



**AUSTRALIAN ATOMIC ENERGY COMMISSION**  
**RESEARCH ESTABLISHMENT**  
**LUCAS HEIGHTS**

**A MODIFIED VERSION OF THE BUSING-MARTIN-LEVY LEAST SQUARES  
PROGRAM FOR THE DIRECT FITTING OF STRUCTURES TO POWDER  
DIFFRACTION PATTERNS BY THE METHOD OF PROFILE ANALYSIS**

by

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ABSTRACT

The Busing-Martin-Levy (BML) crystallographic least squares program has been modified to handle the case of the overlapping diffraction data encountered in powder patterns. Each count along the scan is treated as a single observation and the pattern is considered to be the superposition of the  $(h,k,l)$  Gaussian peaks, as in the method of Rietveld (*Acta Cryst.*, 22, 151 (1967)). In this way the structure is fitted directly to the diffraction pattern, while details of the profiles are not lost. For this reason, together with the fact that a larger number of observations are used, the method is superior to conventional refinements with integrated intensities (which can also be done with the present program).

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COMPUTER CODES; CONFIGURATION; CRYSTALLOGRAPHY; GAUSS FUNCTION;  
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## 1. MODIFICATION OF THE BML PROGRAM

The BML program is designed for non-overlapped diffraction data, e.g. from a single crystal. In this case, the normal equation on  $F^2$  with respect to the shift  $\Delta$  in the n-th variable parameter,  $\rho_n$ , is

$$\sum_{hkl} w_{hkl} \left( F_{ohkl}^2 - s F_{c_{hkl}}^2 \right) \left( \frac{\partial F^2}{\partial \rho_n} \right) - \Delta \rho_1 \sum_{hkl} w_{hkl} \left( \frac{\partial F^2}{\partial \rho_1} \right) \left( \frac{\partial F^2}{\partial \rho_n} \right) - \dots - \Delta \rho_n \sum_{hkl} w_{hkl} \left( \frac{\partial F^2}{\partial \rho_n} \right)^2 - \dots = 0 \quad \dots (1)$$

The sum is over all the reflexions (hkl) and  $w_{hkl}$  and s are weighting and scale factors.

When overlapping of the reflexions (hkl) occurs, intermediate sums over the overlapped intensities must be made, and the number of observations reduced accordingly. If there are q overlapping reflexions in a peak, Equation (1) becomes

$$\sum_{\text{pattern}} \left[ \left( \sum F_o^2 (\text{peak}) - s \sum_q w_q m_q F_q^2 \right) \left( \sum_q w_q m_q \frac{\partial F_q^2}{\partial \rho_n} \right) - \Delta \rho_1 \left( \sum_q w_q m_q \frac{\partial F_q^2}{\partial \rho_1} \right) \left( \sum_q w_q m_q \frac{\partial F_q^2}{\partial \rho_n} \right) - \dots - \Delta \rho_n \left( \sum_q w_q m_q \frac{\partial F_q^2}{\partial \rho_n} \right)^2 - \dots \right] = 0 \quad \dots (2)$$

The factors  $m_q$  are the powder multiplicities, and the number of observations is the number of peaks in the pattern. The BML program has been modified to handle this case - conventional integrated intensity analysis of overlapping data.

With further modification, the pattern-fitting method of Rietveld (1967) can be programmed. Each observation along the scan is now a data point and the factors  $m_q$  are replaced by  $K_q$ 's, where

$$K_q = \frac{m_q \exp - (4 \ln 2 \cdot (\Delta 2\theta)^2 / b^2)}{b \sin \theta \sin 2\theta} \dots (3)$$

,  $2\theta$  is the theoretical diffraction angle for the  $q$ -th reflexion (hkl),  $\Delta 2\theta$  the deviation of this value from the  $2\theta$  value of the observation point on the scan, and  $b$  the half-width of the (hkl) component (the spread of the peak is assumed to have Gaussian form).  $b$ 's over the pattern are obtained by inspection or from standard patterns, and the theoretical diffraction angles  $2\theta$  from a knowledge of the wavelength and cell dimensions. The equation corresponding to (2) for the profile analysis mode has factors  $K_q$  instead of  $m_q$ . Each data point can have  $q$  contributing reflexions, the contributions being modified according to (3). The number of observations is now the number of points along the scan.

## 2. HOW TO RUN THE PROGRAM

### (a) Conventional Integrated Intensity Mode

The data is punched up in the same way as described for the conventional BML program (Busing, Martin and Levy 1962, G.W. Cox, unpublished work), except for the (hkl) reflexion data cards. These are punched as a group for each integrated intensity measurement, in format (1X, 314, 1X, 2F9.3, I3, F9.4) as follows:

	<u>h k l</u>	<u><math>\Sigma F_o^2</math></u>	<u><math>\sigma(\Sigma F_o^2)</math></u>	<u>IQ</u>	<u>m(hkl)</u>
reflexions in a peak	$h_1 k_1 l_1$	1.0	1.0	1	$m_1$
	$h_2 k_2 l_2$	1.0	1.0	1	$m_2$
	.	.	.	.	.
	.	.	.	.	.
	.	.	.	.	.
	.	.	.	.	.
	$h_q k_q l_q$	$\Sigma F_o^2$	$\sigma(\Sigma F_o^2)$	1	$m_q$

The observed intensity of the peak,  $\Sigma F_o^2 = I_{\text{peak}} \sin \theta_{\text{peak}} \sin 2\theta_{\text{peak}}$  (for neutrons) is punched on the last card for the group; for the other members of the group it is set at 1 (as well as the standard deviation). Where there is only one reflexion in a peak, it is punched as for the last member of a group. IQ is the scale factor indicator, set at 1. This mode can also be used with superposed data from twinned crystals, if the  $m_q$  are set at 1 (Taylor, Mueller and Hitterman 1970).

(b) Profile Analysis Mode

A program called Profile Part I was written to generate card images containing the  $K_q$  factors. Each intensity measurement along the scan is taken in turn, and the program computes which reflexions are contributing at that point (the range of a reflexion is taken as 3.1b), and the corresponding  $K_q$  factors. Card images may be punched or transferred via disk to the input of the modified least-squares program. At present, Profile Part I is concatenated with the BML program, so that the observed diffraction pattern can be input and the calculated pattern can be output in the one computer job. The data cards for Profile Part I are:

Card 1. Wavelength and reciprocal cell constants,  $\lambda$ ,  $a^*$ ,  $b^*$ ,  $c^*$ ,  $\cos \alpha^*$ ,  $\cos \beta^*$ ,  $\cos \gamma^*$  (7F10.5).

Card 2.  $h_{\min}$ ,  $k_{\min}$ ,  $l_{\min}$ ,  $h_{\max}$ ,  $k_{\max}$ ,  $l_{\max}$  (6I5). These are the minimum and maximum (hkl) values expected over the pattern.

Card 3. Data points; one card for each point of the pattern containing  $2\theta_i$ ,  $I_i$ ,  $B_i$ ,  $b_i$  where  $I$  is the intensity uncorrected for background,  $B$  is the background and  $b$  the half-width at  $2\theta_i$  (F10.5, 2I10, F10.5). If  $(I_i - B_i) = 1$ , which occasionally happens,  $I_i$  or  $B_i$  can be changed by one count.

Multiplicities and systematic absences are programmed in Part I by the user for the special case being considered. The values of  $b$  as a function of  $2\theta$  are estimated by observing the resolution of the spectrometer being used.

Card 4. Blank card at end of data.

$n$  card images are output by Part I for each part of the pattern, one for each (hkl) reflexion within range of that point. Each card image contains  $h$ ,  $k$ ,  $l$ ,  $I-B$ ,  $\sigma(I-B)$ ,  $IQ$  and  $K_{hkl/10}$  with the format (1X, 3I4, 1X, 2F9.3, I3, F9.4). The first  $n-1$  cards have  $(I-B)$  and  $\sigma(I-B) = 1$ , and the  $n$ -th and last card for the point the true values of these quantities. These cards or images are then input into the modified BML deck, with the rest of the data punched up in the usual way. The variable parameters must now be the same for each cycle.

For example, for the observation at  $2\theta = 13.743^\circ$  of a neutron diffraction pattern of  $UF_6$ , having  $I = 251$ ,  $B = 38$ , and  $b = 0.43^\circ$ , the following 4 records are produced by Profile Part I (multiplicities  $m$  are also recorded on the printed output):

<u>h k l</u>	<u>I-B</u>	<u><math>\sigma(I-B)</math></u>	<u>IQ</u>	<u><math>K/10</math></u>	<u>m</u>
011	1.000	1.000	1	32.334	4
020	1.000	1.000	1	15.559	2
101	1.000	1.000	1	8.839	4
210	213.000	18.083	1	0.409	4

The reflexion contributing most at this point is the (011).

### 3. TESTS OF THE PROGRAM

The program has been tested with neutron diffraction powder patterns for  $UF_6$  and  $K_2NiF_6$ . The observed and calculated profiles for the  $UF_6$  pattern are shown in Figure 1.

The data for  $K_2NiF_6$  were analysed both in the integrated intensity and profile analysis modes. The parameters obtained by the two methods were as follows:

Mode	$x_F$	$B_{Ni}(\text{\AA})^2$	$B_K(\text{\AA})^2$	$B_F(\text{\AA})^2$
Integrated Intensity	0.219(1)	1.5(3)	2.5(5)	2.2(2)
Profile Analysis	0.2190(5)	1.4(1)	2.5(2)	1.9(1)

The profile analysis mode is seen to be about twice as accurate as the conventional integrated intensity mode. The observed and calculated profiles for the  $K_2NiF_6$  pattern are shown in Figure 2. The fit is good, as  $\chi = (\sum w(I_o - I_c)^2 / (NO - NV))^{1/2}$ , where NO is the number of pattern points and NV the number of variables, is 0.84.  $\chi$  should be unity for complete agreement between theory and experiment.

Convergence is better in the profile mode and is usually obtained in 3 or 4 cycles.

### 4. REFERENCES

- Busing, W.R. Martin, K.O., and Levy, H.A. (1962) - ORNL-TM-305.  
 Rietveld, H.M., (1967) - Acta. Cryst. 22, 151.  
 Taylor, J.C., Mueller, M.H. and Hitterman, R.L. (1970) - Acta. Cryst. A26, 559.

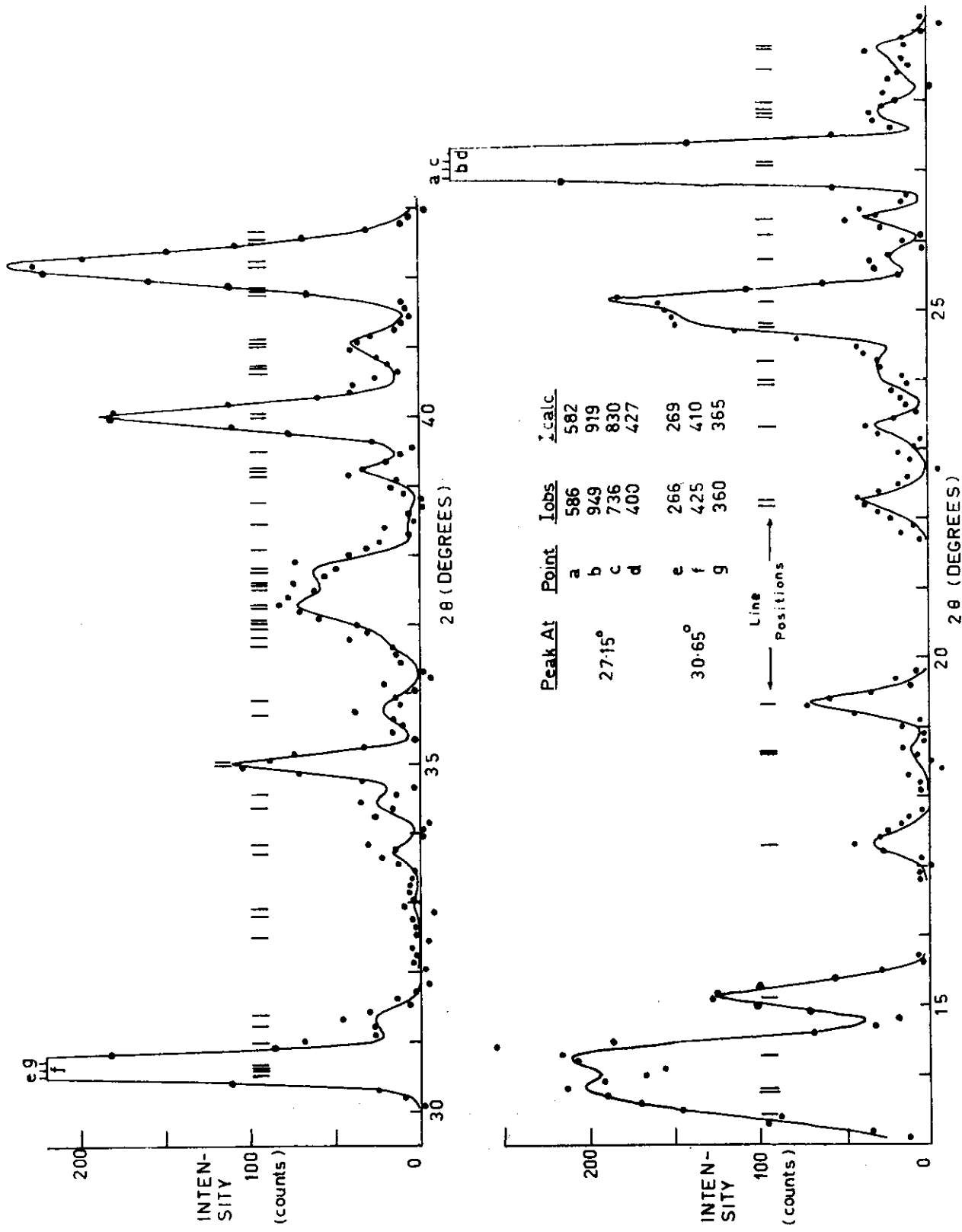


FIGURE 1. OBSERVED AND CALCULATED PROFILES FOR UF<sub>6</sub> NEUTRON DIFFRACTION PATTERN

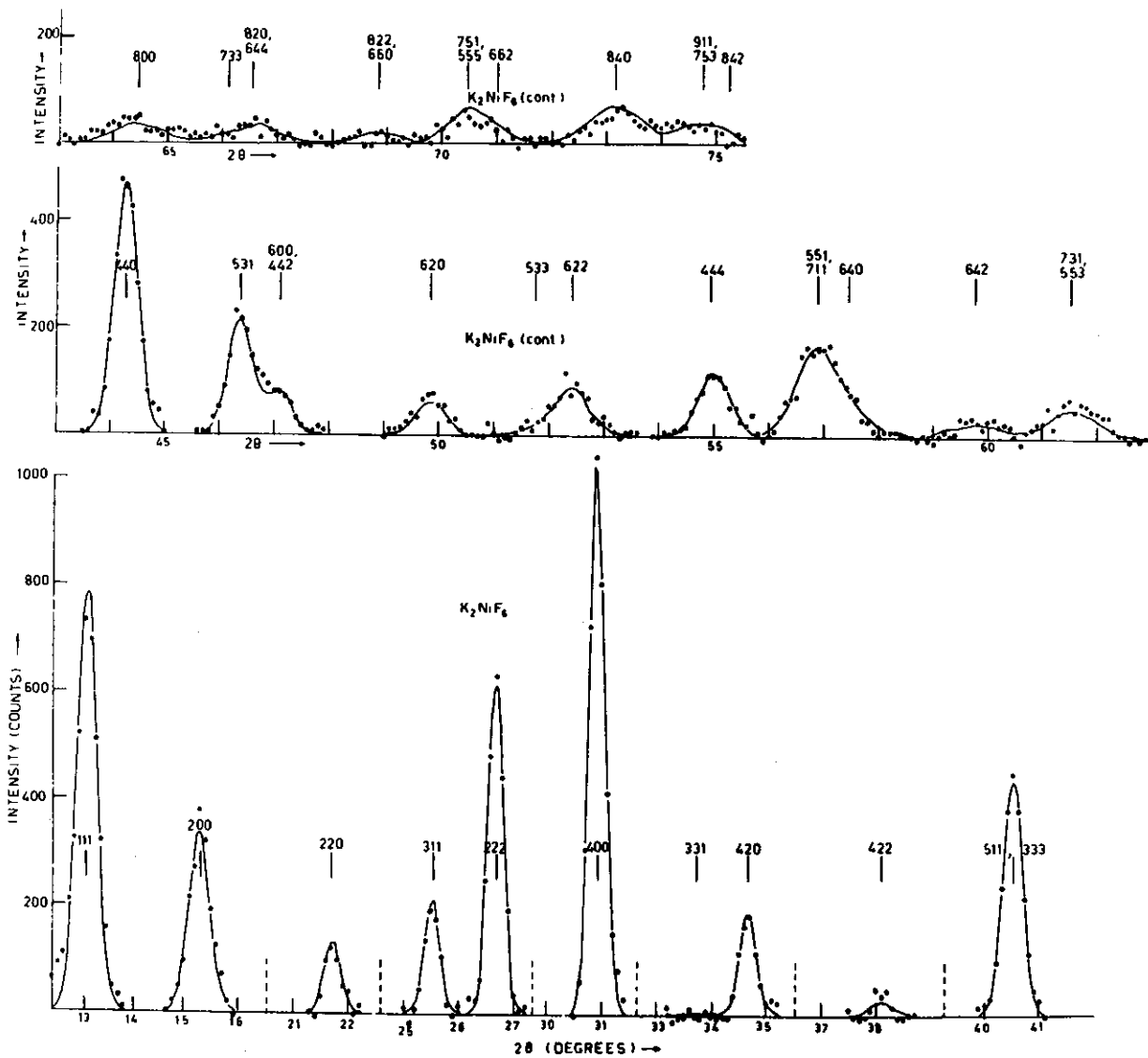


FIGURE 2. OBSERVED AND CALCULATED PROFILES FOR  $K_2NiF_6$  NEUTRON DIFFRACTION PATTERN