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Automatic diffractometer programs: the estimation of intensity errors.

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The paper by Cetlin & Abrahams (1963) describing the PEXRAD programs assumes that in the absence of systematic errors, only statistical counting errors are present in the F^2 values obtained from the measured intensities. This will only certainly be true if absorption errors are negligible, *i.e.* if μR and $\sigma(R)/R$ for the spherical crystals employed are small enough. Typical maximum values are 0·1 for μR and 2·5% for $\sigma(R)/R$ (Jeffery & Rose, 1964). For such crystals the procedure employed will be adequate, although the test for the presence of other errors by calculating $V(\bar{F}^2)$ for symmetry-related reflexions is of doubtful validity in the case of monoclinic symmetry (only 2 symmetry-related reflexions) and completely indeterminate in the case of triclinic symmetry. This has, in fact, now been found in practice (Abrahams, 1964*a*) and the large and improbable variation in $V(\bar{F}^2)$ which can arise with monoclinic crystals is illustrated by Table 1 of that paper.

For those crystals where absorption errors are not negligible (a large class for Cu $K\alpha$ radiation and including most inorganic crystals even with Mo $K\alpha$ radiation), Abrahams (1964*a*) assumes that errors arising from variations in effective radii (r) from the mean radius ($\bar{r}$) for an imperfect sphere, are 'systematic and anisotropic'. That such variations can be partly anisotropic (owing, for instance, to a tendency towards an ellipsoidal shape) is certainly true, but in the crystals investigated by Jeffery & Rose (1964) no such tendency could be directly detected and the agreement between experimental and theoretical results based on the assumption of random variation in r leaves little room for such anisotropic effects. According to Abrahams (1964*b*) the variations in r which he and his co-workers found have always been related to the crystal structure and in this case the variations would, of course, be justifiably regarded as systematic. But in this case such variations may not be fully revealed, if at all, by $V(\bar{F}^2)$. Take the case of an imperfect sphere which is an ellipsoid of revolution about c for a tetragonal crystal. This would, in fact, be the most likely relation to the structure in such a case. For rotation about c all symmetry-related reflexions would have identical relations to the ellipsoid and there would be no differences between them arising from the shape of the crystal. Nevertheless, in general, r would be different from $\bar{r}$ and a systematic error would occur in $\bar{F}^2$ which would not show up in $V(\bar{F}^2)$ at all. For rotation about a only a small part of the error would show up. It is therefore very desirable to be able to produce imperfect spheres with random rather than systematic variations in r. In such cases for orthorhombic and higher symmetry $V(\bar{F}^2)$ should be used in place of $\sigma^2(\bar{F}^2)$ for forming weights, and the variance ratio recorded as a check on consistency. In the case of monoclinic and triclinic symmetry $V'(\bar{F}^2)$ should be estimated from $\sigma(R)$, μR and θ (Jeffery & Rose, 1964).

These alternative procedures can be built into one program and the procedure required and the necessary data for calculating $V'(\bar{F}^2)$ fed in beforehand. This procedure will deal with random errors of shape, counting statistics and instability of the X-ray source and recording system and to some extent with systematic shape errors. There are a number of strictly systematic errors (Abrahams, 1964*a*) of which errors in μ and $\bar{r}$ will normally be the most important. While it is very desirable to have an estimate of such errors it would seem better to keep them separate from the random errors because their effect on the accuracy of the final structure determination is almost certainly different.

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Structure de l'aluminate tricalcique hydraté, $3CaO.Al_2O_3.6H_2O$.

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La structure cristalline de l'aluminate tricalcique hydraté $3CaO.Al_2O_3.6H_2O$ a déjà été étudiée en 1941 par Flint, MacMurdie & Wells (1941). Leur étude a été faite par analogie avec la grossularite au moyen de la méthode des poudres. De plus, une communication concernant la détermination dans l'aluminate hydraté, de la position des atomes d'hydrogène par diffraction neutronique et résonance magnétique nucléaire, a été présentée par Cohen-Addad, Ducros, Durif-Varambon, Bertaut & Delapalme (1963) au VIe Congrès International de Cristallographie.

Dans le présent travail, nous nous sommes proposé de