through only the preliminary stages of a structure determination in order to arrive at an approximate structure, and not to perform a complete structure determination.

If this structure contains mirror planes then packing arguments dictate that all atoms must lie in these mirror planes. (The metallic radii, for coordination number 8 (Pauling, 1947), are: U, 1·463 Å; Ru, 1·283 Å). This is consistent with the observation, from the Weissenberg photographs, that the $h0l$ layer is identical in appearance to the $h2l$ layer but not to the $h1l$ layer. If the space group is assumed to be centrosymmetric then it must be either $P2/m$, with both mirror planes having the same atomic composition (since $F(0k0)$ was observed $=0$, for k odd), or $P2_1/m$.

$H0L$ and $H\frac{1}{2}L$ Harker sections were calculated using an IBM 650 computer and are shown in Fig. 1(*a*) and (*b*). (In both Figs. contours are drawn at the same equal arbitrary intervals. Negative contours are omitted.) A possible solution can be obtained by placing (unidentified) atoms at roughly

$$(x, y, z;\ x, y+\tfrac{1}{2}, z+\tfrac{1}{2}) + ((n/3), 0, 0;\ (2n+1)/(6), 0, \tfrac{1}{2})\ ,\quad n=0, 1, 2\ .$$

This arrangement of atoms may be placed into $P2/m$ by putting a 2-fold axis at $x=0$, $z=0$ or $x=\frac{1}{12}$, $z=\frac{1}{4}$, or into $P2_1/m$ by putting a 2-fold screw axis at $x=\frac{1}{12}$, $z=0$ or $x=\frac{1}{6}$, $z=\frac{1}{4}$. These four cases are exhaustive. In order to locate the atoms of U and Ru structure factors (trigonometric part only) were calculated for all possible ordered arrangements, consistent with the symmetry, for each case, and compared qualitatively with the observed data.

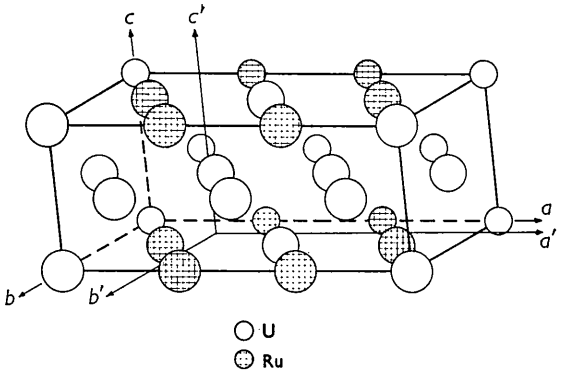

Fig. 2. Suggested atomic packing in U_2Ru. (The size of the circles represents relative distance from the observer.)

The atomic assignments shown in Fig. 2 give the best agreement between the calculated and observed structure factors (Table 2). This configuration can be placed into $P2/m$ by placing the origin at $x=y=z=0$ (axes abc) or into $P2_1/m$ by placing the origin at $x=\frac{1}{12}$, $y=-\frac{1}{4}$, $z=0$ (axes $a'b'c'$). However, the above structure is only approximate as suggested by the Harker sections and as evidenced by the fact that the given atomic positions lead to a calculated intensity of zero for reflections with $h+k=2n+1$ whereas a few are observed as very weak reflections.

Table 2. *Qualitative comparison of observed and calculated structure factors*

Class of reflections		$\|F_o\|$	$\|F_c\|$
$0k0$	$k_{\rm odd}$	0	0
	$k_{\rm even}$	*vs*	912
hkl	$(h+k)_{\rm odd}$	*vw*	0
$k_{\rm even}$	$h=6n,\ l_{\rm even}$	*vs*	912
	$h=6n,\ l_{\rm odd}$	*m*	192
	$h=6n\pm2$	*w*	96
$k_{\rm odd}$	$h=6n+3,\ l_{\rm even}$	*m*	192
	$h=6n+3,\ l_{\rm odd}$	*vs*	912
	$h=6n\pm1$	*w*	96

The structure may be considered to consist of approximate layers of atoms parallel to (001). Alternate layers contain only U atoms with the intermediate layers having the atomic composition $\frac{1}{3}$U, $\frac{2}{3}$Ru.

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References

Dwight, A. E. (1961). To be published.
Heal, T. J. & Williams, G. I. (1955). *Acta Cryst.* **8**, 494.
Pauling, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.
Rough, F. A. & Bauer, A. A. (1958). *Constitution of Uranium and Thorium Alloys.* BMI 1300.

Acta Cryst. (1961). **14**, 1302

The determination of crystallite size from diffraction profiles using standard deviation as a measure of breadth.*

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Methods of X-ray crystallography provide a suitable means of obtaining information about the internal structure of grains in photographic emulsions (Herz, 1960). In particular, the measurement of line broadening can give information about the presence of small crystallites and lattice distortion (Waidelich, 1958). We report here the outcome of some preliminary investigations into this problem.

The unambiguous interpretation of measurements of line broadening is difficult, especially when both distortion and size effects are present together. This was shown

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by Hauk & Hummel (1956) who used the Fourier-coefficient method of Warren–Averbach (1950), the method due to Kochendörfer (1944) and the Hall (1949) method to interpret the same samples, obtaining widely discrepant results. It was therefore clear that an important part of the investigations would be a reexamination of the problem of interpreting line-profiles.

The relationship between the instrumental profile, the diffraction broadening and the observed profile is given by the well-known convolution integral (Jones, 1938)

$$h(x) = \int f(y)g(x-y)dy, \tag{1}$$

where $h(x)$ is the observed broadened profile, $g(x)$ is the instrumental profile, and $f(x)$ is the diffraction broadening. Unless the functions $f(x)$ and $g(x)$ have certain special forms, the derivation of the diffraction profile integral breadth from $g(x)$ and $h(x)$ is not simple. Although in principle this difficulty is avoided by the Fourier-analysis method of Stokes (1948), the uncertainty about the point of merging of the line into the background (Hauk & Hummel, 1956) is in practice a severe limitation, particularly having regard to the amount of labour involved in the method. Some simpler method was therefore sought, and a study of the convolution integral showed that if σ_f, σ_g and σ_h are the standard deviations of $f(x)$, $g(x)$ and $h(x)$ respectively, then the relationship

$$\sigma_f^2 = \sigma_h^2 - \sigma_g^2 \tag{2}$$

holds. This suggested that the breadth of a line might be suitably defined as 2σ, enabling the diffraction breadth $2\sigma_f$ to be derived readily from the experimental determination of σ_h and the standard deviation of the instrumental profile σ_g. The relation (2) is exact, and its independence of the form of the functions makes it unnecessary to separate the $\alpha_1\alpha_2$ components. It was decided to apply this result in experiments designed to check the basic theory of broadening due to crystallite size.

This additive property of the variances has also been noted by Spencer (1949) and Ladell, Parrish & Taylor (1959). The latter also investigated the effect of truncation to define the limits of the profiles.

Samples of photographic emulsion grains were prepared by a technique developed by Dr R. W. Berriman of these laboratories. These were pure silver–bromide crystals of cubic habit, grown in gelatin solution, to produce samples having a narrow size spread about a series of different mean values. Coatings on a flexible support were used as specimens. When the growth was continued to form larger crystals (in the range 3,000 to 10,000 Å in linear dimension) the X-ray diffraction lines produced from these showed no greater broadening than did annealed control specimens. It was assumed that this also indicated an absence of lattice distortion in the size range used in these experiments, namely 500 to 1,700 Å, at least within the limitations of the technique.

X-ray patterns were made from these specimens using a symmetric quartz monochromator and focusing camera in conjunction with a Hilger micro-focus diffraction unit. Using an annealed control specimen, the apparatus gave $\alpha_1\alpha_2$ resolution at about 13°(θ). The intensity between the α_1 and α_2 peaks was a half of the α_2 peak maximum at this Bragg angle. This is believed to be an improvement on the resolution obtained at such a low angle with customary equipment.

Ten diffraction lines in the θ range of approximately 15° to 74° were examined for each specimen and the instrumental broadening was derived from patterns given by the largest grains (10,000 Å). This broadening was then subtracted in accordance with equation (2). The values of $2\sigma_f \cos\theta$ were found to be independent of θ for each specimen within the limits of the experimental error. This result is in agreement with the theory of crystallite-size broadening, in which the breadth β is given by

$$\beta = k\lambda/(L\cos\theta)\ , \tag{3}$$

where λ is the X-ray wavelength, L is the cube root of the volume of a single crystal and k is the Scherrer constant. The value of L was found from electron micrographs of each specimen and compared with that calculated from equation (3) using a value of 1·44 for k. (This was the value of k calculated to give agreement for the 750 Å crystals.) The comparison is shown in Table 1.

Table 1. *Comparison between values of L*

From electron micrographs	From equation (3)
480 Å	490 Å
650	640
750	750
900	870
1700	1810

It will be seen that the agreement is satisfactory when the standard deviation definition of breadth is used. Work is in progress to evaluate the appropriate theoretical value of k. It is hoped that this work will be published later, together with an account of additional experiments involving distortion.

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References

Hall, W. H. (1949). *Proc. Phys. Soc.* A, **62**, 741.
Hauk, V. & Hummel, C. (1956). *Z. Metallk.* **47**, 254.
Herz, R. H. (1960). *J. Phot. Sci.* **8**, 2.
Jones, F. W. (1938). *Proc. Phys. Soc.* A, **166**, 16.
Kochendörfer, A. (1944). *Z. Kristallogr.* A, **105**, 393.
Ladell, J., Parrish, W. & Taylor, J. (1959). *Acta Cryst.* **12**, 561.
Spencer, R. C. (1949). *J. Appl. Phys.* **20**, 413.
Stokes, A. R. (1948). *Proc. Phys. Soc.* **61**, 382.
Waidelich, W. (1958). *Z. angew. Phys.* **10**, 525.
Warren, B. E. & Averbach, B. L. (1950). *J. Appl. Phys.* **21**, 595.