

show that in fact the lattice constant varies significantly when the noble metal atom ( $B$ ) is changed.

The lattice constants of the Pd and Pt compounds indicate that the effective radius for Pd in these compounds is larger than that for Pt. Heumann & Kniep-meyer's (1957) data are also in agreement with this conclusion. However, the lattice constants given by Heumann & Kniep-meyer for the strontium compounds do not agree with those published here within our limits of error. They give the following values:

$$\begin{aligned} \text{SrPd}_2, & 7.800 \text{ \AA} (\Delta = +0.026); \\ \text{SrPt}_2, & 7.742 \text{ \AA} (\Delta = +0.035); \\ \text{SrRh}_2, & 7.695 \text{ \AA} (\Delta = +0.011); \\ \text{SrIr}_2, & 7.849 \text{ \AA} (\Delta = -0.149). \end{aligned}$$

Heumann & Kniep-meyer give the experimental data for one substance, SrRh<sub>2</sub>. When the lattice constant for SrRh<sub>2</sub> is determined from their data by Bradley-Jay extrapolation, the result is  $7.707 \pm 0.005$  Å, which agrees with our lattice constant, similarly determined, within experimental error. This difference in treatment of data may well account for the discrepancy between their results and ours in the cases of SrPd<sub>2</sub> and SrPt<sub>2</sub> as well, but may not account for the different results for SrIr<sub>2</sub>. The larger discrepancy in this case might be due to impurity or off-stoichiometry of material. The results of the spectroscopic analyses of our material and the chemical analyses of their material preclude the presence of appreciable amounts of metallic impurities, but non-metallic impurities

would not have been detected by the spectroscopic analysis. While departure from stoichiometry would have been possible in both cases, it seems unlikely in this structure that one of the constituents would substitute for the other because of the great difference in size and bonding of the two constituents. Vacancies, however, could occur.

The writers wish to thank S. C. Abrahams for his careful reading of the manuscript and helpful criticism. They are also grateful to H. J. Seubert for making the drawings.

### References

- DAUBEN, C. H. & TEMPLETON, D. H. (1955). *A Table of Dispersion Corrections for X-Ray Scattering of Atoms*. University of California Radiation Laboratory UCRL-3061.
- FREVEL, L. K. (1942). *Industr. Engng. Chem. Anal. Ed.* **14**, 687.
- FRIAUF, J. B. (1927). *J. Amer. Chem. Soc.* **49**, 3107.
- HEUMANN, TH. & KNIEMMEYER, M. (1957). *Z. anorg. Chem.* **290**, 191.
- International Tables for the Determination of Crystal Structures* (1935). Berlin: Borntraeger.
- LAVES, F. (1939). *Naturwissenschaften*, **27**, 65.
- LAVES, F. (1956). *Theory of Alloy Phases*. Cleveland: American Society of Metals.
- MATTHIAS, B. T. & CORENZWIT, E. (1957). *Phys. Rev.* **107**, 1558.
- SCHULZE, G. E. R. (1939). *Z. Elektrochem.* **45**, 849.

*Acta Cryst.* (1958). **11**, 433

## A Guide Mechanism for a Single-Crystal X-ray Counter Goniometer

BY A. McL. MATHIESON

*Chemical Physics Section, Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia*

(Received 30 December 1957)

A mechanism has been devised which permits the counter on a X-ray goniometer to scan a selected straight line in reciprocal space within the range of the limiting sphere.

### Introduction

A counter goniometer offers the possibility of increased sensitivity and accuracy in intensity measurements on single crystals, a possibility which can best be adequately exploited if the goniometer is made automatic in operation. In the design of such a goniometer, the principal disadvantage of the counter is that it is a one-point detector, so that the conditions governing its orientation with respect to the crystal to record a sequence of reflexions are much more critical than those required by a goniometer em-

ploying photographic film, i.e., a two-dimensional detector.

In the majority of cases, the problem of satisfying the required conditions has been tackled by hand-setting both the crystal and the counter (see Lonsdale (1948), Wooster, Ramachandran & Lang (1948), Cochran (1950), Clifton, Filler & McLachlan (1951), Evans (1953), Zachariasen (1954), Furnas & Harker (1955)). To make the collection of intensity measurements automatic, it is necessary to devise a linkage between the crystal and counter movements which will enable the whole or a selected part of the recip-

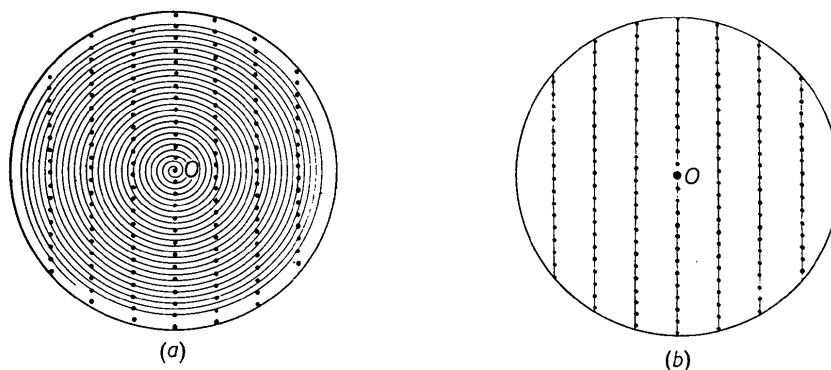


Fig. 1. Part of a typical reciprocal lattice with the limiting circle ( $d = 2.0$ ) outlined. (a) The spiral scan devised by Bond (1955). (b) The scan, linear in reciprocal space, proposed in the present paper.

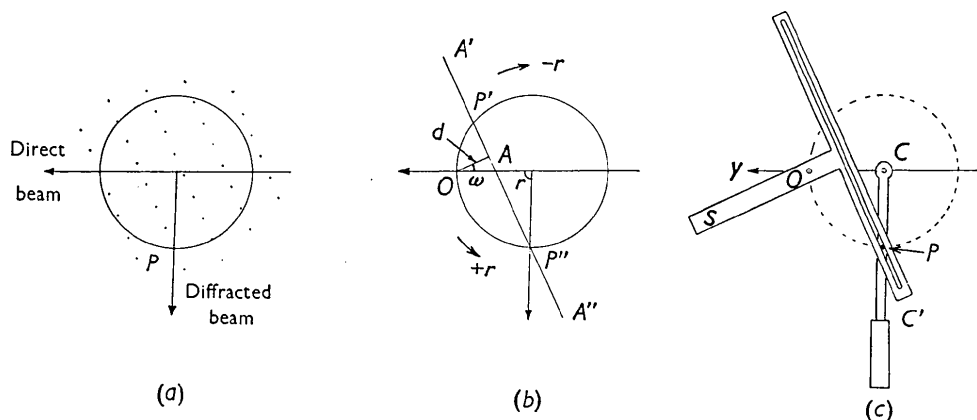


Fig. 2. (a) The geometrical construction of the interaction of the reciprocal lattice and the reflecting circle. Reflecting condition satisfied at point  $P$ . (b) A selected line  $A'A''$  in reciprocal space. The various angular relationships are indicated. (c) The mechanical analogue of (b). The Scotch yoke,  $Y$ , rotates about  $O$ , while the pin,  $P$ , engages in the yoke is but constrained to rotate about  $C$ , the axis of the crystal.

reciprocal lattice to be covered in one run. For this purpose, Bond (1955) has recently designed and built a counter goniometer which searches a layer of the reciprocal lattice by means of a spiral scan from  $\theta = 0$  up to the instrumental limit. Fig. 1(a) illustrates the principle which was converted into mechanical terms by combining a relatively fast rotation of the crystal with a slow rotation of the counter. The large amount of time spent on the background by this type of scan is reduced by using a fast rate of travel when the count rate is low; when it rises in the neighbourhood of a reflexion, the counter is stopped and backed, and restarts travel at the slow rate. This dependence of the rate of travel on the count rate means that reflexions not greatly above the background level will be passed over unless a very sensitive discriminating device is incorporated. For many organic compounds of moderate complexity, experience shows that a large proportion of the reflexions are of weak intensity, and, for such compounds, Bond's device would severely limit the number of reflexions which could be measured. Alternatively, the spiral scan without discrimination would spend too much time on the background.

A more satisfactory approach would be to explore only significant regions of the layers of reciprocal space selected by a preliminary photographic survey, thereby overcoming the need for elaborate discriminating devices. The most natural and economical scan is along the most highly populated rows of the reciprocal lattice, as shown in Fig. 1(b). To achieve this, however, it is necessary to devise a mechanism which will permit the counter to follow a straight line in reciprocal space.

Several years ago the author devised a linkage between counter and crystal which fulfilled most of the requirements of such a guide mechanism. It has now been constructed and found to operate in a satisfactory manner.

### Principle of the mechanism

The principle of operation is based directly on the geometrical construction of the diffraction condition in terms of the reciprocal lattice. The transition from the basic idea to the mechanical set-up is shown in Fig. 2. Considering only the two-dimensional case, the

condition for diffraction to occur is for a reciprocal-lattice point to coincide with the circumference of the reflecting circle (Fig. 2(a)), the angular conditions of the crystal ( $\omega$ ) and the counter ( $r$ ) with respect to the X-ray beam being defined by this construction. Let us focus attention on a line through a row of reciprocal lattice points, e.g.  $A'AA''$ , which is distant  $d$  from the origin  $O$ , Fig. 2(b). As this line intersects the reflecting circle with rotation of the reciprocal lattice, the required conditions between  $\omega$  and  $r$  for this line are continuously specified. Consideration of the geometrical construction suggested the basic essentials of the mechanical arrangement for the guide mechanism, Fig. 2(c). The Scotch yoke,  $Y$ , capable of rotation about  $O$ , represents the line  $A'AA''$  in reciprocal space. The yoke can be adjusted in the direction  $SO$ , i.e. perpendicular to  $A'A''$ , to give any value of  $d$  between zero and 2 (the diameter of the reflecting circle). Since it represents a part of the reciprocal lattice, the yoke is rotated about  $O$  at the same constant rate as the crystal is rotated about  $C$ . The counter, mounted on the arm  $CC'$ , free to rotate about the shaft  $C$  which is concentric with the crystal shaft but independent of it, is linked to the Scotch yoke by the pin  $P$ , which lies at unit distance from  $C$ , i.e. effectively on the circumference of the reflecting circle. As the Scotch yoke rotates about  $O$ , it causes the pin to slide within the yoke and moves the counter so as to satisfy the desired conditions between  $r$  and  $\omega$ . Hence the counter scans the row of reflexions indicated in Fig. 2(a). The pin can be placed in position  $P'$  or  $P''$  (Fig. 2(b)) according as region  $A'A$  or  $AA''$  is being surveyed. The diffracted beams are then

detected in the corresponding regions  $-r$  or  $+r$  (Fig. 2(b)).

Fig. 3 shows the actual guide mechanism, which, for convenience in construction and use, is separated from the goniometer unit. The Scotch yoke is mounted on the helical gear,  $G_1$ , and can be adjusted in its slide from  $d = 0$  to 2.0 (where 1 = 5 cm.). This gear and a similar one on the crystal holder shaft are driven in parallel. Gear  $G_2$ , which is effectively the reflecting circle, carries the pin,  $P$ , which engages in the slide block in the Scotch yoke. This gear,  $G_2$ , is linked through a 1:1 gear train to the counter arm. For the survey of any central row of reciprocal-lattice points the guide mechanism is declutched and a simple 2:1 gear train is brought into action.

### Performance

Assessment of the performance of the guide mechanism is best made by comparison of experimental ( $r, \omega$ ) plots for various values of  $d$  with the theoretical distributions for which Buerger (1942) has already supplied tabulated values in his discussion of the equi-inclination Weissenberg goniometer.

To make the measurements, the counter and crystal angular scales were first adjusted as follows. The Scotch yoke, in the position where  $SO$  is coincident with  $OC$  (Fig. 2), was set at  $d = 1$ . For this position the counter angle is  $r = \pm 90^\circ$ . With the yoke slide in the  $AA''$  region,  $r$  is set at  $+90^\circ$  and the crystal scale at  $\omega = 180^\circ$ . For the alternative region  $A'A$ , the counter is set at  $270^\circ$ . Values of  $r$  were then read off for each  $10^\circ$  interval of  $\omega$  both for increasing and

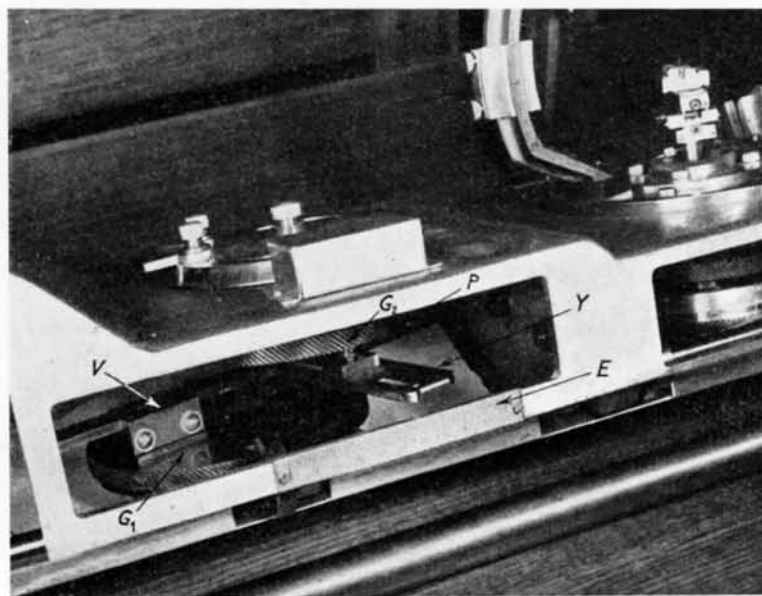


Fig. 3. The guide mechanism in the goniometer. The Scotch yoke,  $Y$ , is mounted on the helical gear  $G_1$ .  $d$  can be adjusted on scale  $E$  by moving the yoke in the slide  $V$ .  $G_2$  (the reflecting circle) carries the pin,  $P$ , which engages with the slide block in the yoke.

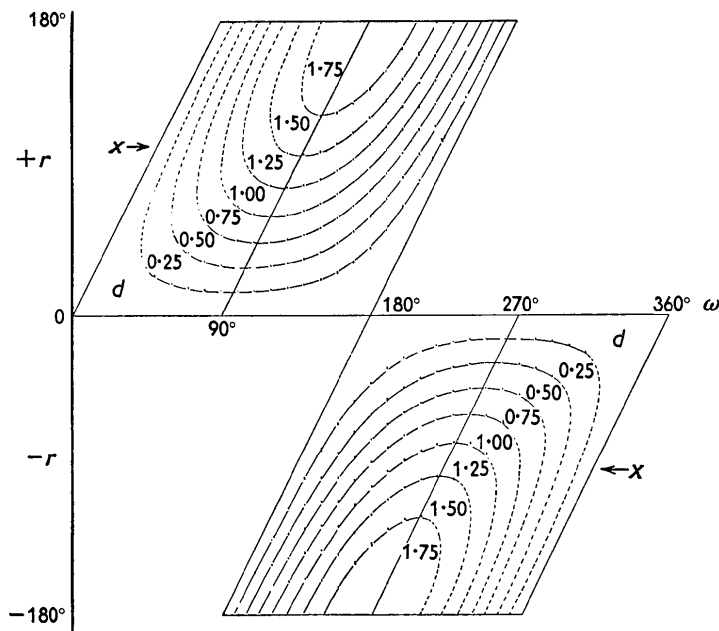


Fig. 4. For the values of  $d$  indicated,  $r$  is plotted against  $\omega$  at  $10^\circ$  intervals of  $\omega$  in the  $+r$  and  $-r$  regions. The vertical spread of the points is the observed backlash in the mechanism. The continuous curves refer to regions where the mechanism is fully effective, dashed curves to regions where measurements were either not made or could not be made (i.e. near the 'noses' of the curves).

decreasing  $\omega$ . The only adjustment required for further sets of readings was a shift of  $d$  to its new value by sliding the Scotch yoke to the appropriate value. This operation automatically adjusts the relative angular positions of the counter and crystal for the new value of  $d$ . The  $(r, \omega)$  measurements for  $d$  from 0.25 to 1.75 by shifts of 0.25 are shown in Fig. 4.

From these results, it is evident that selected values of  $d$  can be set with adequate accuracy by means of the Scotch yoke. Secondly, the guide mechanism is capable of following the curves smoothly over the full range of  $d$ . The mean deviation in  $r$  is of the order of  $1^\circ$ , with a maximum of  $3^\circ$ . A measure of the backlash in this type of mechanism is given by the vertical spread of the readings in Fig. 4, which is not greater than  $2^\circ$ .

The principal limitation of the guide mechanism arises from its mode of operation. Thus, in the region  $X$ , Fig. 4, the  $(r, \omega)$  function is double-valued, since the line  $A'A''$  intersects the reflecting circle at two points which gradually draw together until they coincide at the 'nose' of the curve. At this position the line is tangential to the reflecting circle, and, should it progress further in the  $-\omega$  direction, it would leave the reflecting circle. In the mechanism it is impossible for this to occur, and hence the mechanism cannot operate adjacent to this region. However, in one run, it can cover more than half the line  $A'AA''$ , i.e.  $> AA''$ , and then, by transferring to the  $-r$  range, it can cover the other half, i.e.  $> A'A$ , with an overlap useful to coordinate the data for the two halves. This limitation can be more fully appreciated by study of

Fig. 2 or by reference to the appropriate section in Buerger (1942). The practical extent of the ranges of the line  $A'A''$  in the respective  $r$  regions is indicated in Fig. 4.

The goniometer is designed to operate in the equi-inclination mode so that there is no need to displace the origin of the reciprocal lattice of the layer being studied from its position on the circumference of the reflecting circle. In mechanical terms, the axis of the Scotch yoke does not require to be displaced, which simplifies the construction of the guide mechanism and maintains accuracy. The  $d$  scale is merely modified by a factor  $\cos \mu$  as the equi-inclination angle  $\mu$  is increased.

I would like to express appreciation of the excellent workmanship of Mr R. Venn, who constructed the guide mechanism.

#### References

- BOND, W. L. (1955). *Acta Cryst.* **8**, 741.  
 BUERGER, M. J. (1942). *X-ray Crystallography*, p. 276. New York: Wiley.  
 CLIFTON, D. F., FILLER, A. & MCLACHLAN, D. (1951). *Rev. Sci. Instrum.* **22**, 1024.  
 COCHRAN, W. (1950). *Acta Cryst.* **3**, 268.  
 EVANS, H. T. (1953). *Rev. Sci. Instrum.* **24**, 156.  
 FURNAS, T. C. & HARKER, D. (1955). *Rev. Sci. Instrum.* **26**, 449.  
 LONSDALE, K. (1948). *Acta Cryst.* **1**, 12.  
 WOOSTER, W. A., RAMACHANDRAN, G. N. & LANG, A. (1948). *J. Sci. Instrum.* **25**, 405.  
 ZACHARIASEN, W. H. (1954). *Acta Cryst.* **7**, 305.