nature and orientation of the tetragonal crystal while hot turned out to be exactly the same as in the first case. However, in this second case, since the crystal reverted to the monoclinic structure on cooling, it was possible to obtain some information on the reverse transformation.

As soon as a crystal was heated above $\sim$1200 °C, tetragonal reflections could be observed. There were, of course, three orthogonal axes, and one of these, as predicted, was parallel to the original monoclinic b axis. However, instead of one axis being parallel to monoclinic c and one 9·2° from a, the two tetragonal axes split the difference, *i.e.* the 90° tetragonal angle was inscribed, approximately symmetrically, within the larger monoclinic angle, β. Although somewhat unexpected, this becomes plausible when one considers the next result. The tetragonal crystal was a triplet, and each axial direction gave a reflection both for a^* and for c^*.

Removal of the flame resulted in quenching of the crystal, and the one that was tied with wire reverted to the monoclinic structure. Its reflections were now broad and of low peak height. The extent of twinning was considerably enhanced, and in addition the crystal now consisted of a number of slightly misoriented blocks, still parallel along the original **b** direction but rotated out of register in the $a-c$ plane over a range of about 10°. Since the tetragonal axes must rotate 4 to 5° in the a–c plane to become the monoclinic a and c axes, the various partners of the tetragonal trilling must have rotated their respective axes in opposite senses, thus giving rise to the 10° spread in orientation.

The observational evidence does not furnish a clear decision as to whether the transformation is of the brittle martensitic or the true martensitic type (Wolten 1963), but favors the latter point of view.

If the transformation is martensitic, it should be possible, in principle, to apply the theory of zero average strain by Wechsler, Lieberman & Read (1953) for the calculation of the habit plane. The term 'habit plane', as used here, does not refer to the crystal habit but denotes a crystallographic plane which, in a martensitic phase transformation, is common to both lattices and remains undistorted and unrotated through the transformation. The calculation cannot, at present, be carried out for lack of certain additional data. However, the observations plainly suggest that the habit plane is the monoclinic (101) which becomes (101), (110), and (011) of the tetragonal trilling, indexed on the double cell. The misfit of the lattice parameters is relieved by twinning.

The data that are lacking for the application of the theory are the lattice parameters of the monoclinic phase at the temperature of the transformation. The tetragonal parameters were measured directly by Teufer (1962) at 1250 °C, a little above the transformation range. The lattice parameters of the monoclinic phase are accurately known only at room temperature*. A mean (bulk) coefficient of thermal expansion for zirconia is known (Fulkerson, 1960), but if this is applied to the room temperature cell volume and extrapolated to 1250 °C, a volume difference of about 1 % between the phases is obtained, which is inconsistent with the observed bulk volume change of the transformation of about 7 % (Geller & Yavorsky, 1945). It is clear, therefore, that the coefficient of expansion of the monoclinic phase must change rapidly above 1000 °C. This effect would distort dilatometric curves of the transformation and explain the discrepancy between dilatometric and X-ray transformation temperatures noted by Duwez & Odel (1950).

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* Lattice parameters for monoclinic zirconia were determined by McCullough & Trueblood (1959) using a single crystal of baddeleyite and by Adam & Rogers (1959) using synthetic ZrO_2 powder. The discrepancy between the two sets of data is very slight but results in significant differences in calculated interplanar spacings at low diffraction angles. The spacings observed by the author on many occasions, as well as those reported by Ferguson (1960), for synthetic ZrO_2 consistently agreed with those calculated from the lattice parameters of Adam & Rogers.

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Determination of particle size and strain in a distorted polycrystalline aggregate by the method of variance.

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Recent work by Tournarie (1956 *a*, *b*) and Wilson (1962 *a*, *b*, *c*; 1963) has clearly established the usefulness of the variance of an X-ray diffraction line profile due to an aggregate of distorted crystallites as a measure of the particle size and strain of the aggregate. Langford & Wilson (1963) and Halder & Mitra (1963) have described practical methods of determining particle size and strain from the study of variances of the line profiles. Both the methods are extremely dependent on the choice of the range over which the variance has been determined. The present work describes a graphical method in which this difficulty has been removed.

Wilson (1962 *b*) has shown that, if the entire line broadening is due to particle size effect, the variance of the line profile in 2θ,

Table 1. *Particle size and strain of aluminum at different stages of annealing*

	Particle size (Å)			Strain x10^3		
Temp. of annealing (°C)	Present method	Integral breadth method	Warren & Averbach method Gauss strain	Present method	Integral breadth method	Warren & Averbach method Gauss strain
30	3258	4023	360	1·23	1·02	6·51
100	4112	4219	440	0·86	0·61	3·27
200	4545	4865	740	0·52	0·37	1·19
300	5624	6423	1040	0·47	0·30	0·38

$$W = \frac{K\lambda\sigma}{2\pi^2 t\cos\theta} - \frac{L\lambda^2}{4\pi^2 t^2\cos^2\theta} \tag{1}$$

where θ is the Bragg angle, t the particle size, λ the wave length used, σ the angular range (in 2θ) over which the intensity distribution is appreciable, and K and L are constants for a given particle shape. Wilson (1963) has further shown that if the broadening is due to strain only,

$$W = 4\tan^2\theta\langle e^2\rangle \tag{2}$$

where $\langle e^2\rangle$ is the variance of the strain.

Attributing the broadening to both particle size and strain, we can write, because of the additivity property of the variance,

$$W = \frac{K\lambda\sigma}{2\pi^2 t\cos\theta} - \frac{L\lambda^2}{4\pi^2 t^2\cos^2\theta} + 4\tan^2\theta\langle e^2\rangle\,. \tag{3}$$

For isotropic substances like aluminum and tungsten, the particle shape can be taken to be spherical, for which $K = (9\pi/16)^{\frac{1}{3}}$ and $L = 0$ (Wilson, 1962 *b*) for all reflexions. For other cases, particle size and strain can be determined for a particular direction, *e.g.* 111 and 100 for f.c.c. crystals like copper, nickel *etc.* This can be done by studying multiple reflexions like 111, 222 and 200, 400 as has been done for the method of integral breadths by Michell & Haig (1957), Smallman & Westmacott (1957) *etc.* By a proper change of axes, each of these sets of reflexions can be treated as $00l_0$, $002l_0$, ... *etc.* reflexions for each of which $K = 1$ and $L = 0$ (Wilson, 1962 *b*). With these assumptions, equation (3) can be written

$$W = \lambda\sigma/2\pi^2 p\cos\theta + 4\tan^2\theta\langle e^2\rangle \tag{4}$$

where $p = t/K$ is the apparent particle size. From this, we have

$$\frac{W\cos\theta}{\lambda\sigma} = \frac{1}{2\pi^2 p} + \frac{n^2\lambda}{\sigma\cos\theta}\cdot\frac{\langle e^2\rangle}{a^2} \tag{5}$$

where a is the lattice parameter and $a/n = \lambda/2\sin\theta$. A plot of $W\cos\theta/\lambda\sigma$ against $n^2\lambda/\sigma\cos\theta$ will thus be linear with a slope and intercept which will give $\langle e^2\rangle/a^2$ and $1/2\pi^2 p$ respectively. From these p and $\langle e^2\rangle^{\frac{1}{2}}$ can be determined easily. For different values of σ, there will be different values of W (Langford & Wilson, 1963) but corresponding to each set of (W, σ) values, there will be a separate point on the linear plot represented by equation (5). Fig. 1 shows such plots for super-pure aluminum cold drawn at 30 °C (reduction 99%) and subsequently annealed for half an hour at each of the temperatures 100 °C, 200 °C and 300 °C respectively. The resulting least-square-fitted values of p and $\langle e^2\rangle^{\frac{1}{2}}$ are shown in Table 1 along with the same values obtained by the methods of Williamson & Hall (1953) and Warren & Averbach (1950).

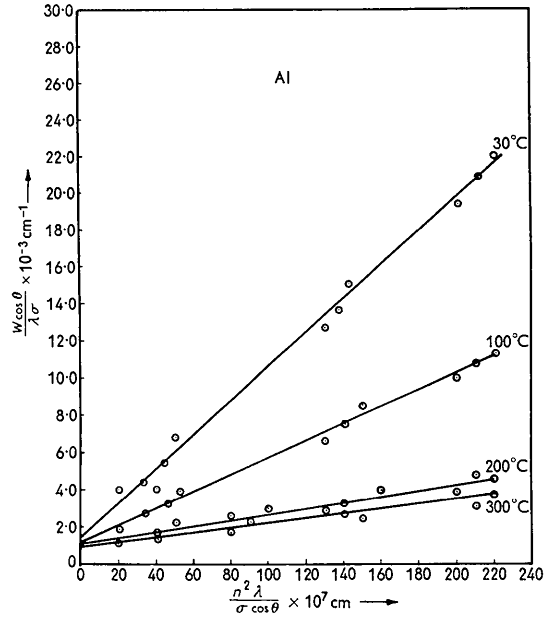

Fig. 1.

It is observed that the values obtained by the present method are intermediate between those obtained by the other two methods but nearer to those obtained by the method of integral breadths due to Williamson & Hall (1953).

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