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Elimination of Extinction Effects by Extrapolation to Zero Wavelength

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Abstract

A model-free approach to extinction correction of single-crystal reflection data has been developed. Single-crystal peak-intensity observations taken over a series of wavelengths in the range 0.25–0.11 Å were extrapolated to zero wavelength. Evaluation of this method by comparison of extrapolated values with accurate kinematic structure factors for Si shows that it is capable of giving approximate independent estimates of extinction effects. The accurate synchrotron data of Hester, Maslen, Spadaccini, Ishizawa & Satow [*Acta Cryst.* (1993), B49, 842–846], which those authors believed to be unaffected by extinction, has been checked using the present method and found to be significantly affected by extinction. The present results give no reason to doubt the validity of widely used extinction models.

1. Introduction

Standard extinction-correction procedures refine one or more extinction parameters as part of a least-squares structure refinement. If the model used for estimating F_c is assumed to be correct and the reflection weights are normally distributed, the refined parameters will have a maximum likelihood of being correct (Hampel, Ronchetti, Rousseeuw & Stahel, 1986). The least-squares approach developed by Zachariasen (1967) and Becker & Coppens (1974) is expected to provide an accurate extinction correction up to reductions in F due to extinction of approximately 30%.

A common model for calculating F_c in least-squares structure refinements assumes spherically symmetric harmonically vibrating free atoms at the nuclear positions. Accurate electron-density experiments acknowledge that this model is approximate by attributing significance to density due to the residual values of $F_o - F_c$. A model parameter that affects F_c in the same way as changes in electron density caused by formation of the crystal affect F_o will appear to refine successfully. For example, in certain cases, anharmonic thermal-motion parameters may refine to non-zero values owing to electron redistribution among d orbitals. This behaviour may occur in the absence of anharmonic potentials. Similarly, if, in a highly symmetric inorganic structure, atoms located at sites of high symmetry were to have strongly depleted cores, the effect on the intense low-angle structure factors might imitate that of extinction. In such cases, a method of extinction correction that is independent of least-squares refinement is required.

The present experiment adopts a model-independent approach to extinction correction. The philosophy of such approaches has been described by Mathieson (1979). Mathieson argues that, when diffracted intensity is zero, extinction is also zero. Therefore, by taking measurements that approach the limit of zero diffracted intensity and then extrapolating to the zero-diffraction condition, the kinematic structure factor can be obtained. Sufficiently close to the zero-diffraction condition, a linear extrapolation gives a good approximation to the true functional behaviour.

For example, in recent experiments by Stevenson (1994), the zero-diffraction condition chosen is an angle of X-ray incidence to the crystal surface of 0°. Alternatively, the crystal size may be reduced to a level for which extinction is small. If the crystal is asymmetric, the range of incident-beam path lengths for a set of equivalent reflections could be plotted against observed intensity and extrapolated to zero path length. Such an approach has been developed by Maslen & Spadaccini (1993) and used in a number of synchrotron-radiation experiments (*e.g.* Maslen, Streltsov, Streltsova & Ishizawa, 1995).

The limit of zero diffracted intensity is also approached as wavelength decreases. Recently, Palmer & Jauch (1995) examined the variation in structure-factor intensity over a series of γ-ray wavelengths. The experimental results were tested against several models. As noted by those authors, the dependence of F on λ at low levels of beam–crystal interaction is linear to a good approximation. The present paper develops an approach based on linear extrapolation of multiple-wavelength data for the more experimentally accessible neighbouring short X-ray wavelength range, with emphasis on practical applications to electron-density experiments.

The present experiment used an X-ray tube source, which implies that data collected at wavelengths away from the characteristic tube wavelength, while measureable, will be relatively less intense and consequently less accurate. It is expected that use of the more intense short-wavelength radiation available from third-genera-

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tion synchrotron sources would significantly improve the accuracy of the method.

2. Experimental procedure

Two experiments are described below. The first experiment, using an Si single crystal, was performed in order to gauge the accuracy of the present approach. The second experiment, on K_2PdCl_4, was carried out in order to assess independently the magnitude of extinction in that compound.

In both experiments described here, crystals were mounted on a glass fibre, placed on a Huber diffractometer cradle and illuminated with unmonochromated radiation from an X-ray generator running at 1.5 kW with stationary W target. Peak integrated intensities were measured by a standard ω-scanning technique with a constant scan width of 0.5° for all data collections. Small spheres of data in reciprocal space were collected at 0.11, 0.15, 0.184 (W $K\beta_1$) and 0.25 Å. A larger reciprocal-space sphere was collected at 0.209 Å (W $K\alpha_1$). Accurate orientation matrices for the samples were obtained at 0.209 Å using the eight-setting method of King & Finger (1979), and did not require recalculation during the experiment.

Unmonochromated radiation from the W X-ray tube was diffracted by the sample into a nitrogen-cooled pure Ge solid-state detector. The resulting voltage spectrum was passed through a single-channel analyser, which had been set for the required energy, before reaching the counting electronics. The energy window was set equal to the width of the W $K\alpha_1$ line. Small variations in the size of this window did not alter the width of the observed peak, confirming that energy dispersion was a negligible contributor to peak shape.

All data were corrected for absorption based on measured crystal shape and using the X-ray absorption coefficients of Sasaki (1990). After merging and Lorentz–polarization correction, scale factors linking the data sets were refined using the method of Monohan, Schiffer & Schiffer (1967). Linear extrapolation of F and F^2 *versus* wavelength was then carried out. The resulting kinematic structure factors are used in the comparisons described below. All crystallographic calculations were performed using the *Xtal*3.2 (Hall, Flack & Stewart, 1992) series of crystallographic programs running under a Unix operating system on an IBM-486 compatible PC. Data collection lasted approximately two weeks in each case.

2.1. *Assessing the procedure*

Silicon was chosen as the test material because accurate kinematic structure factors were already available (Saka & Kato, 1986). A small fragment of Si in the shape of a triangular prism was cut from a large wafer of pure crystalline silicon. Each face was ground flat and the dimensions measured using an electronic micrometer attached to an optical microscope. The triangular faces had dimensions of $0.8 \times 0.5 \times 0.5$ mm and the crystal thickness was 0.4 mm. Further details are contained in Table 1.

A series of conventional least-squares structure refinements was performed using a variety of extinction models, and the results compared using a 'model agreement factor', defined as $[\sum(F_{\rm refine} - F_{\rm exact})^2 / \sum(F_{\rm exact})^2]^{1/2}$, where $F_{\rm exact}$ refers to the accurate values and $F_{\rm refine}$ to values of F_o or F_c after refinement. Model agreement factors between least-squares-refined data sets and the accurate data set are tabulated in Table 2.

Extrapolated structure factors, together with the accurate kinematic structure factors of Saka & Kato (1986) and least-squares structure factors from the 'standard' refinement are presented in Table 3. The first agreement factor quoted in this table is calculated using only those reflections listed, and thus is not directly comparable with those listed in Table 2. The second agreement factor was obtained after substituting the extrapolated values into the W $K\alpha_1$ data set and carrying out least-squares refinement without an extinction parameter and may be compared with the values in Table 2.

Least-squares refinement is clearly superior to simple extrapolation for this crystal. The most intense reflections are also the worst corrected by the present method, presumably because of a breakdown in the assumption of linear dependence of F on λ. This breakdown may be attributable to the presence of significant primary extinction, as typical path lengths are several times larger than typical extinction lengths. The present method is thus not particularly suitable as a replacement for model-dependent approaches. However, extrapolated structure-factor magnitudes, while less precise than the least-squares estimates, are generally within 2σ of the true value, and thus are suitable for determining the acceptability of values resulting from least-squares refinements. Furthermore, extrapolated values appear to provide an upper limit to the kinematic structure-factor intensity.

3. Applying the method

Hester, Maslen, Spadaccini, Ishizawa & Satow (1993) (hereafter HMS) report an accurate electron-density determination of K_2PdCl_4 using synchrotron radiation. In an effort to reduce extinction effects, very small crystals (volume $\simeq 0.016$ mm^3) were used. Comparison of the relative intensities of extinction-affected reflections at 0.7 and 0.9 Å revealed no decrease with increasing wavelength and thus it was concluded that extinction had been reduced to negligible levels.

It is possible to refine an extinction parameter using the data of HMS. Such a refinement gives a maximum

Table 1. *Experimental details for Si data collections*

Wavelength (Å)	0.25	0.209 (W $K\alpha_1$)	0.184 (W $K\beta_1$)	0.15	0.11
Scan speed (° min^{-1})	1	6	6	1	1
Total reflections	411	2355	1952	824	295
hkl range	$0 \le h \le 8$ $-8 \le k, l \le 8$	$-12 \le h, k, l \le 12$	$-12 \le h, k \le 12$ $0 \le l \le 12$	$-8 \le h, k, l \le 8$	$-8 \le h \le 0$ $0 \le k, l \le 8$
Max $\sin\theta/\lambda$ (Å^{-1})	0.86	1.24	1.91	0.86	0.78
Instability factor	*n/a*	1.1×10^{-3}	1.2×10^{-4}	*n/a*	*n/a*
μ (cm^{-1})	0.424	0.314	0.257	0.211	0.165
Absorption max./min.	1.18/1.14	1.13/1.10	1.11/1.08	1.09/1.07	1.07/1.05
$R_{merge}(I)$ (%)	4.6	4.6	5.3	3.7	5.0
Independent reflections	33	82	127	33	26
Scale (F^2)	0.4185 (9)	1.000 (2)	2.340 (8)	2.308 (7)	15.2 (2)
R(scale)	0.38	0.43	1.28	0.79	2.75
R (%)	1.0	1.2	3.3	1.5	4.0
wR (%)	0.5	0.9	1.3	1.4	1.5
S	1.2 (2)	1.3 (1)	1.24 (8)	3.7 (5)	1.9 (2)
y_{min}	0.71	0.79	0.78	0.83	0.95

correction to F of 20%. It is possible, for reasons described in the *Introduction*, that such an apparently successful refinement is consistent with negligible extinction. In order to determine which estimate of extinction is correct, the method described above has been applied to K_2PdCl_4. This method is expected to give results of similar accuracy to those obtained for Si because the degree of extinction in the sample (as estimated by least-squares refinement of an extinction parameter) is broadly comparable.

A sample of dimensions 0.62 × 0.22 × 0.42 mm was chosen from a fresh batch of solution-grown K_2PdCl_4 crystals. Data-collection details for K_2PdCl_4 are presented in Table 4.

Scaled values of F were extrapolated to zero wavelength. Extrapolation was performed using a linear unweighted least-squares fit to the data, which yielded kinematic structure factors F_k and $\sigma(F_k)$. A typical extrapolation is shown in Fig. 1. F_k and $\sigma(F_k)$ values were included in the W $K\alpha_1$ data set and a standard least-squares refinement performed without refinement of an extinction parameter. Values of F_k and ΔF are compared with those of HMS in Table 5.

The results of the silicon experiment do not appear to favour extrapolation against F or F^2. In practice, both extrapolations result in virtually identical values and F was chosen in the light of the linear dependence of F on λ in the γ-ray results of Palmer & Jauch (1995).

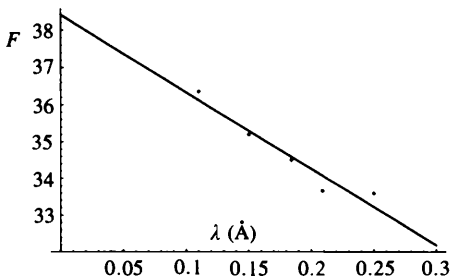

Fig. 1. Extrapolation to zero wavelength for the K_2PdCl_4 220 reflection.

Table 2. *Agreement factors (%) for each refinement*

Standard: Zachariasen extinction parameter, scale factor and harmonic vibration parameters refined together using the full data set, F_o compared with F_{exact}; F_c(std): agreement between F_c and F_{exact}; 0.6: thermal parameters and scale factor determined by refinement of reflections with $\sin\theta/\lambda > 0.6$ Å^{-1}; type 1, type 2, general: Becker & Coppens (1974) extinction models.

Refinement	0.25 Å	$K\alpha_1$	$K\beta_1$	0.15 Å	0.11 Å
Standard	1.88	0.96	1.08	1.38	1.59
F_c(std)	1.83	0.89	0.98	1.38	1.19
0.6	2.27	1.59	0.78	0.81	1.88
Type 1	2.94	1.13	1.81	1.40	1.63
Type 2	4.73	2.86	3.34	2.92	1.80
General	1.67	0.76	0.96	1.44	-

Table 3. *Comparison of extrapolated structure factors with exact and least-squares (W $K\alpha_1$ data) values*

All agreement factors are relative to the exact values. F^2: linear extrapolation of F^2 against λ; F: linear extrapolation of F against λ; y: least-squares extinction factor; F (least squares): F obtained by 'standard' least-squares refinement of extinction parameter; F_{exact}: *Pendellösung* data of Saka & Kato (1986); R_{agree}: agreement factor using listed structure factors; $R_{complete}$: overall agreement factor after least-squares refinement including corrected structure factors (see text).

hkl	y (least squares)	F^2	F	F (least squares)	F_{exact}
1 1 1	0.79	61 (3)	62 (2)	60.7 (4)	60.131 (3)
0 2 2	0.81	68 (2)	69 (1)	66.3 (7)	67.343 (5)
0 0 4	0.88	58 (2)	58 (1)	55.5 (4)	56.234 (3)
1 1 3	0.91	45 (1)	44.7 (6)	43.7 (2)	43.634 (6)
2 2 4	0.92	50 (1)	50.2 (5)	49.1 (2)	49.106 (4)
1 3 3	0.94	38 (1)	38.5 (5)	38.2 (1)	38.224 (5)
0 4 4	0.95	45 (2)	45 (1)	42.3 (2)	42.885 (6)
0 2 6	0.96	38.1 (6)	38.2 (3)	37.4 (1)	37.587 (7)
1 1 5	0.96	33.1 (8)	33.1 (4)	32.8 (1)	32.941 (3)
3 3 3	0.96	31.7 (9)	31.7 (5)	32.7 (2)	32.833 (3)
1 3 5	0.97	28.8 (1)	28.8 (1)	28.68 (8)	28.81 (1)
4 4 4	0.97	32.1 (7)	32.1 (2)	32.9 (2)	33.18 (1)
0 0 8	0.98	25.9 (4)	25.8 (2)	25.9 (2)	26.227 (8)
2 4 6	0.98	28.75 (9)	28.75 (9)	29.40 (9)	29.42 (1)
3 3 5	0.98	25.5 (4)	25.5 (2)	25.2 (1)	25.357 (6)
R_{agree} (%)		2.4	2.7	0.99	0.0
$R_{complete}$ (%)		3.8	2.8	0.96	0.0

Table 4. *Experimental details for K_2PdCl_4 data collections*

Wavelength (Å)	0.25	0.209 (W $K\alpha_1$)	0.184 (W $K\beta_1$)	0.15	0.11
Scan speed (° min^{-1})	1	6	6	1	1
Total reflections	774	1664	1404	816	1003
hkl range	$-6 \le h, k \le 6$	$-8 \le h, k \le 8$	$-8 \le h, k \le 8$	$-6 \le h, k \le 6$	$-6 \le h, k \le 6$
	$-3 \le l \le 3$	$-4 \le l \le 4$	$-3 \le l \le 3$	$-3 \le l \le 3$	$-3 \le l \le 3$
Max $\sin\theta/\lambda$ (Å^{-1})	0.48	0.62	0.75	0.75	0.52
Instability factor	1.1×10^{-4}	4.7×10^{-5}	2.3×10^{-2}	*n/a*	2.1×10^{-3}
μ (cm^{-1})	0.8623	0.5148	0.3622	0.2294	0.1126
Absorption max./min.	1.04/1.02	1.03/1.02	1.02/1.00	1.01/1.00	1.00/1.00
$R_{merge}(I)$ (%)	7.6	5.7	6.3	6.1	3.6
Independent reflections	78	153	193	193	88
Scale (F^2)	0.912 (2)	1.000 (2)	0.672 (1)	3.84 (1)	24.9 (3)
R_{scale} (%)	3.3	1.6	1.7	3.8	8.7
Scale (F, least squares)	2.56 (4)	2.67 (2)	2.26 (2)	5.47 (5)	13.8 (2)
R (%)	3.1	3.2	7.3	3.5	13.8
wR (%)	3.6	2.9	3.7	2.6	5.6
S	4.3 (4)	3.1 (2)	3.7 (2)	2.5 (2)	1.4 (1)
y_{min}	0.86	0.86	0.92	0.94	0.99

4. Discussion

Despite the large errors for the extrapolated reflections, it is clear that the 220 and 002 reflections in the HMS results are significantly affected by extinction at 0.7 Å, as seen from Fig. 1 and Table 5. The extrapolated estimates for these reflections do not contradict those derived from least-squares extinction refinement, especially given that extrapolations for these reflections are expected to overestimate F.

Results for the remaining reflections are less clear. Extrapolated values are all smaller than the corresponding least-squares values, while remaining within 2–3σ of these values. Conversely, the extrapolated values for these reflections are all larger than the HMS values, while remaining within 2–3σ of the HMS values. Given that extrapolation is expected to slightly overestimate extinction effects, this may indicate that, as suggested by HMS, least-squares extinction refinement can cause slight overcorrection of extinction.

The best estimates for extinction-affected structure factors in this compound were assumed to be the least-squares values for the 002 and 220 reflections and, for the remaining reflections, the extrapolated values.

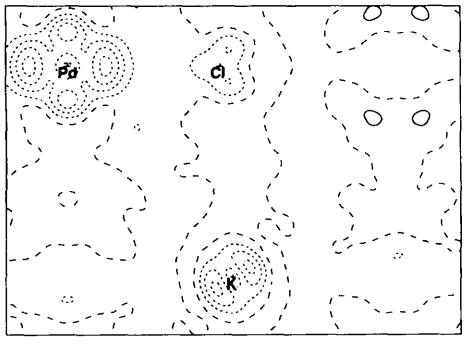

Fig. 2. $\Delta\rho$ in K_2PdCl_4 for the (111) plane using revised values for extinction-affected reflections (see text). Borders 6.9 × 5.0 Å, contour interval at 0.2 e Å^{-3}.

Table 5. *Comparison of strongly extinction affected reflections for K_2PdCl_4*

$\Delta \equiv F_o - F_c$. Extrap: from extrapolation to zero wavelength; HMS: F taken from Hester *et al.* (1993) at 0.7 Å; lsq: least-squares refinement of a Zachariasen extinction parameter.

hkl	F_{extrap}	F(HMS)	F(lsq)	Δ_{extrap}	Δ(HMS)
220	105.7 (15)	91.7 (4)	103.6 (4)	4.8	−9.5
002	89 (2)	79.6 (6)	86.3 (6)	0.4	−9.2
040	76.6 (9)	73.5 (4)	77.4 (4)	0.5	−3.0
111	64.1 (12)	62.4 (6)	66.9 (6)	−3.1	−4.7
001	62.5 (15)	58.3 (4)	63.5 (4)	−2.8	−6.8
010	49.8 (11)	47.9 (2)	52.4 (2)	−2.2	−3.8

Table 6. *Charges calculated by Hirshfeld partitioning of $\Delta\rho$*

	Present result	HMS
K	−0.2 (2)	−0.936 (6)
Pd	+0.8 (2)	+1.894 (7)
Cl	−0.1 (2)	−0.006 (7)

Fig. 2 is a revised version of HMS's Fig. 2 calculated by replacing the six structure factors in Table 5 with these best estimates.

The new $\Delta\rho$ map is more physically reasonable than that published in the original paper. Areas of large negative difference density in regions far from atoms, implying non-physical negative absolute density, are absent in the present maps. The area near the Pd nucleus remains depleted, and the unusual lobes around K identified by HMS remain. An accumulation of positive difference density far from the nuclei, not shown in this section, remains unchanged. None of the broad changes resulting from the present work significantly alter the conclusions of the original paper.

The new extinction correction has, as expected, a pronounced effect on the atomic charges. Charges calculated by Hirshfeld partioning of the difference density are presented in Table 6 together with the published charges of HMS.

There are no changes in signs of the atomic charges. Both K and Pd atoms have become less polar, while the Cl charge does not change significantly. Standard deviations for the present results are much larger, reflecting the larger σ values for the low-angle reflections. These changes do not affect the conclusions of the original paper.

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