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Geiger Counter Measurements of Bragg and Diffuse Scattering of X-Rays by Single Crystals

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The advantages and limitations of the use of Geiger counter equipment for the measurement of scattering intensity from small single crystals are discussed, and the effect of the presence of varying amounts of white radiation in the incident and reflected beams is investigated. Crystals of urea and of oxalic acid dihydrate were studied before and after immersion in liquid air, using Cu K and Mo K radiations, with argon- and krypton-filled counter tubes. It was found that the thermal diffuse scattering is independent of crystal perfection. The ratio of thermal scattering intensity to Bragg scattering for a mosaic crystal increases rapidly with angle of scattering when measured for equivalent groups of thermal waves, and is also much greater for Cu than for Mo radiation.

Introduction

During the summer of 1947, a commercial Geiger counter spectrometer, which had been partially adapted for single crystal observations, was made available to me for about two months. The adaptation consisted of fitting an adjustable goniometer head to the crystal spindle and of uncoupling the Geiger tube arm from the specimen arm, to which it was originally geared, so that they could be moved separately. It was felt that although no extended piece of research could be undertaken the time might profitably be spent in investigating the suitability of the apparatus, in principle and in detail, for single crystal intensity measurements and, in particular, for measurements of thermal diffuse scattering.

Two problems seemed suitable for such measurements: (1) investigation of the variation of the diffuse to Bragg scattering ratio (the diffuse scattering being that corresponding to a group of waves of limited frequencies and directions of propagation) for several orders of reflexion from the same set of crystal planes, using two different wave-lengths of incident X-rays; (2) investigation of the variation of the intensity of diffuse scattering with crystal perfection, by measurements made before and after an abrupt change of texture through liquid-air treatment.

Measurements were made first on single crystals of urea using (1) Cu radiation (filtered Ni); Geiger counter tube filled with an argon-methylene bromide mixture; (2) Cu radiation (filtered Ni); Geiger counter tube filled with a krypton-methylene bromide mixture; (3) Mo radiation (filtered ZrO_2); Geiger counter tube filled with krypton-methylene bromide mixture. Further experiments were carried out using single crystals of oxalic acid dihydrate, with Mo radiation (filtered ZrO_2) and krypton + methylene bromide as detector. In all the experiments automatic traces on a Brown recorder were compared with visual measurements from a mechanical impulse counter, using a scaling circuit on which the rate of recording of impulses could be varied from a scale of 2 to a scale of 64. Lack of workshop facilities made it impossible to monochromatize the radiation (except approximately by filtration) or even to collimate the incident beam satisfactorily, except horizontally. The beam was $\frac{1}{4} \times \frac{1}{4}$ mm. on leaving the slit system, but was about $1{\cdot}6 \times \frac{1}{4}$ mm. at the crystal and was $4{\cdot}9 \times \frac{1}{4}$ mm. on reaching the slit in front of the Geiger tube. The crystals used were about 3 (vertical) $\times \frac{1}{2} \times \frac{1}{2}$ mm., and (except where otherwise stated) the Geiger tube slit was kept at $5 \times \frac{1}{4}$ mm. to collect the scattered beam. It will be seen therefore that no attempt was made to reproduce the ideal conditions for Bragg intensity measurement (a very small crystal bathed in a parallel incident beam), partly because such conditions would have made the crystal adjustment much more difficult and partly because they would not have been best suited to the two particular problems under investigation, especially to the second of them.

Sensitivity and calibration of instrument

In general, the stray radiation in the laboratory gave a reading which varied from 16 to 24 counts per min. It was found advisable to check this by a 10 min. reading at least once every 2 hr. when measurements of low-intensity scattering were being made.

On the same scale, the peak intensity of Bragg reflexion from the (110) planes of the urea crystal used, with Cu radiation, would be over 10^6 counts per min. (A reading as large as this, however, could not be registered directly.) There is, of course, *no upper limit* to the intensity that can be measured, provided that a filter of known absorption is interposed, or some other method is used for cutting down the intensity entering the Geiger counter tube to a quantity that is capable of being resolved and accurately recorded. The *minimum* reading that could be recorded with certainty was one

of about 10 counts per min. (that is, 30 counts per min. with background), but a reading as low as this required a counting period of about 10 min. It may confidently be stated, therefore, that the instrument is, with care, capable of measuring intensities within a practical range of at least 10^5 to 1, and that it is very sensitive to small intensities, so that it can be used to give measurable readings even with a very low-powered X-ray tube. This is not true, however, if the automatic recorder is used. Even at the maximum sensitivity, this instrument ceases to record at a minimum intensity which is certainly more than 100 times the minimum of the mechanical impulse counter. Its intensity range at any given sensitivity is no more than about 300 to 1, and since the linear part of its intensity versus deflexion scale at any sensitivity is quite small, the problem of interpreting the automatic records for accurate intensity measurement over even a limited range of intensities is a very difficult one. This is particularly true of 'integrated intensity' measurements, which involve the recording of both low and high intensities in the same curve. The non-linearity of the scale, the lack of response at low counting rates, and the asymmetry introduced by the 'time factor' combine to make evaluation of integrated intensities by measurement of areas under recorded curves almost meaningless except in a very qualitative way, even when the curves are traced out using the slowest possible motion of the crystal.

Even with the mechanical counter, however, various difficulties arise when accurate measurements of relative intensity are required over a wide range of different intensities. It is well known that the Geiger-Müller tube is not equally sensitive all over its cross-sectional area and that care must be taken to have the tube correctly orientated with the most active area properly placed behind the slit system admitting the reflected beam. Due to the smallness of this area a lack of rigidity in the apparatus, or any kind of strain on the heavy insulated leads, may have a detrimental effect on the recorded intensity, by introducing the possibility of slight displacements of the tube from its optimum position. Moreover, although the characteristic curves (number of counts per min. as a function of applied voltage) for any Geiger counter have a 'plateau' within which the counting rate is almost independent of applied voltage, it is not in fact quite independent, but increases slightly with increasing voltage (Friedman, 1945) at a rate which varies from one counting rate to another. The curve of counting rate versus X-ray intensity (the 'calibration curve' of the instrument used with a mechanical impulse counter) is therefore slightly dependent upon the applied voltage, even within the plateau region. Using the instrument as it stood, it was found that the power unit providing the high potential to the Geiger tube tended to warm up during a long run, with a consequent change of applied voltage. This, however, was not a serious difficulty. It was also found that the 'threshold voltage' varied with counting rate, but this did not affect plateau readings although it might be more serious if the proportional counting method were used. Much the most serious consideration is the fact that the linear part of the calibration curve is relatively small. In the various combinations of Geiger-Müller tubes, amplifying and scaling circuits, and mechanical impulse counters available during the course of this research, the scale was found to be linear only below a counting rate of 100 to 150 counts per sec., although many of the Bragg reflexions corresponded to rates very much higher than this. (Cf. Fig. 11 in Friedman's article, where there seems to be linearity up to about 300 counts per sec. Measurements in other laboratories have shown a linearity up to nearly 1000 counts per sec. It is evident that each equipment must have careful individual calibration before it can be used for intensity measurement.) Above a rate of 2000 to 3000 counts per sec. some mechanical impulse counters cease to resolve even on the scale of 64. That is to say, resolution was found to break down when the impulses to be recorded were separated by less than 0·03 to 0·02 sec. (Fig. 10 in Friedman's article gives about the same figure, though 0·01 is mentioned in the text.) This means that a reflexion of any greater magnitude has to be reduced by absorption in a filter or by a rotating wedge or some other means to an intensity at the Geiger tube corresponding to not more than 1000 counts per sec. and preferably to something under 100 counts per sec. (though not too low, or counting times become unduly high). The method actually used in the present research was to insert n metal foils (usually Ni, but Cu and Al were also tried) so as to reduce the intensity incident on the counter tube to e^{-nx} times its original value, where e^{-x} is the absorption of a single foil. The linearity of the calibration curve could be tested by plotting counting rate against n on semi-logarithmic graph paper and comparing the resulting curve with the straight line e^{-nx} versus n; or even more rigorously by plotting the ratio (counting rate for n foils)/(ditto for $(n-1)$ foils) against n. It was found that no difference could be detected in the results whether the foils were inserted between the X-ray tube and the crystal, or between the crystal and the Geiger tube. The equivalence of the various foils used was tested by measuring their respective absorptions for the same reflexion. Table 1 shows the results obtained for 12 Ni foils cut from the same sheet, each reading being repeated three times and the readings on the three foils numbered 1, 3 and 9 being made a second time. At the point marked with an asterisk there was an interval of 1 hr. in the measurements.

These readings illustrate clearly the statistical nature of this type of measurement, which may of course be due partly to variation of output of the X-ray tube (a variation usually evened out during the course of a photographic exposure), partly to inhomogeneity of the foils (which were used quite at random in the

subsequent experiments), but is mostly due to the mechanism of ionization within the Geiger tube. One consequence of this inevitable scatter of the readings is that if the standard method of measuring the impulses in a given period of time (usually 64 sec.) is adopted, the uncertainty of the readings rises sharply as the intensity falls. This is illustrated by Table 2, which shows five successive readings (in counts per sec.) made at each of three different intensities, the time of the reading being 30 sec. in each case, and the stray radiation (which has been subtracted) being 0·33 counts per sec. measured over a period of 6 min.

Table 1. *Statistical nature of intensity readings measured with Geiger counter spectrometer*

	1	2	3	4	5	6	7	8
I	384	379	392	383	381	360	382	363
II	394	369	397	375	373	370	374	367
III	388	383	384	365	366	357	358	368*
	9	10	11	12	1	3	9	
I	352	375	364	362	371	377	355	
II	353	382	358	364	370	368	364	
III	360	379	370	359	370	378	358	

The reflexion whose intensity was being measured after passage through one Ni foil was the (303) from oxalic acid dihydrate (original $P2_1/n$ description), using filtered Mo $K\alpha$ radiation and a krypton-filled counter, and the actual mean reading was 371 impulses per 64 sec. on a scale of 16, or about 93 counts per sec., after the reduction by absorption.

Table 2. *Relative accuracy of intensity readings made in a constant time period*

I	II	III
853	15·1	1·13
847	17·3	0·87
842	15·8	0·81
838	15·5	1·07
850	17·2	0·97
Mean 848 ± 10	16·2 ± 1·1	0·97 ± 0·16
Total scatter 2·3 %	13·6 %	33·0 %

The alternative method now used in some laboratories of measuring the time for a given number of counts is far more accurate, although much slower for low intensities.

Effect of harmonics in incident X-ray beam

Bragg reflexions. In measuring intensities of reflexion by Geiger counter methods involving the insertion of filters of known absorption, it must not be forgotten that, unless the incident beam is absolutely monochromatic, the reflected beam, even at the Bragg positions, will not be monochromatic either, and its *quality* may therefore be changed during the process of absorption. Even if the incident beam is monochromatized by crystal reflexion, it will almost always contain some $\lambda/2$ and $\lambda/3$ components, and this is certainly true for an incident beam which is not monochromatized at all. The $\lambda/2$ and $\lambda/3$ components will be reflected into the first order spectral position as second and third order spectra. The question then arises as to whether the presence of such harmonics, differentially absorbed, might explain, at least in part, the non-linearity of the intensity calibration scale for high counting rates.

Let S_1, S_2, S_3 ... be the geometrical structure factors of the first, second, third ... order reflexions from a crystal. The intensities of reflexion will be proportional to $I.S^2.f^2.\lambda^3.\phi(\theta)$, where I is the incident intensity, $\phi(\theta)$ depends only on the reflecting angle θ, and f is dependent on $(\sin\theta)/\lambda$; f_1, f_2, f_3 ... will decrease in the same way for the wave-lengths λ, $\lambda/2$, $\lambda/3$ ... reflected at the same angle θ, as for one wave-length λ reflected at the angles θ, $\sin^{-1}(2\sin\theta)$, $\sin^{-1}(3\sin\theta)$ .... We may therefore write for the relative intensities of λ, $\lambda/2$, $\lambda/3$ wave-lengths reflected at the angle θ

$$I_1 : I_2 : I_3 \ldots = S_1^2\,[f\,(\sin\theta)/\lambda]^2.\lambda^3 : x.S_2^2\,[f\,(2\sin\theta)/\lambda]^2 \times \lambda^3/8 : y.S_3^2\,[f\,(3\sin\theta)/\lambda]^2\,\lambda^3/27 \ldots,$$

where x, y are the proportionate amounts of $\lambda/2$, $\lambda/3$ radiation present in the incident beam relative to that of the characteristic wave-length λ.

For the 110 reflexion from urea, $(\sin\theta)/\lambda = 0{\cdot}124$ and

$$S_1^2 : S_2^2 : S_3^2 = 1 : 1{\cdot}6 : 3{\cdot}3 \text{ approximately,}$$

giving $I_1 : I_2 : I_3 = 100 : 7{\cdot}2x : 1{\cdot}4y$.

Now we know that the efficiency of an argon-filled Geiger tube for the detection of wave-lengths 1·54/2 and 1·54/3 A. is only a fraction of that for the wave-length 1·54 A., so that the intensity, *as recorded by the instrument*, will be reduced to

$$I' = I'_1 + I'_2 + I'_3;$$

where

$$I'_1 : I'_2 : I'_3 = 100E_1 : 7{\cdot}2.x.E_2 : 1{\cdot}4.y.E_3,$$

where E_1, E_2, E_3 are the proportions of X-ray photons recorded for wave-lengths 1·54, 0·77, 0·51 A. A reasonable estimate of E_1, E_2, E_3 would be 4 : 2 : 1 (which probably favours the short wave-lengths; see Fig. 6 of Friedman's article, where the ratio is much greater: no allowance is made in his curves, however, for relative absorptions in the Geiger tube window or the dead space).

Suppose that n successive thicknesses t of an absorbing metal foil are inserted in front of the Geiger tube slit (or between the crystal and the X-ray tube: the first method alters $I_1 : I_2 : I_3$, the second alters $1 : x : y$: and there is no practical difference in the result). The total recorded intensity will be

$$I_n = I'_1.e^{-\mu_1 nt} + I'_2.e^{-\mu_2 nt} + I'_3.e^{-\mu_3 nt},$$

where μ_1, μ_2, μ_3 are the linear absorption coefficients of the material of the foil for wave-lengths λ, $\lambda/2$, $\lambda/3$. For Al and $\lambda = 1{\cdot}54$ A., $\mu_1 = 131$, $\mu_2 = 18$, $\mu_3 = 6$ cm.$^{-1}$. For Ni and $\lambda = 1{\cdot}54$ A., $\mu_1 = 438$, $\mu_2 = 490$, $\mu_3 = 178$ cm.$^{-1}$. These therefore represent typically different cases.

We have to investigate the curves of I_n versus n for two cases:

$$I_n^{\mathrm{Al}} = 100.E_1.e^{-131n.t_{\mathrm{Al}}} + 7{\cdot}2.x.E_2.e^{-18n.t_{\mathrm{Al}}} + 1{\cdot}4.y.E_3.e^{-6n.t_{\mathrm{Al}}}$$

and

$$I_n^{\mathrm{Ni}} = 100.E_1.e^{-438n.t_{\mathrm{Ni}}} + 7{\cdot}2.x.E_2.e^{-490n.t_{\mathrm{Ni}}} + 1{\cdot}4.y.E_3.e^{-178n.t_{\mathrm{Ni}}}$$

and to compare them with the ideal linear graphs of $100E_1.e^{-\mu_1 n.t}$ versus n, and with the calibration curves actually observed for urea (110) using Al and Ni filters respectively (Figs. 1 and 2). In the experiments, $t_{\mathrm{Al}} = 0{\cdot}0030$ cm. and $t_{\mathrm{Ni}} = 0{\cdot}0023_5$ cm.

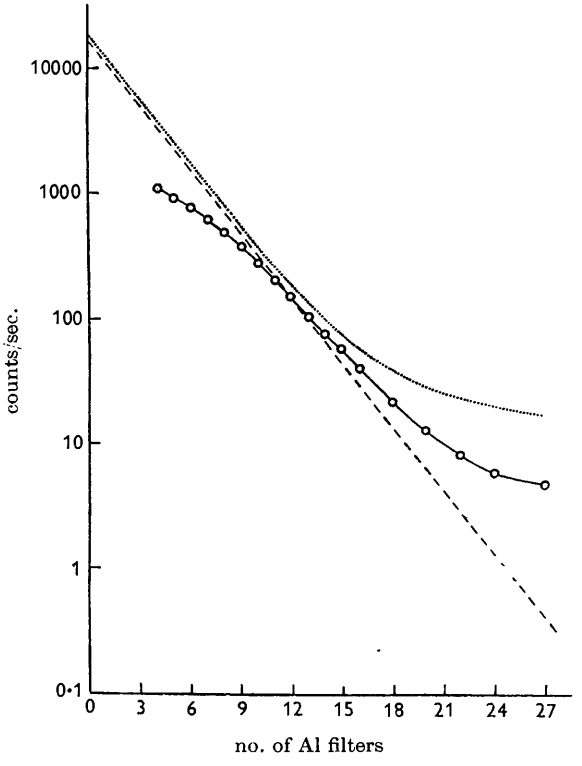

Fig. 1. Calibration of Geiger counter spectrometer. Cu $K\alpha$ radiation: absorption by Al filters. Full line: observed calibration curve. Dashed line: ideal linear relationship. Dotted line: theoretical effect of 0·4 % of $\lambda/2$ and $\lambda/3$ in reflected beam (one Ni filter was always left inserted to absorb Cu $K\beta$ radiation)

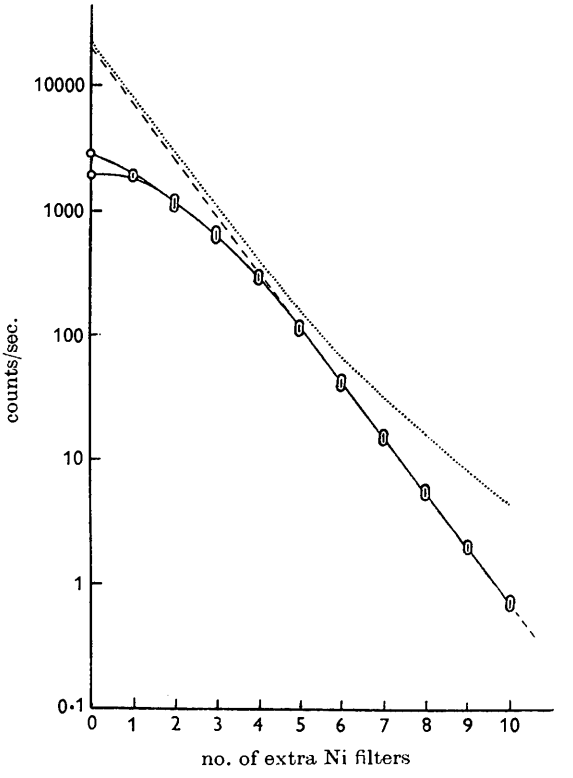

Fig. 2. Calibration of Geiger counter spectrometer. Cu $K\alpha$ radiation: absorption by Ni filters. Full line: observed calibration curves. Dashed line: ideal linear relationship. Dotted line: theoretical effect of 8 % of $\lambda/2$ and $\lambda/3$ in reflected beam (one Ni filter was always left inserted to absorb Cu $K\beta$ radiation)

It is clear from these figures:

(1) That even if the $\lambda/2$ and $\lambda/3$ harmonics were present in equal amounts and were detected with the same efficiency as the characteristic wave-length λ, this could not *reduce* the apparent intensity at high counting rates (n small) for any kind of absorber; that is, the effect of harmonics is to make the whole calibration curve straight or convex towards the origin, whereas the observed curves are concave at high counting rates and straight or convex at low counting rates.

(2) That for a Ni absorber the effect of white radiation is relatively negligible. Al absorbers show the effect more strongly and are therefore less suitable for calibration purposes.

(3) The observed curves correspond to a value of $I_1' : (I_2' + I_3')$ of the order of 100 : 0·1 (which actually may mean up to 5 % or more ($\lambda/2 + \lambda/3$) components in the *incident* beam, depending on the efficiency of the Geiger tube in their detection).

(4) The departure from linearity in the observed calibration curves, which in each case takes place at counting rates above 100 counts per sec., is therefore a property of the detecting mechanism and not of the incident beam and the particular method of obtaining the curves. In the case of the Ni absorber the limits of 'observed' counting rates shown in Fig. 2 correspond to readings obtained with two different sets of Geiger tube, amplifying valve, mechanical impulse counter and scaling circuit. For the lower reading with *no* extra Ni filter (Fig. 2) the new impulse counter was failing badly in resolution at high counting rates, so that the reading was in fact no greater than when the first extra filter was inserted.

Similar data for the Mo X-ray tube and krypton-filled Geiger tube showed the presence of a rather larger percentage of $\lambda/2$ radiation ($\lambda/3$ was not excited) in the incident and reflected beams, but otherwise shared the

same general features of the curves, including the departure from linearity at upwards of 100 counts per sec.

Diffuse scattering. The presence of $\lambda/2$ and $\lambda/3$ harmonics cannot affect the intensity readings of diffuse scattering at all, because the harmonics are reflected with measurable intensity only in the exact Bragg position of the crystal and are detected in the corresponding 2θ position of the Geiger tube. For measurements of diffuse scattering, either the crystal or the Geiger tube or both must be displaced from the Bragg positions, and the effect of the harmonics is then completely negligible. Of course the ordinary Laue reflexion of white radiation must be expected at any setting for which the Geiger tube angle is twice the crystal angle, but this constitutes no observational difficulty. There is considerably more difficulty in knowing what allowance to make for Compton scattering, which will be relatively important for substances such as urea or oxalic acid dihydrate, composed chiefly of the light elements C, O, N, H from which, on the other hand, fluorescent scattering is negligible. However, Compton scattering will provide an overall background intensity which increases as the scattering angle increases, and which is *not concentrated* in the neighbourhood of Bragg reflexions, as the thermal scattering is. It will be of importance only in the regions of very low thermal diffuse scattering, in which we are not now interested .

Crystal adjustment

One major difficulty encountered in the use of the Geiger counter equipment was that of setting the crystal with a zone axis vertical. Failing optical adjustment, the only method possible with the present equipment was to turn the crystal into a position such that the reflexions from pairs of equivalent planes (such as 310, 130 for urea) occurred within the graduated quadrant; and then to adjust the crystal on the arcs until the intensities of these reflexions (as observed on the frequency meter) were equal. But at best this was a 'hit-and-miss' method compared with the standard photographic methods. Yet it is essential to have good crystal adjustment in order that the reflexions in the zone under observation shall lie accurately in the horizontal plane in which the Geiger tube moves. Auxiliary photographic equipment which would allow a series of quick Laue or oscillation photographs to be taken either on a cylindrical or a plane film at known distances from the crystal would have been exceedingly helpful. Alternatively an extension of the span of the graduated quadrant to include a useful range of negative scattering angles would have made problems of crystal setting much less formidable. (Incidentally, a redesign of the equipment to provide angles 2θ greater than $90°$ would be essential for any serious structural analysis of crystals or for any kind of precision measurement of spacings, although that was not needed for my particular problem.)

In order to check the crystal setting, a Laue photograph was, in fact, taken on a film supported just in front of the Geiger tube slit. This also gave the actual cross-sectional area of the reflected beam and the shape of the diffuse reflexions associated with the Bragg reflexion. In the case of $hh0$ reflexions from urea the thermal reflexions were diffuse vertical streaks of approximately the same size and shape as the sharp Laue spots (elliptical $4{\cdot}9 \times \frac{1}{4}$ mm.).

Measurements on urea

Two methods of measuring the diffuse scattering were used:

(1) The crystal was kept stationary at or near the Bragg angle θ and the Geiger tube was moved through a series of positions on either side of 2θ, an intensity measurement being made in each such position. This is

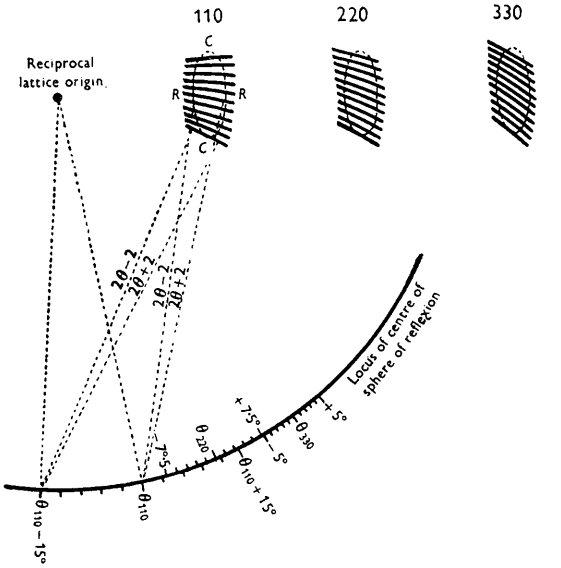

Fig. 3. $hk0$ reflexions from urea. Crystal stationary at various angles; counter moving (equivalent to successive positions of centre of sphere of reflexion, with variation of angle of diffraction on either side of 2θ). The curves show the sections of the sphere of reflexion in the neighbourhood of the 110, 220, 330 reciprocal lattice points

equivalent to a measurement of intensity radially across the diameter of a diffuse spot on the equator of a Laue photograph. A succession of such measurements (corresponding to a succession of Laue photographs) for different crystal positions θ, $\theta \pm \alpha$, $\theta \pm 2\alpha$, etc. will give the intensity over the [001] cross-section of the entire reciprocal lattice region of any $hk0$ reflexion. The curves traced out in reciprocal space for the 110, 220, 330 reflexions by this procedure are shown in Fig. 3.

(2) The Geiger tube was kept stationary at 2θ, $2\theta \pm \beta$, $2\theta \pm 2\beta$, etc. and the crystal was moved through a series of positions on either side of θ. This corresponded to the curves in reciprocal space shown in Fig. 4, and again the entire cross-section could be covered by such curves.

In order that the curves for 110, 220, 330 shall be comparable (though they cannot be made equivalent, since they correspond to different slopes of the surface of the sphere of reflexion) the crystal positions should be θ_{110}, $\theta_{110} \pm \alpha$, $\theta_{110} \pm 2\alpha$..., θ_{220}, $\theta_{220} \pm \alpha/2$, $\theta_{220} \pm \alpha$..., θ_{330}, $\theta_{330} \pm \alpha/3$, $\theta_{330} \pm 2\alpha/3$..., although the Geiger tube angle of mis-setting β need not vary from one order to another. The crystal position can be set accurately to 0·01° or even better, but on the present instrument it is not possible to set the Geiger tube with any accuracy at all; it is not even furnished with a vernier to give 0·1°. For good work with single crystals not only would this be necessary, but it would be very desirable to have a two-circle movement of the Geiger tube. Since there was no possible movement of the Geiger tube except in a horizontal plane during the present experiments, the Geiger tube slit was left with a large vertical aperture (5 mm.), so as to integrate over the [001] direction in reciprocal space for each diffuse spot. The divergence of the incident beam in a vertical direction also helped to integrate along [001].

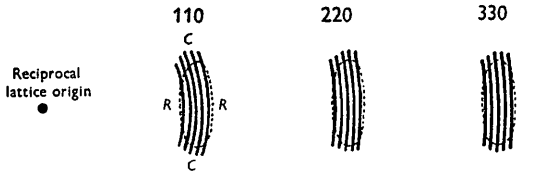

Fig. 4. Counter stationary at various angles; crystal moving (equivalent to rotation of the reciprocal lattice)

The measurements made showed that the (001) cross-section of the diffuse regions in reciprocal space was as shown in Figs. 3 and 4, a movement of $2\theta \pm 2°$ being amply sufficient to reduce the diffuse intensity (background subtracted) in the radial direction *RR* to an amount equal to the irreducible background, though in the directions *CC* movements of the crystals up to $\theta_{110} \pm 15°$, $\theta_{220} \pm 7{\cdot}5°$, $\theta_{330} \pm 5°$ were necessary in order to reduce the intensity to an equal amount. The *extent* of the diffuse regions in reciprocal space did not appear to change very much for the different spectra of the (110) plane.

In order to determine the ratio of diffuse to Bragg scattering it was necessary to reduce the Bragg intensity, by means of absorbing filters, for all three reflexions. The measured peak intensities in counts per sec. were:

Cu $K\alpha$ (argon-filled Geiger tube)	20300 : 4900 : 1770
Mo $K\alpha$ (krypton-filled Geiger tube)	4840 : 1030 : 470

The 110 intensity, using Cu $K\alpha$ radiation and a krypton-filled counter, was of the order of one-third of that using argon. Both sets of readings showed that considerable extinction was present. Measurements on another urea crystal, using Cu $K\alpha$ radiation, gave 15270 : 3000 : 1125. Now Wyckoff (1932), measuring the ratio 110 : 220 on a powder, with Ni *K* radiation, found the value 17·8 : 1, which would correspond to 85500 : [4900] for Cu radiation, or 16500 : [1030] for Mo radiation (taking the second order as standard in each case). The observed 110 intensity is only about one-quarter of the 'mosaic' value. It may be mentioned in passing, that from the usual formula $\rho \sim I_0 . S^2 . f^2 . \lambda^3 . \phi(\theta)$ we would expect the intensities 20300 : 4900 : 1770 for Cu radiation to correspond to 5570 : 1176 : 497 for Mo radiation, so that the observed efficiency of the Mo + krypton combination was approximately equal to that of the Cu + argon. This result is quite surprisingly good, in view of the fact that the X-ray unit was in each case a small air-cooled one, with the X-ray tube passing only 6 mA. at about 35 kV.

Attempts to increase the intensity of the 110 reflexion by sudden immersion of the crystals in liquid air were quite unsuccessful. The urea crystals remained clear, even after repeated immersion, and the 110 : 220 : 330 intensities were almost unchanged, even by this drastic treatment, being 18220 : 4240 : 1660 counts per sec. as compared with 20300 : 4900 : 1770 before immersion. This was an unexpected result, indicating a relatively high heat capacity and thermal conductivity of the urea crystals. Experiments on oxalic acid dihydrate (to be described later) did, however, show that for this substance the extinction in the Bragg scattering could be markedly reduced by liquid-air treatment, but that *the absolute value of the diffuse scattering remained unchanged.* This is to be expected; in the diffuse scattering there are no sharp phase relationships as there are for Bragg reflexion, and perfection or imperfection of the crystal cannot bring about a change in these relationships and in the resulting intensity of the scattered radiation. Clearly, however, the data on Bragg reflexion intensities from a highly perfect crystal showing large extinction cannot be expected to bear any significant relationship to the diffuse scattering, and in order to examine the variation of the diffuse : Bragg intensity ratio with order of spectrum or with wave-length, the Bragg intensities to be considered must be those from a completely *mosaic* crystal.

The investigations on urea are partially summarized in Fig. 5, which shows the change of the ratio diffuse : Bragg intensity (the latter corrected for extinction) with order of reflexion and with change of wave-length, for the case in which the Geiger tube is kept at 2θ and the crystal position varied from $\theta_{110} + 15°$ to $\theta_{110} - 15°$, $\theta_{220} + 7{\cdot}5°$ to $-7{\cdot}5°$, $\theta_{330} + 5°$ to $-5°$. As mentioned before, the curves along which the diffuse intensity was measured are not quite equivalent in the six cases (three orders for Cu $K\alpha$, and three for Mo $K\alpha$), but for positions not too far from the reciprocal lattice points, individual readings at $\theta_{110} \pm \alpha$, $\theta_{220} \pm \alpha/2$; $\theta_{330} \pm \alpha/3$ do correspond to approximately the same groups of thermal waves. Since the (110) spacing is 4·02 A., the angles of mis-setting 15° for 110, 7·5° for 220, 5° for 330 all correspond to transverse thermal waves having a mean wave-length of approximately 12 A. (the shortest for which any certain thermal

scattering could be observed), while the angles 1°, 0·5° and 0·33° respectively for the three orders correspond to waves of length about 180 A. The extent of the actual Bragg reflexion (governed by the size of crystal and of the incident beam) made it impracticable to investigate the effect of waves whose length was much greater than 360 A. for transverse waves travelling along [1$\bar{1}$0], or 720 A. for longitudinal waves along [110]. Generally

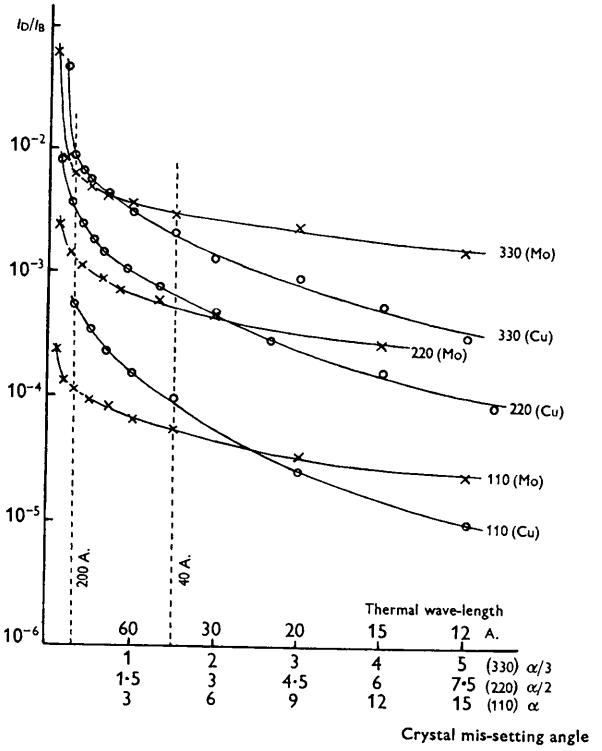

Fig. 5. I_D/I_B (I_B corrected for extinction) versus thermal wave-length in A., for transverse waves along [1$\bar{1}$0], approximately (Geiger tube stationary at $2\theta_{hh0}$). Circles for Cu $K\alpha$ radiation (argon-filled tube); crosses for Mo $K\alpha$ (krypton-filled tube)

speaking, it was found that for the group of waves approximately along [1$\bar{1}$0] having wave-lengths between 200 and 40 A. the ratio I_D/I_B varied as

$$1 : 6 : 18{\cdot}5 \; [1 : 2^{2{\cdot}61} : 3^{2{\cdot}65}]$$

for Cu $K\alpha$ radiation and as

$$1 : 11 : 54 \; [1 : 2^{3{\cdot}46} : 3^{3{\cdot}63}]$$

for Mo $K\alpha$ radiation. This result indicates the same kind of dependence upon order as was observed by Laval (1939) for the 002, 004, 006 reflexions of KCl using Mo radiation. Laval found intensities of diffuse scattering which had the same absolute value for equivalent thermal waves (Lonsdale, 1942–3); his ratios of I_D/I_B were therefore the reciprocals of the Bragg intensities for Mo $K\alpha$ radiation and KCl; that is 1 : 4·6 : 18·8.

The large increase for high orders is not surprising, for the amplitude of thermal vibration is quite large relative to the distance between successive planes of atoms. The ratio of thermal to Bragg scattering and its variation with scattering angle must certainly depend on the absolute value of the thermal wave amplitudes. For very small amplitudes the ratio will be small for all orders of reflexion and will increase fairly slowly with increasing order; the larger the amplitude, the greater is the relative importance of thermal scattering in the higher orders.

The absolute values of the ratios in the case of urea are given in Table 3 for a few mean wave-lengths.

Table 3. *Diffuse to Bragg scattering ratios for some thermal waves in urea*

X-rays	Thermal wave-length	$hh0$	I_D/I_B
Cu $K\alpha$	200 A. along [1$\bar{1}$0] (transverse)	110	$0{\cdot}557.10^{-3}$
		220	$3{\cdot}30.10^{-3}$
		330	$9{\cdot}12.10^{-3}$
	40 A. along [1$\bar{1}$0] (transverse)	110	$0{\cdot}095.10^{-3}$
		220	$0{\cdot}65.10^{-3}$
		330	$2{\cdot}00.10^{-3}$
Mo $K\alpha$	200 A. along [1$\bar{1}$0] (transverse)	110	$0{\cdot}114.10^{-3}$
		220	$1{\cdot}40.10^{-3}$
		330	$6{\cdot}48.10^{-3}$
	40 A. along [1$\bar{1}$0] (transverse)	110	$0{\cdot}056.10^{-3}$
		220	$0{\cdot}55.10^{-3}$
		330	$3{\cdot}0.10^{-3}$

[These values are a mean of the $\pm\alpha$ values, which could differ by as much as 25%, depending on the exactness with which the 'centre' of the Bragg reflexion had been located; it was found that this mean value remained constant for different series of observations even when the latter varied among themselves.]

The fact that the diffuse scattering corresponding to long transverse thermal waves along [1$\bar{1}$0] was almost 0·01 of the Bragg scattering peak intensity for Cu $K\alpha$ radiation shows that the thermal vibrations of this type had really large amplitudes normal to the (110) planes (in which the molecules lie). It would be very desirable to carry out more extensive measurements both on this and on simpler compounds, using apparatus in which the conditions of the experiment (divergence of primary beam, size and position of crystal, position of Geiger tube and size and shape of the associated slit system) could be more readily controlled.

Measurements on oxalic acid dihydrate

Experiments on oxalic acid dihydrate, using Mo $K\alpha$ radiation, were carried out partly because it was known that liquid-air treatment *would* alter the texture of these crystals (Lonsdale, 1947), partly because a previous photographic survey (Lonsdale & Owston, unpublished) had shown the existence of very strong diffuse scattering for a large number of planes, and partly because an extended structural analysis had already been carried out for this substance (Robertson

& Woodward, 1936; Brill, Hermann & Peters, 1942–3; Dunitz & Robertson, 1947).

The diffuse reflexions in this case are not elliptical, as with urea, but show streaks going off at various angles, and a long narrow Geiger tube slit was therefore particularly unsuitable for their observation. Nevertheless, the results are of interest from a qualitative point of view.

Suitable prismatic crystals, about $3 \times \frac{1}{2} \times \frac{1}{2}$ mm., were mounted with their long (b) axis vertical. It was not difficult, by setting the Geiger tube at the correct 2θ angles, to identify the (101) and (10$\bar{2}$) planes (using the original $P\,2_1/n$ description), and attention was then fixed on the various orders of the 101 reflexion. Values of F have been given by Robertson & Woodward for the first five orders, and these could be used to determine the relative intensities for Mo $K\alpha$ radiation; Brill, Hermann & Peters have given actual intensities, using Mo $K\alpha$ radiation, for the first eight orders (corrected for extinction in the first two orders). These values showed that considerable extinction was present in the crystals used in my experiments, and that it might be possible to produce a large change in texture by immersion in liquid air. Table 4 shows the actual observed values of the Bragg and diffuse scattering (in counts per sec.) when the Geiger tube (slit $5 \times \frac{1}{4}$ mm.) was set at $2\theta_B$ and the crystal was set successively at θ_B, $\theta_B \pm 0{\cdot}2°$, $\theta_B \pm 0{\cdot}3°$, $\theta_B \pm 0{\cdot}5°$ for the strongest reflexions, 101, 202 and 404. Column (a) gives the results for crystal I *before* dipping in liquid air, column (b) the results for the same crystal *after* dipping in liquid air, column (c) the results for another crystal II *after* dipping in liquid air.

It is clear that the increase in the Bragg reflexion (decrease in extinction) observed after the liquid-air treatment, has not been accompanied by any corresponding increase in diffuse scattering, which remains approximately constant, difficulties of resetting being taken into account.

The liquid-air treatment caused a certain spreading of the Bragg reflexions, especially for high orders, so that the peak value found with a $\frac{1}{4} \times 5$ mm. slit no longer represented a good approximation to the integrated intensity, as it had previously done. An attempt to improve the mosaic condition of crystal I still further unfortunately resulted in a complete breakdown of the specimen, and all further data were obtained from crystal II.

Table 5 shows a comparison of actual measurements (in counts per sec.) on crystal I (before treatment) and crystal II (after treatment), each taken with a 1×5 mm. slit in front of the Geiger tube, for all the eight observable orders of reflexion.

The first, second, fourth and fifth orders had to be reduced by Ni foil in order to bring them within the linear region below 100 counts per sec., but in fact a complete calibration curve was drawn for each reflexion, using several foils, so that the values given are really the mean of a number of readings. The data given in the column headed B. H. & P. are the values in Table 1 of Brill, Hermann & Peters' paper, multiplied by 40 to bring the value of the 505 intensity approximately to that of the Geiger counter measurements, while Robertson & Woodward's data, given in the column headed R. & W., have been adjusted to be comparable with the other three. It is interesting to note that the intensity observed by Robertson & Woodward for the 505 reflexion, which is clearly too low, was in fact at the limit of visual observation on their photographs (using Cu $K\alpha$ radiation) and was therefore subject to considerable error of estimation. Similarly, Brill, Hermann & Peters, who used an ionization spectrometer, were not able to detect reflexions less than 4·0 units on the scale of Table 5. The

Table 4. *Bragg and diffuse scattering for two* $(COOH)_2 2H_2O$ *crystals*: I (a) *before*, I (b), II (c) *after liquid air treatment*

	101			202			404		
	I		II	I		II	I		II
	(a)	(b)	(c)	(a)	(b)	(c)	(a)	(b)	(c)
θ_B	1632	2247	2752	1615	2172	2463	318	292	324
$\theta_B \pm 0{\cdot}2°$	2·27	1·96	2·17	7·47	6·86	8·00	3·99	3·78	4·52
$\theta_B \pm 0{\cdot}3°$	1·68	1·60	1·74	6·46	5·22	6·13	3·18	2·87	3·39
$\theta_B \pm 0{\cdot}5°$	1·46	1·31	1·35	5·25	4·11	4·93	2·59	2·41	2·67

Table 5. *Comparison of Bragg intensity data for* $(COOH)_2 2H_2O$ (Mo $K\alpha$)

	R. & W. (photography)	B. H. & P. (ionization chamber)	I (before) (Geiger counter and scaling circuit)	II (after) (Geiger counter and scaling circuit)
101	5010	4660	1681	3772
202	6660	6800	2044	5535
303	36·8	50	60·3	61·8
404	750	750	641	858
505	39·6	118·8	120·8	117·8
606	—	< 4·0	8·7	9·0
707	—	5·6	4·5	4·5
808	—	4·0	5·6	2·5

Geiger counter spectrometer (when working satisfactorily) could improve on this by a factor of 20 or more, for its limit of observation was less than 0·2 counts per sec. above the stray radiation.

It will be noted that the drastic liquid-air treatment given did not completely remove all extinction. True mosaic values can be obtained only by the use of a very finely divided powder. Apparently there had also been some extinction present in the relatively strong 404 reflexion, the intensity of which was increased by liquid air immersion, though not to the same extent as that of 101 or 202. The differences in the 808 reflexions are not regarded as significant, because at the time of making these readings the scaling circuit was beginning to give trouble. This took the form of a partial breakdown in the working of the scale of 2^n, which did not affect relatively large readings, but which did affect measurements of low intensity as shown in Table 6. These

Table 6. *Breakdown of the scale of* 2^n

Scale of	2	4	8	16	32	64
(*a*)	30	33	22	11	6	3
(*b*)	304	170	90	46	23	11
(*c*)	1668	947	461	236	120	60

readings were made over a time period of 6 to 8 min. for each of the low counts in row (*a*). Previous measurements of this intensity (the stray radiation in the laboratory) indicated that *all* the readings (*a*) were too high, the correct value being about 20×2, not 30×2 and certainly not 3×64. This kind of defect, obvious as it may seem on paper, was not at all easy to detect in practice, and could be guarded against only by the repetition of a known standard intensity value, *on all the scales*, from time to time.

Conclusion

The general conclusion arrived at in respect of the equipment was that the Geiger counter spectrometer was, in principle, admirably suited to the measurement of diffuse and Bragg intensities for single crystals, but that for accurate determination over a wide range of intensities, a mechanical impulse counter must be used and not an automatic recorder. The present commercial instrument, though excellent for many technical and research problems, does not give reliable measurements of intensity without the exercise of considerable precautions, and would not be suitable for single-crystal observations without a good deal of modification. Probably the ideal arrangement would be a combination of photographic and Geiger counter methods incorporated in the same instrument. With such apparatus there are many interesting and important problems in structure analysis and in crystal dynamics that could be tackled.

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