

been observed because of the enormous increase of the elastic strain energy due to the higher density of α octahedra. Instead, phases with $\{103\}$ CS planes, but with larger n values, are expected to form. Moreover, phases with $n = 8, 9, 10, 12, 14$ and 16 are more stable than others because of the better fit between the octahedra of the different layers.

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The Influence of Systematic Errors in Crystal Structure Refinements Using Guinier Camera X-ray Intensity Data

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Abstract

The effect of systematic errors on the reliability of crystal structure refinements based on Guinier camera powder data has been investigated. Three structures were refined with Guinier integrated intensity data, and the results are compared with published single-crystal determinations. In each case, the effect of systematic errors could be adequately corrected by an overall temperature factor, though in one case a significant decrease in the residual resulted from the inclusion of an idealized specimen absorption correction. Atomic temperature factors determined from the Guinier data were highly correlated with the correction terms: atomic coordinates were insensitive to the corrections,

and agreed well with the corresponding single-crystal values.

Introduction

Structure determination from powder data has been stimulated by the development of the profile refinement technique (Rietveld, 1967, 1969). Applied originally to neutron diffraction data, it has been extended to Guinier camera X-ray powder data by Malmros & Thomas (1977). The technique reduces the problem of overlapping of non-equivalent reflexions, common in powder data, but there is some doubt as to whether current profile refinement programs estimate the stan-

dard deviations of the parameters correctly (Sakata & Cooper, 1979).

The relation between Guinier integrated intensities and structure factors has been given by Sas & de Wolff (1966). In addition to the usual Lorentz, polarization and multiplicity factors, the variation with Bragg angle of the specimen-to-film distance and the obliquity of the diffracted beams to the film plane are taken into account. The obliquity factor requires a knowledge of the absorption coefficient of the film emulsion for the radiation used, but this is easily determined.

It is generally assumed that absorption by the specimen may be a major source of systematic error in Guinier intensity data. Sas & de Wolff (1966) give an idealized correction for this which assumes that the specimen is uniform and flat, but it is common to treat the effects of absorption as though they arose from an overall isotropic temperature factor (Malmros & Thomas, 1977; Werner, Marinder & Magnéli, 1978; Werner, Salomé, Malmros & Thomas, 1979). This paper examines the applicability of the idealized absorption correction to actual specimens (which are often far from uniform), and the effect of different corrections on the values and precision of the refined parameters.

Three compounds for which single-crystal structure determinations have been published were selected for this study. They were quartz-like germanium oxide, yttrium oxide and potassium chloroplatinate: all have simple structures and give well-resolved Guinier powder patterns suited to the determination of integrated intensities.

Experimental

A specimen of each material was prepared by grinding a sample under methyl chloroform: the particle sizes were estimated by microscopical examination to be <10 μm in each case, though the distribution of sizes varied. The powder was sprinkled on the exposed adhesive surface of transparent Scotch tape mounted on an annular metal support, and excess powder was removed by tapping. The mass of each specimen was determined by weighing the support before and after the addition of the sample: since the area was also known, the mean thickness of the specimen could be calculated. Typical specimens had masses from 0.5–1.0 mg and mean thicknesses from 5–10 μm (*i.e.* comparable with the particle size), but because of the small mass the error in these estimates could be as much as 25%.

The data were collected with an XDC 700 camera of Guinier-Hägg design with Cu $K\alpha_1$ radiation. The reflexions were recorded on Ilfex 90 X-ray film, developed in Phenisol for 6 min at 293 K: after fixing,

the back emulsion of the film was removed. Optical densities were measured with a scanning microdensitometer and recorded on a chart: the peak areas were measured with a planimeter. A semi-empirical correction for the non-linearity of the film response was made by multiplying the measured peak areas by a factor $[1 + (D_m + 2D_b)/6]$, where D_m and D_b are the maximum and background densities above fog. This was derived by assuming a triangular peak shape and multiplying measured densities by a factor $(1 + kD)$ (Werner, 1971): for the film used (one emulsion only) a value of $k = 0.25$ was found to give good correction for measured densities up to about 1.0. The validity of this correction was confirmed when $(I_o - I_c)\sqrt{w}$ vs I_o was plotted for each refined structure and showed no significant correlations.

For each specimen, three or four films with exposures differing by factors of about three were prepared. Cross-scaling between films was carried out by comparing those reflexions with maximum densities lying between 0.2 and 1.0 on a pair of films: the intensity of the monochromatized X-ray beam was not sufficiently stable to allow accurate cross-scaling directly from the exposure durations.

Data analysis

The data were analysed by refining the published single-crystal structures (with any anisotropic temperature factors replaced by equivalent isotropic factors) with the Guinier integrated intensity data and the program *POWDER* (Rossell & Scott, 1975). Reflexions which were theoretically observable but which were too weak to detect were given arbitrary intensities of $\frac{1}{4}$ the weakest measured intensity for the specimen, and included in the refinement. The parameters varied were the scale, an overall isotropic temperature factor, isotropic temperature factors for each atom type in the structure except the heaviest, and the relevant atomic coordinates. To facilitate comparisons, the temperature factor for the heaviest atom was given the value obtained in the corresponding single-crystal study, and was not refined: to the extent that this assumption is valid, the overall temperature factor may be regarded as a measure of otherwise uncorrected angle-dependent systematic errors in the Guinier data.

Intensities were calculated from scattering factors for neutral atoms with corrections for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). The calculations took account of Lorentz and polarization factors, reflexion multiplicities and the camera geometry: the absorption coefficient of the film emulsion for Cu $K\alpha_1$ was determined experimentally to be 0.21, and this value was used in the obliquity correction. Corrections for specimen absorption were

made with the expression of Sas & de Wolff (1966) in the form

$$A = z_0 [\exp(\mu t z) - 1] / z [\exp(\mu t z_0) - 1],$$

where μt = specimen absorption coefficient, $z = \sec \beta - \sec(2\theta - \beta)$, $z_0 = \sec \beta - 1$, and β = camera angle (30° in this case). This form is normalized to unity at the Bragg angle for minimum absorption, *i.e.* when $2\theta = \beta$.

Since an object of the study was to determine the effect of specimen absorption on Guinier intensity data, each structure was refined with three different values of the absorption coefficient. In the first model it was set to zero, so that specimen absorption was represented primarily in the overall temperature factor. In the second, the average absorption coefficient calculated from the specimen mass was used; this is the uniform specimen model. Finally, the absorption coefficient was optimized by trial and error to yield the lowest residual for the refined structure. The weighted residual used, $R_w = \frac{1}{2} [\sum w(I_o - I_c)^2 / \sum w I_o^2]^{-1/2}$ with $w = (I_o + I_{\min})^{-1}$, where I_{\min} is about equal to the weakest reflexion measured, is numerically comparable with the conventional single-crystal residual based on F . *POWDER* does not provide for specimen absorption to be refined directly: in any case, Werner *et al.* (1979) found that in profile analysis the specimen absorption term correlated so highly with the overall temperature factors that it was not possible to refine both simultaneously.

Results

The results of the refinements for each of the three materials are set out in Tables 1, 2 and 3, which include the corresponding single-crystal data for comparison: basic crystallographic data for each material are also shown.

It was observed that the data for potassium chloroplatinate showed no evidence of preferred orientation.

Table 1. *Structure refinement of quartz-like germanium oxide with Guinier camera data*

GeO₂, trigonal, $P3_121$, $Z = 3$.

$a = 4.987$, $c = 5.562$ Å, $\mu(\text{Cu } K\alpha) = 24.0$ mm⁻¹.

	Specimen absorption model			Single-crystal comparison*
	Nil	Uniform	Optimized	
μt	0.0	0.13	0.10	—
B_0	0.83 (9)	0.71 (9)	0.74 (9)	—
$B(\text{Ge})$	0.54	0.54	0.54	0.54 (1)
$B(\text{O})$	0.72 (40)	0.77 (40)	0.76 (40)	1.07 (8)
$\text{Ge}(x)$	0.4522 (9)	0.4522 (9)	0.4522 (9)	0.4513 (1)
$\text{O}(x)$	0.398 (4)	0.399 (4)	0.399 (4)	0.3969 (5)
$\text{O}(y)$	0.300 (3)	0.300 (3)	0.300 (3)	0.3021 (5)
$\text{O}(z)$	0.094 (2)	0.095 (2)	0.095 (2)	0.0909 (4)
R_w (%)	2.17	2.17	2.17	1.9
$N(\text{obs})$	31	31	31	194

* Smith & Isaacs (1964).

Table 2. *Structure refinement of yttrium oxide with Guinier camera data*

Y₂O₃, cubic, $Ia\bar{3}$, $Z = 16$.

$a = 10.6026$ (3) Å, $\mu(\text{Cu } K\alpha) = 54.3$ mm⁻¹.

	Specimen absorption model			Single-crystal comparison*
	Nil	Uniform	Optimized	
μt	0.0	0.29	1.57	—
B_0	-1.04 (12)	-1.35 (11)	-2.60 (9)	—
$B(\text{Y})$	0.98	0.98	0.98	0.98
$B(\text{O})$	1.93 (51)	1.95 (64)	2.15 (37)	1.39
$\text{Y}(x)$	-0.0319 (4)	-0.0320 (4)	-0.0322 (3)	-0.0328 (2)
$\text{O}(x)$	0.389 (3)	0.389 (2)	0.389 (2)	0.389 (1)
$\text{O}(y)$	0.150 (3)	0.150 (2)	0.150 (2)	0.154 (1)
$\text{O}(z)$	0.382 (3)	0.382 (2)	0.381 (2)	0.378 (1)
R_w (%)	3.97	3.55	2.78	8.2
$N(\text{obs})$	41	41	41	220

* Paton & Maslen (1965).

Table 3. *Structure refinement of potassium chloroplatinate with Guinier camera data*

K₂PtCl₆, cubic, $Fm\bar{3}m$, $Z = 4$.

$a = 9.7538$ (4) Å, $\mu(\text{Cu } K\alpha) = 52.1$ mm⁻¹.

	Specimen absorption model			Single-crystal comparison*
	Nil	Uniform	Optimized	
μt	0.0	0.25	0.11	—
B_0	1.59 (14)	1.37 (14)	1.49 (13)	—
$B(\text{Pt})$	1.06	1.06	1.06	1.06 (9)
$B(\text{K})$	2.74 (46)	2.70 (46)	2.72 (45)	2.69 (32)
$B(\text{Cl})$	2.59 (32)	2.53 (32)	2.56 (32)	2.44 (21)
$\text{Cl}(x)$	0.2372 (14)	0.2370 (14)	0.2371 (14)	0.2391 (12)
R_w (%)	3.13	3.14	3.12	7.02
$N(\text{obs})$	28	28	28	75

* Williams, Dillin & Milligan (1973).

tation. This is despite the fact that this material forms thin platelets on grinding (Williams, Dillin & Milligan, 1973), and diffractometer data from a pure sample showed pronounced enhancement (by a factor of about four) of the $h00$ and hhh reflexions, indicating cleavage on the (100) and (111) planes. This supports the claim by Malmros & Thomas (1977) that Guinier data is relatively free from preferred orientation effects.

After each structure had been refined with the optimized correction for specimen absorption, $(I_o - I_c)\sqrt{w}$ for each reflexion (or group of reflexions) was plotted against the Bragg angle of the reflexions. These plots showed that any angle-dependent systematic errors not corrected by the absorption and overall temperature factor were small compared to the random errors.

Conclusions

The results given in Tables 1, 2 and 3 show that the atomic positions derived from Guinier data are insensitive to the specimen absorption model. Differences in

the positions for the different models were insignificant, and in all cases the coordinates derived from Guinier data agreed with the corresponding single-crystal results within the e.s.d.'s. The lower precision of the coordinates derived from Guinier data is primarily a consequence of the limited region of reciprocal space which is sampled, $\sin \theta/\lambda < 0.46 \text{ \AA}^{-1}$: the precision of the data itself is comparable with that of the single-crystal data. Temperature factors correlate highly with the absorption corrections and cannot be determined meaningfully from Guinier data: however, the results suggest that the differences between atomic temperature factors may be physically significant, albeit with rather low accuracy.

The absorption correction calculated for a uniform specimen proved a poor approximation, doing little if anything to reduce either R_w or the magnitude of the overall temperature factor (which is considered to be a measure of uncorrected systematic errors) for the structures refined. In one case, yttrium oxide, the absorption correction with an empirically optimized coefficient did significantly reduce R_w and the e.s.d.'s of the parameters: however, the magnitude of the overall temperature factor increased greatly and the optimized absorption coefficient was more than five times the calculated average value, so that the physical significance of this correction is uncertain.

In practice, it appears possible in many cases to correct effectively for systematic errors, including specimen absorption, by a single overall temperature factor (which may be either positive or negative) as proposed by Werner *et al.* (1979). Good agreement between the model and the data was obtained in this

way for the three structures studied here. However, in some cases an improved fit, and hence more precise parameter estimates, may be achieved by including a correction of the form given by Sas & de Wolff (1966) for specimen absorption. Both these corrections are of an *ad hoc* nature, and are not to be considered as the direct physical consequence of thermal or absorption effects.

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Multiple Bragg Reflections of Neutrons in an Elastically Deformed Single Crystal

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Abstract

The large positive diffraction intensity changes on forbidden (222) planes, which are produced by simultaneous diffraction, were observed when a perfect Si single crystal was excited into vibration. The excited *Umweganregung* effect is of the same order as the

diffraction intensity obtained on (111) planes under the same experimental conditions. The theoretical consideration is an extension of the lamellae model usually used in the two-wave approximation. Both the theory and the experimental results demonstrate that such an effect may cause very large errors especially in diffraction experiments with non-perfect single crystals.