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Grain Boundaries in Materials with a Hexagonal, Rhombohedral or Tetragonal Lattice: the Connection Between Different Treatments of Approximate Coincidence

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Abstract

The relative orientation of the lattices of two neighbouring grains of the same phase can be described by a rotation R. It can be decomposed as a product $R = R_\perp R_\parallel$ of two rotations with axes perpendicular and parallel to a given direction. This direction is chosen parallel to the principal symmetry axis in the case of hexagonal, rhombohedral or tetragonal lattices. The parameter ε introduced by Bonnet & Durand [*Philos. Mag.* (1975). **32**, 997–1006] to describe the deformation connected with approximate coincidence in such lattices satisfies $\varepsilon = \Delta \sin \Phi$, where Δ is the relative deviation between the experimental and the coincidence value of the axial ratio c/a and Φ is the angle of $R_\perp$. Addition of the value of $\sin \Phi$ to tables of coincidence rotations makes it possible to compute ε in a simple manner for any experimental value of c/a.

1. Introduction

The success of the coincidence model of grain boundaries in cubic materials has led to the systematic determination of all the rotations that leave a large portion $1/\Sigma$ of the symmetry translations invariant. Such rotations are called coincidence rotations with multiplicity Σ.

The coincidence model has been extended also to hexagonal, rhombohedral and tetragonal lattices. [See Warrington (1975), Bonnet, Cousineau & Warrington (1981), Bleris, Nouet, Hagège & Delavignette (1982), Grimmer & Warrington (1985) and Grimmer (1989*b*) for hexagonal lattices, Doni, Fanides & Bleris (1986) and Grimmer (1989*a,d*) for rhombohedral lattices, Erochine & Nouet (1983) for tetragonal lattices.] In these cases, a coincidence rotation with axis $\mathbf{n}$ and angle Θ has a multiplicity that is independent of the axial ratio $r = c/a$ of the lattice if either $\mathbf{n}$ is parallel to the principal (*i.e.* 6-, 3- or 4-fold) symmetry axis of the lattice or $\Theta = 180°$ and $\mathbf{n}$ is perpendicular to the principal axis. All other rotations can have a small value of Σ only for certain rational values of r^2. The former type of coincidence rotation is called common or exact, the latter specific or approximate because the coincidence of translation vectors is only approximate if the experimental value r_e slightly deviates from the specific value r for which the rotation has a low value of Σ. Low energy boundaries are expected between grains in an exact orientation or in a specific orientation if $r_e = r$.

If $r_e \neq r$ of the specific orientation then the boundary must contain secondary dislocations in order to locally preserve the structure of a coincidence boundary. The minimum density of dislocations is related to the deformation parameter ε introduced by Bonnet & Durand (1975). The purpose of this paper is to derive an analytic expression for ε if the relative deviation between the specific and experimental values of the axial ratio is small, *i.e.* $\Delta = |r - r_e|/r_e \ll 1$. In order to show the connection between ε and Δ, the coincidence rotation R is decomposed as follows: $R = R_\perp R_\parallel$, where $R_\perp$ and $R_\parallel$ are rotations perpendicular and parallel to the principal axis. It is shown that the angles Φ of $R_\perp$ and Ψ of $R_\parallel$ can be chosen smaller or equal to the angle Θ of R and that $\varepsilon = \Delta \sin \Phi$.

2. The splitting of a rotation R into two rotations with axes parallel and perpendicular to the principal axis, $R = R_\perp R_\parallel$

Each rotation R may be considered as a right-handed rotation by an angle $\Theta = 2\theta$ satisfying $0 \leq \Theta \leq 180°$ about an axis characterized by a unit vector $\mathbf{n}$. Introducing an orthonormal coordinate system, one obtains $\mathbf{n} = (n_1, n_2, n_3)$ with $n_1^2 + n_2^2 + n_3^2 = 1$. The rotation R can be characterized by a pair of unit quaternions

$$R \Leftrightarrow \pm(a_0, a_1, a_2, a_3) = \pm(\cos\theta, n_1 \sin\theta, n_2 \sin\theta, n_3 \sin\theta). \quad (1)$$

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Notice that

$$a_0^2+a_1^2+a_2^2+a_3^2=1. \quad (2)$$

Let us show that R can be decomposed as

$$R=R_\perp R_\parallel, \quad (3)$$

where $R_\parallel$ and $R_\perp$ are rotations with axes parallel and perpendicular to a fixed direction. This decomposition is unique unless $a_0=a_3=0$. We shall also show that the angles $\Phi=2\varphi$ of $R_\perp$ and $\Psi=2\psi$ of $R_\parallel$ satisfy $\cos\varphi\cos\psi=\cos\theta$. We choose the fixed direction parallel to the principal (6-, 3- or 4-fold) symmetry axis of the hexagonal, rhombohedral or tetragonal lattice and let it coincide with the third axis of our orthonormal coordinate system. It follows that

$$R_\parallel \Leftrightarrow \pm(\cos\psi, 0, 0, \sin\psi). \quad (4)$$

Consider $R'=RR_\parallel^{-1}$. We shall see that R' is of type $R_\perp$ for a uniquely defined value of ψ and that for this value of ψ the half-angle φ of R' takes its minimum value. The law of quaternion multiplication (see *e.g.* Grimmer, 1974) gives

$$\begin{aligned} R'=RR_\parallel^{-1} &\Leftrightarrow \pm(a_0, a_1, a_2, a_3)(\cos\psi, 0, 0, -\sin\psi)\\ &=\pm(a_0\cos\psi+a_3\sin\psi, a_1\cos\psi-a_2\sin\psi,\\ &\quad a_2\cos\psi+a_1\sin\psi, a_3\cos\psi-a_0\sin\psi). \end{aligned} \quad (5)$$

The rotation R' is of type $R_\perp$ if and only if $a_3\cos\psi=a_0\sin\psi$; R' considered as a function of ψ has minimum angle if $a_0\cos\psi+a_3\sin\psi$ is maximal, *i.e.* if

$$0=\mathrm{d}\,(a_0\cos\psi+a_3\sin\psi)/\mathrm{d}\psi=-a_0\sin\psi+a_3\cos\psi.$$

Both conditions give $\tan\psi=a_3/a_0$, *i.e.*

$$\cos\psi=a_0/(a_0^2+a_3^2)^{1/2}$$

and (6)

$$\sin\psi=a_3/(a_0^2+a_3^2)^{1/2}.$$

The half-angle φ of $R'=R_\perp$ then becomes

$$\cos\varphi=a_0\cos\psi+a_3\sin\psi=(a_0^2+a_3^2)^{1/2}. \quad (7)$$

It follows from $\cos\theta=a_0$ that

$$\cos\varphi\cos\psi=\cos\theta, \quad (8)$$

i.e. $\cos\varphi\geq\cos\theta$ and $\cos\psi\geq\cos\theta$. This implies $\varphi\leq\theta$ and $\psi\leq\theta$ because $0\leq\varphi, \psi, \theta\leq 90°$. The splitting $R=R_\perp R_\parallel$ can be expressed as follows in terms of unit quaternions:

$$\begin{aligned}(a_0, a_1, a_2, a_3)\\ &=(a_0^2+a_3^2)^{-1/2}(a_0^2+a_3^2, a_0a_1-a_2a_3, a_0a_2+a_1a_3, 0)\\ &\quad (a_0^2+a_3^2)^{-1/2}(a_0, 0, 0, a_3). \end{aligned} \quad (9)$$

3. Application to coincidence rotations; computation of the deformation parameter ε

Consider first a hexagonal lattice with axial ratio $r=c/a$. We change from orthonormal to crystal coordinates with

$$|\mathbf{e}_1|=|\mathbf{e}_2|=a,\quad |\mathbf{e}_3|=c,\quad \mathbf{e}_1\mathbf{e}_3=\mathbf{e}_2\mathbf{e}_3=0,\quad \mathbf{e}_1\mathbf{e}_2=-a/2$$

and from quaternions to hexagonal quadruples as in Grimmer & Warrington (1987). The hexagonal quadruple (m, U, V, W) describes a rotation with axis $[U, V, W]$ and half-angle θ given by their equation (26) as

$$\tan\theta=\{[(U^2-UV+V^2)+r^2W^2]/3r^2m^2\}^{1/2}, \quad (10)$$

obviously independent of the normalization of the quadruple. The splitting $R=R_\perp R_\parallel$ becomes in terms of (not normalized) quadruples

$$\begin{aligned}(m, U, V, W)=[&3m^2+W^2, 3mU+(U-2V)W,\\ &3mV+(2U-V)W, 0](m, 0, 0, W).\end{aligned} \quad (11)$$

It has been shown in that article that R is a coincidence rotation if and only if all four components of its hexagonal quadruple are integral multiples of some real number and if in addition either r^2 is rational or the inner two or the outer two components of the quadruple vanish. A coincidence rotation with quadruple of type $(m, 0, 0, W)$ or $(0, U, V, 0)$ is always of the common type. Because $\varepsilon=0$ for common rotations we need not consider these cases any further.

If r^2 is rational and R a coincidence rotation, *i.e.* if all four components of its quadruple are integral multiples of some real number then the same holds also for $R_\perp$ and $R_\parallel$ according to (11). A similar argument holds for rhombohedral and tetragonal lattices.

It remains to compute ε. Let $R=R_\perp R_\parallel$ be a coincidence rotation of a lattice G_1 with r^2 rational. $R_\parallel$ maps G_1 onto G, $R_\perp$ maps G onto G_2,

$$G_1 \xrightarrow{R_\parallel} G \xrightarrow{R_\perp} G_2.$$

Let U_1 be the lattice consisting of the vectors that are common to G_1 and G, $U_1=G_1\cap G$, and let Σ_1 be its multiplicity. Analogously, let Σ_2 be the multiplicity of $U_2=G_2\cap G$, and $\bar\Sigma$ the multiplicity of $\bar U=U_1\cap U_2$.* A primitive cell M of $\bar U$ is therefore simultaneously a cell of G_1, G and G_2 with a volume $\bar\Sigma$ times larger than the volume of primitive cells of these three lattices. Since the vectors of a lattice form an Abelian group, it follows from the 'first theorem on group isomorphisms' (van der Waerden, 1966) that $\bar\Sigma$ is a factor of $\Sigma_1 . \Sigma_2$, a multiple of Σ_1 and a multiple of Σ_2.

The lattice G_1 with axial ratio r can be obtained from a lattice G_1^e of the same Bravais type but with the experimental value r_e of the axial ratio by an elongation D_1 in the direction of the principal

* Notice that $\bar\Sigma$ is a multiple of the multiplicity Σ of the lattice $G_1\cap G_2$.

symmetry axis by an amount

$$\delta = (r - r_e)/r_e. \qquad (12)$$

The transformation D_1 gives the cell M as the image of a cell M_1 of G_1^e. Also, lattice G has a cell M. Reversal of the elongation in the direction of the principal axis leads back to M_1 because the principal axis remained unchanged under $R_\parallel$. However, reversing the elongation in the direction of the principal axis of lattice G_2 transforms its cell M into a cell M_2. In order to determine the linear transformation A mapping M_1 into M_2 it suffices therefore to consider the component $R_\perp$ of R.

Fig. 1 shows the plane perpendicular to the axis of $R_\perp$ and containing the axis of $R_\parallel$. A right-handed orthonormal coordinate system with y axis along $R_\parallel$ is chosen in this plane. The transformation D_1 has an invariant plane perpendicular to the axis of $R_\parallel$. This plane may be chosen to pass through the point O, where the axes of $R_\parallel$ and $R_\perp$ intersect. The mappings D_1 and $R_\perp$ are represented in this coordinate system by the following matrices*

$$\mathbf{D}_1 = \begin{pmatrix} 1 & 0 \\ 0 & 1+\delta \end{pmatrix}, \qquad \mathbf{R}_\perp = \begin{pmatrix} \cos\Phi & \sin\Phi \\ -\sin\Phi & \cos\Phi \end{pmatrix}.$$

The mapping D_2 that transforms M into M_2 is represented in the primed coordinate system of Fig. 1 by the inverse of the matrix $\mathbf{D}_1$:

$$\mathbf{D}_2' = \begin{pmatrix} 1 & 0 \\ 0 & (1+\delta)^{-1} \end{pmatrix} = \mathbf{R}_\perp \mathbf{D}_2 \mathbf{R}_\perp^{-1}.$$

The mapping A that transforms M_1 into M_2 is given by

$$\mathbf{A} = \mathbf{D}_2\mathbf{D}_1 = \mathbf{R}_\perp^{-1}\mathbf{D}_2'\mathbf{R}_\perp\mathbf{D}_1$$
$$= \begin{pmatrix} (1+\delta\cos^2\Phi)(1+\delta)^{-1} & \delta\sin\Phi\cos\Phi \\ (\delta\sin\Phi\cos\Phi)(1+\delta)^{-1} & 1+\delta\sin^2\Phi \end{pmatrix}.$$

The eigenvalues λ of A satisfy $\det(\mathbf{A}-\lambda\mathbf{I})=0$, $\mathbf{I}$ the identity matrix, *i.e.*

$$\lambda^2 - 2[1+\delta^2\sin^2\Phi/2(1+\delta)]\lambda + 1 = 0$$

or

$$\lambda = 1 + \frac{\delta^2\sin^2\Phi}{2(1+\delta)} \pm \left\{\left[1+\frac{\delta^2\sin^2\Phi}{2(1+\delta)}\right]^2 - 1\right\}^{1/2}.$$

Because only those specific rotations are of interest for which $|\delta| \ll 1$, it is sufficient to consider terms up to first order in δ:

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \simeq \begin{pmatrix} 1-\delta\sin^2\Phi & \delta\sin\Phi\cos\Phi \\ \delta\sin\Phi\cos\Phi & 1+\delta\sin^2\Phi \end{pmatrix}$$

and $\lambda \simeq 1 \pm \delta\sin\Phi$. In this approximation, the matrix $\mathbf{A}$ is symmetric and describes a pure (*i.e.* rotation-free) deformation. The eigenvectors $\mathbf{v}$ of A satisfy $(a_{11}-\lambda)v_x + a_{12}v_y = 0$, from which it follows in our approximation that

$$v_y/v_x \simeq (\sin\Phi \pm 1)/\cos\Phi = \tan(\Phi/2 \pm 45°).$$

Taking also the direction perpendicular to the plane of Fig. 1 into account, we introduce a new orthonormal coordinate system as follows. The axes are chosen in the direction of eigenvectors arranged in the order of increasing eigenvalues. Put $\Delta = |\delta|$. The first and third axes lie in the plane of Fig. 1 and have eigenvalues $\lambda_1 = 1-\Delta\sin\Phi$ and $\lambda_3 = 1+\Delta\sin\Phi$, respectively, the second axis lies perpendicular to that plane and has eigenvalue $\lambda_2 = 1$. Expressed in this coordinate system A has the form

$$A = \begin{pmatrix} 1-\Delta\sin\Phi & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1+\Delta\sin\Phi \end{pmatrix}.$$

Let us compare this result with the general result of Bonnet & Durand (1975) and Bonnet & Cousineau (1977), valid also for boundaries between different phases of arbitrary symmetry. They write A as

$$A = R_0 D,$$

where R_0 is a rotation and D a pure deformation. Using an orthogonal coordinate system as described above they obtain

$$D = \begin{pmatrix} 1+\varepsilon_1 & 0 & 0 \\ 0 & 1+\varepsilon_2 & 0 \\ 0 & 0 & 1+\varepsilon_3 \end{pmatrix} \quad \text{with } \varepsilon_1 \le \varepsilon_2 \le \varepsilon_3.$$

If the cells M_1 and M_2 have equal volumes then $\varepsilon_1+\varepsilon_2+\varepsilon_3=0$. For boundaries between grains of the same phase with a hexagonal, rhombohedral or tetragonal lattice we obtained that the rotational part of A is trivial ($R_0 = I$), that $\varepsilon_2 = 0$, *i.e.* $\varepsilon_3 = -\varepsilon_1 = \varepsilon$,*

* The fact that $\varepsilon_2 = 0$ and $\varepsilon_3 = -\varepsilon_1 = \varepsilon$ was stated by Bonnet, Cousineau & Warrington (1981) for grain boundaries in hexagonal materials and by Lartigue (1988) for grain boundaries in rhombohedral materials.

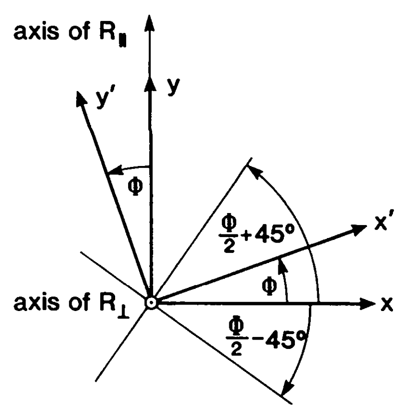

Fig. 1. The directions of the eigenvectors of A in two coordinate systems related by $R_\perp$.

* $\mathbf{D}$ and $\mathbf{D}'$ are used to denote the matrices representing a mapping D in the coordinate systems xy and $x'y'$, respectively.

Table 1. *The equivalence classes of specific rotations with $\Sigma \le 21$ and $6{\cdot}7 \le r^2 \le 6{\cdot}9$*

		Representative				$R_\perp$		Miller–Bravais indices of symmetry planes	
r	Σ	m	u	v . w	Θ (°)	Φ (°)	sin Φ		
2·598	10	1	1	0 . 1	69·51	36·87	0·600	0 1 . 9	1 0 . 1
	12*a*	2	0	3 . 0	60·00	60·00	0·866	1 1 . 3	
	12*b*	3	3	3 . 3	82·82	60·00	0·866	1 1 . 9	
	13	1	0	2 . 1	87·80	67·38	0·923	2 0 . 9	0 1 . 2
	16	9	0	27 . 3	98·99	97·18	0·992	1 2 . 9	
	18*a*	2	3	3 . 0	90·00	90·00	1·000		
	18*b*	3	0	9 . 3	104·48	90·00	1·000	1 0 . 3	0 1 . 3
	21*a*	4	0	9 . 0	81·79	81·79	0·990	2 2 . 9	
	21*b*	1	0	3 . 0	98·21	98·21	0·990	1 1 . 6	
2·611	12	1	0	2 . 1	87·61	67·11	0·921	11 0 . 50	0 1 . 2
	20	11	0	10 . 11	67·98	33·56	0·553	1 0 . 10	0 11 . 10
2·627	11	1	0	2 . 1	87·39	66·80	0·919	5 0 . 23	0 1 . 2
	17	1	1	0 . 1	69·33	36·49	0·595	0 5 . 46	1 0 . 1
	21	10	0	23 . 10	92·73	74·35	0·963	1 0 . 4	0 10 . 23

and that

$$\varepsilon = \Delta \sin \Phi. \qquad (13)$$

This formula provides a simple way to compute the parameter ε. It is the product of two factors, the first of which is independent of R and the second independent of r_e.

If the coincidence rotation R of a hexagonal lattice is described by the quadruple (m, U, V, W) as in Grimmer & Warrington (1985, 1987) and in Grimmer (1989*b*) then sin Φ will be obtained from:

the form (11) of the quadruple representing $R_\perp$;

the formula (10) expressing the half-angle of a rotation in terms of the components of its quadruple;

the relation $\sin \Phi = 2 \tan \varphi/(1+\tan^2 \varphi)$:

$$\sin \Phi = \frac{2(3m^2+W^2)^{1/2}(U^2-UV+V^2)^{1/2}}{r(3m^2+W^2)+r^{-1}(U^2-UV+V^2)}. \qquad (14)$$

Rotation symbols $(m, u, v\,.\,w)$ have been used to describe coincidence rotations R of rhombohedral lattices in Grimmer (1989*a,d*) and of rhombohedral and hexagonal lattices in Grimmer (1989*c*). Such a symbol describes a rotation the axis of which has Weber indices $[u, v\,.\,w]$ and the half-angle θ of which is given by

$$\tan \theta = \{[3(u^2+uv+v^2)+r^2w^2]/3r^2m^2\}^{1/2}. \qquad (15)$$

The splitting $R = R_\perp R_\parallel$ is expressed as

$$(m, u, v\,.\,w) = [3m^2+w^2, 3mu-(u+2v)w, 3mv+(2u+v)w\,.\,0](m, 0, 0\,.\,w). \qquad (16)$$

It follows that the angle Φ of $R_\perp$ is given by

$$\sin \Phi = \frac{2(3m^2+w^2)^{1/2}[3(u^2+uv+v^2)]^{1/2}}{r(3m^2+w^2)+r^{-1}3(u^2+uv+v^2)}. \qquad (17)$$

4. An example: specific coincidence rotations for rhombohedral lattices with axial ratios close to the values for antimony and bismuth

Antimony and bismuth have the same structure type with rhombohedral space group $R\bar{3}m$. Eckerlin & Kandler (1971) give for the lattice parameters at 298 K

	a (Å)	c (Å)	$r_e = c/a$	r_e^2
Sb	4·3084	11·247	2·610	6·815
Bi	4·54590	11·86225	2·609	6·809.

Using the methods of Grimmer (1989*d*) one finds that there are three axial ratios in the range $6{\cdot}7 \le r^2 \le 6{\cdot}9$ that give rise to specific coincidence rotations with $\Sigma \le 21$, *i.e.*

μ	ρ	r^2	r	$\Delta_{\rm Sb}$	$\Delta_{\rm Bi}$
27	6	6·75	2·598	0·00475	0·00435
50	11	6·818	2·611	0·00026	0·00066
23	5	6·9	2·627	0·00625	0·00665.

Representatives of the equivalence classes with $\Sigma \le 21$ and $6{\cdot}7 \le r^2 \le 6{\cdot}9$ are given in Table 1 together with Φ, sin Φ and the Miller–Bravais indices of the planes perpendicular to 180° rotations contained in the equivalence class. [Only planes $(hk\,.\,l)$ satisfying $h \ge 0$, $k \ge 0$, $l \ge 0$ are given.] The rotation symbol $(m, u, v\,.\,w)$ of the representative has been normalized as proposed by Grimmer (1989*d*). [The determination of Σ according to his equation (73) makes use of this normalization.]

Notice that $\varepsilon = \Delta$ in the cases $\Sigma 18a$ and $\Sigma 18b$ of $r = 2{\cdot}598$ and $\varepsilon < \Delta$ in all other cases of Table 1; $\Phi = \Theta$ if $w = 0$ and $\Phi < \Theta$ otherwise.

Doni *et al.* (1986) were the first to give specific coincidence rotations for rhombohedral lattices with axial ratios close to $r_{\rm Sb}$ and $r_{\rm Bi}$. They considered $r = 2{\cdot}627$ (their case $p/q = 5/17$). Notice that $r = 2{\cdot}598$ and $r = 2{\cdot}611$ are closer to the experimental values of Sb and Bi than $r = 2{\cdot}627$ and that $r = 2{\cdot}598$ gives rise to more coincidence rotations with a small value of Σ.

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Measurement of the Structure Factors of Diamond

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Abstract

The absolute values of the structure factors of diamond are determined for nine low-order reflections by measuring the X-ray *Pendellösung* beats on the wavelength scale. Parallel-sided wafers of synthetic diamond single crystals are used for specimens. The deformation charge density and the Debye-Waller B factor are evaluated from the structure factors. The charge density of pile-up electrons is estimated to be $0\cdot44\,(17)\,e\text{Å}^{-3}$ at the midpoint between the nearest-neighbour atoms. The density is slightly smaller than that determined by the powder diffraction method. The obtained B factor, $0\cdot142\,(9)\,\text{Å}^2$, is in good agreement with that evaluated to date from neutron diffraction measurements.

1. Introduction

Diamond is a typical covalent crystal in which each atom is linked tetrahedrally to four neighbouring atoms. The charge distribution is modified in the crystal so as to reflect the site symmetry ($\bar{4}3m$) of the atomic positions. A weak X-ray intensity measured for the forbidden 222 reflection (Renninger, 1955) is clear evidence of this modification. The structure factors of diamond were determined by Göttlicher & Wölfel (1959) (hereafter GW). They carried out an X-ray measurement of integrated intensity diffracted from a fine-powder sample and evaluated the structure factors using kinematical diffraction theory.

Lang & Mai (1979) (hereafter LM) observed the *Pendellösung* fringes in the Bragg case from natural diamond crystals. They determined the structure factor of the 311 reflection from the fringe spacing based on dynamical diffraction theory. The advantage of the *Pendellösung*-fringe method is that no absolute intensity measurement is required but only the extremum positions need to be determined. However, as far as diamond is concerned, no data from the *Pendellösung*-fringe method are available except the value for the 311 reflection by LM.

The present authors have developed a technique of measuring the *Pendellösung* beats on the wavelength scale and determined the structure factors of various substances (Takama & Sato, 1988; Kobayashi, Takama, Tohno & Sato, 1988). In the present study, the technique is applied to determine the structure factors of diamond. The structure factors for the nine low-order reflections are used to evaluate the deformation charge density as well as the temperature factor.

2. Measurements

The synthetic diamond crystals were grown under a pressure of 5·0-5·5 GPa at 1700-1800 K with the help of a metal solvent. Granular crystals were cut to parallel-sided wafers having a {110} surface and about

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