THE EXPERIMENTAL PRECISION OF THE KOSSEL TECHNIQUE IN SEM

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RESUMEN

Recientemente se ha propuesto utilizar la difracción de los rayos X emitidos por una muestra cristalina, bombardeada por un haz de electrones, para determinar su orientación cristalográfica y su parámetro de la red. En este trabajo se correlaciona la precisión en la determinación del patrón de difracción con la precisión obtenible en la orientación y el parámetro de la red. Se muestra que el número de cifras significativas en el parámetro de la red es menor que el de las coordenadas de los puntos de las líneas en el patrón de difracción.

ABSTRACT

Recently, the use of the diffracted X-rays emmited by a cristaline sample, being bombarded with a beam of electrons, has been proposed for determining cristalografic orientation and the lattice parameter. In this paper the precision in the determination of the diffraction patern is corrilated to the obtainable precision of the orientation and the lattice parameter. It is shown that the number of significant digits of the lattice paramter is less than those of the coordinate points of the diffraction patern.

INTRODUCTION

The technique of the diffraction of divergent X rays, known as the Kossel method in honor of its discoverer, offers the possibility of obtaining quantitative crystalografic information of a sample in a scanning electron microscope (SEM), taking advantage of the narrow beam of electrons that bombard the sample, which excit its atoms in a very small region (~ 1 μm.)[1]. The excited atoms emit characteristic X rays, that are diffracted on their way out by the crystalographic lattice.

The way in which the radiation is diffracted, forms the so called Kossel cones, which are detected by means of a photographic film, placed a few centimeters from the sample. The intersection of the general diffracted cones with the film forms the Kossel Pattern, which contains the information of the crystalographic orientation and allows the determination of the interplanar spacing, if the constituent element of the sample is known, that is to say, that the wave length λ of the emmited X rays is known[2].

With today's sufficiently elaborated computational methods, it is possible to obtain a rapid and unique interpretation of the Kossel Pattern's, by the accurate measurement of the relative coordinates of different points of the conics on the pattern, without the need of knowing the location of the center of the pattern nor the distance between the emission point and the film, as was required previously[3].

We need to evaluate the precision, with which the method works experimentally. Therefore and evaluation is required of the uncertainty in the orientation angles and the interplanar spacing, according with the precision with which are measured the coordinates of the different points of the conics, the measured percentage of the total perimeter of the conic line and the number of data distributed over the said percentage.

BRIEF ANALISIS OF THE KOSSEL TECHNIQUE

The interpretation of the Kossel patterns consists essentially of the simultaneous solution of the general equation of Kossel conics, generated by crystalographic planes arbitrarily orientated with respect to the film and at a distance t (fig. 1)[4].

$$(\alpha - \cos^2\gamma_1)x^2 + (\alpha - \cos^2\gamma_2)y^2 + (\alpha - \cos^2\gamma_3)t^2 - 2(\cos\gamma_1 \cos\gamma_2 xy + \cos\gamma_1 \cos\gamma_3 xt + \cos\gamma_2 \cos\gamma_3 yt) = 0 \quad (2.1)$$

($\alpha = \sin^2\Theta = \lambda^2/4d^2$ Bragg's Law) and the second degree equation corresponding to a line of the pattern:

$$S(x,y) = C_1x^2 + C_2y^2 + 2C_3xy + 2C_4x + 2C_5y + C_6 = 0 \quad (2.2)$$

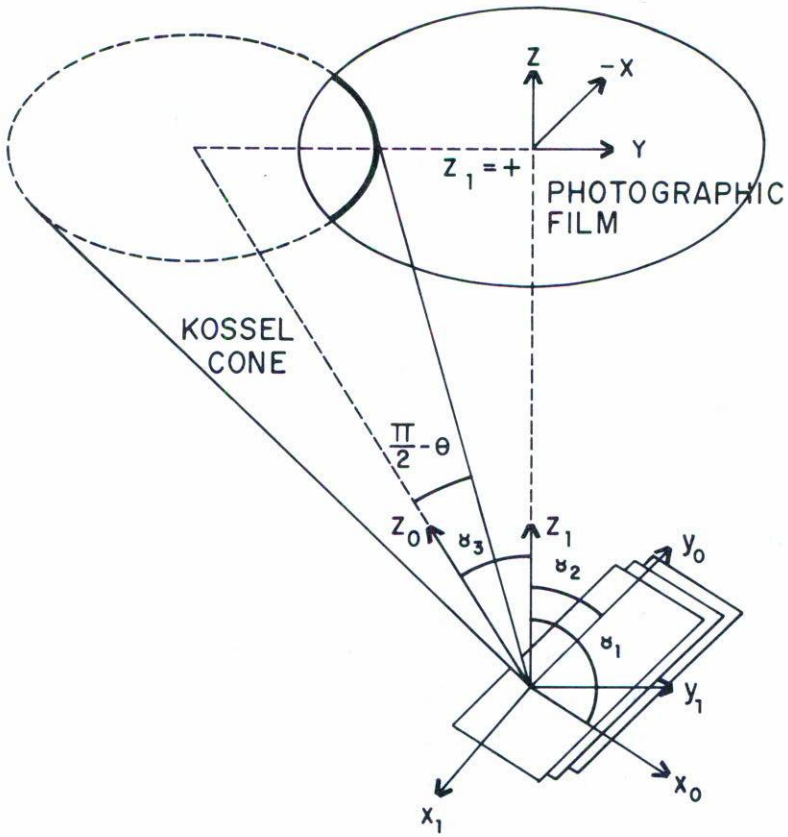

Fig. 1. Attainment of a cone of X rays reflected with a semi-angle $\pi/2 - \theta$ where θ is the Bragg Angle. (x_0, y_0, z_0) is the coordinate system related to the cone with the plane (x_0, y_0) parallel to the crystal's planes (x_1, y_1, z_1) is the coordinate system with center at the APEX of the cone and having the plane (x_1, y_1) parallel to the plane of the photographic film. The system (x, y, t) is placed on the film and on it, the coefficients C_i are given. Cos γ_1, cos γ_2 and cos γ_3 are the directional cosines.

which gives[5]

$$\cos^2\gamma_1 = K\, C_3 C_4 C_5^{-1}, \qquad \cos\gamma_2 = \cos\gamma_1\, C_5 C_4^{-1}$$

$$\cos^2\gamma_3 = 1 - \cos^2\gamma_1 - \cos^2\gamma_2, \qquad t = -KC_4(\cos\gamma_1\cos\gamma_3)^{-1} \quad (2.3)$$

$$\alpha = K\, C_6\, t^{-2} - \cos^2\gamma_3$$

$$K = \frac{2C_4C_5\,(C_3C_6 - C_4C_5)}{(C_4^2 + C_5^2)(3C_3C_4C_5 - 2C_3^2C_6) - C_4^2C_5^2(C_1 + C_2)} \quad (2.3')$$

where (2.3') is the sufficient and necessary condition for the existance and uniqueness of the solution.

From the system of equations (2.3), the uncertainities in the parameters of the lattice may be deduced to depend on the precission with which the coefficients of (2.2) are determined. It has been reported in the literature[6], what seems to us is the theoretical evaluation of the expected precision of the Kossel method, which is far from that experimentally obtainable.

So as to evaluate the experimental precision in a general way, a program was prepared so as to give the coordinates of several points of a theoretical curve:

$$S(x^1,y^1) = a_1x^{1\,2} + a_2y^{1\,2} + a_3x^1y^1 + a_4x^1 + a_5y^1 + 1 = 0 \qquad (2.4)$$

and after, process this data so that it would simulate what is experimentally expected. This was acomplished by introducing a parameter P that corresponds to the number of significant digits that may be read with certainty on a traveling optical microscope and finally generating a random digit for the P+1 decimal position. That is to say, the number of significant digits was cut down to P by means of the INTEGER function and with the aid of the RANDOM function, the next digit was generated:

$$x^1 = 10^{-P}\ \mathrm{INT}\ (x^1 \cdot 10^P + 0.5)$$

accordingly

$$y^1 = 10^{-P}\ \mathrm{INT}\ (y^1 . 10^P + 0.5) + 10^{-(P+1)}\ \mathrm{INT}((9 \cdot \mathrm{RND} + 1) - 5) \qquad (2.5)$$

The data generated in this manner was fed to the computer so that it would adjust the coefficients of the second degree general equation by means of the least squares method:

$$S(x^1,y^1) = E_1x^{1\,2} + E_2y^{1\,2} + E_3x^1y^1 + E_4x^1 + E_5y^1 + 1 = 0 \qquad (2.6)$$

In the same way, 10 groups of data for equation (2.4) were generated, having as fixed parameters, the value of P and the number n of data to be used. This is equivalent to having 10 readings of the coordinates of each point of the line. The values obtained for each coefficient of (2.6) were processed so as to obtain the standard deviation as a function of the number of data and the parameter P:

$$\overline{\Delta E} = \frac{1}{5} \sum_{i=1}^{5} \Delta E_i = \frac{1}{5} \sum_{i=1}^{5} \sqrt{\frac{1}{90} \sum_{j=1}^{10} (E_{ij} - \bar{E}_i)^2} \qquad (2.7)$$

where

$$\bar{E}_i = \frac{1}{10} \sum_{j=1}^{10} E_{ij} \qquad (2.8)$$

In the figure 2, it may be seen, that the standard deviation decreases very slowly as the number n on data increases. Simultaneously

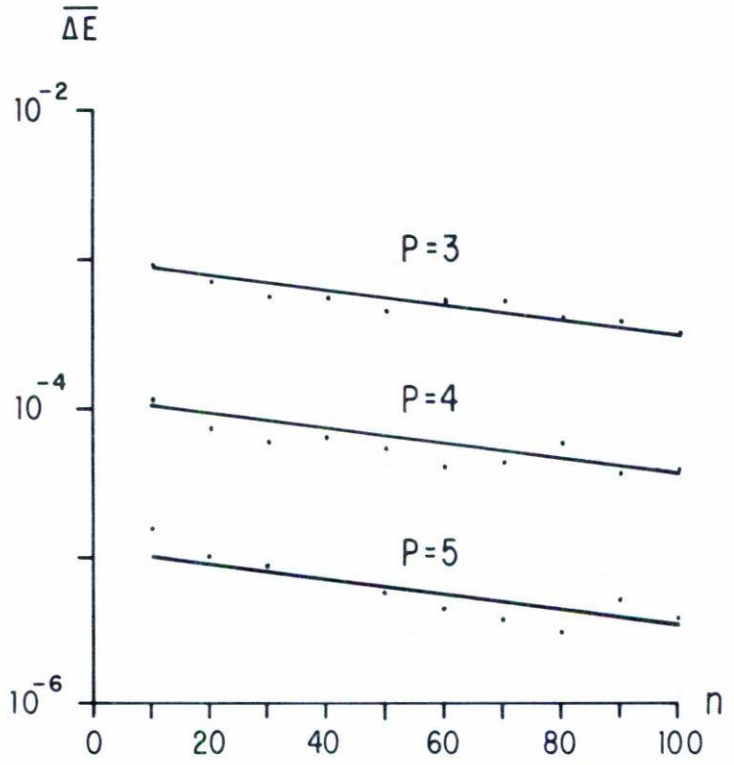

Fig. 2. Dependance of the standard deviation $\overline{\Delta E}$ of the coefficients E_i of the equation (2.6) as a function of the number of significant digits (P) with which the data is read and of the number n of data.

it was observed, that the function (2.6) evaluated for each of the points of the line (x_i^1, y_i^1), differs slightly from zero by a value ΔS_i, in such a manner that the function

$$\overline{\Delta S} = \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^{n} \left(\frac{S(x_i^1, y_i^1)}{\partial S(x_i^1, y_i^1)/\partial y_i^1} \right)^2} \qquad (2.9)$$

is a function from which its minimum value may be taken as indicative of the accuracy with which the coefficients have been adjusted (fig. 3). This permits to avoid the evaluation for the experimental case, of ten different groups of data; because the calculation of $\overline{\Delta S}$ gives information about the value of $\overline{\Delta E}$.

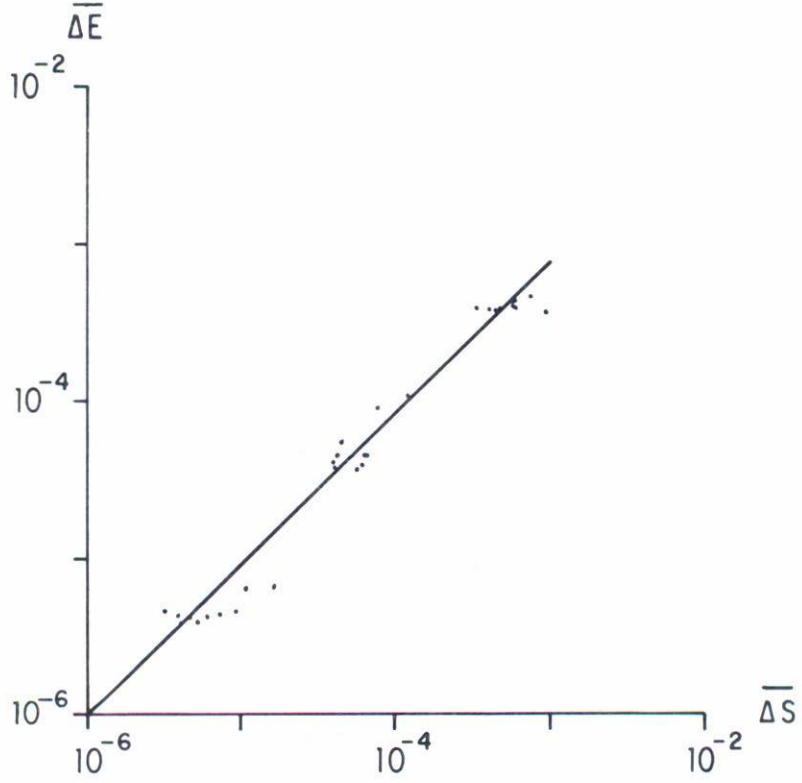

Fig. 3. Relation between the function $\overline{\Delta S}$ and the value of standard deviations of the coefficients ΔE.

Another of the points of interest, in relation with precision, is the dependence of the percentage of the perimeter of the line in which the data is homogeneously distributed, with the precision obtainable in

the coefficients. Figure 4 shows the typical graph of the results obtained in this way; and from it, may be concluded the convinience of measuring at least 40% of the total perimeter of the curve.

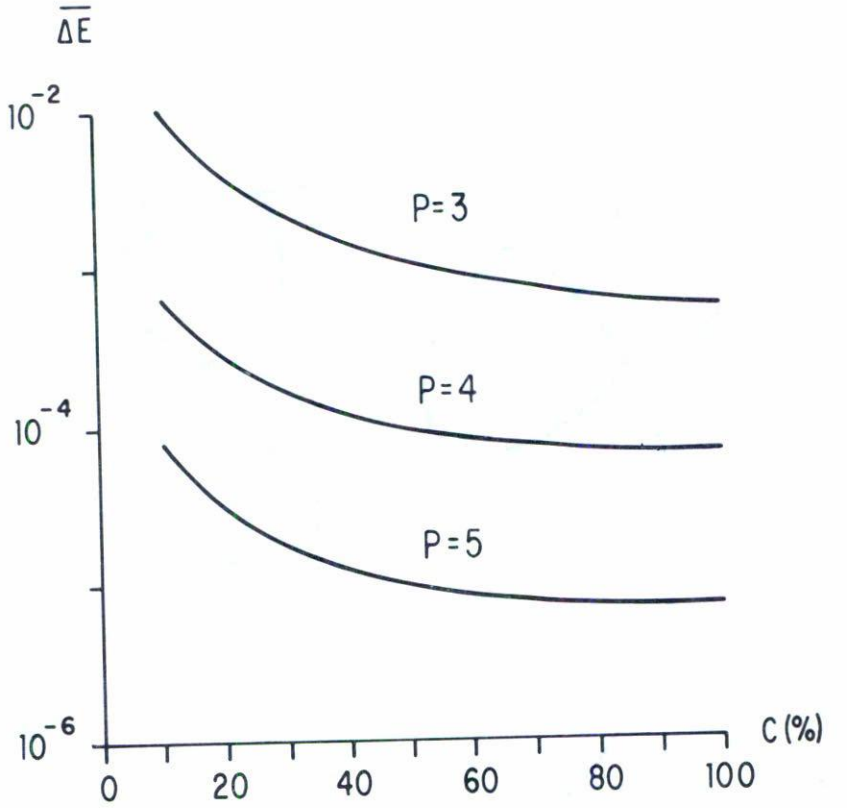

Fig. 4. Variations in the standard deviation as a function of the perimeter of the curve on which the data is distributed homogeneously (n = 40 data).

PROPAGATION OF ERRORS

Experimentally, it is not easy to determine the centre of the pattern, upon which the emission source is projected[8]. This compels having the coordinates of the different points of the curve, referred to an arbitrary system, which generally is that of the travelling optical microscope, with which the measurements are being made.

Therefore, as a final step, the relationship between the coefficients C_i of equation (2.2) refered to the system (x o y) and the coefficients E_i of (2.6) related to the system (x' o' y') should be found and with this, the propagation of error ΔE_i and its influence on the coefficients C_i (Fig. 5) will be determined.

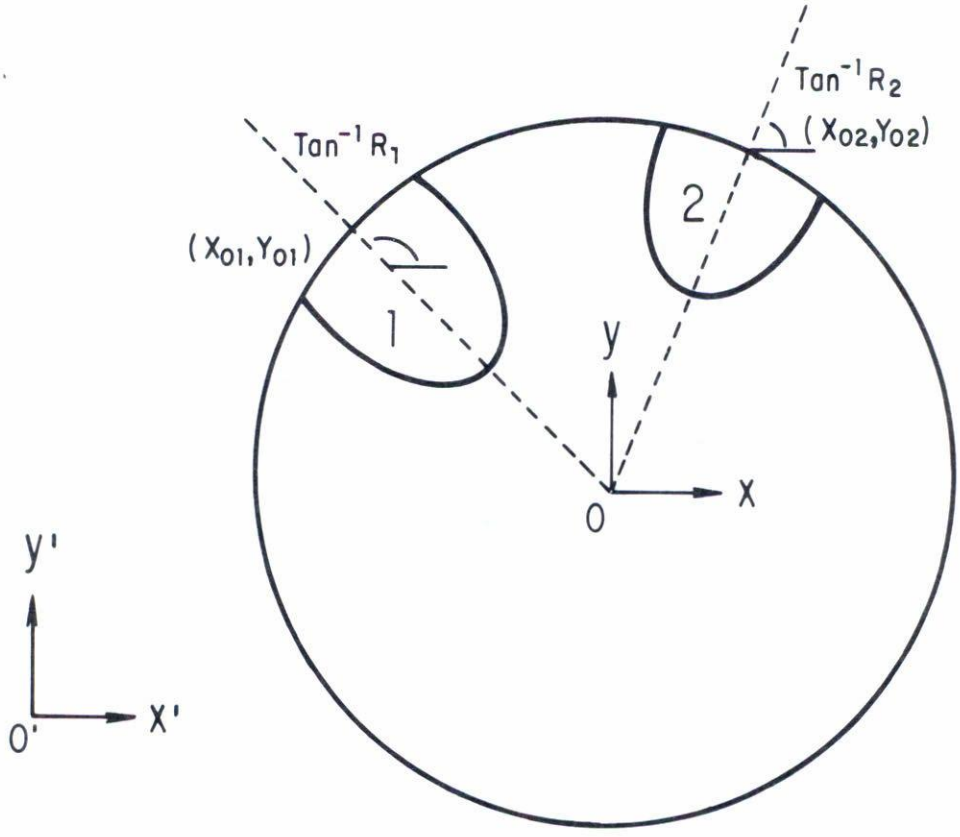

Fig. 5. Squematic diagram of the relation between the coordinate systems (x' o' y') and (x o y) on which the coefficients E_i and C_i are determined respectively.

The center of the pattern is obtained by the interaction of the focal axis of two or more Kossel conics using the following procedure:

a) determination of the center of symmetry of each conic

$$x^1_{o\ell} = (E_3E_5 - E_4E_2) / (E_1E_2 - E_3^2)$$
$$y^1_{o\ell} = (E_3E_4 - E_1E_5) / (E_1E_2 - E_3^2) \qquad (3.1)$$

and of the angle that the mayor axis of the conic has with respect to the coordinate axis

$$\tan \phi_\ell \equiv R_\ell = (E_2-E_1 \pm \sqrt{(E_2-E_1)^2 + 4E_3^2})/2E_3 \qquad (3.2)$$

(the correct sign is determined according to the canonical equation of the curve),

b) the equations of the focal axis, as a function of the center of symmetry and of the correct angle, come as

$$y^1 = a_\ell x^1 + b_\ell \qquad (3.3)$$

where

$$a_\ell = R_\ell$$

$$b_\ell = y^1_{o\ell} - R_i x^1_{o\ell}$$

c) the center of the pattern is then at the intersection of the focal axis

$$(x^1,y^1) = \left(\frac{a_\ell - b_m}{a_m - a_\ell} \;,\; \frac{a_m b_\ell - a_\ell b_m}{a_m - a_\ell}\right) \qquad (3.4)$$

$$\ell \neq m$$

The coordinate system is transfered to the point so obtained and the equation of the line will be given as in (2.2), with its coefficientes C_i related to the coefficients E_i by the equations

$$\begin{aligned} C_1 &= E_1 \;, \\ C_2 &= E_2 \;, \\ C_3 &= E_3 \;, \\ C_4 &= E_4 + E_1 x^1 + E_3 y^1 \\ C_5 &= E_5 + E_2 y^1 + E_3 x^1 \\ C_6 &= S(x^1,y^1) \end{aligned} \qquad (3.5)$$

Applying directly the propagation of error[9] to equations 3.1, 2, 3, 4, 5 and 2.3, the uncertainties in the characteristics parameters of the crystal lattice are obtained: the directional cosines, the distance t and the interplanar spacing (for a given λ). The results obtained for an experimental case which had three curves is shwon in table 1.

CONIC # 1		CONIC # 2		CONIC # 3	
E_i	ΔE_i	E_i	ΔE_i	E_i	ΔE_i
2.75577E-3	3.9E-7	2.47768E-3	5.4E-7	2.47853E-3	3.7E-7
3.40427E-3	4.8E-7	3.29530E-3	7.1E-7	4.21424E-3	6.3E-7
8.5848E- 4	1.2E-7	-7.9317E- 4	7.7E-7	5.58934E-4	8.3E-8
-4.64376E-2	8.5E-6	-4.5151E- 2	1.3E-5	5.5006E- 2	1.1E-5
3.01622E-2	3.7E-6	-2.62975E-2	7.9E-6	-1.7512E- 2	1.5E-5

	x_o^1	Δx_o^1	y_o^1	Δy_o^1	R_i	ΔR_i	b_i	Δb_i	k	Δk
# 1	21.283	2.8E-2	-14.227	1.8E-2	-.69125	2.3E-4	.48473	6.1E-4	230.03	8.6E-1
# 2	22.513	2.1E-2	13.399	1.2E-2	.60960	6.7E-4	-.32460	1.9E-4	244.42	7.2E-1
# 3	-23.843	1.5E-2	7.3179	3.2E-3	-.29416	6.8E-4	.30419	2.5E-4	210.92	4.7E-1

The crystal lattice parameter d is

$d = (1.6358 \pm 2.3E\text{-}3)$ Å

The pattern center was found in (0.59, 0.11) with a standard deviation of $\Delta r = 0.1$ mm.
The distance between the sample and the photographic film was $t = 25.21 \pm 0.11$ mm.

Table 1. Experimental results for three Kossel lines showing the error propagation for the several parameters.

CONCLUSIONS

From what was said before, it may be deduced, that the precision with which the parameters of the crystal lattice may be obtained, depends

fundamentally on the uncertainty with which the coordinates of the different points of the line can be determined. This is because, the error propagates up to these parameters through the different equations. In the same manner, it is deduced, that the precision does not increase notably for perimeters greater than 40%, nor for a number of data greater than 30.

The error introduced by the computer by rounding off digits is neglectable in comparison with the experimental uncertainty (for the BS7500 it is 10^{-13}).

The precision in reading the coordinates of points on the lines is limited fundamentally by the measuring system of the optical microscope and by the grain size of the film, because this determines the minimum width that a line has on a photograph. For example, a film with a resolution of 200 lines per milimeter, would have curves with a 5 μm width and all the coordinates would have a minimum error of ± 2.5 μm.

Besides the grain size, the folding or curvature that the film presents, diminishes the precision of the experiment, therefore the possibility of using glass substrates for the emulsion should be studied.

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