Table 1. *Comparative values of residuals $R_1$ and $R_2$ in least-squares refinements of structures from neutron-diffraction data*

|  | $R_1$ | $R_2$ | $\sigma$ | Remarks |
|---|---|---|---|---|
| α-D-Glucose (Brown & Levy, 1965) | 0·060 | 0·059 | 1·097 | 37 of 1656 data omitted |
| Potassium hydrogen chloromaleate (Ellison & Levy, 1965) | 0·123 | 0·092 | 1·015 | 4 of 1959 data omitted |
| K₂NbF₇ (Brown & Walker, 1966) | 0·090 | 0·081 | 1·20 | All 1355 data, no extinction corrections |
|  | 0·109 | 0·103 | 1·13 | 112 data omitted because of extinction |
|  | 0·087 | 0·070 | 1·11 | All 1355 data, corrected for extinction |

$$f_k \equiv ||F|_o^k - |F|_c^k|/|F|_o^k \qquad (2)$$

and to rewrite $R_k$ in the form

$$R_k = \frac{\Sigma f_k |F|_o^k}{\Sigma |F|_o^k} . \qquad (3)$$

This expression emphasizes that $R_k$ is the weighted average value of the absolute fractional discrepancy, each individual value being weighted by the corresponding $|F|_o^k$. Making use of the approximation $f_1 \simeq f_2/2$, valid for $f_1$ and $f_2$ values in the range of interest, one can write the specific forms for $R_1$ and $R_2$ as follows:

$$R_1 = \tfrac{1}{2} \Sigma f_2 |F|_o / \Sigma |F|_o \qquad (4)$$

$$R_2 = \Sigma f_2 |F|_o^2 / \Sigma |F|_o^2 . \qquad (5)$$

It is well known that for X-ray film data the fractional observational errors are usually approximately constant over a wide range of $|F|_o$ values above a minimum value. From (4) and (5) it follows that the relation $R_1 \simeq R_2/2$ should be expected to hold, in agreement with the usual finding.

In the typical set of neutron-diffraction data, obtained by counter techniques, $f_2$ is by no means constant. Rather, it varies over a very wide range, usually from about 0·03 for the strongest reflections to the order of unity for the weakest observable reflections. In comparison with (4), the expression (5) weights the smaller fractional discrepancies associated with the larger $|F|_o$ values much more heavily than the larger discrepancies associated with the smaller $|F|_o$ values. Given the usual distribution of $|F|_o$ values in a set of data, it is understandable, therefore, that $R_1$ may equal or exceed $R_2$.

For X-ray data recorded by counter techniques higher precision can easily be achieved in measuring the weaker reflections, because of the better resolution against background allowed by the higher intensity of radiation in X-ray beams. Therefore the range of values of $f_2$ is usually not so large as it is for neutron data. It follows that one should expect for such data values of $R_1/R_2$ intermediate between those characteristic of X-ray film data and neutron data. The

precise value in a given case will depend on the distribution of the fractional errors in the data, which will be determined by the details of the recording scheme and by the effects of any systematic errors that may be present.

By systematic analysis of the discrepancies, one may detect in the last stages of a structure refinement with neutron data the presence of extinction errors which are small in magnitude but which may affect fifty or a hundred data of the strongest reflections. The $R_k$ values computed when these data are included in the refinements are always lower than those computed when the data are omitted, though the reverse is true for the corresponding values of the more significant quantity $\sigma$, the standard deviation of an observation of unit weight.[*] At first sight this finding may seem anomalous, but it is readily understood by reference to the expression (3) for $R_x$. When the data in error are included, their fractional discrepancies are reduced by a compensating adjustment of the scale factor on the observations, so that the discrepancies become small relative to those of many of the weak reflections. Then the large weights given these data by equation (3) ensure a value of $R_k$ that is misleadingly low. In fact, the resulting $R_k$ value may even be quite close to the value calculated after refinement on data corrected for extinction.

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[*] This quantity is defined by the equation

$$\sigma = \left[ \frac{\Sigma w(|F|_o^2 - |F|_c^2)^2}{n - p} \right]^{\frac{1}{2}}$$

where the weight $w$ is the reciprocal of the variance of an observation $|F|_o^2$, $n$ is the number of observations, and $p$ is the number of parameters fitted to the data set. See, *e.g.* Hamilton (1964).

## Crystallite size and lattice distortion parameters from X-ray line broadening. By D. R. BUCHANAN, R. L. McCULLOUGH and R. L. MILLER, *Chemstrand Research Center, Inc., Durham, North Carolina, U.S.A.*

In a study of line broadening from gray irons and steels, Hauk & Hummel (1956) obtained vastly differing results for integral breadth analyses and the Fourier transform

analysis of Warren & Averbach (1950). These discrepancies led others (Willets, 1965) to suggest alternate methods of line profile analysis in order to separate the effects of small

crystallite size from those of lattice distortions. Another integral breadth analysis (Bonart, Hosemann & McCullough, 1963) is based on paracrystalline theory and might be expected to yield still another set of values for the size, and especially, the distortion parameters. The purpose of this note is to show that numerical differences in the parameters obtained from the different methods of analysis arise naturally and need not be construed as evidence that a given method is more applicable than others.

For this development: (1) we treat size terms and distortion terms separately, even though they interact to a considerable extent when both small crystallite size and lattice distortion are present in the experiment; (2) we ignore any experimental advantages (or disadvantages) of a given method of size-distortion separation; and (3) we assume that an accurate correction for instrumental broadening has been made.

Consider first the case in which line broadening arises solely from a distribution, $n(i)$, of small crystallite sizes, $L_i\,(=d_{hkl}\cdot i)$. In the following, $s$ is the diffraction space variable ($s_0=1/d_{hkl}$). For the $hkl$ reflection, each size $L_i$ produces a profile of the type:

$$I(s,i)=n(i)A_if(s,i)\,, \qquad (1)$$

where $A_i$ is a scaling factor dependent on the nature of $f(s,i)$, and $f(s,i)$ is so normalized that $f(s_0,i)=1$. The total ($hkl$) intensity from all sizes $L_i$ is:

$$I(s)=\sum_i n(i)A_if(s,i)\,, \qquad (2)$$

and the integral breadth of the total profile is:

$$b=\frac{\int I(s)ds}{I(s_0)}=\frac{\sum_i n(i)A_i\int f(s,i)ds}{\sum_i n(i)A_i}\,, \qquad (3)$$

where the integration is taken over the ($hkl$) profile only.

The integral breadth of the $i$th profile is:

$$b_i=\int f(s,i)ds=1/L_i\,, \qquad (4)$$

which is equivalent to the Scherrer formulation relating crystallite size and integral breadth (Klug & Alexander, 1954). Equation (3) becomes:

$$b=\frac{\sum_i n(i)A_ib_i}{\sum_i n(i)A_i}\,. \qquad (5)$$

The intensity in the $i$th profile must be proportional to the product of the size of the $i$th crystallites, $L_i$, and their number, $n(i)$. Therefore,

$$\int I(s,i)ds=kL_in(i)=n(i)A_i\int f(s,i)ds=n(i)A_ib_i \qquad (6)$$

where $k$ is the proportionality constant. If we assume that the $f(s,i)$ all have the same functional form, we obtain from equations (4), (5) and (6):

$$b=\frac{\sum_i kL_in(i)}{\sum_i kL_in(i)/b_i}=\frac{\sum_i L_in(i)}{\sum L_i^2n(i)}=\frac{1}{\langle L_i\rangle}\,, \qquad (7)$$

where $\langle L_i\rangle$ is a 'weight-average' (i.e. size-average) dimension.

In contrast to this result, the size obtained through the Warren–Averbach technique is a 'number-average' dimension (Warren & Averbach, 1950):

$$L_i=\frac{\sum_i L_in(i)}{\sum_i n(i)}\,. \qquad (8)$$

It is apparent that crystallite dimensions obtained by an integral breadth method are always larger than (or equal to) those obtained by the Fourier transform technique; the two size averages are complementary, rather than competing, parameters.

Next we consider the case in which lattice distortions are the only cause of broadening and compare the integral breadths defined by several theories of distortion broadening. The appropriate integral breadths are:

(1) Wilson's method (Wilson, 1949):

$$b\,(\text{Å}^{-1})=2es_0\,, \qquad (9)$$

where $e=\delta d/d$ represents the (somewhat loosely defined) extent of the lattice distortions.

(2) Paracrystalline method (Bonart, Hosemann & McCullough, 1963):

$$b\,(\text{Å}^{-1})=(1/2d_{hkl})[1-\exp\,(-2\pi^2m^2g_1^2)]\,, \qquad (10)$$

where $d_{hkl}$ is the interplanar spacing of interest, $m$ is the order of reflection, and $g_1=\Delta_1/d$, where $\Delta_1$ is the standard deviation of $H_1(x)$, the probability function describing the paracrystalline lattice in the direction normal to ($hkl$). When the product $2\pi^2m^2g_1^2$ is sufficiently small, equation (10) reduces to:

$$b\,(\text{Å}^{-1})=(1/2d_{hkl})(2\pi^2m^2g_1^2)=\pi^2m^2g_1^2/d_{hkl}\,. \qquad (10a)$$

(3) Fourier transform methods (Warren & Averbach, 1950):

$$b\,(\text{Å}^{-1})=1/\sum_{t=-\infty}^{+\infty}F(t)\,,$$

where $F(t)$ is the Fourier transform of the observed profile, $f(s)$, and is given by:

$$F(t)=\exp\,(-2\pi^2s_0^2t^2\overline{\varepsilon_t^2})\,,$$

where $\overline{\varepsilon_t^2}$ is the mean square value of the lattice distortion over the domain, $t(\text{Å})$.

Thus:

$$b\,(\text{Å}^{-1})=1/\int_{-\infty}^{+\infty}\exp\,(-2\pi^2s_0^2t^2\overline{\varepsilon_t^2})dt=s_0\sqrt{2\pi\overline{\varepsilon_t^2}}\,. \qquad (11)$$

Note that $\sqrt{\overline{\varepsilon_t^2}}$ is the r.m.s. value of $\varepsilon_t$, averaged over all $t$. If the lattice distortions are microstrains, equations (9) and (11) indicate that:

$$e\simeq1\cdot25\sqrt{\overline{\varepsilon_t^2}}\,. \qquad (12)$$

We note from equations (9), (10), and (11) that the relationships between integral breadth and order of reflection are not the same for the various treatments. Paracrystalline theory requires that the integral breadth be proportional to the square of the order of reflection, while both Wilson's method and the Fourier transform method require that the integral breadth be proportional to the first power of the

order of reflection. Clearly at least three orders of reflection are required in order to decide which of the two types of distortion broadening theory is applicable to the data.

Thus for size broadening, two quite different (but precisely defined) parameters may be obtained from integral breadth methods and from the Fourier transform method. When lattice distortions are the only cause of broadening, different results, which are not all compatible, will be obtained from the different analyses. Clearly the situation is further complicated by the simultaneous presence of both size and distortion broadening.

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# The crystal structure of terpyridylzinc chloride: a refinement. By FREDERICK W. B. EINSTEIN and BRUCE R. PENFOLD,

*Chemistry Department, University of Canterbury, Christchurch, New Zealand*

The crystal structure of terpyridylzinc chloride has been reported by Corbridge & Cox (1956). The monoclinic space group of the form investigated was $P2_1/a$ with $a=16\cdot21$, $b=8\cdot25$, $c=10\cdot97$ Å and $\beta=93\cdot5°$. Each zinc atom was shown to be at the centre of a distorted trigonal bipyramidal group of three nitrogen and two chlorine atoms. The published atomic coordinates, particularly those of carbon and nitrogen atoms, were however of low precision, having been determined directly from three-dimensional electron density maps. The exact configuration of the terpyridyl ligand was therefore uncertain. In conjunction with a structure analysis of the tin(IV) complex $[Sn(CH_3)_2Cl_2]_2$ . terpyridyl (Fergusson, Roper & Wilkins, 1965) we wished to know these details and therefore have carried out a least-squares refinement of the data of Corbridge & Cox.

Refinement commenced with the published atomic coordinates and, of the 554 listed structure factors, all were used except one thought to be affected by extinction and four others for which $F_{obs}$ was indicated as uncertain. The block-diagonal least-squares procedure was used (the program being that written for the IBM 1620 computer by G. A. Mair) and each atom was assigned an independent

isotropic thermal parameter. Least-squares weights were as follows: $\sqrt{W}=10/F_{obs}$ for $F_{obs}>10$; $\sqrt{W}=F_{obs}/10$ for $F_{obs}<10$. Unobserved reflexions were assigned a value of $0\cdot6$, all these numbers referring to the original scale. Self-consistent field model scattering factors were used for all atoms except zinc, for which anomalous dispersion 'in phase' corrections were applied to the Thomas–Fermi–Dirac scattering factors (*International Tables for X-ray Crystallography*, 1962).

After two preliminary refinement cycles during which only zinc and chlorine positions and an overall scale factor were varied, seven further cycles were computed during which all positional and thermal parameters were allowed to vary. During this refinement, which was aided by an acceleration procedure (Hodgson & Rollett, 1963), the discrepancy index $R$ decreased from $0\cdot24$ to $0\cdot14$. The final

Table 1. *Atomic coordinates and isotropic thermal parameters*

|  | $x/a$ | $y/b$ | $z/c$ | $B$ |
|---|---|---|---|---|
| Zn | 0·1181 | 0·0955 | 0·2171 | 2·09 Å² |
| Cl(1) | 0·2383 | 0·0239 | 0·1389 | 2·90 |
| Cl(2) | 0·1318 | 0·3226 | 0·3342 | 2·03 |
| N(1) | 0·1169 | −0·101 | 0·359 | 1·0 |
| N(2) | −0·0059 | 0·027 | 0·224 | 1·5 |
| N(3) | 0·0520 | 0·203 | 0·058 | 1·4 |
| C(1) | 0·1893 | −0·162 | 0·415 | 2·5 |
| C(2) | 0·1805 | −0·286 | 0·505 | 2·8 |
| C(3) | 0·1099 | −0·334 | 0·543 | 4·0 |
| C(4) | 0·0321 | −0·260 | 0·480 | 2·0 |
| C(5) | 0·0468 | −0·147 | 0·391 | 1·7 |
| C(6) | −0·0291 | −0·070 | 0·325 | 1·0 |
| C(7) | −0·1118 | −0·094 | 0·343 | 1·5 |
| C(8) | −0·1699 | −0·016 | 0·266 | 2·3 |
| C(9) | −0·1504 | 0·089 | 0·175 | 2·1 |
| C(10) | −0·0647 | 0·101 | 0·155 | 1·5 |
| C(11) | −0·0325 | 0·200 | 0·060 | 4·1 |
| C(12) | −0·0834 | 0·279 | −0·030 | 2·1 |
| C(13) | −0·0466 | 0·360 | −0·122 | 2·1 |
| C(14) | −0·0421 | 0·372 | −0·120 | 2·4 |
| C(15) | 0·0921 | 0·290 | −0·026 | 2·6 |

Table 2. *Interatomic distances and angles*

| | | | |
|---|---|---|---|
| Zn–Cl(1) | 2·25 Å | $\sigma=0\cdot01$ Å | (2·28 Å)* |
| Zn–Cl(2) | 2·27 | 0·01 | (2·29) |
| Zn–N(1) | 2·24 | 0·04 | (2·19) |
| Zn–N(2) | 2·09 | 0·04 | (2·11) |
| Zn–N(3) | 2·18 | 0·04 | (2·34) |
| Cl(1)ZnCl(2) | 112° | (111°) | |
| Cl(1)ZnN(1) | 97 | | |
| Cl(1)ZnN(2) | 143 | | |
| Cl(1)ZnN(3) | 101 | | |
| Cl(2)ZnN(1) | 102 | | |
| Cl(2)ZnN(2) | 105 | | |
| Cl(2)ZnN(3) | 98 | | |
| N(1)ZnN(2) | 74 | (79) | |
| N(1)ZnN(3) | 145 | | |
| N(2)ZnN(3) | 73 | (72) | |
| N(1)C(1) | 1·38 Å | N(3)C(15) | 1·36 Å |
| N(1)C(5) | 1·27 | N(3)C(11) | 1·37 |
| N(2)C(6) | 1·43 | N(2)C(10) | 1·32 |
| C(1)C(2) | 1·44 | C(14)C(15) | 1·44 |
| C(2)C(3) | 1·30 | C(13)C(14) | 1·44 |
| C(3)C(4) | 1·53 | C(12)C(13) | 1·38 |
| C(4)C(5) | 1·37 | C(11)C(12) | 1·41 |
| C(6)C(7) | 1·38 | C(9)C(10) | 1·42 |
| C(7)C(8) | 1·38 | C(8)C(9) | 1·37 |
| C(5)C(6) | 1·53 | C(10)C(11) | 1·45 |

* Values in parenthesis are those reported by Corbridge & Cox (1956).