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Characterization of Grain Boundaries in the Hexagonal System Based on Tables of Coincidence Site Lattices (CSL's)*

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Abstract

A method for the characterization of coincidence cells is proposed for hexagonal crystals. It is based on a simple formulation of the orientation relationships for coincidence site lattices. Therefore tables of coincidence orientation are established for different axial ratios with rational values of $(c/a)^2$. Possible practical cases of coincidence are characterized by their comparison with these tables. This comparison is preferably performed using the description given by a rotation angle of 180°.

1. Introduction

A new formulation for the generation of coincidence site lattices (CSL) has been proposed in a previous paper (Bleris & Delavignette, 1981). It was proved there for the first time that there is a strict connection between Ranganathan's (1966) generating function for the cubic system and the rotation matrix describing a CSL according to Warrington's (1975) approach.

The connection between these two approaches has the following consequences:

(*a*) the generating function may be constructed for a CSL described by a rotation matrix;

(*b*) the multiple Σ values for a given multiplicity are well defined;

(*c*) the construction of the CSL matrix for a given multiplicity becomes a systematic procedure based on three parameters: m, n and α.

The first of these points gave a better insight into the original proposition of Ranganathan, the other two solved different computational difficulties for the construction of the rotation matrix.

The general ideas of the previous paper will be extended here to the hexagonal system, for which the generating function, as far as we know, has not yet been established.

2. The general rotation matrix in the hexagonal system

If p_1, p_2, p_3 are the direction cosines of a direction, the general rotation matrix in an orthogonal system has the form:

$$\mathrm{R}_0 = \begin{bmatrix} p_1^2(1-\cos\theta) & p_1p_2(1-\cos\theta) & p_1p_3(1-\cos\theta) \\ +\cos\theta & -p_3\sin\theta & +p_2\sin\theta \\ p_1p_2(1-\cos\theta) & p_2^2(1-\cos\theta) & p_2p_3(1-\cos\theta) \\ +p_3\sin\theta & +\cos\theta & -p_1\sin\theta \\ p_1p_3(1-\cos\theta) & p_2p_3(1-\cos\theta) & p_3^2(1-\cos\theta) \\ -p_2\sin\theta & +p_1\sin\theta & +\cos\theta \end{bmatrix}, \quad (1)$$

where θ is the rotation angle. If the direction is crystallographic its direction cosines may be expressed as a function of integral numbers by introducing the Miller indices $[uvw]$ by means of the relations:

$$p_1 = \frac{2u-v}{2\sqrt{d^*}}, \quad p_2 = \frac{\sqrt{3}v}{2\sqrt{d^*}}, \quad p_3 = \rho\,\frac{w}{\sqrt{d^*}}, \quad (2)$$

where

$$d^* = u^2 + v^2 - uv + \rho^2 w^2 \quad (3)$$

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and $\rho = c/a$ is the hexagonal axial ratio. Using relation (2) and by a similarity transformation $\mathrm{S}^{-1}\mathrm{R}_0\mathrm{S}$, where S is

$$\mathrm{S} = a\begin{bmatrix} 1 & -1/2 & 0 \\ 0 & \sqrt{3}/2 & 0 \\ 0 & 0 & \rho \end{bmatrix}, \tag{4}$$

we may transform the rotation matrix R_0 into the matrix $\mathrm{R}_h = [R_{ij}]$, which expresses the same rotation operation in the hexagonal system. The matrix elements R_{ij} have the form:

$$\mathrm{R}_h = \begin{bmatrix} \frac{(2u-v)u}{2d^*}(1-\cos\theta) + \frac{w}{\sqrt{3d^*}}\rho\sin\theta + \cos\theta & \frac{(2v-u)u}{2d^*}(1-\cos\theta) - \frac{2w}{\sqrt{3d^*}}\rho\sin\theta & \frac{uw}{d^*}\rho^2(1-\cos\theta) + \frac{2v-u}{\sqrt{3d^*}}\rho\sin\theta \\ \frac{(2u-v)v}{2d^*}(1-\cos\theta) + \frac{2w}{\sqrt{3d^*}}\rho\sin\theta & \frac{(2v-u)v}{2d^*}(1-\cos\theta) - \frac{w}{\sqrt{3d^*}}\rho\sin\theta + \cos\theta & \frac{vw}{d^*}\rho^2(1-\cos\theta) - \frac{2u-v}{\sqrt{3d^*}}\rho\sin\theta \\ \frac{(2u-v)w}{2d^*}(1-\cos\theta) - \frac{v\sqrt{3}}{2\sqrt{d^*}}\rho^{-1}\sin\theta & \frac{(2v-u)w}{2d^*}(1-\cos\theta) + \frac{u\sqrt{3}}{2\sqrt{d^*}}\rho^{-1}\sin\theta & \frac{w^2}{d^*}\rho^2(1-\cos\theta) + \cos\theta \end{bmatrix}. \tag{5}$$

3. An extension of the generation function for the cubic system to the hexagonal system

By reference to the form of Σ and θ for the cubic system:

$$\Sigma = (m^2 + dn^2)/\alpha, \quad \tan\left(\frac{\theta}{2}\right) = \frac{n}{m}\sqrt{d}, \tag{6}$$

we shall seek expressions of the type:

$$\Sigma = (xm^2 + yn)^2/\alpha, \quad \tan\left(\frac{\theta}{2}\right) = \frac{n}{m}\sqrt{\frac{y}{x}}, \tag{7}$$

where the parameters x, y will be determined in such a way that the matrix elements (5) are rational numbers with the common denominator being the integer Σ. The parameters m, n and α are, as in the cubic system, integers used for the generation of the coincidence's descriptions. Using (7) we easily see that

$$1 - \cos\theta = \frac{2yn^2}{\alpha\Sigma}; \quad \sin\theta = \frac{2\sqrt{xy}\,mn}{\alpha\Sigma};$$

$$\cos\theta = \frac{xm^2 - yn^2}{\alpha\Sigma}, \tag{8}$$

and introducing (8) into (5), we have

$$\mathrm{R}_h = \frac{1}{\Sigma}\begin{bmatrix} \left[(2u-v)u\frac{yn^2}{d^*} + 2w\rho\sqrt{\frac{xy}{3d^*}}mn + xm^2 - yn^2\right]/\alpha & \left[(2v-u)u\frac{yn^2}{d^*} - 4w\rho\sqrt{\frac{xy}{3d^*}}mn\right]/\alpha & \left[2uw\rho^2\frac{yn^2}{d^*} + 2(2v-u)\rho\sqrt{\frac{xy}{3d^*}}mn\right]/\alpha \\ \left[(2u-v)v\frac{yn^2}{d^*} + 4w\rho\sqrt{\frac{xy}{3d^*}}mn\right]/\alpha & \left[(2v-u)v\frac{yn^2}{d^*} - 2w\rho\sqrt{\frac{xy}{3d^*}}mn + xm^2 - yn^2\right]/\alpha & \left[2vw\rho^2\frac{yn^2}{d^*} - 2(2u-v)\rho\sqrt{\frac{xy}{3d^*}}mn\right]/\alpha \\ \left[(2u-v)w\frac{yn^2}{d^*} - v\rho^{-1}\sqrt{\frac{3xy}{d^*}}mn\right]/\alpha & \left[(2v-u)w\frac{yn^2}{d^*} + u\rho^{-1}\sqrt{\frac{3xy}{d^*}}mn\right]/\alpha & \left[2w^2\rho^2\frac{yn^2}{d^*} + xm^2 - yn^2\right]/\alpha \end{bmatrix}. \tag{9}$$

The following symbolism will be used:

$$\mathrm{R}_h = [R_{ij}] = \frac{1}{\Sigma}[r_{ij}] = \frac{1}{\Sigma}[r^*_{ij}/\alpha]. \tag{10}$$

From (3) it is obvious that for $\rho = 1$, d^* is an integer. The following values:

$$x = 3, \quad y = u^2 + v^2 - uv + w^2 \tag{11}$$

eliminate the non-integral parts of (9). Then the rotation matrix takes the general form (10), where r^*_{ij} are integers, α has the same meaning as in the cubic system and

$$\Sigma = [3m^2 + (u^2 + v^2 - uv + w^2)n^2]/\alpha. \tag{12}$$

For the case $\rho \neq 1$, in order to describe ideal CSL's in any hexagonal system, the axial ratio should obey the following relation:

$$\rho^2 = \mu/\nu, \tag{13a}$$

$$(\mu,\nu) \doteq 1,† \tag{13b}$$

where μ and ν are integers. These new parameters will be introduced in (5). The d^* expression (3) is transformed into

$$d = (u^2 + v^2 - uv)\,\nu + w^2\,\mu = d^*\,\nu, \tag{14}$$

where d is an integer. Using (14) and choosing $x = 3\mu$, $y = d$, we have for the elements r^*_{ij} (10) integral

† $(\mu,\nu) \doteq 1$ means that the greatest common divisor of μ and ν is 1.

expressions, and Σ takes the form

$$\Sigma = (3\mu m^2 + dn^2)/\alpha. \tag{15}$$

We have already seen that there is a quadratic expression of the multiplicity Σ, as for the cubic system which transforms the general rotation matrix of the hexagonal system in a rotation matrix with integral elements times Σ^{-1}. The existence of a generating function such as (15) for the hexagonal system does not ensure the unique character of the decomposition of Σ in a quadratic expression. We shall treat this problem in the next paragraph.

4. The application of Warrington's condition

Let the matrix (5) describe a CSL rotation operation. Then this matrix should be of the form $\mathsf{R} = (1/\Sigma)[r_{ij}]$, where r_{ij} are integral expressions, without a common factor, and Σ is the corresponding multiplicity. In such where the r_{ij} should be integers without any common factor in order that the matrix $\mathsf{R}_h = (1/\Sigma)[r_{ij}]$ describes a CSL.

Let us consider first the case $\rho = 1$, $d^* = d$. In this case the values of the nine products $12dr_{ij}$, where d is the integral number (14), should be integers for every i, $j = 1, 2, 3$. We may easily see that the only non-obvious integral expressions are the square roots:

$$\sqrt{3\Sigma - S}; \quad \sqrt{\Sigma + S}; \quad \sqrt{3d}, \tag{18}$$

which means there must be relations of the form

$$(3\Sigma - S)(S + \Sigma) = 3dz^2; \quad 3\Sigma - S = dz'^2, \tag{19}$$

where z and z' are integers. The substitutions

$$3\Sigma - S = fdn^2; \quad \Sigma + S = f3m^2, \tag{20}$$

where m, n, d are integers and f is an integer without square factors, obey the relation (19) and by introducing this substitution into r_{ij} we have:

$$[r_{ij}] = \begin{bmatrix} [(2u-v)un^2 + 2wmn + 3m^2 - dn^2]f/4 & [(2v-u)un^2 - 4wmn]f/4 & [2uwn^2 + 2(2v-u)mn]f/4 \\ [(2u-v)vn^2 + 4wmn]f/4 & [(2v-u)vn^2 - 2wmn + 3m^2 - dn^2]f/4 & [2vwn^2 - 2(2u-v)mn]f/4 \\ [(2u-v)wn^2 - 3vmn]f/4 & [(2v-u)wn^2 + 3umn]f/4 & [2w^2n^2 + 3m^2 - dn^2]f/4 \end{bmatrix} \tag{21}$$

a matrix the trigonometric functions may be expressed as

$$1 - \cos\theta = \frac{3\Sigma - S}{2\Sigma} \tag{16a}$$

$$\cos\theta = \frac{S - \Sigma}{2\Sigma} \tag{16b}$$

$$\sin\theta = \frac{(3\Sigma - S)^{1/2}(\Sigma + S)^{1/2}}{2\Sigma}, \tag{16c}$$

where $S = r_{11} + r_{22} + r_{33}$. These relations introduced into rotation matrix (5) transform their elements into expressions:

$$\mathsf{R}_h = \frac{1}{\Sigma}\begin{bmatrix} (2u-v)u\dfrac{3\Sigma-S}{4d^*} + w\rho\dfrac{(3\Sigma-S)^{1/2}(\Sigma+S)^{1/2}}{2\sqrt{3d^*}} + \dfrac{S-\Sigma}{2} & (2v-u)u\dfrac{3\Sigma-S}{4d^*} - w\rho\dfrac{(3\Sigma-S)^{1/2}(\Sigma+S)^{1/2}}{\sqrt{3d^*}} & uw\rho^2\dfrac{3\Sigma-S}{2d^*} + (2v-u)\rho\dfrac{(3\Sigma-S)^{1/2}(\Sigma+S)^{1/2}}{2\sqrt{3d^*}} \\ (2u-v)v\dfrac{3\Sigma-S}{4d^*} + w\rho\dfrac{(3\Sigma-S)^{1/2}(\Sigma+S)^{1/2}}{\sqrt{3d^*}} & (2v-u)v\dfrac{3\Sigma-S}{4d^*} - w\rho\dfrac{(3\Sigma-S)^{1/2}(\Sigma+S)^{1/2}}{2\sqrt{3d^*}} + \dfrac{S-\Sigma}{2} & vw\rho^2\dfrac{3\Sigma-S}{2d^*} - (2u-v)\rho\dfrac{(3\Sigma-S)^{1/2}(\Sigma+S)^{1/2}}{2\sqrt{3d^*}} \\ (2u-v)w\dfrac{3\Sigma-S}{4d^*} - v\rho^{-1}\sqrt{3}\dfrac{(3\Sigma-S)^{1/2}(\Sigma+S)^{1/2}}{4\sqrt{d^*}} & (2v-u)w\dfrac{3\Sigma-S}{4d^*} + u\rho^{-1}\sqrt{3}\dfrac{(3\Sigma-S)^{1/2}(\Sigma+S)^{1/2}}{4\sqrt{d^*}} & w^2\rho^2\dfrac{3\Sigma-S}{2d^*} + \dfrac{S-\Sigma}{2} \end{bmatrix}, \tag{17}$$

and

$$\Sigma = \frac{f}{4}(3m^2 + dn^2).$$

The factor $f/4$ is eliminated in a similar way as previously presented (Bleris & Delavignette, 1981), the rotation matrix takes the form (10):

$$\mathsf{R} = \frac{1}{\Sigma}[r^*_{ij}/\alpha] \quad \text{and} \quad \Sigma = (3m^2 + dn^2)/\alpha \tag{22}$$

and α has the usual meaning.

For the case $\rho \neq 1$ we introduce the integral expression of d from (14). Then the square-root expressions (18) are transformed and contain the factor

μ. The following substitutions are necessary and sufficient:

$$3\Sigma - S = dn^2 f; \quad \Sigma + S = 3\mu m^2 f. \tag{23}$$

In this case we have

$$\Sigma = \frac{\Sigma^*}{\alpha} = \frac{1}{\alpha}(3\mu m^2 + dn^2);$$

$$\cos\theta = \frac{3\mu m^2 - dn^2}{3\mu m^2 + dn^2} \quad \text{or} \quad \tan\frac{\theta}{2} = \frac{n}{m}\sqrt{\frac{d}{3\mu}}, \tag{24}$$

and the matrix elements become

$$[r_{ij}] = \begin{bmatrix} \begin{matrix}[(u^2\nu - v^2\nu - w^2\mu)n^2 \\ + 2w\mu mn + 3\mu m^2]/\alpha \\ \text{or} \\ [(2u - v)u\nu n^2 \\ + 2w\mu mn + 3\mu m^2 - dn^2]/\alpha\end{matrix} & \begin{matrix}[(2v - u)u\nu n^2 \\ -4w\mu mn]/\alpha\end{matrix} & \begin{matrix}[2uw\mu n^2 \\ + 2(2v - u)\mu mn]/\alpha\end{matrix} \\ \begin{matrix}[(2u - v)v\nu n^2 \\ + 4w\mu mn]/\alpha\end{matrix} & \begin{matrix}[(v^2\nu - u^2\nu - w^2\mu)n^2 \\ - 2w\mu mn + 3\mu m^2]/\alpha \\ or \\ [(2v - u)v\nu n^2 \\ - 2w\mu mn + 3\mu m^2 - dn^2]/\alpha\end{matrix} & \begin{matrix}[2vw\mu n^2 \\ - 2(2u - v)\mu mn]/\alpha\end{matrix} \\ \begin{matrix}[(2u - v)w\nu n^2 \\ - 3v\nu mn]/\alpha\end{matrix} & \begin{matrix}[(2v - u)w\nu n^2 \\ + 3u\nu mn]/\alpha\end{matrix} & \begin{matrix}[(w^2\mu - u^2\nu - v^2\nu + uv\nu)n^2 \\ + 3\mu m^2]/\alpha \\ \text{or} \\ (2w^2\mu n^2 \\ + 3\mu m^2 - dn^2)/\alpha\end{matrix} \end{bmatrix}. \tag{25}$$

5. The parameter α

Possible values for the parameter α are determined in the Appendix on the basis of numerical properties of the nine terms of the rotation matrix. It is shown that α is of the following form:

$$\alpha = \alpha_i k, \tag{26}$$

where $\alpha_i = 1, 3, 4$ or 12; k is any factor of the product $\mu\nu$.

All values of the parameter α are not determined, but (26) defines the form the parameter α must obey. Therefore all the values of α are obtained by selecting those values of the form (26) that give to terms of the rotation matrix (25) integral values, relatively prime.

6. The smallest rotation angle description

Suppose that for a given multiplicity Σ_0 the numbers m, n and d have been found such that $\Sigma_0 = (3\mu m^2 + dn^2)/\alpha$ for a convenient value of α. If θ_0 is the corresponding rotation angle there are eleven other angles θ_i which correspond to other descriptions of the same CSL. The angle θ_0 could be the smallest one between the twelve descriptions if

$$\cos^2\theta_0/2 > \cos^2\theta_i/2, \quad i = 1, \ldots, 11. \tag{27}$$

Let R_0 be the matrix which corresponds to the m, n and d data. The application of the twelve symmetry elements (see for example Hagège, Nouet & Delavignette, 1980) to the R_0 gives the following transformations of the trace S of the matrix R_0:

$$\begin{aligned} &S_1 = r_{11} + r_{22} + r_{33}; && S_2 = -r_{12} + r_{21} + r_{22} + r_{33}; && S_3 = -r_{11} - r_{12} + r_{21} + r_{33}; \\ &S_4 = -r_{11} - r_{22} + r_{33}; && S_5 = r_{12} - r_{21} - r_{22} + r_{33}; && S_6 = r_{11} + r_{12} - r_{21} + r_{33}; \\ &S_7 = r_{12} + r_{21} - r_{33}; && S_8 = -r_{11} + r_{21} + r_{22} - r_{33}; && S_9 = -r_{11} - r_{12} + r_{22} - r_{33}; \\ &S_{10} = -r_{12} - r_{21} - r_{33}; && S_{11} = r_{11} - r_{21} - r_{22} - r_{33}; && S_{12} = r_{11} + r_{12} - r_{22} - r_{33}. \end{aligned} \tag{28}$$

The relations (28) are functions of the m, n and d values, so we may introduce them into (27) by taking into account the expression

$$\cos^2\left(\frac{\theta}{2}\right) = \frac{S + 3\mu m^2 + dn^2}{4\Sigma}, \tag{29}$$

which may be easily deduced from (16*b*).

From the eleven different inequalities which (29), (28) and (27) imply, the following independent inequalities must be fulfilled in order that the description R_0 is the description with the smallest angle:

$$\frac{m}{n} > \frac{w}{2\sqrt{3} - 3}; \quad \frac{m}{n} > \frac{u}{3\rho}; \quad \frac{m}{n} > \frac{2u - v}{2\sqrt{3}\rho}. \tag{30}$$

7. The 180° rotation angle description

From (24) it is obvious that $m = 0$ ($n = 1$) implies $\theta = 180°$. When these values are introduced into the matrix elements (25), the rotation matrix becomes

$$R_{180} = \frac{1}{\Sigma}\begin{bmatrix} (u^2\nu - v^2\nu - w^2\mu)/\alpha & (2v-u)u\nu/\alpha & 2uw\mu/\alpha \\ (2u-v)v\nu/\alpha & (v^2\nu - u^2\nu - w^2\mu)/\alpha & 2vw\mu/\alpha \\ (2u-v)w\nu/\alpha & (2v-u)w\nu/\alpha & (w^2\mu - u^2\nu - v^2\nu + uv\nu)/\alpha \end{bmatrix} \quad (31)$$

and the Σ expression takes the form

$$\Sigma = [(u^2 + v^2 - uv)\,\nu + w^2\,\mu]/\alpha = d/\alpha. \quad (32)$$

From (31) and (32) we see the well known property that the 180° description around the $[uv0]$ directions is independent of the hexagonal axial ratio c/a.

8. Systematic generation of tables of CSL's

The method presented for the generation of CSL's in the cubic system is applicable to particular hexagonal systems without change: relations (24) are used, maximum m and n values are determined, authorized α values are calculated and the tables are generated for particular μ and ν values (particular c/a values), the selection rules introduced for the cubic system are replaced here by compatibility conditions on the r_{ij} elements and the d value (they must be integers), which is a more time consuming approach than for the cubic system.

This generation method gives all the descriptions of all the CSL's corresponding to a particular multiplicity Σ but does not differentiate all different CSL's having the same multiplicity. Moreover, their detection on the form of the rotation matrix is not obvious, in contrast to the cubic case. Therefore every description is transformed into its twelve equivalent descriptions using the symmetry-element rotation matrices and compared to the other generated descriptions, allowing a final determination of all existing CSL's.

An establishment of tables of CSL's on this basis for $c/a = \sqrt{8/3}$ and $c/a = 1$ confirmed the already published tables by Warrington (1975) and by Hagège, Nouet & Delavignette (1980). Tables of coincidence have been published more recently for twenty-two different axial ratios (Bonnet, Cousineau & Warrington, 1981), in the range of the hexagonal close-packed metals (Be, Ti, α-Zr and Mg), also for less densely packed metals (Zn and Cd), and for graphite. It is an interesting approach for the determination of coincidence grain boundaries in hexagonal structures based on the concept of near-coincidence, which is similar to the present approach, although we insisted more on the comparison with ideal models, similar to that which has been developed for cubic crystals. For the range $12/5 \leq (c/a)^2 \leq 27/10$ and $\Sigma \leq 25$ we found fifteen coincidences which are not mentioned by Bonnet, Cousineau & Warrington (1981).

It is evident that all tables established for different axial ratios contain common CSL's for rotations around the [001] axis (or 180° rotations around $[uv0]$), since these are independent of the axial ratio. These are the multiplicities $\Sigma = 7, 13, 19, 31, 37, 43, 49$, *etc.*

From any predetermined axial ratio, expressed in the fractional form $\mu/\nu = c^2/a^2$, the formulation presented here allows a rapid determination of *all ideal* existing CSL's. Such an idealized approach is essential for the characterization of a grain boundary. The form of the formulation (the Σ expression is a function of μ and ν) indicates that the lowest multiplicities Σ in all axial ratios will appear for the lowest μ and ν values. This statement is evident, and easily deduced from the CSL concept: only special axial ratios for low μ and ν values give rise to three-dimensional coincidence lattices of low multiplicities. This is also confirmed by the calculations.

9. Characterization of a grain boundary

No practical systematic analyses of grain boundaries (or bicrystals) in terms of CSL's have been presented up till now. This is essentially due to the difficulty in presenting an idealized model of a CSL, and to the time consuming procedure for the determination of ideal CSL's for a large variety of c/a values. The approach of Bonnet, Cousineau & Warrington (1981) is a first attempt in that direction, but it does not present a completely developed method for systematically characterizing CSL's in hexagonal structures. Its fundamental interest is to have presented for the first time a large variety of CSL's for different c/a values, in spite of some missing values. It also presents a way of characterizing coincidences by the determination of near coincident cells.

We do not suggest approaching the problem first by defining a 'best' axial ratio approximation for a particular material, but we will show that *different* μ/ν ratios may be competitively considered for describing the same material.

Considering the hexagonal compact metals, such as α-Ti, α-Zr, Re, α-Co or Mg, characterized by an axial ratio around 1·6 or close to the μ/ν values of 5/2 or 8/3, it is clear that any of these two ratios might give rise to possible approximative CSL's. It is clear also that a significant deviation of this μ/ν value is of no physical meaning. Therefore different tables of CSL's will be established for different μ/ν values in the neighbourhood of these ratios. Restricting ourselves to deviations of μ/ν of $\pm 10\%$ (*i.e.* deviations of c/a of $\pm 5\%$) and considering CSL's with lower multiplicities than $\Sigma = 21$ (higher multiplicities have a limited physical meaning), it has been verified that only 11 different μ/ν values give rise to possible CSL's (neglecting of course the trivial cases independent of the μ/ν value). It is therefore concluded that the CSL's

Table 1. *Rotation axes of all CSL's in the* 180° *description with* $\Sigma \leq 20$ *for hexagonal crystals with* $1{\cdot}5 < c/a < 1{\cdot}7$

c/a	μ/ν \ Σ		7	9	10	11	12	13	14	15	16	17	18	19	20
any			3 1 0 5 1 0					4 1 0 7 2 0						5 2 0 8 1 0	
1·55	12/5			2 1 1 8 4 5			4 2 1 4 2 5				2 0 1 6 0 5	1 0 1 12 0 5		3 0 1 4 0 5	
1·56	39/16											2 1 2 26 13 8			
1·57	27/11														2 1 1 18 9 11
1·58	5/2	*a*	1 0 1 5 0 2			1 0 2 5 0 1		2 1 2 10 5 3				2 1 3 10 5 2		3 1 1	
		b				2 1 1 10 5 6		2 0 1 5 0 4				3 1 2		3 0 2 5 0 3	
1·60	18/7							2 1 1 12 6 7				4 2 1 6 3 7			
1·61	13/5												1 0 1 13 0 5		
1·62	21/8	*a*		2 1 2 14 7 4				3 0 2 7 0 4		2 1 4 14 7 2		3 0 4 7 0 2			
		b								2 1 1 14 7 8					
1·63	8/3				2 0 1 4 0 3	1 0 1 8 0 3			2 0 3 4 0 1			2 1 1 16 8 9	4 2 3 8 4 3		
1·64	27/10													2 1 1 18 9 10	
1·66	11/4						1 0 2 11 0 2		2 1 2 22 11 6	1 0 1 11 0 4			3 1 2		3 0 2 11 0 6
1·67	14/5											2 0 1 7 0 5		1 0 1 14 0 5	

existing within these two limits on μ/ν and on Σ are given by Table 1 in their 180° rotation description. There are 40, which could actually be considered as 18 different CSL's, since for several cases different multiplicities describe 180° rotations around the same rotation axis for different μ, ν values, as for example rotations around [211]. There is no CSL in these limits which has no 180° rotation description.

The following steps will be considered in a grain boundary analysis:

(1) from a bicrystal calculate its 180° rotation description; if this does not exist, it is doubtful that it is a coincidence grain boundary:

(2) determine its exact rotation axis (180°) using Table 1;

(3) determine the corresponding μ and ν values;

(4) determine the grain boundary plane and compare the lattice constants for the material (for its c/a value) and for the corresponding ideal CSL (for the corresponding μ and ν values);

(5) verify that the misfit in point (4) is accommodated by misfit dislocations;

(6) the deviation of the ideal CSL relationship is accommodated by intrinsic boundary dislocations, which may be analysed in terms of a tilt component and a twist component.

Practically, the determination is considerably simplified by using the stereographic projection of all 180° rotation axes in a reference triangle, Fig. 1. The corresponding axial ratios only are mentioned in Table 1.

10. Presence of at least one 180° description

Tables of CSL's corresponding to more than 200 different μ and ν values have been established in all their equivalent descriptions. The property established by Friedel (1926), that a twin always has at least one description of the type symmetry plane or binary axis, means that special attention has been paid to the 180° rotation description (considering lattices and not structures and taking into account that the CSL concept is a generalization of the twin concept). In our determinations, most of the CSL's for which $\Sigma \le 50$ have at least one 180° description. There is one exception for the special case $\mu/\nu = 1$ already analysed and for which out of the 99 CSL's for which $\Sigma \le 50$, there are 20 CSL's with no 180° description.

11. Conclusion

The expressions (24) and the form of the rotation matrix (25) are simple tools for the rapid and simple automatic calculation of tables of CSL in the hexagonal system. Their systematic use for the calculation of CSL's for a large number of μ/ν values has shown that it is possible, for the hexagonal crystals, to establish complete tables of CSL, for any particular material within pre-established deviations of the axial ratio c/a and up to a maximum Σ value. The hexagonal case may therefore be treated in a similar way to the cubic case.

The description using a rotation angle of 180°, if present, is an easy approach to the coincidence, since this may be visually presented by the projection of its rotation axis in the reference stereographic triangle. Indeed, when, for a practical bicrystal, a rotation description exists with an angle close enough to 180°, it is a first criterion for the existence of a coincidence. If moreover the rotation axis transposed on the reference triangle is close enough to a rotation axis of a coincidence, the determination is complete. It may then be quantified by the matrix product of these experimental and tabulated matrices which may be a small-angle rotation matrix.

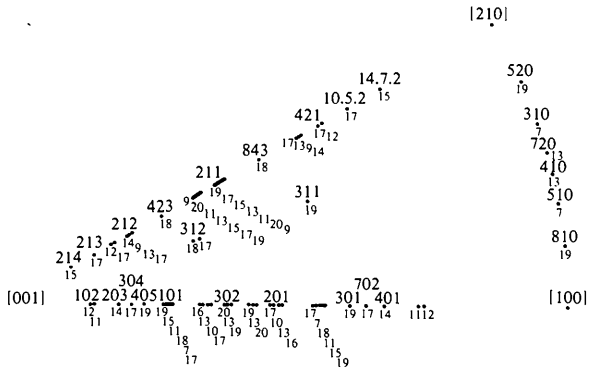

Fig. 1. Stereographic projection in the reference triangle of all the 180° rotation axes defining a CSL and mentioned in Table 1 (the corresponding axial ratios are not reproduced on the projection). $\Sigma = 20$, $1{\cdot}5 < c/a < 1{\cdot}7$. Rotation axes and Σ are given. The groups of points for which *no* Miller indices are given have *different* indices for different c/a ratios; these are given in Table 1.

APPENDIX

Possible values for the parameter α

It is not the purpose here to determine all the values, but only possible values, for the parameter α, excluding any other form for this parameter. In fact we shall prove that α may be $\alpha = \alpha_i k$, where $\alpha_i = 1, 3, 4$ or 12 and k is any factor of the product $\mu\nu$.

Since α is a common factor of the nine elements r^*_{ij} and the Σ^* expression (24), we shall treat the problem looking at all possible divisors of the Σ^* which are divisors of the r^*_{ij} elements. We may first see that all the r^*_{ij} are homogeneous expressions in m, n variables and the same is obvious for the Σ expression, so that one must have

$$(m,n) \doteq 1. \qquad (A1)$$

Let us consider first the case where the numbers $3\mu m^2$, dn^2 are relatively prime:

$$(3\mu m^2, dn^2) \doteq 1. \qquad (A2)$$

From the sum S^* ($S^* = \alpha S$) of the diagonal elements (25) and the Σ^* expression we have

$$\alpha | 3\mu m^2 + dn^2 \dagger \quad \text{since } \Sigma^* = 3\mu m^2 + dn^2 \qquad (A3)$$

$$\alpha | 9\mu m^2 - dn^2 \quad \text{since } S^* = 9\mu m^2 - dn^2, \qquad (A4)$$

from which one obtains necessarily $\alpha | 12\mu m^2$ since $\Sigma^* + S^* = 12\mu m^2$, and from ($A1$), ($A2$), ($A3$) ($\alpha \nmid 3\mu m^2$)† one concludes $\alpha = 1, 2$ or 4.

Let us examine the case $\alpha = 2$. From ($A3$, $A4$), it is obvious that $\alpha | 3\mu m^2 - dn^2 = S^* - 6\mu m^2$ and from the elements (25) we may easily deduce that if $\nu \equiv 0 (\text{mod } 2)$ then $k = 2$, which is a factor of ν. If $\nu \not\equiv 0 (\text{mod } 2)$ we shall show that $\alpha_i \ne 2$. If α_i is an even number from the elements r^*_{12}, r^*_{21} we may see that the conditions $\alpha_i | r^*_{12}$ and $\alpha_i | r^*_{21}$ imply

$$u \equiv 0 (\text{mod } 2) \quad v \equiv 0 (\text{mod } 2) \quad \text{and} \quad w \equiv 1 (\text{mod } 2). \qquad (A5)$$

Since α_i may not divide one of the numbers ($A2$), one concludes that neither m nor n may be an even number.

Taking into account that the square of an odd number is of the type $1 (\text{mod } 8)$, the following conditions may be deduced using ($A5$):

$$\left.\begin{aligned} r^*_{11} - (u^2 - v^2)\nu n^2 &\equiv 0 (\text{mod } 4) \rightarrow r^*_{11} \equiv 0 (\text{mod } 4) \\ r^*_{22} - (v^2 - u^2)\nu n^2 &\equiv 0 (\text{mod } 4) \rightarrow r^*_{22} \equiv 0 (\text{mod } 4) \\ r^*_{31} + v\nu n(wn + 3m) &\equiv 0 (\text{mod } 4) \rightarrow r^*_{31} \equiv 0 (\text{mod } 4) \\ r^*_{32} - u\nu n(wn + 3m) &\equiv 0 (\text{mod } 4) \rightarrow r^*_{32} \equiv 0 (\text{mod } 4), \end{aligned}\right\} \qquad (A6)$$

and all the other elements (25) are obviously of the type

† $p|q$ means $q \equiv 0 (\text{mod } p)$ and $p \nmid q$ means $q \not\equiv 0 (\text{mod } p)$.

0(mod 4). On the other hand:

$$\Sigma^* = 3\mu m^2 + dn^2$$
$$= 3\mu(8p + 1) + d(8p + 1)$$
$$= 4[\pi + \mu(2p + 1)] \equiv 0(\text{mod } 4)$$

[where (8p + 1) means 'a multiple of p plus one'], which implies $\alpha_i = 4$.

Finally when the condition (A2) is fulfilled, α_i may be 1 or 4.

Let us now consider the case where the numbers $3\mu m^2$ and dn^2 are not relatively prime. The existence of a common factor may be obtained from one or more of the following cases (a last case is excluded according to the relation A1):

$$\begin{array}{ll} \text{(i) } (3, d) \div 3 & \text{(iv) } (3, n) \div 3 \\ \text{(ii) } (\mu, d) \div q & \text{(v) } (\mu, n) \div p \\ \text{(iii) } (m, d) \div t & q, p, t \neq t. \end{array} \quad (A7)$$

We shall examine every condition (31) as an independent one.

(i) $(3,d) \div 3$. Since $3|d$ and 3 should divide r^*_{33} we have $3|2w^2\mu n^2$ which means $3|w$, then we have

$$3|u^2 + v^2 - uv \quad (A8)$$

or $3|v$. The last condition leads to the fact $k = 3$ and in particular this k value is a factor of v. The condition (A8) implies $3|(u + v)^2 - 3uv$ from which we have $u + v \equiv 0(\text{mod } 3)$. On the other hand, $2u - v + v + u = 3u \equiv 0(\text{mod } 3)$ which implies $2u - v \equiv 0(\text{mod } 3)$ and also $2v - u \equiv 0(\text{mod } 3)$, thus the r^*_{ij} elements are of the form 0(mod 3) which implies $\alpha_i = 3$. Taking into account the case $\alpha_i = 4$ which is fulfilled for the conditions u and $v \equiv 0(\text{mod } 2)$ and m and $n \equiv 1(\text{mod } 2)$ we have that α_i may have the value 12.

(ii) $(\mu,d) = q$. We shall prove that k may have the value q which in particular is a factor of μ. Since $d \equiv 0(\text{mod } q)$ and since $\mu w^2 \equiv 0(\text{mod } q)$ from (14) we have

$$u^2 + v^2 - uv \equiv 0(\text{mod } q), \quad (A9)$$

taking into account the condition (13b). For (A9), if $(u,v) \div 1$ then q may be only 3, and $k = 3$; in particular 3 is a factor of μ. If u and v are not relatively prime then $k = q$ if $(u,v) = q$.

(iii) $(m,d) \div t$. From the r^*_{33} element we may see that $t|2w$. The case $t = 2$ implies u and $v \equiv 0(\text{mod } 2)$ (from r^*_{12} and r^*_{21}) but since $d \equiv 0(\text{mod } t)$ we have $w \equiv 0(\text{mod } 2)$ which is improper, or $\mu \equiv 0(\text{mod } 2)$. The last condition implies $k = 2$. The condition $t|w$ together with the condition $d \equiv 0(\text{mod } t)$ implies $t|u^2 + v^2 - uv$ or $t|v$. The first of these two conditions may be fulfilled if $t = 3$ and $(u,v) \div 1$ a known value of α_i. Any other condition implies the improper relation $(u,v,w) \div t$. The case $t|v$ implies $k = t$ as may be easily seen from (25).

(iv) The condition $(3,n) \div 3$ implies $\alpha_i = 3$ since all the matrix elements become of the form 0(mod 3).

(v) The condition $(\mu,n) \div p$ implies $k = p$ since all the r^*_{ij} elements become of the form 0(mod p).

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SHORT COMMUNICATIONS

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Acta Cryst. (1982). A**38**, 557–558

Intermolecular energy, structure and stability of regular stacks of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ): erratum.

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Abstract

Previous calculations of the stack structure of TTF and TCNQ by Govers [*Acta Cryst.* (1981), A**37**, 529–535] are corrected for a program error.

New results

During our calculation of the three-dimensional crystalline structure of TTF–TCNQ (Govers, 1982) we met a venomous program error. This error proved important only

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