

Joint Refinement of Neutron and X-ray Diffraction Data

BY J. A. K. DUCKWORTH AND B. T. M. WILLIS

A.E.R.E., Harwell, England

AND G. S. PAWLEY

Department of Natural Philosophy, The University, Edinburgh, Scotland

(Received 10 September 1968)

A least-squares method of analysing joint neutron and X-ray diffraction data from the same crystal is described. The procedure is applied to hexamethylenetetramine, where it is shown that a more satisfactory refinement is obtained than by analysing each set of data independently.

Introduction

There is a great deal of current interest in the collection of highly accurate neutron and X-ray diffraction data, and in the interpretation of these data to give results of chemical or physical significance. Where neutron and X-ray data are available on the same crystal, it may be preferable to analyse both sets of data together. In this note we describe one such method of analysis, and we show one example in which this procedure is used. A recent example of the comparison of separate refinements is that of Hamilton & La Placa (1968).

Joint refinement procedure

We start with two sets of diffraction data taken by use of neutrons and X-rays on crystals at the same temperature. We can then assume that the temperature parameters for both sets of data are the same. However, the positional parameters obtained with these two sets may be different. The neutron data set determines the nuclear positions and the X-ray set the centroids of the electron clouds surrounding the nuclei. We would expect, therefore, that separate refinement of the data sets would yield the same thermal parameters but positional parameters which may be different.

In no crystallographic refinement problem is correlation absent, and if for the two separate refinements the thermal parameters are significantly different, we cannot be sure that the positional parameter differences are not correlation-induced artifacts. To avoid this difficulty we refined both data sets together in such a way that the thermal parameters were identical. The list and meaning of the parameters is as follows.

- s_n . . . neutron data scale factor,
- \mathbf{x}_n^i . . . neutron data positional parameters,
- \mathbf{b}^i . . . thermal parameters common to both sets of data,
- \mathbf{x}_x^i . . . X-ray data positional parameters,
- s_x . . . X-ray data scale factor.

The index i ranges over all the independent atoms, and the thermal parameter matrix \mathbf{b}^i gives the temperature

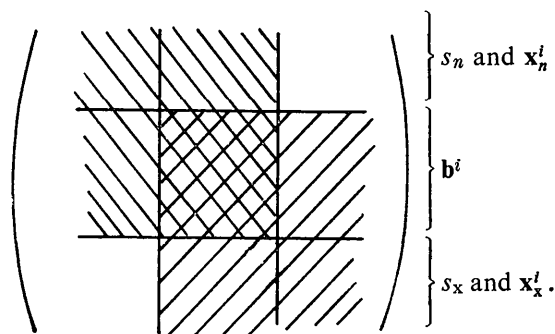
factor for the i th atom,

$$\exp(-h^2 b_{11} - \dots - 2klb_{23} - \dots).$$

The interaction between the two data sets is interesting. Let p_j represent any parameter, and let h be an index for labelling the observations. For any one set of reflecting planes it is likely that there are two observations, one from each set, and these observations must have a separate label h . The calculated structure factor for any observation can then be written F_h , and depending on the value of h , neutron or X-ray scattering factors must be employed. We need make no further distinction between the data sets. The jk element of the least-squares matrix is

$$\sum_h \left(\frac{\partial |F_h|}{\partial p_j} \right) \cdot \left(\frac{\partial |F_h|}{\partial p_k} \right) \cdot \text{weight}(h).$$

Clearly this sum is zero if $p_j = s_n$ or \mathbf{x}_n^i when $p_k = s_x$ or \mathbf{x}_x^i . The least-squares matrix is therefore



Here one cross-hatched region comes from neutron data and the other cross-hatched region from X-ray data. The blank regions are zero, and the double cross-hatched region corresponds to the interaction between the data sets through the thermal parameters. The correlation between the parameters is given by the inverse of this matrix. This will not contain areas of zeros so that all the parameters must be correlated.

It might be thought that trouble would arise from the closeness of \mathbf{x}_n^i and \mathbf{x}_x^i . The difference between these positions will be much less than the resolution of the

data. Resolution difficulty was encountered in the disordered structure of azulene (Robertson, Shearer, Sim & Watson, 1962) and high correlation prohibited a chemically reasonable result. However, we find no such difficulty in the joint refinement, and this should be the result of a difference in topology of the parameter spaces.

Example of joint procedure

Accurate neutron diffraction measurements have been made by the present authors on hexamethylene-tetramine (HMT), and have been refined by customary procedures to a reliability index $R=2.23\%$. This work, and its relation to the neutron diffraction study of HMT by Andresen (1957), will be described in a later publication. In the present paper, we are concerned only with the technique of joint refinement of neutron and X-ray data, and we choose data from HMT to illustrate the kind of results to be expected.

X-ray data on HMT have been published by Becka & Cruickshank (1963), who refined their room-temperature measurements, taken with Mo $K\alpha$ radiation, to $R=2.33\%$. These X-ray measurements were corrected for absorption and extinction, whereas our neutron data were corrected, in addition, for the effect of thermal diffuse scattering. As this last correction is known to be highly correlated with the thermal parameters, the joint analysis was also performed with neutron data uncorrected for thermal diffuse scattering. The differences in the results for the two joint refinements were small (see Table 1) and do not affect any of the main conclusions. This suggests that our conclusions would be the same if we had corrected the X-ray results for thermal diffuse scattering, for although this correction would be different from the neutron correction it would have a similar magnitude. The neutron and X-ray data sets were given equal weights in the analyses.

Table 1. Final parameters in the joint refinement

The scale factor is given as a ratio between the refined value and the value obtained in the original separate refinement. The customary R values for the neutron and X-ray diffraction data are calculated separately. Neutron data sets differ, as set (1) is set (2) corrected for thermal diffuse scattering.

| Parameter | Neutron data set (1) | Neutron data set (2) | Standard deviation |
|--------------------|----------------------|----------------------|--------------------|
| $v_n(\text{N})$ | 0.1221 | 0.1220 | 0.0005 |
| $u_n(\text{C})$ | 0.2378 | 0.2384 | 0.0008 |
| $x_n(\text{H})$ | 0.0901 | 0.0897 | 0.0011 |
| $z_n(\text{H})$ | -0.3262 | -0.3254 | 0.0012 |
| $b_{11}(\text{N})$ | 0.0204 | 0.0201 | 0.0003 |
| $b_{12}(\text{N})$ | -0.0048 | -0.0049 | 0.0003 |
| $b_{11}(\text{C})$ | 0.0121 | 0.0119 | 0.0004 |
| $b_{22}(\text{C})$ | 0.0253 | 0.0251 | 0.0004 |
| $b_{23}(\text{C})$ | -0.0005 | 0.0010 | 0.0007 |
| $b_{11}(\text{H})$ | 0.0453 | 0.0451 | 0.0022 |
| $b_{33}(\text{H})$ | 0.0218 | 0.0211 | 0.0019 |
| $b_{12}(\text{H})$ | 0.0000 | 0.0014 | 0.0022 |
| $b_{23}(\text{H})$ | 0.0096 | 0.0081 | 0.0014 |

Table 1 (cont.)

| Parameter | Neutron data set (1) | Neutron data set (2) | Standard deviation |
|-----------------|----------------------|----------------------|--------------------|
| $v_x(\text{N})$ | 0.1237 | 0.1237 | 0.0002 |
| $u_x(\text{C})$ | 0.2376 | 0.2374 | 0.0003 |
| $x_x(\text{H})$ | 0.0814 | 0.0790 | 0.0020 |
| $z_x(\text{H})$ | -0.3298 | -0.3286 | 0.0030 |
| s_n original | 1.019 | 1.041 | 1.0% |
| s_x original | 0.996 | 0.985 | 0.6% |
| R_n | 2.75% | 3.40% | 49 observations |
| R_x | 1.87% | 1.80% | 39 observations |

HMT crystallizes in the cubic space group $I\bar{4}3m$, with cell edge $a_0=7.021 \text{ \AA}$ (Becka & Cruickshank, 1963). The carbon atom in the asymmetric unit is at $(0,0,u)$, the nitrogen at (v,v,v) and the hydrogen at (x,x,z) . The b^i have elements $b_{11}, b_{22}=b_{33}, b_{23}, b_{12}=b_{31}=0$ for C, $b_{11}=b_{22}=b_{33}, b_{23}=b_{31}=b_{12}$ for N and $b_{11}=b_{22}, b_{33}, b_{12}, b_{23}=b_{31}$ for H. $U^i=b^i \cdot a_0^2/2\pi^2 \text{ \AA}^2$. After four cycles of joint least-squares refinement the values obtained for these parameters are those listed in Table 1.

A number of results are worthy of discussion, the first concerning the correlations. A summary of these is given in Table 2, where the maximum correlation magnitudes and the averages are given between parameters of different classes. Here we have reassurance that the correlation between x_n^i and x_x^i is minimal and that the problem is very stable.

Table 2. Correlations between the parameters in the joint refinement, maximum magnitude/average magnitude

The sign for the single s_n, s_x correlation is given, but the signs varied within each of the other correlation groups. Self correlation is +1 and is ignored.

| $x_{i,n}$ | b_i | $x_{i,x}$ | s_x | |
|-----------|-----------|-----------|-----------|-----------|
| 0.13/0.09 | 0.29/0.16 | 0.24/0.10 | +0.40 | s_n |
| 0.32/0.17 | 0.30/0.09 | 0.13/0.04 | 0.07/0.04 | $x_{i,n}$ |
| | 0.58/0.14 | 0.52/0.18 | 0.38/0.16 | b_i |
| | | 0.54/0.31 | 0.67/0.28 | $x_{i,x}$ |

Returning to Table 1 we find that the X-ray data refine much more satisfactorily than in the unconstrained separate analysis. We have done the unconstrained refinement achieving a fit not significantly different in its R value from those reported in Table 1. However, the standard deviations for the hydrogen positional and thermal parameters were about 1.7 and 3.2 times larger respectively than those quoted in Table 1. The improvement cannot be a result of the introduction of more parameters, as the thermal parameters for the hydrogen atom will be determined almost entirely by the neutron data. The X-ray refinement is, therefore, considerably constrained, which is equivalent to a reduction in the number of parameters.

Our result indicates that this constraint is physically sensible, resulting in improved values for the parameters we wish to determine. It is crystal clear that analyses of future accurate X-ray data in terms of non-spherical electron density functions will have enhanced success if this joint refinement procedure can be used.

This work was carried out during the tenure of an S.R.C. studentship by one of us (J.A.K.D.), who was

on attachment to Harwell from the University of Oxford.

References

- ANDRESEN, A. F. (1957). *Acta Cryst.* **10**, 107.
 BECKA, L. N. & CRUICKSHANK, D. W. J. (1963). *Proc. Roy. Soc.* **A273**, 435.
 HAMILTON, W. C. & LA PLACA, S. J. (1968). *Acta Cryst.* **B24**, 1147.
 ROBERTSON, J. M., SHEARER, H. M. M., SIM, G. A. & WATSON, D. G. (1962). *Acta Cryst.* **15**, 1.

Acta Cryst. (1969). **A25**, 484

Contribution of the Thermal Diffuse Scattering to the Integrated Intensities of Cubic Powder Patterns

BY F. R. L. SCHOENING

Department of Physics, University of the Witwatersrand, Johannesburg, South Africa

(Received 21 October 1968)

The contribution of the thermal diffuse scattering to the measured X-ray intensities of cubic powder patterns is calculated without making the approximation that $T \geq \theta$. Correction curves are given which are valid at all temperatures.

When recent measurements of the integrated intensities of diamond powders (Schoening & Vermeulen, 1969) had to be corrected for thermal diffuse scattering (TDS) it appeared that for low temperatures no simple method existed in the literature. The work by Chipman & Paskin (1959*a,b*) which is valid for moderately high temperatures ($T \geq \theta$) was therefore extended to cover low temperatures. The results are of interest because an easy correction procedure has been derived which, within certain limitations, is applicable to cubic powders at all temperatures.

The first-order TDS per cubic unit-cell for a monatomic crystal is (James, 1948)

$$I_2 = F^2 e^{-2M} \frac{4 \sin^2 \theta}{nmg^2 \lambda^2} \sum_j \frac{\bar{E}_{\phi j}}{v_{\phi j}^2} \cos^2 \alpha_{sj}, \quad (1)$$

where n is the number of atoms of mass m in the unit cell and the other symbols are as defined by James (1948). Equation (1) can be applied to f.c.c. or b.c.c. crystals by setting $n=4$ or 2 respectively. For crystals with more than one atom in the primitive cell (e.g. diamond cubic structure for which $n=8$) it remains valid for the acoustic modes. The sum in equation (1) will now be approximated by $\bar{E}_{\phi} v_m^{-2}$ where \bar{E}_{ϕ} and v_m are suitable mean values. Without this approximation it would not be possible to continue without making reference to a specific material.

With $x = hv/KT = g\theta/g_m T$ equation (1) becomes

$$I_2 = F^2 e^{-2M} \frac{4KT \sin^2 \theta}{nmg^2 v_m^2 \lambda^2} \left(\frac{x}{e^x - 1} + \frac{x}{2} \right).$$

Following Warren (1953) the TDS background of the powder patterns is obtained by integrating for constant $2\lambda^{-1} \sin \theta$ over the Brillouin zone which is assumed to be spherical with radius g_m . After summing the contributions of the hkl reflexions, the TDS becomes

$$I_{TD} = F^2 e^{-2M} \frac{2aK\theta \sin \theta}{nmg_m v_m^2 X \lambda^2} \sum_{hkl} \frac{j_{hkl}}{X_{hkl}} \left\{ \frac{1}{2}(ag_m - |X - X_{hkl}|) - ag_m \frac{T}{\theta} \ln \left[1 - \exp \left(-\frac{\theta}{T} \times |X - X_{hkl}|/ag_m \right) \right] + \frac{T}{\theta} ag_m \ln \left[1 - \exp \left(-\frac{\theta}{T} \right) \right] \right\}, \quad (2)$$

where a is the cubic lattice parameter and j_{hkl} , X and X_{hkl} are as defined by Warren (1953). The result agrees with that by Herbstein & Averbach (1955).

The TDS contribution to the measured integrated intensity can now be obtained by following Chipman & Paskin (1959*b*). They separate the TDS into that part, say B_{TDS} , which is subtracted together with the background, and that part, say P_{TDS} , which remains with the integrated intensity. The sum $A_{TDS} = P_{TDS} + B_{TDS}$ can be obtained by integrating equation (2). B_{TDS} is found by: (1) calculating the TDS from equation (2) at the two positions corresponding to the beginning and end of the measured reflexion, (2) connecting the resulting two intensities by a straight line and (3) cal-