Precision Peak Determination in X-ray Powder Diffraction*

T. C. Huang

IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, U.S.A.

Abstract

A systematic study of the derivative methods for peak search analysis of X-ray powder diffraction data was made to evaluate the relative merits of the methods. Results of analysing computer simulated diffraction peaks show that the peak positions can be precisely determined by the first derivative of a least-squares fitted cubic polynomial. The technique has an accuracy of 0.001° and precisions ranging from $\pm 0.003^{\circ}$ to 0.02° depending on the levels of counting statistical noise. The study also shows that reliable resolution of overlaps has been obtained using the second derivative of a quadratic/cubic polynomial. A method of combining the first derivative of a cubic polynomial and the second derivative quadratic/cubic polynomial has thus been used for precision peak search analysis. The combined first/second derivative method has been tested with experimental diffraction patterns recorded with various step sizes, levels of counting statistical noise and degrees of overlaps. Analysis results agree with those obtained from the computer simulated data. A comparison between the peak search and the profile fitting results showed good matches in the peak positions but relatively poor agreements in the peak intensities especially for the heavily overlapping peaks.

1. Introduction

Peak search analysis is one of the basic data reduction processes in X-ray powder diffraction studies. Precision peak identification and accurate position determination are important in a wide variety of analyses such as phase identification, powder pattern indexing, lattice parameter determination, residual stress analysis, stacking fault calculation, etc. Techniques include a parabolic fitting to the maxima (Koistinen and Marburger 1959), a profile fit to an entire peak (Huang and Parrish 1975), use of mid-chord bisection of a peak profile (Segmuller 1969), and a derivative method (Sonneveld and Visser 1975). These have been used for peak determination of powder diffraction patterns with various degrees of success (Mallory and Snyder 1979). To obtain the maximum advantage of computers for routine peak search analysis, it is necessary to use a data reduction technique which can rapidly and precisely reduce the experimental data. The derivative method is well suited for this purpose.

The aim of this paper is to report the results of evaluating the performances of peak search by first, second and higher order derivatives. The relative merits of the derivative methods in terms of accuracy, precision and resolution were determined

^{*} Paper presented at the International Symposium on X-ray Powder Diffractometry, held at Fremantle, Australia, 20–23 August 1987.

using computer simulated diffractometer peaks. The results were subsequently used to develop an algorithm for high precision and resolution peak search analysis of X-ray powder diffractometer data. The technique has been tested using experimental data obtained with various step sizes, overlaps, counting statistical noises and profile widths. Peak search results were also compared with those obtained by profile fitting to study the different characteristics between these two methods.

2. The Derivative Methods

At the peak position of a diffraction profile where the X-ray intensity reaches a maximum, the slope is zero. A diffraction peak can therefore be identified at the location where the value of the first derivative crosses zero from positive to negative, the second derivative reaches a negative minimum, or the third derivative crosses zero from negative to positive. In principle, values of derivatives can be calculated directly from the experimental data. However, this technique is not widely used because of its strong dependence on the counting statistical noise. To minimise possible errors caused by the random noise, Savitzky and Golay (1964) have developed an effective method of smoothing and differentiation of data by the least-squares technique in which the values of first, second and/or higher order derivatives can be calculated



Fig. 1. Derivatives of a seven-point cubic polynomial: (a) original Si(220) Cu K $a_{1,2}$ doublet; (b) the first (circles), second (crosses) and third (triangles) derivatives.

using a set of tabulated integers. The method is rapid and simple to apply, and was used in this study.

Values of the derivatives and the peak search results determined from the Savitzky-Golay procedure depend on the order of the derivative, the degree of the polynomial and the number of convolute points used in the calculation. An experimental diffractometer Si(220) Cu K $\alpha_{1,2}$ doublet (see Fig. 1*a*) is used to illustrate the differences between the first, second and third derivatives. The derivative curves obtained from a seven-point cubic polynomial calculation are plotted in Fig. 1*b*. The peak positions of the K $\alpha_{1,2}$ doublet obtained from these three derivative curves are significantly different from one another (see Table 1). Peak search results also depend on the number of convolute points N used in the calculation. As shown in Table 1, the different values of 2θ have been obtained by the 7, 15 and 25 point cubic polynomial calculations. Results also show a failure to resolve the K α_2 peak from the Si(220) doublet by the first derivative method with N = 15 and 25, and by the third derivative when N = 25.

Peak	Convolute			
	point N	First	Second	Third
Ka ₁	7	47.302	47.294	47.293
-	15	47.304	47.300	47.299
	25	47.311	47.298	47.308
Ka ₂	7	47.416	47.448	47.447
-	15		47.445	47.445
	25		47.462	

Table 1. Results of peak search by derivatives of a cubic polynomial

There are two types of error commonly generated by reduction of experimental data; namely, the intrinsic or systematic error introduced solely by the data analysis technique and the random error resulting from the counting statistical fluctuation obtained during an experiment. [The term 'systematic error' is not used here so there is no confusion with the well-known systematic errors arising from instrument misalignment, geometric aberration, etc. (Parrish 1965).] The accuracy of an analysis depends on how well we can control or compensate for intrinsic errors, and the precision of an experiment relies on how well we can overcome or analyse random errors.

The effects of intrinsic and random errors can be properly evaluated using computer simulated single diffractometer peaks. For peaks generated by a computer, the peak positions are exactly known and the levels of counting statistical noise can be precisely added. To study the effect of asymmetric profiles commonly observed in powder diffractometry, diffraction peaks with various degrees of asymmetry at 20°, 50° and 80° 2θ have been used. (The profile fitting method was used to generate diffractometer peaks whose shapes are identical to those observed experimentally.) Counting statistical noise was added when required. Computer simulated overlaps with known separations have also been used to determine the minimum resolution limits. A study of the relative merits of the derivative methods in terms of intrinsic and random errors, and the overlap resolution have provided a better understanding of the peak search analysis by derivatives.

(a) Intrinsic Error

The intrinsic errors associated with the derivative methods were first determined using computer simulated peaks without random counting statistical noise. Cu K α_1 diffraction peaks at 20°, 50° and 80° with step sizes $\Delta 2\theta = 0.01^\circ$, 0.02° , 0.03° , 0.04° and 0.05° were used. Analysis showed that the peak positions were dependent on the peak search parameters used, i.e. the order of the derivative, the degree of the polynomial and the product $N\Delta 2\theta$. The value $N\Delta 2\theta$ represents the angular range used in the Savitzky–Golay calculation and is called the convolute range (CR). The peak positions $2\theta_{PS}$ obtained by the first derivative of a quadratic polynomial, the first derivative of a cubic polynomial, and the second derivative of a quadratic/cubic polynomial as a function of CR are plotted in Fig. 2. (The term 'quadratic/cubic



Fig. 2. Peak search results $2\theta_{PS}$ for the first derivative of a quadratic polynomial (open circles); the first derivative of a cubic polynomial (solid circles); and the second derivative of a quadratic/cubic polynomial (crosses).

Table 2. Intrinsic errors Δ of peak search by

Derivative	Peak)	
method	(2θ ₀)	$\frac{1}{2}W$	W	$\frac{3}{2}W$
First deriv.	20°	0.001°	-0.004°	-0.009°
quadratic	50°	0.001°	0.004°	0∙014°
1	80°	-0.001°	-0.000°	-0.000°
First deriv.	20°	-0.001°	-0.001°	-0.002°
cubic	50°	-0.000°	0.000°	0.002°
	80°	-0.001°	-0.001°	-0.001°
Second deriv.	20°	0.003°	0.004°	0.002°
quad./cubic	50°	0.005°	-0.006°	-0.007°
	80°	-0.001°	-0.001°	-0.001°

polynomial' stands for either quadratic or cubic polynomial, and CR is expressed in units of both $^{\circ}2\theta$ and the full-width-at-half-maximum W.) Fig. 2 shows that the results obtained by each method vary systematically with CR, and values of $2\theta_{PS}$ determined from the first derivative of a cubic polynomial are closest to the true value of $2\theta_0 = 20^{\circ}$.

Results of analysing the 20°, 50° and 80° peaks are summarised in Table 2, showing that the discrepancies Δ between $2\theta_{PS}$ values and the true peak position $2\theta_0$ depend on the derivative method and the value of CR chosen. This is especially true for asymmetric peaks located at small 2θ (e.g. 20° and 50°). For nearly symmetric peaks at high 2θ (e.g. 80°), values of Δ gradually approach one another. Since the Δ were obtained from simulated peaks with zero counting statistical noise, these discrepancies were introduced solely by the derivative method used, and therefore they are the intrinsic errors associated with the method. Among these three methods, the results obtained by the first derivative of a cubic polynomial have the smallest intrinsic errors with $\Delta = 0.001^\circ$ on the average, and 0.002° at maximum.

Analyses with higher-order derivatives and higher-degree polynomials have also been studied. In general, the intrinsic error decreases with the order of the derivative and the value of CR, but increases with a decreasing degree of the polynomial. These dependencies on peak search parameters are most pronounced for highly asymmetric peaks.

Derivative	P/σ	P/B				
method		100	10	1	0.1	
First deriv.	25	19.996(2)	19.996(2)	19.996(2)	19.996(2)	
quadratic	10	19.996(4)	19.997(5)	19.997(5)	19.996(5)	
-	3	19.997(15)	19.995(14)	19.997(17)	19.995(17)	
First deriv.	25	20.000(3)	19.999(3)	20.000(3)	19.999(3)	
cubic	10	20.000(8)	20.000(7)	20.000(8)	19.999(8)	
	3	19.999(20)	20.000(20)	20.000(21)	19.998(21)	
Second deriv.	25	20.005(5)	20.005(5)	20.005(5)	20.005(6)	
quad./cubic	10	20.004(13)	20.005(12)	20.005(14)	20.004(23)	
	3	20.000(31)	20.001(31)	19.999(98)	20.005(159)	

Table 3. Random errors of peak search by derivatives $(2\theta_0 = 20^\circ \text{ and } CR = W)$

(b) Random Error

The effect of counting statistical error on peak search by derivatives has also been studied using computer generated diffraction peaks. To simulate a wide range of experimental conditions, diffraction peaks at 20°, 50° and 80° with values of P/B ranging from 100 to 0.1 and P/σ from 25 to 3 were used, where P is the net peak intensity above the background B and the estimated standard deviation is $\sigma = (P+B)^{1/2}$. For each combination of P/B and P/σ , a total of 360 peaks (120 each for $\Delta 2\theta = 0.01^{\circ}$, 0.02° and 0.03°) were added with different amounts of noise generated by a computer following Poisson statistics. Typical peak search results of the 20° peaks analysis with CR = W are listed in Table 3. Results of the 360

 $2\theta_{\rm PS}$ values obtained from peaks having the same P/B and P/σ are summarised in terms of the average $2\theta_{\rm PS}$ value and its standard deviation (in parentheses). The average $2\theta_{\rm PS}$ obtained by the derivative methods each remains approximately the same regardless of the levels of P/B and P/σ . In other words, the averages are not affected by the counting statistical noise and therefore can also be used for studying the effect of intrinsic error. Among the three derivative methods, the first derivative of a cubic polynomial has the lowest intrinsic error. As shown in Table 3, the average of the twelve $2\theta_{\rm PS}$ obtained by the method is within 0.001° of the true peak position $2\theta_0 = 20^\circ$. Both the first derivative of a quadratic and the second derivative of a quadratic/cubic polynomial methods have slightly larger intrinsic errors (i.e. $\Delta = -0.004^\circ$ and $+0.004^\circ$ respectively). It should be noted that these results agree with those previously obtained from noise-free diffraction peaks (see Table 2).



Fig. 3. Plot of the average standard deviation against P/σ .

Values of the standard deviation represent the random errors associated with the derivative methods. As shown in Table 3, the standard deviations of each individual method are approximately the same for peaks having the same levels of P/σ , even through their P/B values differ by three orders of magnitude. (Results on peaks with $P/\sigma < 3$ will not be discussed here because a significant number of the noisy peaks are below the detection limits.) The effect of counting statistical noise can be shown clearly from the plot in Fig. 3 of the average value of the standard deviations against P/σ . As shown, the standard deviation of a derivative method varies systematically with P/σ ; the larger the P/σ , the smaller the standard deviation. In other words, the random error is smaller and the precision is higher for a peak with lower counting noise. Compared with other derivative methods, the first derivative of a quadratic polynomial consistently gives the smallest random error and the highest precision. On the other hand, the second derivative of a quadratic/cubic polynomial has the largest random errors and the lowest precision because it is most sensitive to the counting noise.

The effects of peak search parameters on both the intrinsic and the random errors can be summarised as follows: (1) the lower the order of the derivative, the smaller the intrinsic and random errors; (2) the higher the degree of the polynomial, the lower the intrinsic error, but the larger the random error; and (3) the larger the value of CR, the larger the intrinsic error, but the smaller the random error.



Fig. 4. Overlaps of three peaks with intensity ratios $1:1:\frac{1}{2}$ and separations $\Delta = W$ (left), $\frac{3}{4}W$ (centre), and $\frac{1}{2}W$ (right).

(c) Overlap Resolution

Detection of overlapping peaks is an important process in X-ray powder diffraction analysis. In this study, the resolution limits are determined from computer generated overlaps with known separations. The degree of overlap between two peaks depends on the separation and the relative intensity ratio. Fig. 4 shows the severity of overlaps for clusters of three peaks with separations $\Delta = W$, $\frac{3}{4}W$ and $\frac{1}{2}W$, and relative intensity ratios $1:1:\frac{1}{2}$. In the case of $\Delta = W$ (left of Fig. 4), the two stronger peaks with equal intensities are clearly visible from the cluster, but the third weaker peak appears only as a shoulder next to the stronger peak. As the separation decreases to $\Delta < \frac{3}{4}W$ (centre of Fig. 4), the overlaps become much more severe. At $\Delta = \frac{1}{2}W$, the peaks are so close to each other that no visible evidence of overlap can be observed from the cluster.

Peak search results show that all three methods are successful in resolving overlaps when the separations are large. As Δ decreases, the first derivative of a quadratic polynomial is the first to fail, followed by the first derivative of a cubic polynomial. The second derivative of a quadratic/cubic polynomial has the highest resolution. The minimum separation for a successful resolution obtained by the second derivative of a quadratic/cubic polynomial and $CR = \frac{1}{2}W$ is $\Delta = \frac{1}{2}W$. The minimum separations for the first derivative methods are twice as large, i.e. $\Delta = W$. The minimum resolution increases with CR. A detailed discussion of the resolution limits of the derivative methods and their dependencies on CR have been given elsewhere (Huang and Parrish 1984) and will not be repeated here. A resolution better than $\frac{1}{2}W$, in principle, can be obtained using higher orders of derivative (e.g. quartic, quintic etc.). However, these methods are too sensitive to the counting noise and probably give false peaks. Taking into account both resolution and reliability, the second derivative of a quadratic/cubic polynomial is most effective for the detection of overlapping peaks.

(d) Combined First/Second Derivative Method

The above results show that the peak positions of an X-ray powder diffraction pattern can be accurately and precisely determined by the first derivative of a cubic polynomial. The analysis also shows that overlaps are best resolved by the second derivative of a quadratic/cubic polynomial. An algorithm combining these two methods has therefore been used for high precision and resolution peak search of X-ray powder diffraction data (Huang and Parrish 1984). In the method, peak identifications and 2θ locations are first determined by the first derivative of a cubic polynomial, and the unresolved overlaps are then re-examined and identified by the second determining peak positions with an accuracy of 0.001° and precisions ranging from $\pm 0.003^{\circ}$ to 0.02° depending on the levels of counting statistical noise, and resolving overlaps with separations $\gg \frac{1}{2}W$.



Fig. 5. Diffraction pattern of a mineral mixture recorded with $\Delta 2\theta = 0.01^{\circ}$ and $\Delta t = 10$ second per step. Peaks identified by the combined first/second derivative method are also marked: $CR = \frac{1}{2}W$ and the first derivative (pluses); $CR = \frac{1}{2}W$ and the second derivative (crosses); CR = W and the first derivative (open circles); CR = W and the second derivative (solid circles); CR = 2W and the first derivative (open diamonds); CR = 2W and the second derivative (solid diamonds).

3. Analysis of Experimental Patterns

The combined first/second derivative method has been used to analyse experimental patterns and to illustrate its use to analyse difficult cases occurring in peak search analysis of X-ray powder diffractometer data (Huang *et al.* 1984).

(a) Peak Identification

A diffraction pattern of a mineral mixture of quartz, orthoclase and albite, recorded with a step size $\Delta 2\theta = 0.01^{\circ}$ and count time $\Delta t = 10$ second per step, was used for the study of peak detection and overlap resolution (see Fig. 5). Peak search analyses by the combined first/second derivative method were done with $CR = \frac{1}{2}W$, W and 2 W. The diffraction peaks identified by first and second derivatives are marked in Fig. 5. In general, peaks that are easily visible from the pattern were found by the first derivative. The remaining peaks and the unresolved overlaps were then detected by the second derivative. The resolution achieved depends on the value of CR. The smaller the value of CR, the better the resolution; for example, a weak peak (marked by the cross at 20.89° in Fig. 5), which is separated by $\Delta = \frac{1}{2} W$ or 0.06° from the strong peak at 20.83°, was resolved by the second derivative when a small CR = $\frac{1}{2}W$ was used. Another peak at 21.00°, which is separated by $\Delta = W$ or 0.11° from the 20.89° peak and by $\Delta = \frac{3}{2}W$ or 0.16° from the 20.83° peak, was identified by the first derivative with both $\tilde{CR} = \frac{1}{2}W$ and W. However, when CR increases to 2W, only the second derivative could detect the peak at 21.00°. Similar resolution limits have been obtained previously from computer simulated data (Huang and Parrish 1984). The number of peaks identified by the first and second derivatives as well as their sums are also listed in Table 4, which shows that the larger the value of CR, the smaller the number of identified peaks. The successful resolution of $K\alpha_1$ and $K\alpha_2$ overlaps with separation $\Delta \sim \frac{1}{2} W$ by the second derivative was mainly responsible for the large increase in the number of peaks from 26 at CR = W to 38 at $\frac{1}{2}W$.

CR	First deriv. cubic	Second deriv. quad./cubic	Total
$\frac{1}{2}W$	20	18	38
Ŵ	19	7	26
2 W	15	5	20

Table 4. Effect of CR on the number of identified peaks

Table 5. Effect of step size on the maximum number of identified pe	eaks
---	------

$\Delta 2\theta$	N	CR,	nin	No. of peaks	
(deg.)		°20	W	identified	
0.01	5	0.05	0.5	38	
0.02	5	0.10	0.9	29	
0.03	5	0.15	1.3	25	
0.04	5	0.20	1.7	23	

The step size used to record an experimental pattern also has an effect on the resolution of the peak search analysis. As the step increases, details of overlaps wash out and fewer peaks become visible. In addition, the smallest value of CR which can be used in a peak search analysis is limited by the minimum requirement of five convolute points in the Savitzky–Golay calculation. Diffraction patterns similar to Fig. 5 obtained with steps of 0.01° to 0.04° have been used to illustrate its effect on resolution. As shown in Table 5, the smallest value of CR which can be used varies

Peak	P/σ		range (CR)		
		$\frac{1}{2}W$	W	$\frac{3}{2}W$	2 W
Α	28	22.002(4)	22.003(3)	22.006(3)	22.005(2)
	9	21.996(11)	22.002(8)	22.003(6)	22.003(4)
В	8	22.276(13)	22.278(8)	22.277(6)	22.275(5)
	2.5	22.264(20)	22.276(20)	22.280(14)	22.273(15)

Table 6. Effect of counting noise on peak position

(b) Peak Position Determination

Diffraction patterns of the three-mineral mixture recorded with a count time of 1 and 0.1 s were used to evaluate the peak search precision in 2θ determination. Results of two K α_1 peaks at 22.00° and 22.28° (marked A and B in Fig. 5 respectively) are summarised in Table 6, where the average of twenty $2\theta_{PS}$ (ten for $CR = \frac{1}{2}W$) is listed first and its standard deviation is given in parentheses. The average values of 2θ are approximately the same for the same peak, while the standard deviation which is a measurement of the random error increases as the ratio of P/σ decreases. For example, the standard deviation obtained with CR = W increases from 0.003° to 0.020° as P/σ decreases from 28 to 3. The results agree with those obtained previously from synthesised peaks (see Table 3). The standard deviation for peaks having the same value of P/σ decreases with increasing CR. In other words, the larger the value of CR, the smaller the random error and the higher the precision.



Fig. 6. Diffraction pattern of the fosterite (222), (402) and (231) reflections: experimental data (circles); individual reflections resolved by the profile fitting method (dashed curves); and sum of profile fitted data (solid curve).

A section of three overlapping fosterite reflections was used to study the differences between the peak search and the profile fitting method. The diffraction pattern of the six peak cluster is plotted in Fig. 6. The experimental data are shown as open circles and the solid curve was determined by profile fitting. The individual reflections obtained by profile fitting are shown as dashed curves. The six $K\alpha_1$ and $K\alpha_2$ peaks of the (222), (402) and (231) reflections in the cluster have approximately equal separations and $\Delta \sim W$. Since the separations between peaks are within the resolution limit of the first derivative of a cubic polynomial, precise peak search results can therefore be obtained and compared with the profile fitting results.

Method	(222)		(402)		(231)	
	Ka_1	Ka ₂	Ka ₁	Ka ₂	Ka ₁	Ka ₂
		Peak	position ($^{\circ}2\theta$)			
PS	52.144	52.282	52.431	52.574	52.731	52.864
PF	52.144		52.435		52.735	
PS - PF	0		-0.004		-0.004	
		Peak in	ntensity (count	s)		
PS	13774	8127	5216	2815	1308	680
PF	13550		4477		1033	
(PS - PF)/PF	2%		17%		27%	

Table 7. Comparison between peak search (PS) and profile fitting (PF) results

Results obtained by both the peak search and the profile fitting methods are listed in Table 7. Peak search analysis successfully resolved the cluster into six peaks. Values of $2\theta_{PS}$ were determined by the first derivative of a cubic polynomial with CR = W and the peak intensities were estimated by fitting a Lorentzian curve to the top three experimental data of each peak. The main difference between the two methods is that the profile fitting method can resolve individual reflections and gives results as though there were no overlaps (Parrish and Huang 1979), while the peak search method cannot correct for the overlap interferences. Consequently, the results obtained by peak search are different from those by profile fitting by an amount depending on the degree of overlap. For example, the peak positions of the (222) $K\alpha_1$ peak obtained by both methods are the same because it is relatively free of interference from the adjacent reflection. However, the peak search angles of both the (402) and the (231) K α_1 peaks are 0.004° smaller than the profile fitting values due to the interferences from the $K\alpha_2$ tails of the stronger overlapping reflections. The effect of overlap on peak intensity is much larger and increases rapidly with the degree of overlap. A 2% increase in the peak search intensity over that of the profile fitting has been obtained for the (222) K α_1 peak. The increase in the peak search intensity reached 27% for the severely overlapping (231) $K\alpha_1$ peak.

4. Conclusions

A comprehensive study of the derivative methods for peak search analysis of X-ray powder diffraction patterns has been made to evaluate the relative merits of the methods. The accuracy, precision and overlap resolution of the methods were

determined using computer simulated diffraction patterns in which the peak positions, the levels of counting statistical noise and the degrees of overlap were exactly known. The study showed that the results are dependent on the peak search parameters as follows: (1) the lower the order of the derivative, the smaller the intrinsic and random errors: (2) the higher the degree of the polynomial, the lower the intrinsic error, but the higher the random error; and (3) the larger the value of CR, the larger the intrinsic error, but the smaller the random error. Taking into account both the intrinsic (or accuracy) and the random (or precision) errors, the first derivative of a cubic polynomial is most effective for the peak position determination. The analysis also showed that reliable overlap resolutions have been obtained by the second derivative of a quadratic/cubic polynomial. The method of combining the first derivative of a cubic polynomial for peak position determination and the second derivative for detection of unresolved overlaps has been used for peak search analysis. The method is capable of determining peak positions with an accuracy of 0.001° and precisions of $\pm 0.003^{\circ}$ to 0.020° depending on the levels of counting noise, and resolving overlaps with separations $\Delta \ge \frac{1}{2} W$.

The combined first/second derivative method has been used to analyse complex experimental diffraction patterns of a mineral mixture of quartz, orthoclase and albite. Results agreed with those obtained from the computer simulated data. A comparison between the peak search and the profile fitting analyses of the fosterite diffraction pattern showed that good agreements in the peak position have been obtained and the matches in 2θ were $<0.004^{\circ}$. However, the agreements in the peak intensity were relatively poor, and a maximum discrepancy of 27% has been obtained for the severely overlapping (231) K α_1 peak.

The results of analysing both the computer simulated and the experimental patterns showed that the combined first/second derivative method has been used effectively for analysing X-ray powder diffraction data. The method should also be applicable to the analysis of other spectra such as γ -rays, X-ray fluorescence, optical, infrared, Mössbauer, etc.

Acknowledgment

The author thanks Dr W. Parrish for supplying the mineral mixture and the fosterite powder specimens.

References

Huang, T. C., and Parrish, W. (1975). Appl. Phys. Lett. 27, 123-4.

Huang, T. C., and Parrish, W. (1984). Adv. X-ray Anal. 27, 45-52.

Huang, T. C., Parrish, W., and Lim, G. (1984). Adv. X-ray Anal. 27, 53-60.

Koistinen, D. P., and Marburger, R. E. (1959). Trans. Am. Soc. Met. 51, 537-55.

Mallory, C. L., and Snyder, R. L. (1979). Adv. X-ray Anal. 22, 121-31.

Parrish, W. (1965). 'X-ray Analysis Papers' (Centrex: Eindhoven).

Parrish, W., and Huang, T. C. (1979). Proc. Symp. on Accuracy in Powder Diffraction (Eds S. Block and C. R. Hubbard), pp. 95–110 (NBS: Washington, D.C.).

Savitzky, A., and Golay, M. J. E. (1964). Anal. Chem. 36, 1627-38.

Segmuller, A. (1969). Adv. X-ray Anal. 13, 455-67.

Sonneveld, E. J., and Visser, J. W. (1975). J. Appl. Crystallogr. 8, 1-7.

Manuscript received 21 August, accepted 9 October 1987