In this structure (Fig. 1) the cadmium ions have roughly octahedral coordination. The octahedra occur in pairs, each pair sharing the face which lies in the mirror plane. All octahedra share edges with both neighbours in the **c** direction. Finally, the infinite double strings thus formed share corners with 4 neighbouring strings. Hydroxyl groups (1), (2) and (3) are bonded to 4, 2 and 3 cadmium ions respectively. The bond distances are given in Fig. 1.

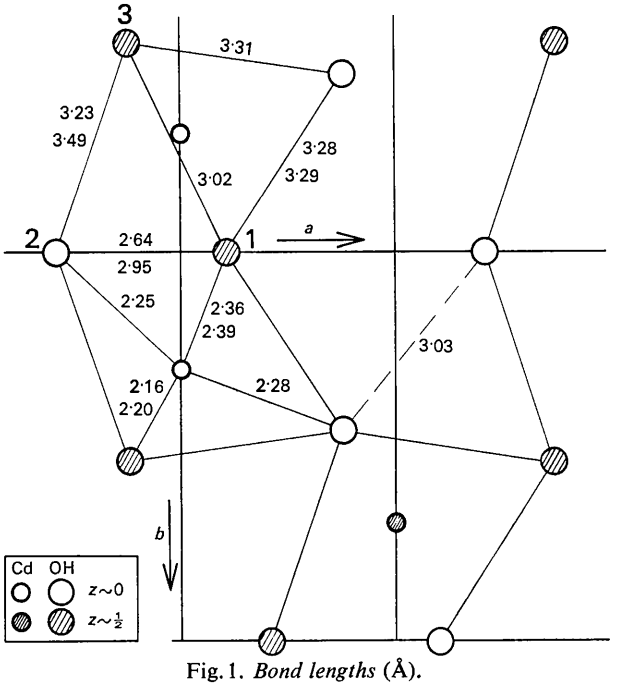

Fig. 1. *Bond lengths* (Å).

The r.m.s. errors in the positions are estimated to be 0·04 Å for the oxygen atoms and 0·01 Å for cadmium. The deviations of z from 0 or ½ are insignificant except for OH(2). This deviation was already apparent as an elongation of the corresponding maximum in the difference Fourier synthesis. It is the only structural aspect preventing the symmetry from becoming orthorhombic (*I*2*mm*); its cause may be a constraint resulting from the – unknown – proton configuration.

I wish to thank Dr Oswald for valuable criticism, Drs Visser and Ir W. Peterse for taking care of all automatic computations, and Ir B. Tideman for his cooperation in the early stages of this investigation.

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Uncertainties in crystal size computed from the standard deviation of the X-ray line breadth.

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(*Received* 7 *October* 1965)

The breadths of X-ray diffraction lines which are used in the Scherrer equation for computing the sizes of small crystals are usually either the half-breadth or the integral breadth. Recently, it was proposed by Pitts & Willets (1961, 1965) that the standard deviation be used. They defined the breadth as twice the standard deviation, 2σ, which is obtained from the variance, σ^2. The variance is defined by the equation:

$$\sigma^2 = \frac{\int_{-\infty}^{\infty} y^2 I(y)dy}{\int_{-\infty}^{\infty} I(y)dy},$$

in which I is the X-ray intensity and y is twice the Bragg angle. Since the theoretical diffraction functions for small crystals have asymptotic values of $(1/y^2)$ at large values of y (Wilson, 1962), the variance and standard deviation do not have finite values. If the range of integration is restricted to a finite value, then this difficulty can be avoided. Using this approach, Tournarie (1956) discussed some theoretical aspects of the use of the variance as a measure of line breadth. He required that the breadth be expressed in terms of σ^2/L, where the integration was restricted between the specific limits $-L$ and $+L$. Langford & Wilson (1963) used a variance measurement of line breadth for specific ranges of integration for a few reflections from metal powders. Their preliminary measurements on line profiles at small Bragg angles indicated that the variance function could be made linear as a function of the range of integration over a considerable change in the range of integration but only by properly choosing the background level. It is evident that the approach taken by Langford & Wilson is workable, but it is not clear that the added effort leads to more reliable results than are obtained by using the simpler half-breadth or integral breadth.

The approach used by Pitts & Willets to achieve finite, reproducible values of standard deviation was simply to set subjectively a baseline (for zero intensity). Since no theoretical values of the Scherrer coefficient were available for this procedure, they deduced an empirical value of 1·44 for small monodisperse cubes whose size was known from electron-microscopic measurements. The amount of error which can enter this subjective type of measurement will

be indicated by the following computation which shows that the correct Scherrer coefficient for this measurement is actually 0·69. This conclusion is based on the fact that for small cubes the diffraction function for $h00$ reflections is given by Murdock (1928, 1930, 1943) as $I(y)=\sin^2(ay)/(ay)^2$. This function goes to zero at $y=\pm\pi/a$. Although there are additional peaks at larger values of y, none of them is as high as 5 % of the primary maximum. On this account, it would only be reasonable experimentally and theoretically to terminate the variance integral at the limits $y=\pm\pi/a$. Such a diffraction function has breadths which are $2\sigma=1{\cdot}05\times 2/a$, $\beta_{1/2}=1{\cdot}38\times 2/a$, and $\beta_I=1{\cdot}44\times 2/a$. Since the Scherrer coefficient for the half-breadth for this case is given by Murdock (1930) as 0·90 and for the integral breadth by Stokes & Wilson (1942) as 1·00, then the Scherrer coefficient for the standard deviation measurement should be (by eliminating $\lambda/V^{1/3}\cos\theta$ from the Scherrer equations) $K_{1/2}2\sigma/\beta_{1/2}=0{\cdot}69$, compared to Murdock's value, and $K_I 2\sigma/\beta_I=0{\cdot}73$, compared to Stokes & Wilson's value. The slightly larger value obtained by using the Scherrer coefficient given by Stokes & Wilson is caused mostly by our neglecting the area lost from the integral breadth by truncation. The value 0·69 is remarkably different from the value given by Pitts & Willets (1961, 1965) of 1·44. Although they consider that the consistency of their experimental results shows the standard-deviation method to be suitable for line-broadening measurements, the discrepancy between the value of 1·44 for the Scherrer coefficient and our computed value of 0·69 shows what a large subjective factor there may be in the experimental determinations.

Table 1. *Line breadths for Cauchy function with baseline placed at different heights*

Baseline position, T	Line breadth $\beta_{1/2}$	β_I	2σ
$\pm 3/a$	$1{\cdot}81\times 1/a$	$2{\cdot}11\times 1/a$	$1{\cdot}89\times 1/a$
$\pm 4/a$	1·88	2·31	2·28
$\pm 5/a$	1·93	2·46	2·62
$\pm\infty$	2·00	3·14	∞

Uncertainty of the baseline position in determinations of line breadth is frequently the source of some error. The extent to which uncertainty in the baseline may affect the determination of line breadth can be illustrated by any of a number of functions. For this purpose we choose the Cauchy distribution, $I(y)=1/(1+a^2y^2)$, which was found by Schoening and his co-workers (1952) to represent quite accurately the shape of their corrected experimental diffraction lines. Such a curve is shown in Fig. 1. The integral breadth and half-maximum breadth of this function are easily obtained but the variance does not have a finite value. However, if the baseline is moved up slightly, a truncated Cauchy function results which does have a finite value of variance. Such a function may be written as $I(y, T)=1/(1+a^2y^2)-1/(1+a^2T^2)$ for values of y in the interval $-T\leq y\leq T$, and the value is made zero when y is not in this interval. The various values of line breadth obtained from this function are given in Table 1. It is seen that the half-breadth changes by only a small amount with different values of T, the value of integral breadth changes somewhat more, and the standard deviation changes quite rapidly. Since the position of the baseline is always somewhat uncertain in a diffraction experiment, a preference for the use of the half-breadth rather than the integral breadth has been expressed for the cases of recording the diffraction lines both photographically (Berry, 1947) and by a Geiger counter (Alexander & Klug, 1950). Since the value of the standard deviation depends so strongly on the position of the baseline, it appears to be the least reliable method of measuring line breadth.

In view of the subjective nature of the standard deviation as a measure of line breadth and the consequent uncertainty in the value of Scherrer coefficient which is to be used, it is concluded that the method is not as satisfactory as other methods for measuring the breadths of diffraction lines.

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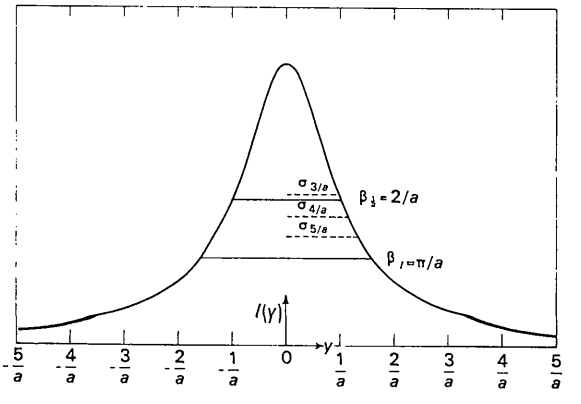

Fig. 1. The Cauchy distribution: $I(y)=1/(1+a^2y^2)$. The half-intensity breadth, $\beta_{1/2}$, and integral breadth, β_I, have finite values; but the standard deviation is infinite, except when the interval of integration is restricted by setting the baseline at values of $I(y)$ where $y=3/a$, $4/a$, $5/a$ *etc.*