 19\cdot 4$.

A further correction to the lower limit may be applied in some cases. A straight-line extrapolation from the experimental points at the peak of the curve may be made to give a value of $J(1)$; this must be regarded as a lower limit since the slopes of the theoretical curves are increasing in this region.

The final mean values of the structure amplitudes for these two reflexions from quartz are

$$F_{10\bar{1}1} = 36\cdot 4 \pm 2\cdot 5\ ,$$
$$F_{20\bar{2}2} = 18\cdot 65 \pm 0\cdot 75\ .$$

These values may be compared with those calculated by Wei (1935) from his structural investigation of quartz, namely

$$F_{10\bar{1}1} = 37\cdot 8\ ,$$
$$F_{20\bar{2}2} = 19\cdot 3\ .$$

The agreement is remarkably good, the calculated F values lying within the experimental range.

8. Conclusions

It has been found that the experimental variation of the integrated reflexion with asymmetry for two natural quartz crystals is similar to that predicted by the dynamical theory for perfect, absorbing crystals.

Using the results of the theoretical investigation, it has been possible to obtain experimental F values with an accuracy of $\pm 10\%$ from one crystal, without the necessity for making detailed assumptions about the degree of perfection of its texture. From the combination of observations from a series of crystals it may be possible to increase the accuracy of this method. Higher accuracy may be obtained if the absorbing effect of any projections on the crystal surface can be found from the experimental variation of $J(\beta)$ with β for a weak reflexion.

A disadvantage of the method is that the crystals used must be quite large, and show faces suitable for mounting. However, wherever applicable the method leads to far more accurate results than any previous investigation.

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References

Darwin, C. G. (1914). *Phil. Mag.* **27**, 675.
Darwin, C. G. (1922). *Phil. Mag.* **43**, 800.
Evans, R. C., Hirsch, P. B. & Kellar, J. N. (1948). *Acta Cryst.* **1**, 124.
Ewald, P. P. (1924). *Z. Phys.* **30**, 1.
Gay, P. (1951). Dissertation for the degree of Ph.D., Cambridge University.
Gay, P. & Hirsch, P. B. (1951). *Brit. J. Appl. Phys.* **2**, 218.
Gay, P., Hirsch, P. B. & Kellar, J. N. (1952). *Acta Cryst.* **5**, 7.
Hirsch, P. B. & Ramachandran, G. N. (1950). *Acta Cryst.* **3**, 187.
Kohler, M. (1933). *Ann. Phys., Lpz.* **18**, 265.
Renninger, M. (1934). *Z. Krystallogr.* **89**, 344.
Thorp, J. S. (1951). *J. Sci. Instrum.* **28**, 239.
Tolansky, S. (1948). *Multiple Beam Interferometry.* Oxford: University Press.
Wei, P. (1935). *Z. Krystallogr.* **92**, 355.
Wooster, W. A. & Macdonald, G. L. (1948). *Acta Cryst.* **1**, 49.
Zachariasen, W. H. (1945). *Theory of X-ray Diffraction in Crystals.* New York: Wiley.

Acta Cryst. (1952). **5**, 530

The Structure of Urea. Interatomic Distances and Resonance in Urea and Related Compounds*

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The interatomic distances in urea have been redetermined by Fourier and least-squares analysis of complete data obtained with Cu $K\alpha$ radiation. The results are C=O = 1·26 Å, C–N = 1·34 Å, $\angle$ N–C–O = 121°, N–H · · · O = 2·99 Å and N–H · · · O′ = 3·04 Å. Evidence for the position of the hydrogen atoms is found in the electron-density sections. Improved agreement of calculated with observed structure factors was obtained by including the hydrogen scattering in the calculations, and by use of anisotropic temperature factors.

Revised values for carbon–oxygen and carbon–nitrogen double bonds are suggested, and these values are used to discuss the effect of resonance on interatomic distances in urea and related compounds.

Introduction

Because of its simplicity, the structure of urea was one of the first organic structures to be determined by X-ray crystallographic methods (Mark & Weissenberg, 1923; Hendricks, 1928; Wyckoff, 1930, 1932; Wyckoff & Corey, 1934). These early studies agreed on the space group, unit cell, and approximate parameters. The space group is D_{2d}^3–$P\bar{4}2_1m$; the unit cell contains two molecules of $CO(NH_2)_2$, with atoms in the following positions: 2 C in (c): $(0, \frac{1}{2}, z)$, $(\frac{1}{2}, 0, \bar{z})$; 2 O in a second set of positions (c); 4 N in (e):

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