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## The reliability of equi-inclination counter-diffractometer data.

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Present-day crystallography is increasingly concerned with the refinement of crystal structures to a high degree. In this laboratory, final values for the disagreement factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for silicate structures have commonly ranged from the order of 9% to as low as 4%. This level of agreement may perhaps begin to approach the overall reliability of the data. Very few studies of the consistency of diffractometer data have been reported. Without this information, it is not possible to assess the significance of low disagreement factors.

The majority of the crystal structures investigated in this laboratory have been of fairly low symmetry. Recently, however, the crystal structure of tetrahedrite, $Cu_{12}Sb_4S_{13}$, was investigated and refined to $R = 3{\cdot}9\%$. This mineral is isometric, and has space group $I\bar{4}3m$. The independent intensities are contained within 1/48 of reciprocal space (*i.e.* $h \geq k \geq l$). Each general reflection therefore occurs as 24 equivalent mates, excluding those which are related by Friedel's Law. The comparison of structure factors required by symmetry to be equivalent thus provided an opportunity to examine ordinary diffractometer data for random and systematic error.

The diffracted intensities were obtained from a specimen of 0·144 mm radius ($\mu_l r = 7{\cdot}39$ for Cu $K\alpha$) which was spherical to $\pm 1{\cdot}7\%$. A proportional counter was used as a detector. The associated electronics were standard Norelco equipment and included pulse-height analysis circuitry. Integrated intensities were determined by recording the total number of counts accumulated as the crystal was rotated through 6° $\varphi$. Background intensity was counted for 100 sec on either side of the diffraction peak, and a suitable deduction of integrated background was made from the measured integrated intensity.

Using a representative sample of reflections, ranging from the weakest detectable to those with a maximum intensity of 2,000 counts per second, three varieties of checks were performed.

(1) Measurement of certain reflections was repeated over a period of several weeks. The degree of agreement of these measurements is affected by reproducibility of the diffractometer settings ($\mu$, $\nu$, $\varphi$, $\Upsilon$), counting statistics, and drift in the electronic equipment.

(2) Equivalent reflections of the form *hkl* and *khl* were examined within a given level, *l*. The agreement between these data involves the above errors, plus variations in the absorption correction required, because of deviations of the crystal shape from a true sphere.

(3) Equivalent reflections of the form *hkl* and *hlk*, *lhk* were compared between different levels. Agreement between these data is affected by all of the above errors, plus systematic errors incurred from level to level. Examples of the latter are errors in the computed values of $\mu$, incorrect evaluation of Lorentz and polarization factors, or differences in the manner in which the white-radiation streak was crossed.

All of the sets of reflections compared in these tests are related by the true point-group symmetry of the crystal. Anomalous dispersion, which is appreciable, therefore does not affect the comparisons.

The results of the study are summarized in Table 1. The deviation between equivalent structure factors occurring in different levels exceeds the reproducibility of the data. This deviation is, however, of the same order of magnitude as the deviation between structure factors occurring within the same level. The main source of error in the set of structure factors obtained for tetrahedrite is therefore most likely the uncertainty in the absorption correction. The 1·7% variation in radius causes an uncertainty in the transmission factor which varies from 5·4% at $\theta = 0°$ to 1·8% at $\theta = 90°$. This would result in a variation of from 2·7 to 1% in the structure factors, which is about the right order of magnitude to account for the increase in error of tests (2) and (3) above the reproducibility of the data. It would appear that with a more favorable value of $\mu_l r$, and with an accurate correction for absorption, standard equi-inclination counter diffractometry is capable of providing a set of structure factors with an over-all precision of better than 2%.

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Table 1. *Comparison of equivalent isometric structure factors for tetrahedrite*

| Test | Range of intensities (integrated peak intensity: integrated background intensity, counts $\times 10^4$) | Range of deviations from mean, $F^2$ | r.m.s. deviation from mean, $F^2$ | Range of deviations from mean, $F$ | r.m.s. deviation from mean, $F$ |
|---|---|---|---|---|---|
| Reproducibility ($F_{hkl}$, $F_{hkl}$) | 8·29/2·13–1·17/6·32 | 0·032–5·7% | 2·31% | 0·016–2·8% | 1·15% |
| Symmetry within a given level ($F_{hkl}$, $F_{khl}$) | 8·29/2·13–0·103/0·751 | 0·13–14·9% | 5·82% | 0·066–7·5% | 2·92% |
| Symmetry between levels ($F_{hkl}$, $F_{hlk}$, $F_{lhk}$) | 8·29/2·13–0·103/0·751 | 0·86–11·9% | 5·63% | 0·43–6·0% | 2·82% |