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Anisotropy in the Variation of Serially-Measured Integrated Intensities

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Abstract

The variation (often decline) in intensity standards measured during a typical X-ray diffraction structure determination is commonly corrected by means of an isotropic polynomial expression of the form $I_t = I_0(1 - \sum_n A_n t^n)$, where t is the exposure time in hours, I_0 is the integrated intensity at zero exposure and $1 \leq n \leq 7$. A linear decline corresponding to $n = 1$ is reported in many studies. In the simplest (linear) anisotropic case, the variation may be represented by

$$I_t = I_0[1 - t(\alpha_{11}h^2 + \alpha_{22}k^2 + \alpha_{33}l^2 + 2\alpha_{12}hk + 2\alpha_{13}hl + 2\alpha_{23}kl)/(h^2 + k^2 + l^2)]$$

where the α_{ij} are coefficients of a radiation-damage-effect ellipsoid. Higher-order and exponential time dependences have also been investigated. The results of applying the anisotropy relation both to an organometallic and an inorganic structure, as evalu-

ated by the method of least squares, are presented. For each case the linear anisotropic correction leads to significant reductions in R_{int} and wR_{int} , with additional improvement resulting from inclusion of quadratic decline correction terms. The smallest number of experimental data required to evaluate the radiation damage anisotropy consists of two sets of symmetry-equivalent reflections.

Introduction

Sequential measurement of integrated intensities is often accompanied by systematic change in the values of standard reflections measured at fixed exposure intervals. Indeed, a request for including the intensity variation observed throughout the diffraction experiment in papers reporting crystal structure determinations is to be found in the IUCr's *Notes for Authors* (1983). The observed variation in standards is

commonly used as a basis for correcting the complete set of measurements. The technique frequently used is to fit the set of successive integrated intensity values measured for each standard reflection to a polynomial expression of degree n :

$$I_t = I_0 \left(1 - \sum_n A_n t^n \right), \quad (1)$$

where t is the exposure time in hours, I_0 is the initial intensity at zero exposure and $1 \leq n \leq 7$. Values of $R' = \sum |I - \langle I \rangle| / \sum I$ are thereupon successively evaluated for each standard reflection over the full range of n and also with the uncorrected I_t values ($n = A_0 = 0$). Inspection of R' versus n usually reveals a consistent pattern among the standard reflections, in which R' for each decreases sharply at the same order of polynomial with much smaller subsequent decreases noted at higher order. Measurement of at least nine standard reflections well distributed in reciprocal space facilitates recognition of the pattern. A sharp decrease commonly occurs at $n = 1$, indicative of a linear change in intensity with exposure. Lack of such a decrease indicates negligible radiation-exposure dependence. For crystals with a sharp decrease at order n , the weighted mean of each A_n coefficient over all standards is taken as the final value in (1). The corresponding weights are derived from the counting statistical variance in the intensity of each standard and the number of measurements of that standard. An illustrative linear correction for an inorganic crystal is $I_t = I_0(1 - 0.00006801t)$, as reported for congruent LiNbO_3 (Abrahams & Marsh, 1986). An earlier approach proposed by Ibers (1969) replaces the normal scale factor S_0 by $S_t = S_0 + a_1 t + a_2 t^2$ for each reflection measured at t h, and the coefficients a_1, a_2 are subsequently determined in the course of least-squares structural refinement.

The origin of the intensity change may be traced to several effects, two of which tend to predominate. The first is mechanical, caused by slight changes in the relative position of X-ray source and crystal during the experiment. Dimensional instability over long time periods is not necessarily negligible. The second and probably larger effect is due to radiation damage. An IUCr Single-Crystal Radiation Damage Survey (Abrahams, 1973) illustrated the pervasiveness of radiation damage in normal crystal structure determination experiments. A major challenge posed by the survey, to investigate the physical and chemical processes leading to radiation damage in single crystals, remains largely open well over a decade later. A second challenge posed therein, to develop methods for correcting radiation effects more adequately, is taken up in this communication.

Correction for anisotropic radiation damage

The reliability of techniques such as that outlined in the *Introduction* for correcting changes in the

integrated intensity magnitudes caused by radiation damage rests on the validity of two major assumptions. The first is that 'standard' reflections measured repeatedly undergo radiation-induced changes that are identical to those of the much larger number of 'nonstandard' reflections generally measured only once for subsequent use in structural refinement. The second assumption is that the intensity variation is dependent only on the radiation exposure. Neither assumption is justifiable in a given case without further investigation. In considering these two, it became apparent that our normal technique of measuring the full sphere of reciprocal space handily provides the information required to investigate the first assumption.

Consider the structure amplitude $F^2(hkl)$ measured at time t h, F_t^2 , with all other members of the hkl form measured later. These measurements sample both reciprocal space and exposure time. The spatial effect of change owing to radiation damage may be represented as ellipsoidal with form

$$B_{ij} = (\alpha_{11}h^2 + \alpha_{22}k^2 + \alpha_{33}l^2 + 2\alpha_{12}hk + 2\alpha_{23}kl + 2\alpha_{13}hl) / (h^2 + k^2 + l^2),$$

where the denominator eliminates scattering-angle dependence. Setting $F_t^2 = F_0^2(1 - tB_{ij})$, the α_{ij} coefficients may be evaluated in principle by means of a least-squares program that minimizes $\sum w(F_t^2 - \langle F_t^2 \rangle)^2$. The weights w used here and later in structural refinement by least squares are the reciprocal variances of $\langle F_t^2 \rangle$, taken as the larger of V_1 or V_2 where V_1 is the variance due to counting statistics, absorption, attenuation effect and variation in the standards and V_2 is calculated from the differences among each equivalent form [see also Abrahams, Bernstein & Keve (1971)]. The α_{ij} coefficients varied should, by Neumann's principle, conform to the point-group symmetry: a better fit may however be possible with a generalized ellipsoid owing to the presence of residual systematic error in the F_t^2 magnitudes. The temporal and spatial dependences may be represented either by a combination of an exponential factor of the form $\exp(-\sum_n A_n t^n)$ together with the tB_{ij} term,

$$F_t^2 = F_0^2 [1 - tB_{ij} \exp(-\sum_n A_n t^n)], \quad (2)$$

or by the general polynomial

$$F_t^2 = F_0^2 (1 - tB_{ij} - t^2 B_{ijkl} - t^3 B_{ijklmn} - \dots), \quad (3)$$

where

$$B_{ijkl} = (\alpha_{1111}h^4 + 4\alpha_{1112}h^3k + 6\alpha_{1122}h^2k^2 + \dots) / (h^2 + k^2 + l^2)^2,$$

$$B_{ijklmn} = (\alpha_{111111}h^6 + 6\alpha_{111112}h^5k + 15\alpha_{111122}h^4k^2 + \dots) / (h^2 + k^2 + l^2)^3, \dots$$

A least-squares program in which the α_{ij} and A_n coefficients of (2) are variable parameters converges to a stable solution with $n=0$ to 2 ($A_0=0$) even for severe radiation damage. Similarly, least-squares variation of the α_{ij} and α_{ijkl} coefficients in (3) is also found to converge strongly. Sixth- (B_{ijklmn}) and higher-order coefficients, however, have not been investigated; neither has the possibility of correlation between coefficients of different order in point groups of high symmetry. By contrast, representation of the temporal dependence by a polynomial similar to that in (1), in conjunction with the spatial dependence, led to indeterminacy for second and higher orders of t .

The effectiveness of the resulting anisotropic corrections, which give rise to a set of structure amplitudes F_0^2 equivalent to those having zero X-radiation exposure, is followed by the indicators $R_{\text{int}} = \sum |F_i - \langle F_i \rangle| / \sum F_i$ and $wR_{\text{int}} = \sum [w(|F_i - \langle F_i \rangle|)^2 / \sum wF_i^2]^{1/2}$, as the corrected values of F_i^2 and the corresponding average $\langle F_i^2 \rangle$ over all members of the form converge to their final F_0^2 magnitudes. Since $\sum |F_i^2 - \langle F_i^2 \rangle|$ is a major component in the evaluation of $\sigma(\langle F_i^2 \rangle)$, the resulting change in w after each iteration, as the fit improves, tends to slow the convergence rate.

The presence of anisotropic extinction necessarily causes correlation with the anisotropy determined in the radiation damage. Isotropic extinction present in the measured set of structure factors is expected to remain unchanged in the corrected set, provided the time dependence in (2) and (3) also fits any extinction variation present.

Application to an organometallic structure

A set of 10 339 $F_i^2 > 3\sigma(F_i^2)$ measured on a crystal of $[(C_2H_5)_4N]^+[ReH_8P(C_6H_5)_3]^-$ in point group 222 at 295 K over $0 < t \leq 610.7$ h (Abrahams, Marsh & Ginsberg, 1987) is used to illustrate the results of correcting the intensity decline in an organometallic crystal caused by severe radiation damage. Nine intensity standards, well distributed in reciprocal space and differing by an order of magnitude between weakest and strongest amplitudes, were measured at 6 h intervals. A graphical display of the sequential intensity values for each standard suggests that all have an approximately linear decline of comparable magnitude. A least-squares fit to (1) for each standard confirms that a linear fit gives the major improvement in R' , with $n \geq 2$ giving only marginal further improvement. The final weighted mean coefficient $A_1 = 0.0010887$ in (1) was generally within 6% of the A_1 magnitude for each individual standard. Application of this linear isotropic coefficient has a major effect on the internal agreement indicators, reducing R_{int} from 0.0952 without correction to 0.0225 with correction.

The magnitude of the correction given by (1), based on a limited number of standard reflections, may be compared with that derived from all reflections by assuming that the decline due to radiation damage is isotropic. A least-squares fit to (2) for $n = A_0 = 0$ and $B_{ij} = A_1$ in the present organometallic structure corresponds to the assumption of a linear exposure and a spherical spatial dependence. Taken over a set of 10 318 $F_i^2 > 3\sigma(F_i^2)$, the resulting value of $A_1 = 0.0010878(18)$ together with the indicators given under 'Linear isotropic' in Table 1. This table also gives wR_{int} for comparison with the corresponding weighted indicators as derived from least-squares structural refinement. It may be noted that this A_1 coefficient corresponds to a decrease of 66.4% in the intensity of an average reflection at the end of the diffraction experiment, and also that the values of A_1 derived either from the limited number of standards or from the entire measurement set are in excellent agreement.

Structural refinement based on the set of $2383 \langle F_0^2 \rangle \geq 3\sigma(\langle F_0^2 \rangle)$ resulting from the linear isotropic correction led to a model in which all eight hydrogen atoms bonded to Re were refinable but with one that had an unacceptably long H-Re distance of 2.7 Å and a small residual in the difference electron density that was possibly attributable to partial occupation by a solvate molecule. The corresponding final values are $R = 0.0151$, $wR = 0.0195$ and $S = 0.675$.

A linear anisotropic radiation-damage correction, with $\alpha_{ij} (i \neq j) = 0$ as required in point group 222, results in $R_{\text{int}} = 0.0220$ and $wR_{\text{int}} = 0.0179$ for 10 321 $F_i^2 > 3\sigma(F_i^2)$. The corresponding coefficients are $\alpha_{11} = 1.091(6)$, $\alpha_{22} = 1.107(6)$ and $\alpha_{33} = 1.084(3) \times 10^{-3}$, suggestive of significant anisotropy although the internal agreement indicators are nearly identical to those for the isotropic correction based upon three fewer structure amplitudes. The indicators are substantially improved on allowing the coefficients with $i \neq j$ to vary, as given under 'Linear anisotropic' in Table 1: it is notable that α_{23} does not differ significantly from zero, as expected from consideration of the point-group symmetry, whereas α_{12} and α_{13} have appreciable magnitudes. The symmetry violation clearly originates in small residual systematic errors in the I_i measurements. A likely source of such error lies in the transmission factors calculated for this capped prismatic crystal, which range from a minimum of 21.06 to a maximum of 39.67%. Correction of residual error by allowing the ellipsoid to rotate from alignment along the crystal axes is expected to result in more-accurate $\langle F_0^2 \rangle$ magnitudes. It may be observed that the α_{ii} magnitudes do not differ significantly from those obtained with $\alpha_{ij} = 0$; see Table 1.

Structural refinement based on the linear anisotropic radiation-damage correction with coefficients as given in Table 1 led to an improved model with

Table 1. Internal agreement indicators and coefficients for several radiation-damage-correction models for $[(C_2H_5)_4N]^+[ReH_8P(C_6H_5)_3]^-$ and $0 \leq t \leq 610.7$ h

Model	No correction	Linear isotropic*	Linear anisotropic†	Quadratic anisotropic‡	Exponential anisotropic§	Exponential quadratic anisotropic¶
R_{int}^{**}	0.0952	0.0219	0.0203	0.0187	0.0192	0.0187
wR_{int}^{**}	0.0550	0.0179	0.0155	0.0146	0.0152	0.0150
$A_1(10^{-3})$	—	1.088 (2)	—	—	-0.024 (12)	1.16 (6)
$A_2(10^{-6})$	—	—	—	—	—	-1.6 (6)
$\alpha_{11}(10^{-3})$	—	—	1.081 (6)	0.907 (14)	1.016 (5)	1.30 (1)
$\alpha_{22}(10^{-3})$	—	—	1.114 (5)	1.211 (11)	1.068 (5)	1.37 (1)
$\alpha_{33}(10^{-3})$	—	—	1.085 (3)	1.003 (9)	1.093 (7)	1.30 (1)
$\alpha_{12}(10^{-3})$	—	—	-0.066 (4)	-0.067 (6)	-0.067 (2)	-0.083 (3)
$\alpha_{13}(10^{-3})$	—	—	-0.068 (3)	-0.102 (6)	-0.064 (2)	-0.080 (2)
$\alpha_{23}(10^{-3})$	—	—	0.002 (3)	-0.060 (6)	0.001 (2)	0.001 (2)

* Equation (1).

† Equation (2), with $n = A_0 = 0$. For $t \leq 314.6$ h (see text), the generalized ellipsoid has coefficients $\alpha_{11} = 0.970(4)$, $\alpha_{22} = 1.097(3)$, $\alpha_{33} = 1.080(3)$, $\alpha_{12} = -0.047(3)$, $\alpha_{13} = -0.072(3)$, $\alpha_{23} = -0.041(3)(\times 10^{-3})$.‡ Equation (3), with B_{ij} and $B_{ijkl} \neq 0$. Only the six α_{ij} coefficients, not the remaining 15 α_{ijkl} coefficients, are listed here for this generalized quadratic anisotropic case.§ Equation (2) with $n = 1$. The magnitude of $A_1 (= B_{ij})$ is not comparable with A_1 in equation (1).¶ Equation (2) with $n = 2$.** The indicators R_{int} and wR_{int} defined in the text, are calculated for all observed F_i corrected to F_0 , with four members per form in space group $P2_12_12_1$ and resulting $\langle F_0^2 \rangle > 3\sigma(\langle F_0^2 \rangle)$.

all H-Re distances in the range 1.76–2.36 Å, the hydridic atoms completing a distorted equatorially tricapped trigonal-prismatic array in which Re-P forms one of the apical bonds. With $2378 \langle F_0^2 \rangle \geq 3\sigma(\langle F_0^2 \rangle)$, the final refinement indicators became $R = 0.0135$, $wR = 0.0120$ and $S = 0.914$. The increased value of S , in comparison with the value above, is due to the smaller spread in magnitudes among members of a form and the resulting reduction in average magnitude of $\sigma(\langle F_0^2 \rangle)$.

Inclusion of the 15 general quadratic anisotropic $t^2 B_{ijkl}$ terms in (3) led to a small additional improvement in fit within each form and hence in internal agreement indicators as compared with the linear anisotropic correction, see Table 1. Refinement with the resulting $2381 \langle F_0^2 \rangle \geq 3\sigma(\langle F_0^2 \rangle)$ gave slightly larger indicators than those based on the linear anisotropic correction but reduced the range of Re-H distances to 1.81–2.08 Å, with an average of 1.97 (9) Å.

Application of (2) with $n = 1$ to the organometallic structure factors gives an exponential anisotropic radiation-damage correction, that to second order gives an exponential quadratic anisotropic correction, as presented in Table 1. The resulting improvement in R_{int} and wR_{int} , as compared with the linear or quadratic anisotropic corrections, is small at best and suggests that the additional effect of the exponential correction on the structural refinement would be similarly small.

Application to an inorganic structure

A set of 5913 $F_i^2 > 3\sigma(F_i^2)$ measured on a ground sphere of $Pb_5W_3O_9F_{10}$ in point group 4 at 295 K over $0 < t \leq 750.3$ h (Abrahams, Marsh & Ravez, 1987) is taken as a typical example of an inorganic structure

in which moderate radiation damage results in the course of the complete exposure. Six standard reflections, measured at 6 h intervals, were found to decline regularly. A least-squares fit of the decline in all standards measured to first order in (1) gave $A_1 = 0.000165$, with resulting $R_{int} = 0.0321$. Elimination of a small number of individual standards with measured value less than $0.7F_0$ gave $A_1 = 0.0001818$ and reduced R_{int} to 0.0281, in excellent agreement with the results obtained by application of (2) to the nearly full set of 5910 observations: with $n = A_0 = 0$ and $B_{ij} = A_1$ to give a linear isotropic correction, $A_1 = 0.0001816(23)$ and the corresponding $R_{int} = 0.0281$, $wR_{int} = 0.0253$. The maximum correction to I_i of 13.6% for this case hence considerably improves R_{int} , which increases to 0.0313 if no correction is made for radiation damage.

The linear anisotropic correction based upon (2) with $n = A_0 = 0$ or upon (3) with $B_{ijkl} = 0$, and with $\alpha_{11} = \alpha_{22}$, α_{33} , $\alpha_{12} = \alpha_{13} = \alpha_{23} = 0$ as required by the point group, gives minor additional improvement with $R_{int} = 0.0280$ and $wR_{int} = 0.0252$. The corresponding quadratic anisotropic correction [(3) with only the three symmetry-allowed B_{ijkl} coefficients varied] results in $R_{int} = 0.0271$, $wR_{int} = 0.0241$. The generalized linear anisotropic correction, however, without point-group-symmetry constraints, gave substantial improvement with $R_{int} = 0.0253$ and $wR_{int} = 0.0233$. The corresponding generalized quadratic anisotropic correction, with all fifteen α_{ijkl} coefficients varied, gave $R_{int} = 0.0225$ and $wR_{int} = 0.0211$. Application of the exponential anisotropic correction in (2) with $n = 1$ gave $R_{int} = 0.0251$, $wR_{int} = 0.0232$: with $n = 2$, $R_{int} = 0.0247$ and $wR_{int} = 0.0231$. It may be observed that the improvement in R_{int} on inclusion of a quadratic time dependence in (3) is highly sig-

nificant at the 99.5% probability level in comparison with other corrections, both for the organometallic and inorganic examples considered. Investigation of further sets of F_i^2 measured on other materials is necessary to determine the generality of this dependence.

Full form versus partial form measurement

In a recent important paper, Hamor, Steinfink & Willis (1985) recommended that all data sets be obtained by merging the intensities from *at least* two sets of symmetry-equivalent reflections other than Friedel pairs, and pointed out some of the advantages that accrue from such averaging. An additional major advantage obtained by following this recommendation is the option it provides of correcting either for isotropic or for anisotropic radiation-damage dependence in the integrated intensities by means of (2) or (3).

An investigation of this option was undertaken by restricting the data measured on the organometallic structure above from the initial full form of four equivalent reflections to a partial form of two equivalents. Since the measurement of one hemisphere of reciprocal space was completed before the second was started, the exposure time investigated was also essentially reduced by a factor of two, to 314.6 h, in selecting the first hemisphere. For the resulting set of 2567 ($\langle F_0^2 \rangle \geq 3\sigma(\langle F_0^2 \rangle)$), based on the linear isotropic correction with $A_1 = 0.989(2) \times 10^{-3}$, $R_{\text{int}} = 0.0142$ and $wR_{\text{int}} = 0.0105$. Corresponding results with the linear generalized anisotropic correction gave $R_{\text{int}} = 0.0133$ and $wR_{\text{int}} = 0.0096$; the quadratic generalized anisotropic correction gave $R_{\text{int}} = 0.0118$ and $wR_{\text{int}} = 0.0090$. The resulting anisotropy based on the partial form, as given by the ratio of α_{11} to α_{22} for the case $n = A_0 = 0$ (see footnote to Table 1), is acceptably comparable to that obtained with the full form, since identity is not required in view of the difference in exposure times. Use of a minimum data set consisting of two symmetry-equivalent measurements of each reflection for the determination of anisotropic radiation-damage dependence in the structure factors is hence shown to be valid, although use of the full set may be expected to offer higher reliability.

The effect on structural refinement of applying a simple linear radiation-damage correction such as (1) to the I_i measured in the first quadrant of reciprocal space was investigated at the Co-editor's suggestion. Reflections measured in the first and second quadrants were interspersed in time: application of (1) to the corresponding standards measured in the initial 314.6 h exposure thereupon led to $A_1 = 0.001387(12)$ and $R' = 0.0165$. The weights used in the following

least-squares refinement were taken as $1/V_1$, see *Correction for anisotropic radiation damage*. Substitution of the resulting set of 2457 modified $F_i^2 > 3\sigma(F_i^2)$ for the amplitudes derived with the linear anisotropic radiation-damage correction led to normal refinement, provided the four parameters for each of the eight hydridic atoms were kept constant, with final $R = 0.0239$, $wR = 0.0277$ and $S = 3.583$ for a total of 446 variables as compared with the values calculated for the best model (see *Application to an organometallic structure*), of $R = 0.0135$, $wR = 0.0120$ and $S = 0.914$ for 478 variables. Simultaneous variation of all parameters, including those of the hydridic atoms, led to oscillatory shifts and indicators, with typical $R = 0.0251$, $wR = 0.0285$ and $S = 3.679$ for a range in H-Re distance of 1.53–2.18 Å, with an average of 1.97(20) Å.

Relation of radiation-damage anisotropy to molecular orientation

Extraction of the orientation and dimensions of the principal axes of the radiation-damage-effect ellipsoid, as determined by means of (2) or (3), opens the possibility of comparison with the shape and orientation of the molecular content of the unit cell undergoing radiation exposure. A close relationship in the case of the present organometallic salt is not to be expected, in view of the cation and anion shapes and the relatively small anisotropy in the radiation damage. It may, however, be speculated that revealing relationships might appear in the case of radiation damage suffered by molecular crystals with highly anisotropic molecular shape, particularly in crystals of low point symmetry.

The results obtained above based on determination of the partial form suggest that structural measurement made following Hamor *et al.*'s (1985) recommendation would provide a minimum data set from which the shape and orientation of the correction for possible ellipsoidal radiation damage may conveniently be derived for comparison with the molecular contents of the crystal.

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