Acta Cryst. (1971). A**27**, 665

Choice of Scans in Neutron Diffraction

BY S. A. WERNER

Scientific Research Staff, Ford Motor Company, Dearborn, Michigan, U.S.A.
and Department of Nuclear Engineering, University of Michigan, Ann Arbor, Michigan, U.S.A.

(*Received* 13 *April* 1971)

Neutron-diffraction experiments on single-crystal samples are generally carried out using either an ω-scan (crystal rotating, detector fixed) or a θ–2θ scan (detector coupled 2:1 to the crystal). In order for the center of the diffracted beam to enter the detector on its centerline at all angular settings of the crystal during the scan of a Bragg reflection, neither of these conventional scanning techniques is optimum. A formula is derived which gives the optimum coupling between the detector and the crystal motions, and it is suggested this mode of scanning should be implemented in performing neutron-diffraction experiments on single crystals.

Introduction

Neutron-diffraction experiments on single-crystal samples are generally carried out using either an ω-scan (crystal rotating, detector fixed) or a θ–2θ scan (detector coupled 2:1 to the crystal). Coupling the detector and the crystal motions in either of these two ways is not a constraint dictated by most diffractometers currently in use, since the crystal and the detector are usually driven by separate stepping motors which are individually programmable. The question of whether there is in general a better way to scan Bragg reflections is the subject of this note.

In view of the fact that in recent years considerable attention has been given to the problem of obtaining highly accurate diffraction data (see for example Willis, 1969), it would seem to be important to scan the Bragg reflections in the most ideal manner possible. Numerous papers have been published over the years on the resolution of neutron crystal spectrometers (Caglioti, Paoletti & Ricci, 1958, 1960; Caglioti & Ricci, 1962; Caglioti, 1964; Caglioti & Tocchetti, 1964, 1965; Willis, 1960; Cooper & Nathans, 1968). However, none of these authors has suggested that there is an optimum scanning procedure for the measurement of the integrated intensity of each Bragg reflection, and that this procedure can be easily implemented. Whether or not the accuracy of the integrated intensities will be improved by using this optimum scanning procedure will depend on the geometry and instrumental parameters of the spectrometer.

Derivation of the optimum scanning ratio

A schematic diagram of a typical neutron diffractometer is shown in Fig. 1. Neutrons from the reactor, which are uncorrelated in angle and energy, pass through an in-pile collimator and impinge upon a monochromating crystal. A small fraction of these ($\sim 1\%$) are Bragg reflected at an angle $2\theta_M$ and pass through the secondary collimator. This forms a beam incident on the sample crystal which has an energy angle correlation. As a result of this correlation in the incident beam, the center of the angular distribution of reflected wave vectors will shift in a particular way dependent on the scattering angle $2\theta_S$ as the sample crystal is rotated through a Bragg reflection. In order to obtain the integrated intensity, it is necessary for the detector to accept all of these Bragg scattered neutrons for each angular setting of the crystal φ (with essentially equal efficiency). If the detector is 'wide-open' and large, this will be accomplished without moving the detector. However, in order to reduce the background counting rate due to incoherent scattering and the correction necessary for thermal diffuse scattering, a slit (or a collimator) is generally placed in front of the detector. Ideally this slit should be sufficiently wide to accept all of the Bragg scattered neutrons, but no wider. Under these conditions the detector must be moved as a function of crystal angle φ. It is apparent that the optimum scanning ratio is obtained if the detector is moved through an angle $\Gamma(\varphi)$ which keeps the center of the diffracted beam aligned with the centerline of the detector. This is illustrated in Fig. 2. This Figure is drawn for a narrow mosaic monochromator. The collimation is assumed to be due primarily to the secondary collimator. $\mathbf{G}_M$ is the monochromator reciprocal-lattice vector. $\mathbf{k}_1$ and $\mathbf{k}_2$ are the wave-vectors incident on and scattered from the sample respectively. The two spheres of reflection centered at A and B are drawn for incident wave-vectors oriented at the edges of the secondary collimation $2\alpha_1$. As the sample is rotated through the Bragg reflection corresponding to the reciprocal-lattice vector $\mathbf{G}_S$, intensity is first obtained when the tip of $\mathbf{G}_S$ falls on sphere A at the point a. The detector should be positioned to accept the scattered ray $\mathbf{k}_2$ at the point a'. As the crystal is rotated from the point a to the point b, the detector should move from the point a' to the point b'. Thus, the scanning ratio should be

$$g = \frac{\Gamma(\varphi)}{\varphi} = \frac{\Delta\gamma}{\Delta\varphi}. \qquad (1)$$

We will now derive an expression for g for any scattering angle $2\theta_S$. We will assume that the collimator transmission functions and the crystal reflectivities are Gaussian in shape as has been done in the papers by Caglioti and coworkers and by Cooper & Nathans. Thus, the transmission of the in-pile collimator for a neutron of wave-vector $\mathbf{k}_0$ oriented off the nominal ray direction by an angle γ_0 is given by

$$T_0(\gamma_0)=\exp\{-\gamma_0^2/2\alpha_0^2\}\,. \tag{2}$$

The reflectivity of the monochromator as a function of mosaic orientation angle Δ_M and its mosaic spread η_M is

$$P_M(\Delta_M)=p_M\exp\{-\Delta_M^2/2\eta_M^2\}\,. \tag{3}$$

Similarly the transmission of the secondary collimator for a ray γ_1 is

$$T_1(\gamma_1)=\exp\{-\gamma_1^2/2\alpha_1^2\}\,, \tag{4}$$

and the reflectivity of the sample crystal in terms of the mosaic orientation angle Δ_S and its mosaic spread is

$$P_S(\Delta_S)=p_S\exp\{-\Delta_S^2/2\eta_S^2\}\,. \tag{5}$$

The intensity $I(\gamma,\varphi)$ of the Bragg beam scattered off the sample at an angle γ (away from the nominal $2\theta_S$) for a given setting of the crysral $\varphi=\theta-\theta_S$ involves an integration over wave-number, since the detector does not distinguish between the energies of the scattered neutrons. That is,

$$I(\gamma_1\varphi)=\int T_0(\gamma_0)P_M(\Delta_M)P_S(\Delta_S)T_1(\gamma_1)\mathrm{d}\left(\frac{\Delta k}{k}\right). \tag{6}$$

In order to do this integration, the variables γ_0, Δ_M, Δ_S, and γ_1 must be expressed in terms of γ, φ and $\Delta k/k$. This is easily done using the Bragg conditions for the monochromator and the sample (see, for example, Willis, 1960), the results are

$$\gamma_0=\gamma-2\frac{\Delta k}{k}(\varepsilon_M\tan\theta_M+\varepsilon_S\tan\theta_S) \tag{7a}$$

$$\Delta_M=\gamma-\frac{\Delta k}{k}(\varepsilon_M\tan\theta_M+2\varepsilon_S\tan\theta_S) \tag{7b}$$

$$\Delta_S=\gamma-\varphi-\frac{\Delta k}{k}(\varepsilon_S\tan\theta_S) \tag{7c}$$

$$\gamma_1=\gamma-2\frac{\Delta k}{k}(\varepsilon_S\tan\theta_S)\,. \tag{7d}$$

θ_M and θ_S are the nominal Bragg angles of the monochromator and sample respectively. ε_M and ε_S give the sense of scattering [left $(+1)$, or right (-1)] from the monochromator and sample respectively.

Using these results, we find that the intensity of the scattered beam as a function of γ for a given crystal setting $\varphi=\theta-\theta_S$ is

$$I(\gamma_1\varphi)=I_0\exp\{-\tfrac{1}{2}[(\gamma-\Gamma(\varphi))^2/\delta^2+\varphi^2/\sigma^2]\}\,. \tag{8}$$

A schematic plot of this function is shown in Fig. 3. The angular width δ of the scattered beam is independent of φ. That is, as the crystal is rotated, the angular shape of the scattered beam remains the same. When the crystal is set at the nominal Bragg angle ($\varphi=0$) the counting rate is given by the area A_1, and when the crystal is set at some other angle φ the counting rate

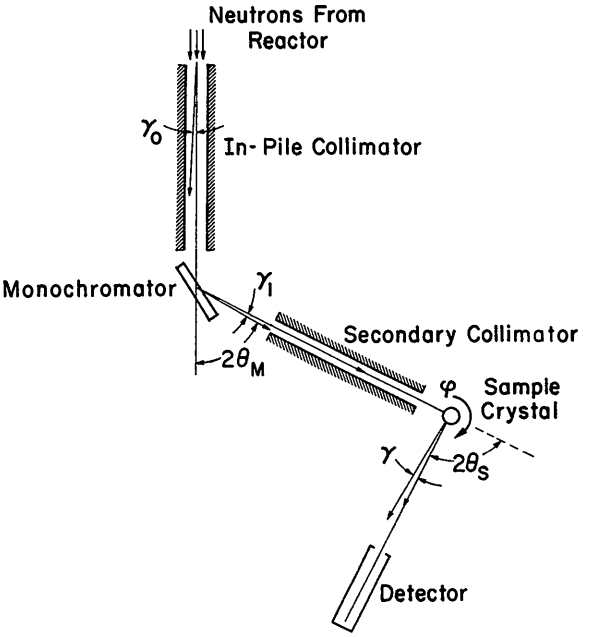

Fig. 1. Schematic diagram of a typical neutron diffraction experiment.

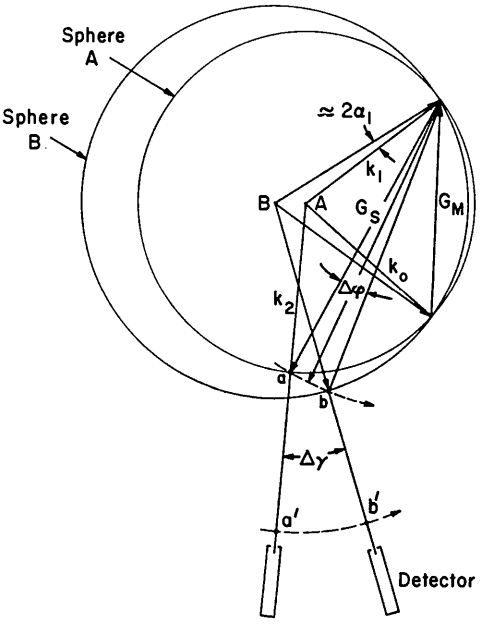

Fig. 2. Diagram in $\mathbf{k}$ space illustrating that the detector must be moved by an angle $\Delta\gamma$ when the sample crystal is rotated through an angle $\Delta\varphi$. The optimum scanning ratio g is given $\Delta\gamma/\Delta\varphi$ which is seldom 2.

is given by the area A_2 in Fig. 3. This is only true if the detector accepts all of the Bragg scattered neutrons for each φ. To insure that this is the case, and that the beam enters the detector symmetrically for each setting of the crystal φ, the detector should be moved by the angle $\Gamma(\varphi)$. The width of the crystal rocking curve is then given by σ. (Expressions for δ, and σ are given in the Appendix.) We are only concerned here with the function $\Gamma(\varphi)$ which determines the optimum scanning ratio g.

We find that

$$g \equiv \frac{\Gamma(\varphi)}{\varphi} = \frac{2\eta_M^2\alpha_1^2(a^2+3a+1)+\alpha_0^2\alpha_1^2(2a^2+3a+1)+2a^2\eta_M^2\alpha_0^2}{\alpha_1^2\eta_S^2+\alpha_1^2\eta_M^2(a+2)^2+4\eta_M^2\eta_S^2+\alpha_0^2\alpha_1^2(1+a)^2+\eta_M^2\alpha_0^2a^2+\alpha_0^2\eta_S^2}. \tag{9}$$

The variable a determines the scattering angle $2\theta_S$,

$$a \equiv \frac{\varepsilon_S \tan\theta_S}{\varepsilon_M \tan\theta_M}. \tag{10}$$

Discussion

The expression for the optimum scanning ratio g is rather complicated. However, for a given experiment with a definite set of instrumental parameters, it is simply a known function of the Bragg angle θ_S. In order to obtain an understanding of the wide variation of the scanning ratio as a function of scattering angle, we will consider the case where the most important collimation in the system is the secondary collimator (*i.e.* $\alpha_0 \to \infty$). In this case

$$g = \frac{\alpha_1^2[1+3a+2a^2]+2\eta_M^2a^2}{\eta_S^2+\alpha_1^2(1+a)^2+a^2\eta_M^2}. \tag{11}$$

The two width parameters are then

$$\delta^2 = \frac{(1+2a)^2\alpha_1^2\eta_S^2+4a^2\eta_M^2\eta_S^2+a^2\alpha_1^2\eta_M^2}{\eta_S^2+\alpha_1^2(1+a)^2+a^2\eta_M^2} \tag{12}$$

and,

$$\sigma^2 = \eta_S^2+\alpha_1^2(1+a)^2+a^2\eta_M^2. \tag{13}$$

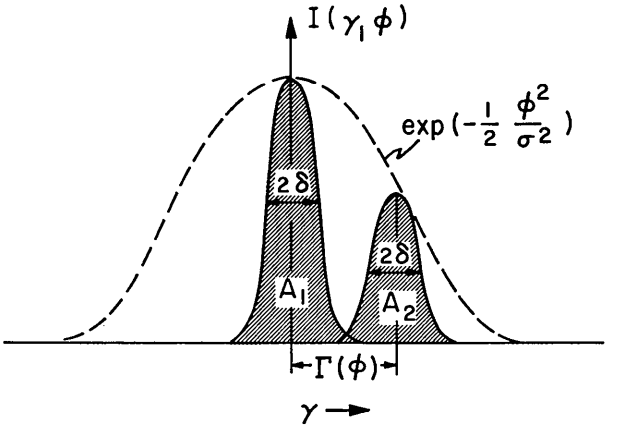

Fig. 3. Schematic diagram of the diffracted beam intensity $I(\gamma,\varphi)$ as a function of the outgoing ray direction γ for various crystal angle settings.

On the 'parallel' side of the origin, the variable a is negative, that is $\varepsilon_M = +1$, $\varepsilon_S = -1$, or $\varepsilon_M = -1$, $\varepsilon_S = +1$. This is the configuration in which most diffraction experiments are done, although in the determination of the collimation parameters it is quite often expedient to scan some Bragg reflections on the antiparallel side of the origin.

The scanning ratio, g, given by equation (11), can be written as a function of η_M/α_1 and η_S/α_1. In Fig. 4 we show how g varies as a function of scattering angle in the case where the mosaic spreads of the monochromator and sample are equal. We see that for large scattering angles (large $|a|$), the optimum scanning ratio g is very close to 2 (*i.e.* a θ–2θ scan is best). When the ratio of the mosaic spreads to the collimation angle α_1 is small, the optimum scanning ratio deviates rapidly from 2, increasing to a large positive value just outside the 'parallel focusing' condition ($a = -1$), and then to a large negative value just inside the parallel position. As the ratio of the mosaic spread to the collimation angle increases, the large variation of g near $a = -1$ becomes less pronounced. However, in the region where a large fraction of diffraction data is taken (say between $a = -3$ and 0), the optimum scan is seldom θ–2θ or θ-rotation.

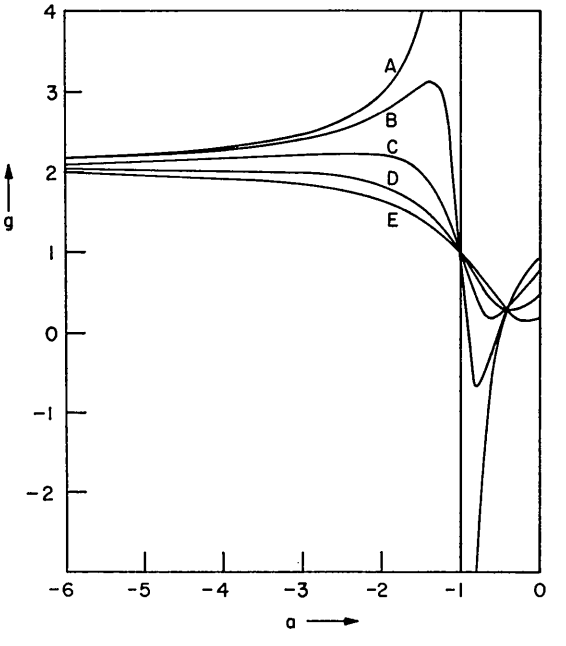

Fig. 4. This Figure shows the optimum scanning ratio g as a function of the parameter $a = \varepsilon_S \tan\theta_S/\varepsilon_M \tan\theta_M$. In this case we have set the mosaic spreads of the monochromator η_M and sample η_S equal. Curve A is for $r = \eta_S/\alpha_1 = \eta_M/\alpha_1 = 0{\cdot}01$, where α_1 is the collimation angle of the secondary collimator. B is for $r = 0{\cdot}2$, C for $r = 0{\cdot}5$, D for $r = 1{\cdot}0$, E for $r = 2{\cdot}0$.

The fact that in a limited region between $a=0$ and $a=-1$, the detector should actually be rotated in a direction *opposite* to the crystal motion is curious. That this is in fact correct is shown in Fig. 5 which is drawn for the case of a narrow mosaic monochromator. The two spheres A and B are drawn again as in Fig. 2. For a reflection just outside the parallel position having a reciprocal-lattice vector $\mathbf{G}_1$, the diffracted beam moves from the point a' to b' as the tip of $\mathbf{G}_1$ is swept from a to b. However, for the reflection just inside the parallel position, the reciprocal-lattice vector $\mathbf{G}_2$ sweeps through the sphere B first and then the sphere A such that the tip of $\mathbf{G}_2$ moves from b to a and the diffracted beam moves from b' to a'. That is, the detector should move in a clockwise sense when the crystal moves in a counterclockwise sense.

In Fig. 6 we show how the optimum scanning ratio in g changes as a function of scattering angle for the case when the monochromator mosaic spread η_M and the collimation angle α_1 are equal. In this case when the sample mosaic spread η_S is small, there is again a rapid variation of the optimum scan in the region $a=-2$ to $a=0$. As the sample mosaic spread becomes larger, the optimum scanning ratio is consistently less than 2 and approaches zero near the parallel position.

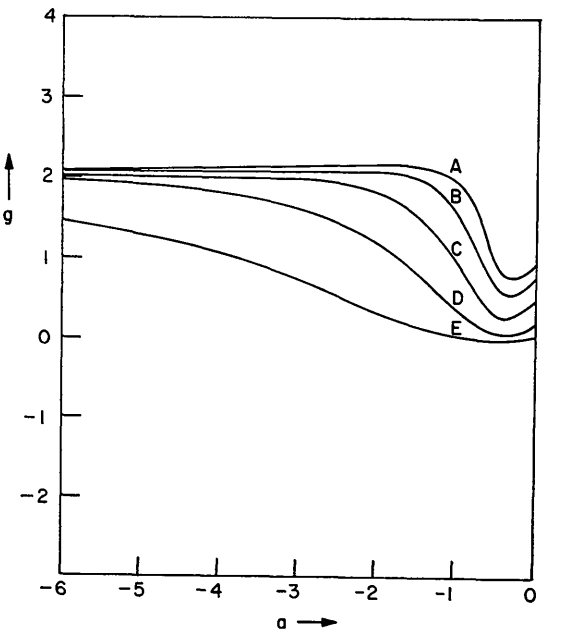

Fig. 6. This Figure is similar to Fig. 4. However the monochromator mosaic spread η_M is set equal to the collimation angle α_1. Curve A is for $\eta_S/\alpha_1=0{\cdot}01$, B for $\eta_S/\alpha_1=0{\cdot}5$, C for $\eta_S/\alpha_1=1$, D for $\eta_S/\alpha_1=2$, E for $\eta_S/\alpha_1=5$.

Conclusions

We have shown in this paper that the optimum scan in single-crystal neutron diffraction experiments is seldom either a θ-rotation or a θ–2θ scan. The question of course arises as to the importance of performing the optimum scan in measuring integrated Bragg reflections. Under what condition will the measurement of all the Bragg reflections using a given fixed mode of scanning lead to errors?

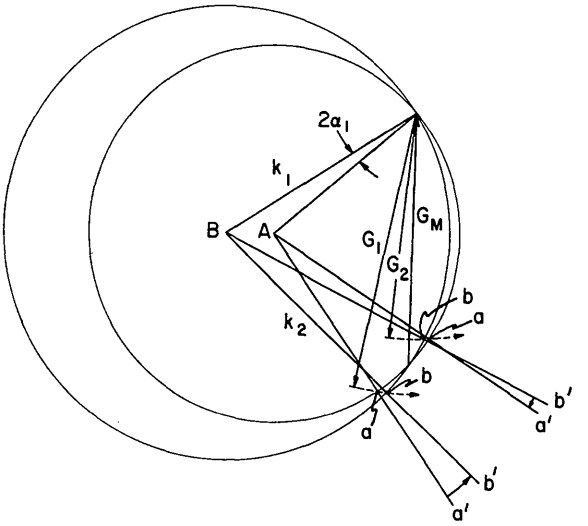

Fig. 5. This diagram shows that for a certain region inside the parallel position, the detector should actually be rotated in a direction opposite to the rotation direction of the crystal.

It is clear that in the case where the monochromator and sample mosaic spreads are both small compared with the collimation α_1, the suggested large scanning ratio g near $a=-1$ is not necessary since the rocking width σ is very narrow and consequently the net shift in the optimum detector position Γ is very small. Thus, either a θ-rotation or a θ–2θ scan is acceptable. However in the region $a=-3$ to $a=-2$, the rocking widths σ will become fairly broad, and the detector must be moved to accept the scattered beam symmetrically. Curve A in Fig. 4 shows that the detector should be moved from 2·5 to 3·0 times faster than the crystal in this region. It will be noted that in this case, the angular divergence δ of the outgoing beam is very small (see Fig. 2), so that the aperture on the detector can, in principle, be made rather small.

In the case where the sample mosaic spread is large, the rocking curve widths σ will consistently be large. The net motion of the detector necessary to accept all of the reflected beam at each crystal setting will also be large. A coupling between the detector and the crystal of 2:1 is not a good choice in this case. As shown by curve E in Fig. 6, the optimum scanning ratio varies from about 1·5 at large angles ($a=-6$) to near zero at small angles.

It is difficult to make a general statement of the range of scattering angles when a θ-rotation is better than a θ–2θ scan, although it is clear that at high angles the θ–2θ scan is preferable, and at small angles a θ-rotation may be better as pointed out by Arndt & Willis (1966).

Our recommendation is that the optimum scanning ratio as given by equation (9) should always be used. This will leave little doubt in the experimenter's mind of whether a θ-rotation or a θ–2θ scan is best for a given reflection, since the diffracted beam will always be entering the detector symmetrically on its centerline. It is anticipated that most experimentalists will be reticent about adopting this variable mode of scanning, since it is commonly thought that all of the data for a given experiment should be accumulated without changing the experimental technique. However, careful consideration will show that employing the optimum scanning ratio appropriate for each scattering angle $2\theta_S$ is the only technique which measures all Bragg reflections in the same way.

Implementing this idea for tape controlled or computer controlled spectrometers is straightforward. The precise scanning ratio g given by equation (9) cannot always be achieved because of the minimum angular increments allowed by stepping motors. However, it is clear that the optimum scan can generally be adequately approximated.

It is a pleasure to thank Dr A. Overhauser for his criticisms and suggestions during the course of preparing this manuscript. I would also like to thank Mr E. Gürmen for checking some of the equations.

APPENDIX

Expressions for δ, σ

The width of the Bragg scattered beam is given by

$$\delta^2=\frac{\left[\frac{4(1+a)^2}{\alpha_0^2}+\frac{(1+2a)^2}{\eta_M^2}+\frac{a^2}{\eta_S^2}+\frac{4a^2}{\alpha_1^2}\right]}{\left[\frac{1}{\alpha_0^2\eta_M^2}+\frac{(a+2)^2}{\alpha_0^2\eta_S^2}+\frac{1}{\eta_M^2\alpha_1^2}+\frac{4}{\alpha_0^2\alpha_1^2}+\frac{(a+1)^2}{\eta_M^2\eta_S^2}+\frac{a^2}{\eta_S^2\alpha_1^2}\right]}. \tag{A1}$$

The width of the crystal rocking curve is given by

$$\sigma^2=\frac{\left[\frac{4(1+a)^2}{\alpha_0^2}+\frac{(1+2a)^2}{\eta_M^2}+\frac{a^2}{\eta_S^2}+\frac{4a^2}{\alpha_1^2}\right]}{\frac{1}{\eta_S^2}\left[\frac{4(1+a)^2}{\alpha_0^2}+\frac{(1+2a)^2}{\eta_M^2}+\frac{4a^2}{\alpha_1^2}\right]-\frac{g^2}{\delta^2}\left[\frac{4(1+a)^2}{\alpha_0^2}+\frac{(1+2a)^2}{\eta_M^2}+\frac{a^2}{\eta_S^2}+\frac{4a^2}{\alpha_1^2}\right]}. \tag{A2}$$

Expressions similar to these for δ and σ have been given by Caglioti, Paoletti & Ricci (1960) and Caglioti & Ricci (1962) for the case when there is collimation on the detector. However, care must be exercised in reducing their expressions to these. Their expression for $B_{\frac{1}{2}}$ will be our σ if the detector collimation parameter is made large, and their $A_{\frac{1}{2}}$ will be our δ if this parameter is made small. There is no equivalent expression for g.

References

ARNDT, U. W. & WILLIS, B. T. M. (1966). *Single Crystal Diffractometer*, p. 265. Cambridge Univ. Press.
CAGLIOTI, G. (1964). *Acta Cryst.* **17**, 1202.
CAGLIOTI, G., PAOLETTI, A. & RICCI, F. P. (1958). *Nucl. Instrum. Meth.* **3**, 223.
CAGLIOTI, G., PAOLETTI, A. & RICCI, F. P. (1960). *Nucl. Instrum. Meth.* **9**, 195.
CAGLIOTI, G. & RICCI, F. P. (1962). *Nucl Instrum. Meth.* **15**, 155.
CAGLIOTI, G. & TOCCHETTI, D. (1964). I. A. E. A. International Symposium on the Inelastic Scattering of Neutrons, Bombay.
CAGLIOTI, G. & TOCCHETTI, D. (1965). *Nucl. Instrum. Meth.* **32**, 181.
COOPER, M. J. & NATHANS, R. (1968). *Acta Cryst.* A**24**, 481, 619.
WILLIS, B. T. M. (1960). *Acta Cryst.* 13, 763.
WILLIS, B. T. M. (1969). *Acta Cryst.* A**25**, 277.