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On least-squares estimation of extinction corrections

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Abstract. Extinction corrections from published studies of the electron density in α-Al_2O_3 (corundum) do not show the crystal-size and wavelength dependence expected of extinction, as is now confirmed by values determined for small crystals. Corrections evaluated by minimizing differences between observed and calculated structure factors are sensitive to the weights of the observations to a degree that precludes accurate results. That sensitivity helps to obscure strong dependence of the extinction corrections on the structure-factor models used in structure refinements. A model-independent determination indicates that model-dependent corrections can exaggerate the effects of extinction on the measured structure factors.

The unknown reliability of extinction corrections limits the accuracy of strong structure factors measured in single-crystal diffraction experiments but the relative merits of alternative correction procedures are still unclear. Among several approaches to evaluating extinction corrections, those by Zachariasen (1967) and Becker & Coppens (1974) are widely used. The values determined depend on the size and mosaic spread of the perfect crystallites of which real crystals are comprised. Because it is difficult to measure those quantities directly, the corresponding parameters in extinction-correction formulae are often evaluated by least-squares minimization of a weighted sum of squares of differences between observed and calculated structure factors. This is justified provided the measurements and their analysis satisfy conditions on the validity of the least-squares principle. The most probable parameters minimize the weighted sum of squares if the terms contributing to the residual are independent and distributed normally with unit variance.

Least-squares evaluation of structural parameters can be justified using the Gauss–Markov theorem (see, for example, Prince, 1982). When extinction parameters are determined simultaneously, the least-squares residual may be dominated by the strong low-angle reflections. Statistical uncertainty will be high and the validity of the least-squares procedure less clear cut if the number of strong reflections is small. We investigated this matter for the analyses of the electron density in α-Al_2O_3 by Lewis, Schwarzenbach & Flack (1982), Tsirelson, Antipin, Gerr, Ozerov & Struchkov (1985), Aslanov (1989) and Kirfel & Eichhorn (1990), referred to below as LSF, TAGOS, A and KE respectively. The three 152 μm diameter crystals studied by A and TAGOS were supplied by E. J. Gabe (National Research Council of Canada). The extinction corrections of A and TAGOS differ significantly and there are large discrepancies between the deformation density maps from those studies.

Kinematic diffraction conditions are necessarily fulfilled for crystals with dimensions less than 1 μm (Zachariasen, 1967). The kinematic limit is approached asymptotically as the crystal size is reduced, at a rate determined by the size and distribution function for the perfect-crystal microdomains. The degree of reproducibility expected in crystal structure analysis was checked by measuring diffraction data for small α-Al_2O_3 crystals. Two crystals with natural faces were prepared by flux growth. They had average dimensions of 33 μm (crystal 1) and 38 μm (crystal 2). One diffraction data set was measured for crystal 1 and two sets were measured for crystal 2 using Mo $K\alpha$ radiation on a Syntex $P2_1$ four-circle diffractometer. Two further data sets were measured for crystal 1 with synchrotron radiation at 0.7 and 0.9 Å using the Tsukuba Photon Factory BL14A four-circle diffractometer (Satow & Iitaka, 1989). Details will be published elsewhere (Streltsov, Maslen, Ishizawa & Satow, 1992).

Our concern here is with the extinction corrections. Those determined by least-squares analyses of the diffraction data with the approaches of Zachariasen (1967) and Becker & Coppens (1974) were similar. Table 1 lists the smallest extinction factor y_{min}, which is for the $30\bar{3}0$ reflection in all cases. The evidence that y varies systemati-

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Table 1. *Extinction factors for the* α-Al_2O_3 $30\bar{3}0$ *reflection versus crystal size and wavelength*

Reference	Wavelength λ (Å)	Crystal diameter (μm)	y_{min} ($F_o = yF_k$)
A (crystal 1)	Mo $K\alpha$ (0.71069)	152(5)	0.82
A (crystal 2)	Mo $K\alpha$	152(5)	0.73
TAGOS	Mo $K\alpha$	152(5)	0.7†
LSF	Mo $K\alpha$	200	0.76
LSF	Ag $K\alpha$ (0.56083)	130	0.85
KE	0.5599	200	0.64
Present work			
Crystal 1	Mo $K\alpha$	33	0.89
Crystal 1	0.6991	33	0.85
Crystal 1	0.9	33	0.82
Crystal 2 (set 1)	Mo $K\alpha$	38	0.90
Crystal 2 (set 2)	Mo $K\alpha$	38	0.89

† Estimated value from $r^* \lambda = 0.875(6)$ μm given by TAGOS.

cally with the crystal dimensions or radiation wavelength is not conclusive. Data from very small crystals should be virtually extinction free, but the y_{min} range in Table 1 of 0.82 to 0.90 for crystals 1 and 2 overlaps the range 0.64 to 0.85 for the larger crystals.

Table 1 does not show the dependences for various levels of interaction predicted by Mathieson (1979) or the crystal-size and wavelength dependence estimated from the Zachariasen formula $y = \left(1 + r^* \delta \lambda^3 \overline{T}\right)^{-1/4}$ for the extinction factor applicable to $|F|$. $\overline{T}$ is the mean path length of the radiation in the crystal and δ is approximately 0.83×10^{33} m^{-4} for the $30\bar{3}0$ reflection. The synchrotron-radiation data for crystal 1 should be the most reliable indicator of the wavelength dependence of extinction. If r^* is wavelength independent the y_{min} value for $\lambda = 0.7$ Å should be 13% less than that for 0.9 Å, but the decrease indicated in Table 1 is only 2.4%. Other y_{min} values listed in Table 1 (for LSF and KE) show a similar lack of wavelength dependence. It is also questionable whether these y_{min} values correlate closely with the crystal size. The y_{min} range 0.85 to 0.90 for the tube-data r^* value for crystals 1 and 2 extrapolates, with the 0.7 Å synchrotron value for crystal 1, to a range of 0.6 to 0.7 for A and TAGOS. The observed range is 0.7 to 0.82.

The intrinsic reliability of the extinction parameters from least-squares structure refinements was tested by adjusting the statistical uncertainties of the observations to simulate altered measurement conditions. Structure-factor magnitudes were unchanged; only the weights were modified. Weights for 15 strong reflections from the 0.7 Å data for crystal 1 were reduced to satisfy the Gauss–Markov conditions for validity in least-squares processes. The significant y_{min} change from 0.85 to 0.89 shown in Table 2 shows that the statistical precision of the measurements influences extinction corrections determined during a structure refinement.

Dependence of y_{min} on statistical precision would explain why values from data with similar precision for crystals 1 and 2 agree more closely than the values determined for crystal 1 using Mo $K\alpha$ tube and 0.7 Å synchrotron-radiation data that differ in precision. Similar behaviour would account for the wide range of r^* values for the A and TAGOS crystals. The resulting uncertainty in the corrections could account for the large discrepancies reported for the difference density maps. It does not explain why the y_{min} range does not vary more systematically with crystal size.

Small-crystal y_{min} values substantially less than 1.0 suggest that the poor correlation of y_{min} with the crystal dimensions and the wavelength is due to deficiencies in model structure factors interacting with extinction corrections determined by least-squares structure refinements. High statistical uncertainty due to the limited number of strong reflections would be compounded if those reflections were significantly affected by the redistribution of bonding electron density.

Interaction with extinction corrections in least-squares refinements, which is obvious for structure factors modelled by a superposition of independent spherical atoms [the independent-atom model (IAM)], persists even for flexible refinements. In principle, structure-factor models can be invoked to describe the electron density more appropriately. In practice, this may be difficult if the parameters describing extinction and those describing electron redistribution correlate strongly, as can occur for extended models. The extent to which multipole coefficients can compensate for extinction errors must be considered when assessing the reliability of local multipole models. Least-squares minimization of a residual may be so ill conditioned that small adjustments to the weights of the observations alter the extinction corrections drastically.

The LSF and KE y_{min} values in Table 1 were based on a multipole expansion model. The dependence of the extinction factor y on the KE model was assessed using the program *VALRAY* (Stewart & Spackman, 1983) in a least-squares refinement of the 0.7 Å data set for crystal 1. Table 2 shows the result of refining the 40 multipole coefficients and the structural parameters, including the extinction parameter, in two different sequences. In sequence 1, the extinction parameter was refined ($\Delta/\sigma < 0.0001$) before the multipole coefficients were determined. The resulting y_{min} value in Table 2 is equal to that from conventional IAM refinement. The order of determining the parameters was reversed in sequence 2, with multipole coefficients and structural parameters refined to convergence before extinction was included. The results differ dramatically, showing that there are at least two distinct minima on the least-squares error surface and highlighting possible consequences of strong correlation of extinction corrections with the electron density model.

It is unlikely that these α-Al_2O_3 analyses are atypical. Attempts to correct diffraction data for extinction *a posteriori* involve significant uncertainties. An approach that does not require theoretical structure factors is desirable. In a method proposed by Maslen & Spadaccini (1992), differences between intensities for equivalent reflections

Table 2. *Variation of* y_{min} *for the* $30\bar{3}0$ *reflection and the* 0.7 Å *crystal* 1 *data with the electron density model and least-squares weighting*

Model	Weighting	y_{min}	R	R_w	GoF
IAM	$1/\sigma^2(F_o)$	0.85	0.015	0.017	2.72
	*	0.89	0.016	0.012	1.69
Multipole model†					
1	$1/\sigma^2(F_o)$	0.85	0.011	0.010	1.75
2	$1/\sigma^2(F_o)$	0.92	0.020	0.022	3.87

* Weights for low-angle reflections satisfying Gauss-Markov conditions.

† Model 1: extinction refined before multipole parameters; model 2: extinction included after multipole refinement.

with different path lengths in small crystals are minimized by optimizing parameters in an extinction formula. A similar analysis applies to intensities for the same Bragg reflection measured at different angles ψ, which is the preferred technique for low-symmetry crystals with a limited number of equivalents. In this approach the dependence on theoretical structure factors of the extinction factors y determined during structure refinement is eliminated. The equality hypothesis for equivalent structure factors and ψ scans is exact. The number of observations, being larger than that for structure refinement using symmetry-unique reflections, improves the statistical precision of the determination. This applies *a fortiori* to ψ scans, which can provide a large number of measurements for each Bragg reflection.

When applied to crystals 1 and 2 this approach showed far less extinction than that determined by comparing observed and calculated structure factors. This conclusion is supported by other studies.

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