A method to obtain orientation curves in Euler space for a second diffraction process in polycrystals

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A method is presented to obtain the orientation curve in the Eulerian space, of crystallites which diffract in one point of a Debye-Scherer ring in a second diffraction process. The incident beam is therefore the reflected beam of a previous diffraction process, and the sample has a general orientation for a pole figure measurement, given as usual by two angles, χ around the sample Y axis, and φ around the sample normal. Two solutions are found for all secondary reflections. The method proposed here was outlined somewhere else for the measurement of pole figures by neutron diffraction [1], and here important improvements are made, especially regarding the mathematical methods.

Keywords: X-ray diffraction; texture; extinction.

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1. Introduction

Multiple scattering is generally not considered in X-ray or neutron diffraction from polycrystals, due to the negligibly low intensity expected from this effect; however, measurements of pole figures show significant differences in many cases when density maxima from first and second orders are compared to each other, indicating that primary or secondary extinction could be present [1-3]. If secondary extinction is dominant, a way to verify it could be to test if the curve of crystallite orientations for the second diffraction coincides with high populated zones of the Orientation Distribution Function (ODF) of the textured sample. As well known of diffraction from polycrystals, the intensity at a point of a Debye-Scherrer ring hkl, or the pole density at a point on the pole figure, is caused by the superposition of the intensities diffracted by many crystallites, all of which satisfy the Bragg condition for the planes (hkl). This crystallites have in common the normal direction of planes (hkl), but differ otherwise in orientation so that their orientations lie along a curve in the Eulerian space, *i.e.* the pole figure is a projection of pole densities along a path through the ODF corresponding to a 2π-rotation around the diffraction vector [5]. This happens also for the second diffraction process, being the incident vector orientation the only difference, so that the diffracting crystallites lie also along a curve in the Eulerian space. So the aim of this work is to evaluate the orientation curves for the main reflections for a secondary diffraction, and for a general sample orientation given by the conventional angles (χ, φ). This scope was proposed by Palacios *et al.*, [1], however, the mathematical method used allowed only one solution of the main equation expressing the Laue condition for a second reflection (Eq. (7) of [1]), and no modifications were made for especial cases where no solution (for example reflections where $h = k = 0$) could be obtained. This work aims to solve this deficiencies, and to improve solutions. For the sake of completeness, the figures and the background of the main equation are repeated here.

2. The method

Let $\boldsymbol{k}_0$ be the wave vector of an X-ray photon, which has already been diffracted by planes $(h_0k_0l_0)$. If θ_0 is the Bragg angle of the first diffraction, and $k = 2\pi/\lambda$ with λ the radiation wave length, this is in the sample reference system

$$\boldsymbol{k}_0 = k(0, \cos\theta_0, \sin\theta_0). \tag{1}$$

To determine possible secondary diffraction processes this wave can produce in the polycrystalline sample, the orientation curve of crystallites contributing to the intensity registered at a general point of a Debye-Scherrer ring produced by diffraction from plane (hkl) is to be calculated. Figure 1 shows the primary diffraction layout, and Fig. 2 shows the sequence of both diffraction processes.

It is convenient to rotate the reference system an angle α around X_0, to make $\boldsymbol{k}_0$ to coincide with the Z axis. Let ω be an angle characterizing a point of a Debye-Scherrer ring, as shown in Fig. 3. The wave vector of the second diffracted wave is then in the new reference system

$$\boldsymbol{k}_0' = k(\sin 2\theta\cos\omega, \sin 2\theta\sin\omega, \cos 2\theta).$$

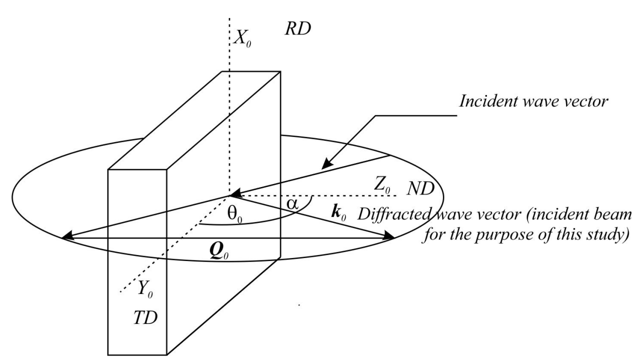

FIGURE 1. Reference frame for the sample at the orientation $\chi = 0$ and $\varphi = 0$.

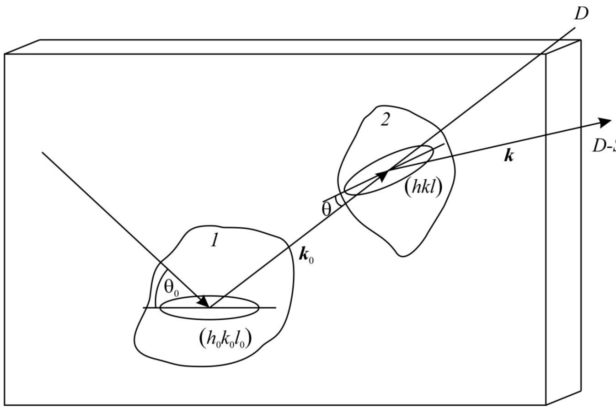

FIGURE 2. Sequence of primary and secondary reflections by crystallites 1 and 2 respectively. D indicates the detector direction, and $D-S$ the direction of the point of afrom which Debye-Scherrer ring which this particular event affects.

And expressed in the sample reference system, it is

$$\boldsymbol{k}_0' = k(\sin 2\theta\cos\omega, \sin\theta_0\sin 2\theta\sin\omega + \cos\theta_0\cos 2\theta,$$
$$-\cos\theta_0\sin 2\theta\sin\omega + \sin\theta_0\cos 2\theta). \qquad (2)$$

If $\boldsymbol{Q}_0 \equiv \boldsymbol{k}_0' - \boldsymbol{k}_0$, then

$$\boldsymbol{Q}_0 = k(q_x^0, q_y^0, q_z^0) \qquad (3)$$

with

$$q_x^0 = \sin 2\theta\cos\omega$$
$$q_y^0 = 2\sin\theta(\sin\theta_0\cos\theta\sin\omega - \cos\theta_0\sin\theta)$$
$$q_z^0 = -2\sin\theta(\cos\theta_0\cos\theta\sin\omega + \sin\theta_0\sin\theta) \qquad (4)$$

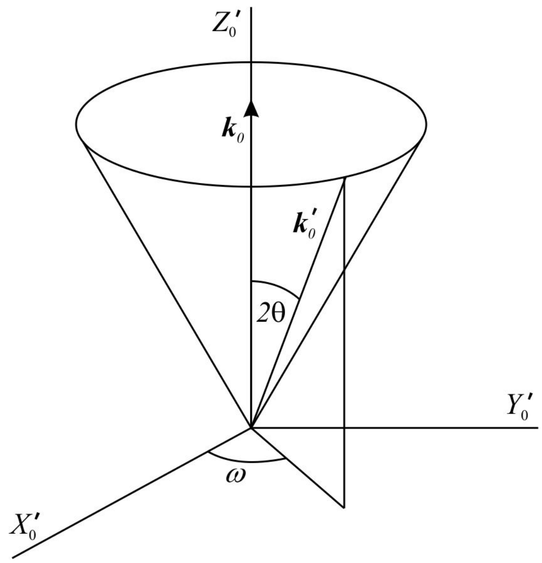

FIGURE 3. Debye-Scherrer ring for a general secondary reflection.

where the superindex 0 indicates that the sample is in its initial orientation (0,0).

Q_0 in terms of the pole figure angles (χ, φ)

As in a measure of a pole figure, let the sample be rotated an angle χ around the Y axis (TD), followed by a rotation of an angle φ around the normal direction of the sample. Figure 4 shows the sample in this general orientation for the measurement of a point (χ, φ) of the pole figure. $\boldsymbol{Q}$ is the vector $\boldsymbol{Q}_0$ as seen by the sample in its new orientation after both rotations:

$$\boldsymbol{Q} \equiv \begin{pmatrix} Q_x \\ Q_y \\ Q_z \end{pmatrix} = k\begin{pmatrix} \cos\chi\cos\varphi q_x^0 + \sin\varphi q_y^0 - \sin\chi\cos\varphi q_z^0 \\ -\cos\chi\sin\varphi q_x^0 + \cos\varphi q_y^0 + \sin\chi\sin\varphi q_z^0 \\ \sin\chi q_x^0 + \cos\chi q_z^0 \end{pmatrix} = k\begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} \qquad (5)$$

Crystallites for which Q satisfies Laue conditions

Let hkl be a particular reflection, and C a crystallite such that the vector Q satisfies Laue conditions for a certain reciprocal vector $\boldsymbol{G}_{hkl}$. The vector Q as seen by C is

$$\boldsymbol{Q}_C = M_{\varphi_1\phi\varphi_2}\boldsymbol{Q} \qquad (6)$$

where φ_1, ϕ, φ_2 are the Eulerian angles of the crystallite; *i.e.* those which bring the sample system to coincidence with C, and $M_{\varphi_1\phi\varphi_2}$ is the rotation matrix [6] (Eq. (2.50)):

$$M_{\varphi_1\phi\varphi_2} = \begin{pmatrix} \cos\varphi_1\cos\varphi_2 - \sin\varphi_1\sin\varphi_2\cos\phi & \sin\varphi_1\cos\varphi_2 + \cos\varphi_1\sin\varphi_2\cos\phi & \sin\varphi_2\sin\phi \\ -\cos\varphi_1\sin\varphi_2 - \sin\varphi_1\cos\varphi_2\cos\phi & -\sin\varphi_1\sin\varphi_2 + \cos\varphi_1\cos\varphi_2\cos\phi & \cos\varphi_2\sin\phi \\ \sin\varphi_1\sin\phi & -\cos\varphi_1\sin\phi & \cos\phi \end{pmatrix} \qquad (7)$$

Then

$$\boldsymbol{Q}_C = \boldsymbol{G}_{hkl} \qquad (8)$$

where $\boldsymbol{G}_{hkl} = h\boldsymbol{A} + k\boldsymbol{B} + l\boldsymbol{C}$ is the reciprocal lattice vector corresponding to the reflection hkl. For a cubic system with lattice constant a:

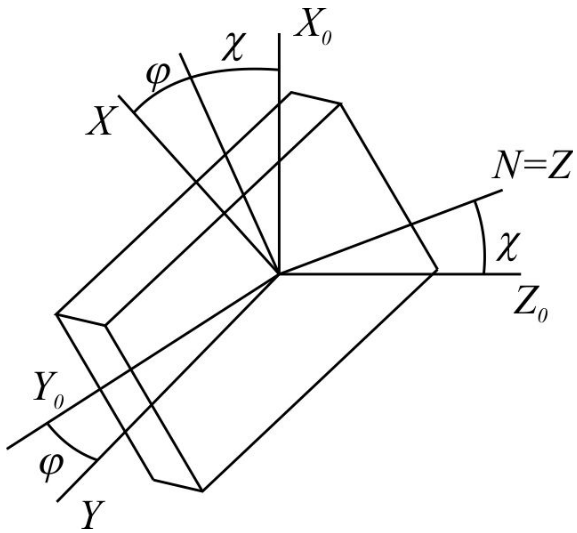

FIGURE 4. Sample in a general orientation (χ,φ). Axis X_0, Y_0 and Z_0 are those of the sample in its initial symetric orientation. X, Y y Z are the axis after rotation. N is the sample normal.

$$\boldsymbol{G}_{hkl}=\frac{2\pi}{a}(h\hat{\mathbf{\imath}}+k\hat{\mathbf{\jmath}}+l\hat{\boldsymbol{k}}) \tag{9}$$

where $\hat{\mathbf{\imath}}$, $\hat{\mathbf{\jmath}}$ and $\hat{\boldsymbol{k}}$ are unit vectors of C.

After applying matrix $M_{\varphi_1\phi\varphi_2}$ to (6), with $k2\pi/\lambda$, and from (8) and (9), it follows

$$A\sin\varphi_2+B\cos\varphi_2=\frac{\lambda}{a}h \tag{10a}$$

$$-B\sin\varphi_2+A\cos\varphi_2=\frac{\lambda}{a}k \tag{10b}$$

$$C\sin\phi+D\cos\phi=\frac{\lambda}{a}l \tag{10c}$$

where

$$\begin{aligned}A(\varphi_1,\phi)&=\cos\varphi_1\cos\phi q_y\\&\quad-\sin\varphi_1\cos\phi q_x+\sin\phi q_z\end{aligned} \tag{11a}$$

$$B(\varphi_1)=\cos\varphi_1 q_x+\sin\varphi_1 q_y \tag{11b}$$

$$C(\varphi_1)=q_x\sin\varphi_1-q_y\cos\varphi_1 \tag{11c}$$

Some properties of coefficients A, B, C and D

From (11a) and (11c) it can be readily be seen that

$$A=-C\cos\phi+D\sin\phi \tag{12a}$$

Multiplying (10a) by $\sin\varphi_2$, (12b) by $\cos\varphi_2$, and adding

$$A=\frac{\lambda}{a}(h\sin\varphi_2+k\cos\varphi_2) \tag{12b}$$

and similarly for B

$$B=\frac{\lambda}{a}(h\cos\varphi_2-k\cos\varphi_2) \tag{12c}$$

It follows then

$$A^2+B^2=\left(\frac{\lambda}{a}\right)^2(h^2+k^2). \tag{12d}$$

Also, from (11b) and (11c)

$$B^2+C^2=q_x^2+q_y^2$$

And with (11d)

$$B^2+C^2+D^2=q_x^2+q_y^2+q_z^2 \tag{12e}$$

Since rotations do not change the magnitude of vectors

$$Q^2=Q_c^2$$

from which, using (5), (8), and (9)

$$q_x^2+q_y^2+q_z^2=\left(\frac{\lambda}{a}\right)^2(h^2+k^2+l^2)$$

Using (12e), this equation gives

$$C^2+D^2-\left(\frac{\lambda}{a}\right)^2 l^2=\left(\frac{\lambda}{a}\right)^2(h^2+k^2)B^2$$

and using (12d),

$$C^2+D^2-\left(\frac{\lambda}{a}\right)^2 l^2=A^2 \tag{12f}$$

Solution of Equations (10)

Equations (10) are not independent, and the way adopted here to solve them is as follows:

1) φ_1 is given as an independent variable.

2) From (11b) and (11c), B(φ_1) and C(φ_1) are obtained, and (10c) is solved for ϕ.

3) From (10a) and (10b) φ_2 is obtained.

To solve (10c) the following method is proposed for a general equation with coefficients a, b and c:

$$a\sin\gamma+b\cos\gamma=c \tag{13}$$

Let

$$\sin\gamma=\frac{e^{i\gamma}-e^{-i\gamma}}{2i}$$
$$\cos\gamma=\frac{e^{i\gamma}+e^{-i\gamma}}{2}$$

Equation (13) is then:

$$e^{i\gamma}\left(\frac{a}{2i}+\frac{b}{2}\right)+e^{-i\gamma}\left(-\frac{a}{2i}+\frac{b}{2}\right)=c$$

Multiplying by $2ie^{i\gamma}$

$$e^{2i\gamma}(a+ib)-a+bi=2ice^{i\gamma}$$

$$e^{2i\gamma}(a+ib)-2ice^{i\gamma}+(-a+bi)=0$$

This is a quadratic equation in $e^{i\gamma}$ whose solutions, after multiplying by $a-ib$, and separating real and imaginary parts are

$$e^{i\gamma}=\frac{cd\pm a\sqrt{a^2+b^2-c^2}}{a^2+b^2}+i\frac{ac\mp b\sqrt{a^2+b^2-c^2}}{a^2+b^2}$$

From which

$$\cos\gamma=\frac{cd\pm a\sqrt{a^2+b^2-c^2}}{a^2+b^2} \tag{14a}$$

$$\sin\gamma=\frac{ac\mp b\sqrt{a^2+b^2-c^2}}{a^2+b^2} \tag{14b}$$

Applying this to (10c) with $a=C$, $b=D$, $\gamma=\phi$ and $c=(\lambda/a)l$

$$\cos\phi=\frac{\frac{\lambda}{a}lD\pm C\sqrt{C^2+D^2-\left(\frac{\lambda}{a}\right)^2l^2}}{C^2+D^2}$$

$$\sin\phi=\frac{C\frac{\lambda}{a}l\mp D\sqrt{C^2+D^2-\left(\frac{\lambda}{a}\right)^2l^2}}{C^2+D^2}$$

From (12f) these equations become

$$\cos\phi=\frac{\frac{\lambda}{a}lD\pm C|A|}{C^2+D^2} \tag{15a}$$

$$\sin\phi=\frac{\frac{\lambda}{a}lC\mp D|A|}{C^2+D^2} \tag{15b}$$

Let $\phi^{1,2}$ be the angles obtained for upper and lower signs respectively. A is then obtained from (12a), and (15a) and (15b):

$$A=-C\cos\phi+D\sin\phi=-C\frac{\frac{\lambda}{a}lD\pm C|A|}{C^2+D^2}+D\frac{\frac{\lambda}{a}lC\mp D|A|}{C^2+D^2}=\mp|A|$$

i.e

$$A(\phi^{1,2})=\mp|A| \tag{16}$$

This means $A(\phi^1)<0$, and $A(\phi^2)>0$.

Equations (10a) and (10b) form a system of two linear equations whose solution is

$$\sin\varphi_2=\frac{\lambda}{a}\frac{hA-kB}{A^2+B^2}$$

$$\cos\varphi_2=\frac{\lambda}{a}\frac{kA-hB}{A^2+B^2}$$

Using (12d), expressing $A=A(\phi)$, and applying (16)

$$\sin\varphi_2^1=\frac{a}{\lambda}\frac{-h|A|-kB}{h^2+k^2} \tag{17a}$$

$$\cos\varphi_2^1=\frac{a}{\lambda}\frac{hB-|A|k}{h^2+k^2} \tag{17b}$$

$$\sin\varphi_2^2=\frac{a}{\lambda}\frac{h|A|-B|k|}{h^2+k^2} \tag{17c}$$

$$\cos\varphi_2^2=\frac{a}{\lambda}\frac{hB+|A|k}{h^2+k^2} \tag{17d}$$

with the condition

$$h^2+k^2>0$$

Especial case $h=k=0$

If $h=k=0$ then, from (12b) $B=0$, and from (11b)

$$\tan\varphi_1=-\frac{q_x}{q_y} \tag{18a}$$

And from (12a) $A=0$, *i.e.* from (11a)

$$\tan\phi=\frac{\sin\varphi_1 q_x-\cos\varphi_1 q_y}{q_z}$$

Which, using (18a) can be written

$$\phi=\tan^1\{-\frac{1}{q_z}\sqrt{q_x^2+q_y^2}\} \tag{18b}$$

Which means that for this case there is only one value for φ_1 and one forϕ, and φ_2 can take any value. The orientation curve is a straight line, but its value depends of q_x, q_y and q_z.

Equation (18a) has no solution if $q_x=q_y=0$. This can come from (5) for the especial case $\chi=\varphi=0$, and $q_x^0=q_y^0=0$, which corresponds to the symmetrical sample orientation, and it can readily be seen that $\phi=0$ and $\varphi_1+\varphi_2$ can take any value.

Total of solutions

Except for the especial case $h=k=0$, following solutions $g_{i,j}$ are obtained:

$$g_1=(\varphi_1,\phi^1,\phi_2^1)$$
$$g_2=(\varphi_1,\phi^2,\phi_2^1) \tag{19}$$

These are two curves if $h^2+k^2>0$, or a straight line along φ_2 if $h=k=0$.

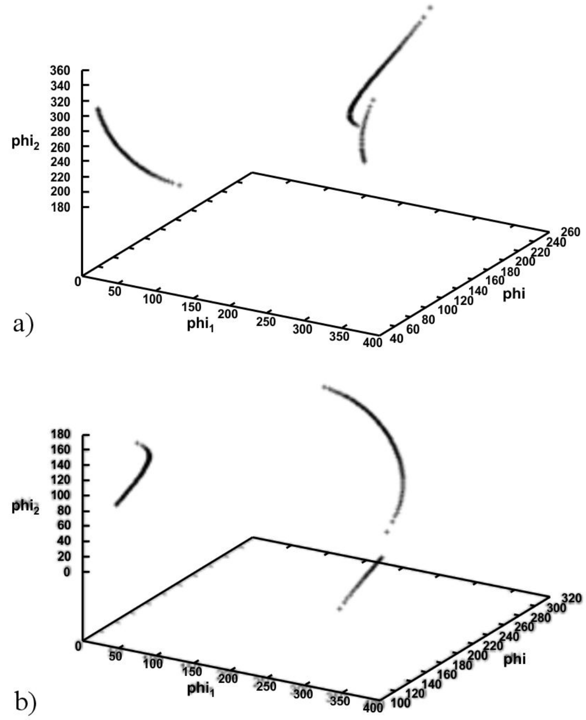

FIGURE 5. Curves obtained for a general orientation of the sample: $\chi = 35^{\circ}$ and $\varphi = 45^{\circ}$ planes 111 for both reflections, primary and secondary. Copper radiation was used, and the sample is silver.

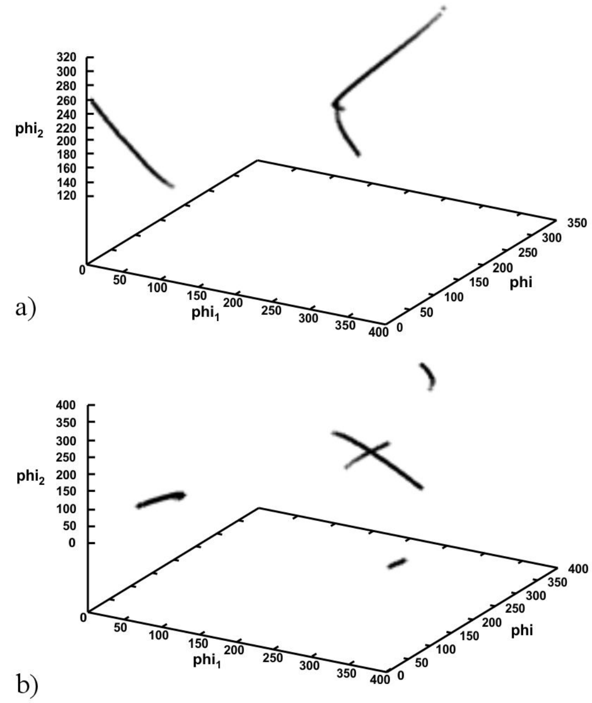

FIGURE 6. Curves obtained for the symmetrical orientation of the sample: $\chi = 0^{\circ}$ and $\varphi = 0^{\circ}$, and planes 111 as the plane causing the first reflection, and 202 as the plane causing the second reflection. Copper radiation was used, and the sample is silver.

3. The computer program

A program in Dev C^{++} has been written, as follows:

1) Primary data are given: Pole figure affected, *i.e.* $(h_0k_0l_0)$, secondary reflection (hkl), point ω of the Debye-Scherrer ring of secondary reflection, lattice constant of sample a, sample orientation (χ, φ), and wavelength λ. From these data, Bragg angles θ_0 and θ for primary and secondary reflections respectively are calculated. Initial φ_1 and an increment $\Delta\varphi_1$ are also given.

2) q_x^0, q_y^0 and q_z^0 are obtained from (4), and q_x, q_y and q_z from (5).

3) B, C and D are then obtained from Eqs. (11), and A from (12.f).

4) ϕ and φ_2 are then calculated through Eqs. (15) and (17) respectively.

5) The especial cases $h = k = 0$ is solved from Eqs. (18).

4. Results

Figures 5 and 6 show some results for a silver sample using copper radiation. Curves are usually closed but they appear fragmentary when some angle reaches the 2π value. Particularly not every value of φ_1 has a solution. Two curves result for each sample orientation, and for first and second reflections since every orientation of the sample is represented by two sets of Eulerian angles $(\varphi, \varphi, \varphi)$ ([6], Eq. (2.4)).

5. Conclusions

A method has been developed to determine the orientation curves of crystallites able to produce a second diffraction of an incident photon. Calculations require only modest computer capabilities, and they could be applied in future work to determine the integrated intensity of the whole Debye-Scherrer rings, as a measure to evaluate the intensity loss due to a possible effect of secondary extinction.

The aim of this work is thus fulfilled; however, to know if these curves pass through high pole density zones, further calculations will be necessary since on the one hand, due to symmetric properties of the samples, only a part of this cube of side length 2π will be sufficient, and on the other hand, every curve should be first subdivided in segments of equal length. Both aspects require careful operations, and for the moment they are beyond the scope of this work.

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