

Using (19), HDS averaged over all possible orientations of a given defect configuration can be written as

$$I_{\text{HDS}} = C \left\{ \frac{f}{V_C} \sum_k \exp [i\mathbf{h} \cdot \mathbf{x}(k)] \right\}^2 \sum_{\nu=1}^5 \gamma_{\nu} \pi_{\nu}. \quad (20)$$

π_{ν} represent the five independent parameters in the tensor $\overline{p_{ij}p_{kl}}$, which is an average over the product of dipole force tensors p . γ_{ν} can be calculated from the elastic constants and the direction of \mathbf{q} and \mathbf{h} .*

In order to compute HDS using (16), we require Kanzaki forces due to the defect, the dynamical matrix and the perfect-lattice Green functions for zinc. Since the interstitial in zinc has a large relaxation volume (3.6 atomic volumes), the defect forces are expected to be long range. Kanzaki forces, extending up to the third neighbour around the defect, were calculated using the experimental values of the force dipole tensor (Ehrhart *et al.*, 1979).* We computed the dynamical matrix and the lattice Green functions for zinc (Khanna, 1982) using a modified axially symmetric force constant model due to Dewames *et al.* (1965).

For the sake of comparison, the HDS was computed for the O , T and S_c configurations near the 002 reflection in the [001] direction. Since the experimental value of dipole force tensor was used for the computation, all of them yielded identical HDS close to Bragg peaks. This is to be expected since these defects have the same long-range symmetry. The computed HDS also showed the expected $1/q^2$ behaviour very close to Bragg peaks.

* A list of γ_{ν} for some high-symmetry reflections and directions and specific forms of π_{ν} and a table containing general expressions for the dipole force tensor components have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36990 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

From elasticity theory, the HDS close to a 002 reflection in the [001] direction is

$$I_{\text{HDS}} = C \left| \frac{f}{V_C} \sum_k \exp [i\mathbf{h} \cdot \mathbf{x}(k)] \right|^2 \left(\frac{h}{q} \right)^2 \frac{p_{33}^2}{C_{33}^2}. \quad (21)$$

Substituting the computed value of I_{HDS} for a given p_{33} in (21) we get $C_{33} = 67.8 \text{ GN m}^{-2}$. This is exactly the value quoted by Dewames *et al.* (1965) based on their atomic force constants. Thus the general theory valid over the entire q space correctly predicts the Huang diffuse scattering close to Bragg peaks.

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References

- DEREDICHS, P. H. (1973). *J. Phys. F*, **3**, 471–496.
 DEWAMES, R. E., WOLFRAM, T. & LEHMAN, G. W. (1965). *Phys. Rev. A*, **138**, 717–728.
 EHRHART, P. & SCHONFELD, B. (1979). *Phys. Rev. B*, **19**, 3896–3904.
 KANZAKI, M. (1957). *J. Phys. Chem. Solids*, **2**, 24–36.
 KHANNA, R. (1982). *Phys. Status Solidi*. Accepted for publication.
 KRIVOGLAZ, M. A. (1969). *Theory of X-ray and Thermal Neutron Scattering by Real Crystals*, pp. 114–155. New York: Plenum.
 MARADUDIN, A. A., MONTROLL, E. W., WEISS, G. H. & IPATOVA, I. P. (1971). *Theory of Lattice Dynamics in the Harmonic Approximation*, pp. 6–38. London: Academic Press.
 TRINKAUS, H. (1972). *Phys. Status Solidi B*, **51**, 307–319.

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On Structure Refinement Using Data from a Twinned Crystal

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Abstract

Refinements leading to accurate structural parameters are possible by using the measured data F_o^2 of a twinned

crystal with exactly superimposed reciprocal lattices and accumulating the sum for the n twin domains, $\sum_i^n \alpha_i |kF_{ci}|^2$, of the calculated squared structure factors, $|kF_{ci}|^2$, weighted according to the fractional contribution α_i of twin i to the total squared structure factor $|kF_c|^2$. The derivatives with respect to structural parameters and the overall scale factor (k) may be

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accumulated similarly. The $(n - 1)$ independent α_i should also be refined; here the derivatives are of the form $\partial|kF_c|^2/\partial\alpha_i = |kF_{ci}|^2 - |kF_{cn}|^2$ since $\alpha_n = 1 - \sum_{i=1}^{n-1} \alpha_i$. These procedures have been incorporated into a standard least-squares program for the successful refinement of the low-temperature structure of $\text{Ni(en)}_3\text{SO}_4$. Two domain systems with partial overlap of reciprocal lattices may also be handled.

Introduction

Two approaches exist for the utilization of data from twinned crystals where some or all of the measured intensities may be expressed as

$$F_o^2 = \sum_i^{n-1} \alpha_i F_{oi}^2 + \left(1 - \sum_i^{n-1} \alpha_i\right) F_{on}^2, \quad (1)$$

where the α_i is the independent fractional volume component of the twin and where there are n twin components of which $n - 1$ are independent. In the first approach, the diffraction data are detwinned to provide a set of observations free from the contributions of the minor components. Methods for estimating the twinning parameter, α , in a two-component system, including cases where the reciprocal lattices are completely superimposable, have been described (Britton, 1972; Murray-Rust, 1973). However, this approach, which is the one usually adopted, has several serious deficiencies. The covariance of this parameter with other structural parameters is ignored. A more serious deficiency lies in the propagation of errors as described in detail by Grainger (1969). The error of a component ('detwinned') intensity cannot be less than the error of the measured intensity. Unless the twinning parameter α is quite large (~ 0.75), poor agreement between observed and calculated structure factors and resultant low precision are ineluctable. Thirdly, as α approaches a value of 0.5, separation of the intensity components becomes impossible as the pairs of simultaneous equations become degenerate.

In the second approach, the data are used as measured. The combined squared structure factor, F_c^2 , is calculated as indicated in (1). In a similar manner the derivatives for the p_j structural parameters including the overall scale factor k ,

$$\frac{k|F_c|^2}{\partial p_j} = \sum_i^{n-1} \frac{\partial}{\partial p_j} (\alpha_i |kF_{ci}|^2) + \frac{\partial}{\partial p_j} \left[\left(1 - \sum_i^{n-1} \alpha_i\right) |kF_{cn}|^2 \right], \quad (2)$$

and the derivatives for the α_i twin factors,

$$\frac{\partial |kF_c|^2}{\partial \alpha_i} = \frac{\partial}{\partial \alpha_i} (\alpha_i |kF_{ci}|^2) + \frac{\partial}{\partial \alpha_i} (-\alpha_i |kF_{cn}|^2), \quad (3)$$

$$i = 1, \dots, n - 1,$$

may be accumulated in a manner analogous to that employed by Pratt, Coyle & Ibers (1971) for the specific case of $n = 2$. As (3) manifests, the method adopted by Grainger (1969) and Grainger & McConnell (1969 and references therein to the work of Kennicott) of refining for each twin component a separate scale factor is not rigorously correct since these scale factors are not strictly separable. However, this method works in much the same way that two occupancies β and γ , where $\gamma = 1 - \beta$, can be successfully refined such that refined values for β and γ do indeed equal unity within the estimated standard deviations.

Hawthorne (1974) has reported an alternative method, that of transforming atomic parameters rather than structure-factor indices as adopted by Grainger (1969), in order to generate the components of the twinned crystal. In addition to the greater conceptual difficulties posed by transforming atomic parameters, particularly for trigonal systems, the simple incorporation of the linear constraints into least-squares refinements using the programs suggested would lead to refinement of a disordered structure [the left-hand term in (4)] and not of a twinned one [the right hand term in (4)];

$$\left\{ \sum_i^n \beta_i \sum_j^{\text{atoms}} f_j \exp(-TF) \exp[-2\pi i(hx_j^i + ky_j^i + lz_j^i)] \right\}^2$$

$$\neq \sum_i^n \alpha_i \left\{ \sum_j^{\text{atoms}} f_j \exp(-TF) \times \exp[-2\pi i(hx_j^i + ky_j^i + lz_j^i)] \right\}^2 \quad (4)$$

(n : the number of atom parameter sets corresponding to n twin or disorder components; x_j^i, y_j^i, z_j^i : coordinates of atom j in atom parameter set i ; TF : temperature factor; β_i : left-hand side of (4) occupancy parameter for atoms of set i).

Here we wish to report the incorporation of general procedures allowing mathematically rigorous refinement of twinning parameters into the Northwestern (Waters & Ibers, 1977) and Zürich Universities' version of the Oak Ridge least-squares refinement program *ORFLS*. This method has been demonstrated with the accurate determination of the structure of tris(ethylenediamine)nickel(II) sulphate at 113 K using diffractometer data from a twinned crystal with near-perfectly superimposed reciprocal lattices (Jameson, Schneider, Dubler & Oswald, 1982).

Results and discussion

Program modification

Fig. 1(a) illustrates the flow diagram for a standard least-squares program. Fig. 1(b) shows the modified

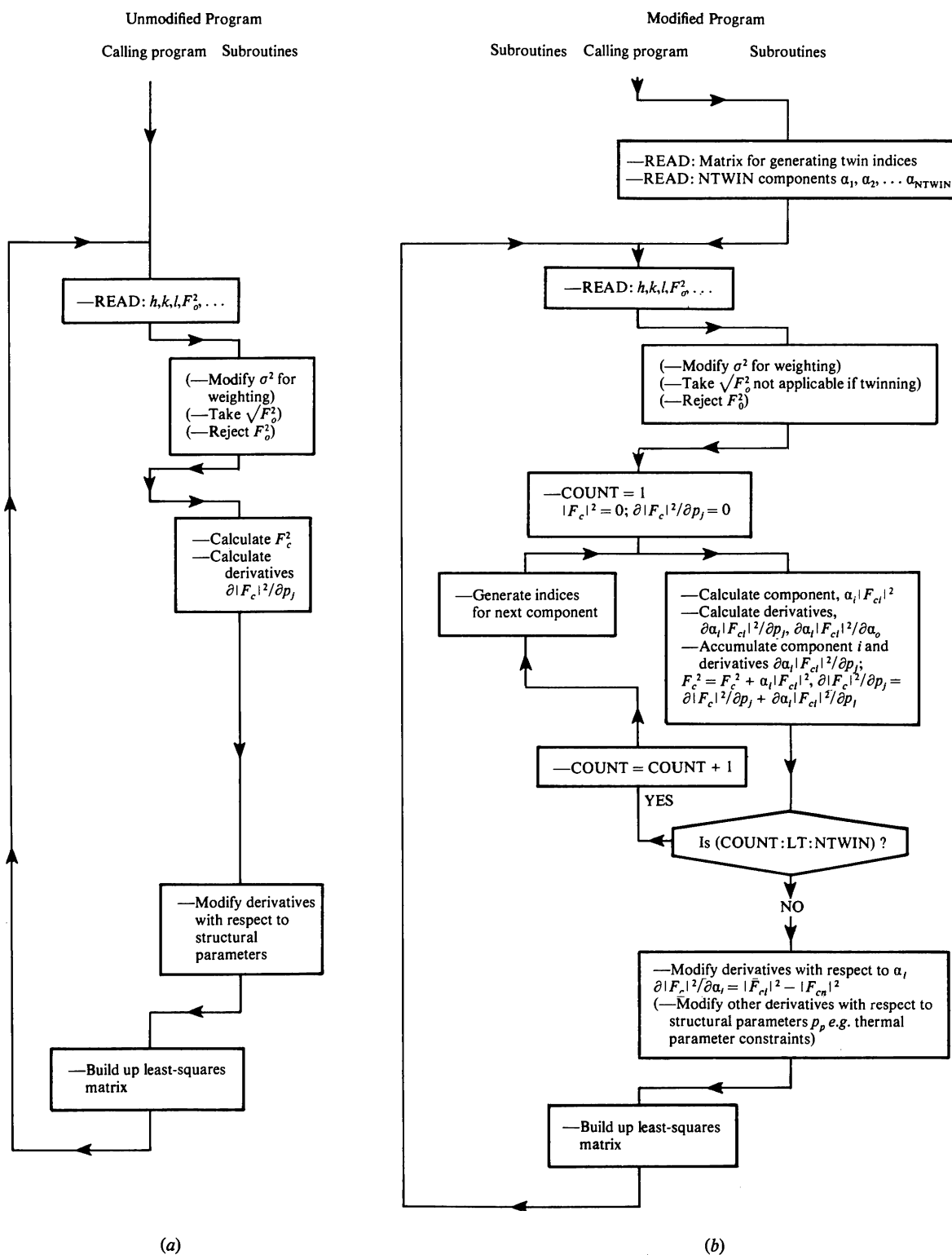


Fig. 1. Flow diagram illustrating the paths followed in the refinement of (a) non-twinned and (b) twinned (accumulated components) structures. Entries in parentheses are optional depending upon the type of refinement in the absence of twinning, e.g. weighting scheme, symmetry constraints on thermal and/or atomic parameters. The case of only partially overlapped data is not illustrated. The scale factor k is omitted for clarity.

path of the calculations should consideration of twinning be desired. A two-domain system with partially overlapping reciprocal lattices can also be accommodated if a mathematical relationship separating composite from non-composite reflections can be defined.* Thus with minimal modification to the calling program and its main subroutines, we were able to test various twinning laws. This was particularly useful in finding the twinning law for the data collected from a crystal of $[\text{Ni}(\text{en})_3][\text{SO}_4]$ at low temperature (Jameson *et al.*, 1982). In particular, with an eye to the cupric analogue (Bertini, Dapporto, Gatteschi & Scozzafava, 1979), we were able to test and reject various triclinic trillings involving three 120° rotations to give an overall $\bar{3}$ diffraction symmetry.

With the exception of one structure where it was assumed and fixed that $\alpha_1 = \alpha_2 = 0.5$ (Wei, 1969), there appears to be only one other structure successfully solved and refined where the twin ratio is less disparate than about 0.65:0.35 (Pratt, Coyle & Ibers, 1971).

Comparison with refinements using detwinned data

It was decided to examine the results of refinements using detwinned data – the data were detwinned (Britton, 1972),

$$F_1^2(hkl) = \frac{\alpha F^2(hkl) - (1 - \alpha) F^2(khl)}{2\alpha - 1}$$

$$F_2^2(khl) = \frac{(1 - \alpha) F^2(hkl) - \alpha F^2(khl)}{1 - 2\alpha},$$

using the refined value for the twinning parameter α [0.5663 (1)]. Table 1 illustrates the undesirability of this process. Refinements were markedly less stable (see Table 2) with oscillating behaviour (shifts of up to 0.9 of their e.s.d.'s) being observed at convergence; hydrogen atoms were even more affected.

It may be noted that early refinements of the structures, ignoring twinning, also lead to the same basic structure. Electron density maps did of course contain ghosts of sulphate groups at nickel sites and *vice versa* as well as enormous positive and negative peaks along the z axis. Given proper refinement techniques, data from a twinned crystal need not lead

* Additional details of this and other programming aspects have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38017 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Error generation involved in detwinning data for selected reflections (F^2)*

			Composite reflections			Detwinned reflection		
h	k	l	Obs*	Calc	%Diff	'Obs'	Calc	%Diff
2	0	-6	346 (16)	335	3.2	637	591	7.2
0	2	-6	254 (12)	257	-1.2	-40	2	105.
5	-2	2	1262 (52)	1256	0.05	2287	2212	3.3
-2	5	2	948 (39)	963	-1.6	-77	8	110.
1	0	8	1017 (43)	1029	1.3	1872	1816	3.0
0	1	8	754 (32)	788	-4.5	-102	0	100.

* Estimated standard deviation in F^2 in parentheses is given by $\sigma^2 = \sigma^2(\text{counting}) + (0.04I)^2$, where I is the raw intensity corrected only for background scattering. The twinning ratio used was 0.5663 (1):0.4337.

Table 2. *Comparison of refinement methods for $\text{Ni}(\text{en})_3\text{SO}_4$*

	Detwinned data	Unmodified data
$R(F^2), R_w(F^2)$ including $F_0^2 < 0$	0.130, 0.077*	0.043, 0.064
Number of data	1282	1353
Number of variables	79	80
Behaviour at convergence	Strongly oscillatory	Stable
Mean shift/error	0.369 1.765	0.110 (non-H atoms) 0.595 (H atoms)

* Unit weights.

to an imprecise, inaccurate crystal-structure determination.

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References

- BERTINI, I., DAPPORTO, P., GATTESCHI, D. & SCOZZAFAVA, A. (1979). *J. Chem. Soc. Dalton Trans.*, pp. 1409–1414.
 BRITTON, D. (1972). *Acta Cryst.* A **28**, 296–297.
 GRAINGER, C. T. (1969). *Acta Cryst.* A **25**, 427–434.
 GRAINGER, C. T. & MCCONNELL, J. F. (1969). *Acta Cryst.* B **25**, 1962–1970.
 HAWTHORNE, F. C. (1974). *Acta Cryst.* A **30**, 603–604.
 JAMESON, G. B., SCHNEIDER, R., DUBLER, E. & OSWALD, H. R. (1982). *Acta Cryst.* B **38**. In the press.
 MURRAY-RUST, P. (1973). *Acta Cryst.* B **29**, 2559–2566.
 PRATT, C. S., COYLE, B. A. & IBERS, J. A. (1971). *J. Chem. Soc. A*, pp. 2146–2151.
 WATERS, J. M. & IBERS, J. A. (1977). *Inorg. Chem.* **16**, 3273–3277.
 WEI, C. H. (1969). *Inorg. Chem.* **8**, 2384–2397.