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A Single-Crystal Automatic Diffractometer. II

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This paper describes the design and construction of the electronic recording and detecting circuits used in the single-crystal automatic X-ray diffractometer described by Bond. Test experiments are discussed which show the operation of the instrument, using NaCl as the diffraction sample.

1. Introduction

The principal objective of the counter and associated circuits used in this apparatus is that of giving a true integrated intensity of a given diffraction line from a single crystal. This involves a number of difficulties, the primary one being that the counter must be sensitive and linear over a very wide range of counting rates. It is believed that an instrument of the type described here would be generally useful for crystal analysis if intensities which varied by a factor of 100 could be faithfully recorded. A convenient lower limit for the intensity was found to be about 100 counts per second (c.p.s.). This limit is determined by such things as the crystal rotation speed, the time required to shift gears and practical circuit time constants. In order to achieve the measurement of the 100:1 ratio in intensity, it is necessary that the counter* be able to count at an average rate as high as 10^4 c.p.s. and that the output of the X-ray source be sufficiently high when monochromatized with a crystal† to give nearly this counting rate for the highest intensity reflection. With this objective in mind, it becomes clear that stringent requirements are also placed on the resolution of the recording circuits and on the speed of the recording pen itself.

The following sections describe the circuitry used in the apparatus and the tests carried out on the original model to determine the reliability and accuracy of the instrument. A later section gives a discussion of some corrections which must be made on the recorded intensities. A crystal of NaCl was used as a test specimen to compare the measured and calculated intensities in order to show the operating characteristics of the apparatus.

2. Description of circuits

The circuits are designed to perform three main functions: (*a*) the shifting of the crystal speed at the proper time to allow recording of the diffraction-line intensity; (*b*) the recording of the integral of a given reflection on a logarithmic scale; and (*c*) the calibration of the instrument in a simple and fast way.

The general operation of the circuits is illustrated in Fig. 1. The clutch-shifting circuit, which consists of

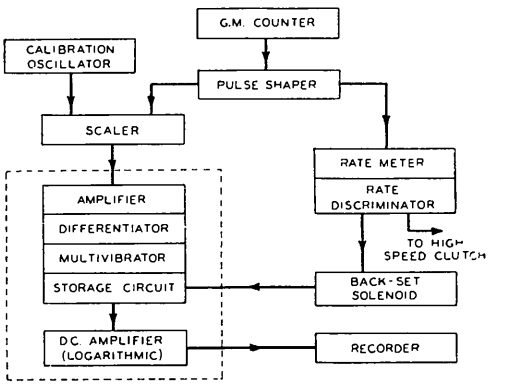


Fig. 1. Block diagram of circuits.

the rate meter and discriminator, controls the speed of the crystal through the high-speed clutch 2* and also energizes the back-set solenoid 18. The integrating and recording circuits shown in the dashed lines of Fig. 1 serve to standardize and store the pulses in order to produce a d.c. voltage which may be recorded. The storage circuit is also connected to a microswitch 39 on the back-set solenoid so that pulses may be stored only when the crystal is passing through a reflection.

We shall consider first the clutch-shifting circuit. Negative pulses are fed from a multiple chamber G.M. counter, the dead time of which is about 10 μsec., to a preamplifier and shaping circuit 20 which shapes them into negative square pulses† a few volts high and about 4 μsec. wide. These pulses are then fed into the ratemeter (Fig. 2(*a*)) whose output is a d.c. voltage approximately proportional to the counting rate. This

* The G. M. counter used on the original apparatus was the General Electric 1 SPG argon-filled counter.

† It is necessary to use a crystal monochromator to eliminate the white radiation, which is particularly troublesome with Mo $K\alpha$ radiation, and also to increase the diffraction angle range through which the counter can swing by about 20°.

* Component numbers refer to Fig. 2 of the companion paper by Bond (1955).

† Negative instead of positive pulses are used to avoid the high currents in the thyratron which would occur if the bias were allowed to go positive to a high value determined by the maximum counting rate.

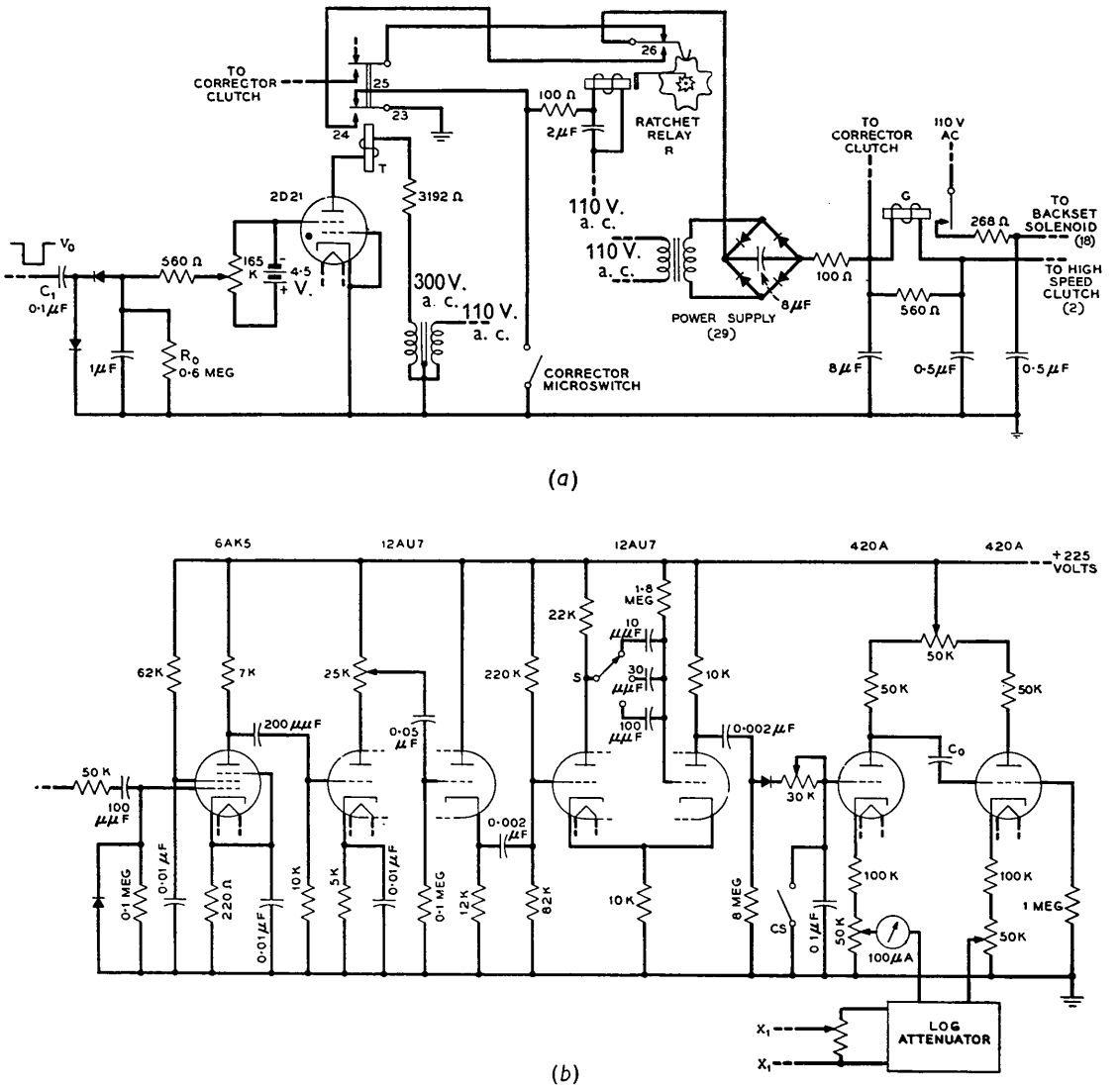


Fig. 2. (*a*) Rate meter and discriminator. The side of the line voltage not shown is grounded. The contact numbers shown are the same as those shown in Fig. 2 of the companion paper by W. L. Bond. (*b*) Integrating and recording circuits.

d.c. voltage in series with the voltage furnished by the battery determines the bias of the a.c.-operated thyratron. When the counting rate reaches a value of about 80 c.p.s., the voltage across R_0 reaches $V \simeq nC_1V_0R_0 \simeq 5$ V. and the thyratron is cut off, opening the relay (T) in the plate circuit. Alternating current is used in the plate circuit in order to make the bias level the same for both firing and extinction. This relay then actuates the ratchet relay R, which energizes the back-set solenoid 18, which turns the crystal back approximately 2°. The counting rate thus drops below the 80 c.p.s. threshold. At the time of the back-set the crystal speed is changed by de-energizing the high-speed clutch 2. As the crystal approaches the proper angle for reflection the second time, the thyratron is again extinguished but the ratchet relay R merely recocks, without shifting the speed, in preparation for the next time the counting rate falls below 80 c.p.s., i.e. when the crystal passes through the proper position for reflection. It should be noted that the integration time of the rate-meter must be long compared to the time between pulses and also to the 60 cycle period of the thyratron.

In the above circuit the integration time was taken as 1 sec., which is found to be sufficiently long to smooth out the statistical fluctuations in the counts coming from the G.M. counter. This long time constant is necessary to avoid any chattering in the plate circuit relay T, which would cause the sequence of operation to get out of phase. One of the difficulties encountered in this part of the circuit is that at the start or end of each form it is possible for a reflection to fall near the edge of the counter window and show an intensity near the threshold. In this case the

sequence could get out of phase. This kind of failure will be considered later.

The recording circuits (Fig. 2(*b*)) are designed to display the integrated intensity of the diffraction line. A signal is taken from a binary scaler at the seventh stage, i.e. after the input pulse has been scaled by a factor of 64. By using every '64th count' in the recording, advantage is taken of the smoothing action of the scaler. This signal, whose rise time is of the order of 0·1 μsec., is fed into the 6AK5 amplifier (Fig. 2(*a*)) and differentiated by the *RC* network whose time constant is about 2 μsec. This pulse is then fed through an amplifier (inverter) and cathode follower and is then used to trigger the multivibrator. The multivibrator then produces an essentially square pulse which is practically independent of the size of the step pulse coming from the scaler. These pulses are then fed through a diode whose back resistance is about 10^{11} ohms to a good quality 0·1 μf. condenser (resistance $\simeq 10^{11}$ ohms). The condenser will then store the charge without appreciable loss for about 5 or 10 min. The voltage across the condenser serves as the grid bias for the W.E. 420 A. The recorder is placed between the cathodes of the two balanced 420 A's. In order to give the recorder a logarithmic response, a commercial logarithmic attenuator was placed between the recorder driver circuit and the recorder. The condenser short switch (CS) is a microswitch connected to the back-set solenoid. The condenser C_0 is used to prevent the pulse that occurs at the time the condenser is shorted from being recorded. The operation of the circuit is then as follows: at the time of back-set the condenser is unshorted and every 64th pulse from the G.M. counter triggers a standard pulse which places a charge on the condenser; the recorder starts recording the integration and continues to do so until the condenser is shorted again by the deactivation of the back-set solenoid. The selector switch S serves to change the length of the pulse (10, 30, 100 μsec.) coming out of the multivibrator. This allows one to pick the proper length pulse for a given crystal depending upon the peak intensity and breadth of the line. The calibration of the recorder may be changed by adjusting the two 50,000 ohm potentiometers which are ganged together to maintain the balance.

The pen speed of the recorder is an important consideration when choosing the scale factor for the instrument. The initial pulse which is fed to the recorder after the storage condenser has been unshorted causes a deflection of about 1 mm. in normal operation. The maximum velocity of the pen is given by $0{\cdot}1 \times N/S$, where N is the maximum counting rate and S the scale factor. Assuming $N = 10{,}000$ c.p.s. and the maximum pen velocity of 20 cm.sec.$^{-1}$, the scale factor must be greater than 50 to avoid appreciable pen lag. For this reason a scale factor of 64 was chosen to assure reliable recordings. Since the integral is recorded on a logarithmic scale, the deflection per 64 counts decreases as the recorder reading increases. The pen therefore moves quite slowly at the end of the integration.

A further advantage of scaling the pulses initially is that it gives the instrument a wide range of usable output pulse length for the multivibrator without making an appreciable error in the integrated intensity of the reflection.

By choosing the scale factor of 64 an error is introduced because as many as 63 counts may be stored in the scaling stages at the end of the integration. These counts will not be recorded. For the minimum intensity line which may be recorded (1000 counts), this error will therefore be less than 6·3%.

The thyratron oscillator in Fig. 3 serves as a calibration oscillator. The signal (~ 3 μsec. long) is fed into the first stage of the scaler and every 64th pulse is taken off the scaler and proceeds by the path described above for the actual pulses. The repetition rate of the thyratron oscillator can be varied from 100 p.p.s. to 5000 p.p.s. by changing the condensers shown and the 1 megohm potentiometer in the plate circuit. The scaler itself (whose total scale factor is 2^{14}) is then used to determine the actual repetition rate being used during the calibration.

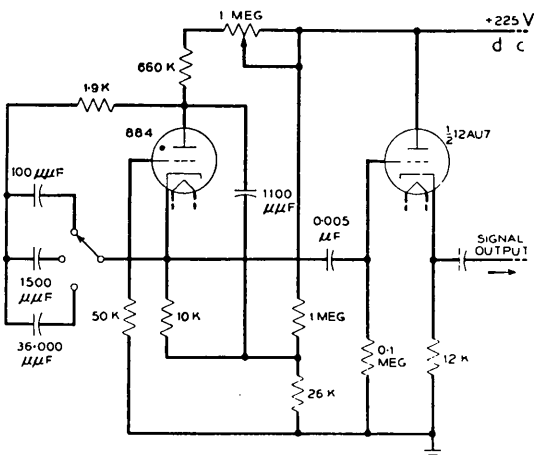
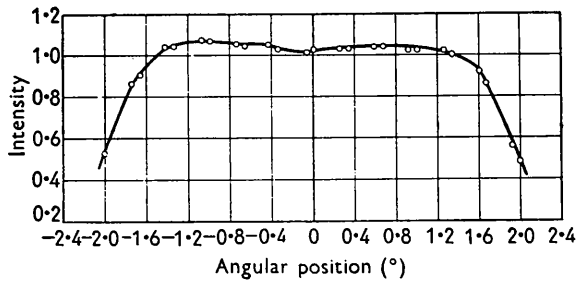


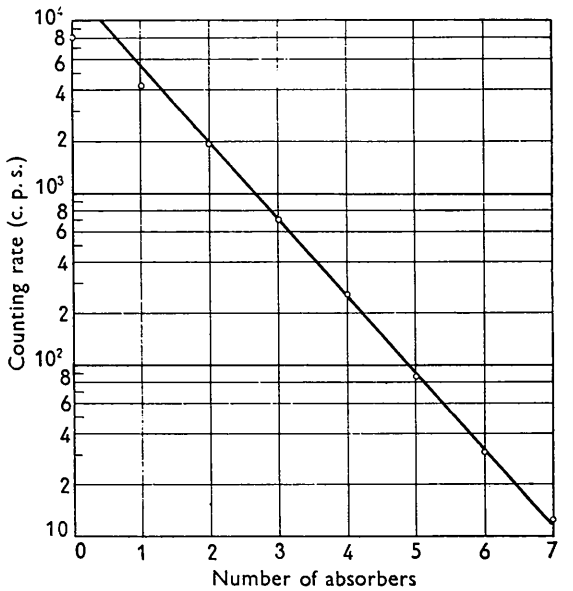
Fig. 3. Calibration oscillator.

Because faulty operation of a relay or big surges in the line voltage can cause failures, it was necessary to use a time delay relay (corrector)* which is activated when the slow-speed clutch is in operation and there is only a small signal (< 80 c.p.s.) coming from the G.M. tube. This relay is connected to the alternating relay and the relay in the plate circuit of the thyratron. Since the delay relay is actuated after the back-set has taken place, it is necessary to make the delay time longer than the back-set time. When the delay relay fires, the system is pushed up one notch in the sequence and is back in phase with a loss of time of only about 1 min.

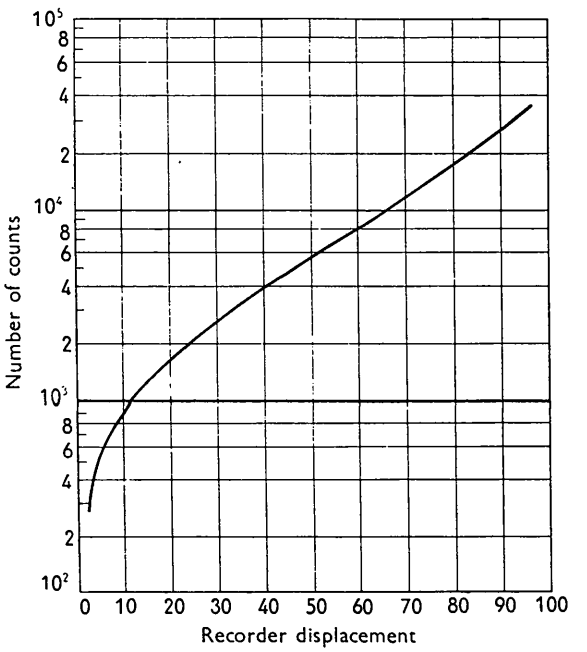
* The time delay relay consists of a motor-driven magnetic clutch to which is fastened a lever. The lever rotates when the clutch is operating until it closes the microswitch (Fig. 2(*a*)).



(*a*)



(*b*)



(*c*)

Fig. 4.

3. Test experiments

A number of experiments were performed to check the linearity, reproducibility, calibration, etc. One important requirement of the G.M. counter is that it must give the same response to a given reflection at all points within the area of the window (approximately 1 cm. × 1 cm.). In order to determine this response, a recording of the (23.0) reflections of quartz was taken. Since the overlap was designed to be 100%, this line will give about 24 lines on the recording or, in effect, will cut the counter window into 24 segments. Fig. 4(*a*) shows a plot of counter response versus position on the window of the reflection. Twenty-five reflections appear within the 4° angle subtended by the counter window. The intensities of the first and last reflections are about one-half of the intensity of one of the lines which falls entirely within the window. We therefore have an experimental check of the design conditions set forth in the previous paper (Bond, 1955).* The counter was moved left and right about the center of a reflection. It was found that the response of the counter at all positions is uniform to a few per cent.

The linearity of the counter was checked by inserting a number of absorbers in front of the counter window and obtaining the absorption curve shown in Fig. 4(*b*). It is seen that the counter is linear to about 2000 c.p.s. The linearity of the recording circuits was checked by recording a fixed number of counts (as determined by the scaler) at various counting rates (as determined by the number of foils inserted in front of the G.M. counter window). The displacements of the pen over a range of about 3 logarithmic cycles varied by only about 5% owing to the speed of response of the recorder, missed counts, etc. The recorder was also checked using the calibrating oscillator from 100 p.p.s. to 5000 p.p.s. and was found to agree with the absorption experiment.

The dead time of the G.M. counter is about 10 μsec., as measured on a Tektronix oscilloscope; this means that the counter should be linear to 10% to counting rates of the order of 10,000 c.p.s. The non-linearities shown in Fig. 4(*b*) occur because the power supply of the X-ray machine is full-wave rectified but unfiltered; therefore the X-rays are on for only a fraction of each

* The apparent variation observed near the center of the window on Fig. 4(*a*) is due to irregularities in the shape of the sample crystal. If the lines are taken in some other sequence, the dip in the curve would appear at a different position on the window.

Fig. 4. (*a*) Plot of counter response versus angular position of G. M. counter measured relative to the position where the center of the counter window is set at the Bragg angle. The quartz crystal is set for Bragg reflection from the 23.0 plane. (Cu $K\alpha$ radiation).

(*b*) Absorption curve showing the response of the G. M. counter as a function of number of absorbers.

(*c*) Calibration curve (integrated counts versus recorder deflection).

cycle. The counter is counting at an average rate which is below the instantaneous rate at the peak of the a.c. cycle (Arndt, 1949). The effective dead time is therefore much longer than the 10 μsec. dead time which it would have for a steady (filtered) X-ray beam. The effective dead time may be minimized by operating the X-ray tube at high voltage (50 kV.p. for Cu). The duty cycle is thus increased for a given power and the amount of 'pile up' taking place in the counter is decreased. In going from 25 kV.p. to 50 kV.p. with Cu radiation, the effective dead time of the counter is decreased by a factor of 3. Steps are being taken now to eliminate this error by means of a proportional counter with a dead time of less than 1 μsec.

The calibration curve shown in Fig. 4(*c*) was obtained with the oscillator run at 100 p.p.s. With this curve it is possible to make a calibration ruler which one can use to read the integrated intensities of the reflections directly from the recording. The calibration curve is not truly logarithmic because of the method of storing charge on the condenser and the shape of the characteristic curves of the 420 A vacuum tubes.

4. Corrections to line intensities

Back-set correction (lost counts at end of reflection)

It is clear that a correction must be made for the finite value (80 c.p.s.) of the back-set counting rate; this correction is made in the following way:

Assume that the diffraction line has a shape given by

$$n(t) = \frac{A}{1+a^2t^2} . \tag{1}$$

The counting rate at the back-set position is

$$n_0 = \frac{A}{1+a^2t_0^2} , \tag{2}$$

where t_0 is the half width of the reflection at the intensity n_0. The number of counts lost owing to the finite counting rate n_0 required to back-set the crystal is then

$$I_{\text{lost}} = \int_{t_0}^{\infty} \frac{A}{1+a^2t^2}\,dt = \frac{A}{a}\left[\frac{\pi}{2} - \tan^{-1}at_0\right] , \tag{3}$$

but, for $at_0 > 1$, we have on expanding

$$I_{\text{lost}} \simeq A/a^2t_0 \tag{4}$$

and, substituting for A from (2),

$$I_{\text{lost}} \simeq n_0t_0[1+1/a^2t_0^2] \tag{5}$$

or

$$I_{\text{lost}} \simeq n_0t_0 . \tag{6}$$

In practice the full width at half maximum of the recorded integral curve is used as an approximation to t_0 in equation (6).

Dead time correction

The dead time correction may be obtained in the following way:

Let $n_m(t)$ be the measured counting rate, $n_a(t)$ the true counting rate, and τ the dead time of the counter. Then, by the usual formula,

$$n_a \simeq n_m(1+n_m\tau) . \tag{7}$$

Assume that

$$n_m = \frac{A}{1+a^2t^2} . \tag{8}$$

Then we have

$$n_a = \frac{A}{1+a^2t^2} + \frac{A^2\tau}{(1+a^2t^2)^2} \tag{9}$$

and

$$I_a = \int n_a dt = I_m + \int_{-\infty}^{\infty} \frac{A^2\tau}{(1+a^2t^2)^2}\,dt , \tag{10}$$

where

$$I_m = \pi A/a \text{ is the measured integrated intensity.} \tag{11}$$

Then

$$I_a - I_m = \Delta I = \frac{A^2\tau}{a}\int_{-\infty}^{\infty} \frac{dx}{(1+x^2)} = \frac{\pi A^2\tau}{2a} . \tag{12}$$

Since the power supply for the X-ray generator is unfiltered, a $\tau_{\text{eff.}}$ deduced from Fig. 4(*a*) must be substituted for τ in the above equation. Therefore

$$\Delta I/I = \tfrac{1}{2}A\tau_{\text{eff.}} . \tag{13}$$

If it is assumed that the integrated intensity of a given line is approximately proportional to the peak intensity, then

$$I = \beta A .$$

It is necessary to read one maximum counting rate while the pattern is being taken to calculate the proportionality constant β. It should be pointed out that β varies from 10 to 16 for the zero layer of NaCl, which does not, however, introduce an appreciable error in the dead-time correction.

$$\frac{I_{\text{lost}}}{I_{\text{total}}} = \frac{I_{\text{int.}}}{\beta}\frac{\tau_{\text{eff.}}}{2} .$$

A typical value of β is about 10 and from formula (7) and Fig. 4(*a*) we obtain $\tau_{\text{eff.}} \simeq 50$ μsec.

For an integrated intensity of 50,000 counts we have

$$\Delta I/I \simeq 12\% .$$

The first three layers of NaCl were recorded using the diffractometer and were compared with the calculated intensities. It was found that the intense lines showed a lower intensity than expected. This could indicate one of two things: (1) the counter dead-time correction was too small, or (2) the secondary extinction was responsible for the discrepancy. A second analysis of the zero layer was made using Co $K\alpha$ instead of Cu $K\alpha$ radiation. It was found that the results were explicable in terms of the secondary extinction phenomenon (James, 1948).

Background corrections

Two types of background which may be troublesome in the instrument are (*a*) incoherent scattering and (*b*) the white radiation which is in the neighborhood of the harmonics of the $K\alpha$ radiation. The correction for the incoherent scattering at present must be obtained from the measured background rate and the time required to traverse a reflection. This correction could be made electronically by the addition of another circuit which samples the background between reflections and feeds a signal to the second 420 A of the balanced output circuit which would in effect decrease the recorder reading by the amount of the background. The contribution to the integrated intensities arising from the harmonics of the $K\alpha$ radiation is small because the efficiency of the G.M. counter is lower than that at the $K\alpha$ wavelength by about a factor of 4. When the proportional counter is installed, it will be possible to eliminate the harmonics completely by pulse-height discrimination if necessary.

5. Conclusions

The data for an 'average' layer line for inorganic crystals (NaCl) can be taken in about 2 hr. If an intensity ratio of greater than 100:1 is desired, an absorber can be inserted in the diffracted beam. The ratio, however, is limited by the 5 μsec. dead time of the electronic circuits at high intensity and the finite back-set counting rate at low intensity. If the diffraction lines are narrow and of low intensity, some extension of the range of applicability can be obtained by using a slower motor to drive the gear train.

Future improvements which will be made on the diffractometer include the elimination of the back-set correction by delaying the clutch-shifting mechanism after passing through the reflection, and using a digital recorder with a print-out device in addition to the present recorder.

The primary limitation of the instrument at present is the uncertainty of the back-set correction. However, it is felt that the diffractometer is now capable of giving integrated intensity data on single crystals to an accuracy of about 10%. After the proportional counter has been installed, the error in the integrated intensity will be decreased to less than 5%. This instrument has most of the advantages of the Weissenberg camera with the added advantages of more accurate intensity data obtained automatically and, for many crystals, a considerable saving in time.

The author wishes to express his appreciation to Dr S. Geller for helpful suggestions and criticism during the development of this instrument and to Mr J. Durand for his help in the construction and testing of various parts of the apparatus.

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Zur Struktur des β-Wollastonits, des Maddrellschen Salzes und des Natriumpolyarsenats

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The similarity of the lattice constants and of the disorder phenomena observed in monoclinic β-wollastonite and $(NaPO_3)_x$(I) and of the lattice constants of triclinic β-wollastonite and $(NaAsO_3)_x$, as well as the similarity of certain Patterson projections of all these, shows the structural similarity of these substances. The chain character of anions which had been established by chemical investigation for the $(NaPO_3)_x$(I) was confirmed by structure analysis of the $(NaAsO_3)_x$. Hence the ring structure proposed for β-wollastonite has to be rejected. A discussion of the symmetries present shows that β-wollastonite and $(NaPO_3)_x$(I) are isomorphous, whereas $(NaAsO_3)_x$ is not isomorphous with these two but seems to contain the same kind of chains. Neighbouring chains are connected by a symmetry centre in the arsenate; in β-wollastonite and the phosphate they are connected in pairs by screw diads parallel to the chains. This difference explains the occurrence of disorder in β-wollastonite and $(NaPO_3)_x$(I) and the absence of such disorder in $(NaAsO_3)_x$.

Nachdem Thilo & Plaetschke (1949) auf chemischem Wege einen Beweis für die Kettenstruktur der Hochtemperaturform des Maddrellschen Salzes $(NaPO_3)_x$(I) (Boullé, 1935) erbracht hatten, erschien es wünschenswert, diesen Beweis durch eine röntgenographische Strukturanalyse zu erhärten. Es stellte sich sehr bald