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Diffraction Pattern of Crystals with Numerous Stacking Faults

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Abstract

A model for crystals with stacking faults is given; it takes account of interaction up to the vth neighbor; it is reduced to a first-order Markov chain. It is shown that the diffraction pattern can be split into spots, the shape of which depends on three parameters (intensity, width, 'asymmetry'). Group theory is used. Application is given for hexagonal–rhombohedral stacking faults (as in graphite) for interactions up to third order.

Introduction

Stacking faults can produce diffraction diagrams quite different from those of perfect crystals, when they are numerous; this is especially the case in lamellar species such as graphite, clays, heavy-metal halides or chalcogenides.

Models have been given only for some simple cases. Méring (1949) has treated the case where the stacking faults are only translations, the probabilities of which are governed by a single factor; *i.e.* when this probability depends only upon first-neighbor interaction. It can be also applied to rhombohedral faults in hexagonal stacks (or the reverse), *i.e.* when an *ABA* stack has an *ABC* fault (Méring, 1949). It has also been applied by Plançon & Tchoubar (1975) to some kinds of kaolinites.

Extension to more general faults (translations and rotations) has been treated by Hendricks & Teller (1942) and Kakinoki & Komura (1952) and with a more powerful method by Plançon & Tchoubar (1976), with an application to other kinds of kaolinites. But the probability of a fault depends here also only upon the first neighbors.

Plançon & Tchoubar (1976) also consider a long-range interaction. Indeed, calculations taking into account further neighbors are needed. For example, in graphite Méring can only produce diagrams with widened hexagonal spots or with wide spots near rhombohedral spots, but not both of them together. Nevertheless, numerous carbon blacks (*e.g.* exfoliated graphite) exhibit the two spot systems together; earlier, Wyckoff (1965) explained composite Debye–Scherrer diagrams as a mixture of the two types of crystals, but as pure rhombohedral carbon has never been observed this interpretation is not very satisfactory.

We show here how to calculate the diffraction of a stack of layers with the following conditions:

the number of layer types is finite;

the layers are equidistant;

the probability that a layer is of a certain type depends on its first v neighboring layers (interaction with the vth neighbor).

We show that the diffraction figure can be decomposed into a sum of spots with definite shapes, and give the applications to hexagonal–rhombohedral stacks (generalized compact pile problem) up to the third-neighbor interaction.

The stacks as a Markov chain

A stack consists of N layers numbered $n (n = 1, N)$. Two layers n and m are said to be of the same type if they are related by a translation $(n - m)\mathbf{c}$;‡ the number of types of layers will be taken as finite.

We consider an ensemble of such N-stacks where layers of the same type in different stacks are related also by a translation; *i.e.* they have the same orientation and $\mathbf{c}$ is also the same for all stacks. This ensemble could be called a 'monocrystalline' ensemble. The probability of finding a layer of type i in position n is $p_i(n)$. Our solutions are given for a sufficiently large ensemble (thermodynamic limits).

It can be shown that when interaction with the v neighboring layers is taken into account the stacks can

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‡ For convenience $\mathbf{z}$ is taken vertically and a layer can be above or under another one but the layers are not necessarily horizontal.

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be considered as homogeneous Markov chains of νth order. But the trick (this point was drawn to our attention by D. Revuz) used to study such chains is to reduce them to first order by taking as elementary events or states not the occurrence of a type of layer, but the occurrence of a certain succession of ν layers. Henceforth we choose as a base the τ allowed succession of ν layers, calling them $\mathbf{e}_i$. For example, in graphite, layers can be of type A, B or C; for a second-neighbor interaction the base will be (AA, BB, CC are forbidden)

$$\mathbf{e}_1 = AB; \quad \mathbf{e}_2 = BC; \quad \mathbf{e}_3 = CA;$$
$$\mathbf{e}_4 = AC; \quad \mathbf{e}_5 = CB; \quad \mathbf{e}_6 = BA,$$

AB being a B layer on an A layer.

We call $P_i(n)$ the probability of finding the layers n to $n + \nu - 1$ (*i.e.* in position n) in the state $\mathbf{e}_i$. The probability that the layers $(n + 1)$ to $(n + \nu)$ (*i.e.* in position $n + 1$) are *then* in the state j is Q^i_j; the transition probability matrix Q does not depend on n (homogeneity of the chain). Q has numerous zeros because the layers $(n + 1)$ to $(n + \nu - 1)$ must be the same.

The probability of layers $n + 2$ to $n + \nu + 1$ being in the state j when the layers n to $n + \nu - 1$ are in the state i is (applying Einstein's summation rule)

$$Q^i_k Q^k_j = (Q^2)^i_j$$

and step by step the transition probability in q steps is

$$(Q^q)^i_j,$$

where Q^q is the qth power of Q.

This expression is the definition of a homogeneous Markov chain of first order (Takács, 1964). Note that the reduction of the problem to first-order chains was not obtained by simply subdividing the stack into substacks of ν sheets; this method would naturally also give a first-order chain but the transition probability matrix would be much more tedious to write (fewer zeros); indeed it would be Q to the νth power. The physical meaning of transition probabilities would be more difficult to understand. If the problem has sufficient symmetry (*e.g.* if the layers have a 'horizontal plane' of symmetry), the probability of finding j above or below i is the same. This is always the case in the examples of the *Introduction*; thus q may be negative but Q has to be raised to the power $|q|$, the absolute value of q. But this is not necessary (polar crystals), and probabilities in the opposite directions may be different.

Now the best way to solve problems in Markov chains is to solve the eigenvalue problem of the transition probability matrix Q

$$Q^i_j A^j_k \equiv \lambda_{\underline{k}} A^i_{\underline{k}}$$

or

$$QA = A\Lambda.$$

(Underlined indices do not obey the Einstein summation rule.) If each eigenvalue is simple, Λ is diagonal; if not, Λ can be divided into smaller matrices of the type

$$\begin{pmatrix} \lambda & 1 & 0 & . & . & 0 & 0 \\ 0 & \lambda & 1 & . & . & . & 0 \\ . & . & . & . & . & . & . \\ 0 & 0 & 0 & 0 & 0 & \lambda & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & \lambda \end{pmatrix}.$$

In all cases A is not singular; it is therefore possible to write

$$Q^q = (A\Lambda A^{-1})(A\Lambda A^{-1}) \ldots (A\Lambda A^{-1})$$
$$= A\Lambda^q A^{-1}.$$

As Q is real the eigenvalues and eigenvectors are real or conjugate. As $\sum_j Q^i_j = 1$, one eigenvalue is always $\lambda_1 = 1$ with eigenvector $A^1_i \equiv 1/\sqrt{\tau}$ and no eigenvalue has a modulus greater than 1.

We shall make the hypothesis that the chain is irreducible, *i.e.* a state can always be reached from another state; when the chain is reducible a closed set of states exists, *i.e.* a subspace in which the study can be done independently of the other states.

If there is no stacking fault, *i.e.* if the stacks are perfect crystals, for each i only one $Q^i_j \neq 0$ (and therefore is equal to 1). If the chain is irreducible other eigenvalues than λ_1 with modulus equal to 1 cannot exist, except if the stack is a perfect crystal. We shall also suppose that the probability distribution $P_i(n)$ is stationary, *i.e.*

$$P_i(n) \equiv P_i.$$

P_i is a solution of

$$P_i = P_j Q^j_i$$

or

$$P_i = \frac{1}{\sqrt{\tau}} (A^{-1})^1_i.$$

This hypothesis can be false for perfect crystals (for example, in graphite, layers alternate) but in other cases we think that it is equivalent to the thermodynamic limit. On the other hand, the distribution

$$P^r_i = (A^{-1})^r_i / \sum_{r=1}^{\tau} (A^{-1})^r_i$$

would decay as $(\lambda_r)^n$ and one can introduce for it a coherence length $r = 1/(\lambda_r)$.

The diffraction problem

We want to calculate the intensity of diffraction for a diffusion vector

$$\chi = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*,$$

$\mathbf{a}^*$ and $\mathbf{b}^*$ are orthogonal to $\mathbf{c}$ and

$$\mathbf{c}^* = 2\pi(\mathbf{a} \times \mathbf{b})/(\mathbf{a},\mathbf{b},\mathbf{c}).$$

When the layer is a piece of a two-dimensional crystal (with possibly some thickness) $\mathbf{a}^*$ and $\mathbf{b}^*$ are the base vectors of the two-dimensional reciprocal lattice. But our calculation can be applied to liquid layers or even nonplanar layers. We shall call the diffraction amplitude of a state the amplitude for only the lower sheet; *i.e.*, for a state i in position n (layers from n to $n + \nu - 1$) it is $\varphi^i(hkl) \exp(2i\pi ln)$.

The intensity of diffraction of a certain stack is

$$\sum_{m,m'=1}^{N} \xi^*(m)\, \xi(m') \exp[2i\pi l(m' - m)],$$

where $\zeta(m)$ is the amplitude of diffraction of the mth layer. The physical quantity is the mean intensity on the set of stacks.

We invert the order of summation; *i.e.* instead of summing in one stack over each pair of layers in positions m and m', and then summing over all possible stacks (we can also say on all configurations of sheets), we are allowed to choose first a pair of positions to sum over all configurations and then only to sum on the pairs of layers. More precisely, we choose m and m' and the states i and j, to which the layers belong, contributing to the intensity by

$$\varphi_i^*\, \varphi_j \exp[2i\pi l(m' - m)].$$

We calculate the number of configurations for which the layers m and m' are in the state i and j (or, better, the probability of these configurations); then we are only left with summing over the pairs of states and the pairs of positions.

Suppose that $m' > m$. The probability of finding states i and j in positions m and m' is the probability of finding state i in position m, *i.e.* $P_i(m)$, multiplied by the probability of thereafter finding the state j in position m', *i.e.* $(Q^{m'-m})^i_j$. The probability of the pair is

$$P_i(m)\, (Q^{m'-m})^i_j.$$

Now if $m' < m$ we begin with m' and the composite probability is

$$P_i(m')\, (Q^{m-m'})^i_j.$$

As $P_i(m) = P_i(m') = P_i$ in both cases the composite probability is

$$P_i(Q^{|m'-m|})^i_j.$$

This formula could have been found immediately in the case of sufficient symmetry (non-polar sheets).

On the whole, the mean intensity is

$$I(hkl) = \sum_{n,m=1}^{N} \sum_{i=1}^{\tau} P_{\underline{i}}(n)(Q^{|n-m|})^{\underline{i}}_{j} \times \varphi^{\underline{i}^*}(hkl)\, \varphi^j(hkl) \exp[2i\pi l(n - m)]$$

(j varies as i from 1 to τ).

This formula is similar to the calculation in Plançon & Tchoubar (1976), but here the summation is over states and not layers; for first-neighbor interactions they are identical.

In Plançon & Tchoubar (1976) a summation of the powers of Q is made. They introduce $(E - Q)^{-1}$, with E the identity matrix; as Q always has a unity root this formulation is in principle mathematically forbidden. We prefer to use first the diagonalization of the matrix, which overcomes the mathematical difficulty, but mainly shows how the diffraction figure can be split into spots with more physical meaning. The mean intensity is then

$$I(hkl) = \sum_{m,n=1}^{N} \sum_{i=1}^{\tau} P_{\underline{i}} A^{\underline{i}}_{k} (A^{|m-n|})^k_{k'} \times (A^{-1})^{k'}_{j}\, \varphi^{\underline{i}^*}(hkl)\, \varphi^j(hkl) \times \exp[2i\pi l(n - m)].$$

To simplify the expression we shall now suppose that A is fully diagonal. The generalization to multiple eigenvalues is straightforward; A is the matrix of coordinate changes. We introduce

$$U_r(hkl) = \sum_{i=1}^{\tau} \varphi^{\underline{i}^*}(hkl)\, P_{\underline{i}} A^{\underline{i}}_{\underline{r}} (A^{-1})^r_j\, \varphi^j(hkl),$$

then

$$I(hkl) = \sum_r I_r$$

with

$$I_r(hkl) = U_r(hkl) \sum_{n,m=1}^{N} \lambda_r^{|n-m|} \exp[2i\pi l(n - m)].$$

Note that

$$\varphi^i(hkl) \equiv \varphi^{i^*}(\bar{h}\bar{k}\bar{l});$$

for real or conjugate eigenvalues A^i_r and $(A^{-1})^r_j$ are real or conjugate; *i.e.*

$$U_r(hkl)^* = U_{r^*}(\bar{h}\bar{k}\bar{l})$$

and

$$I_r(hkl)^* = I_{r^*}(\bar{h}\bar{k}\bar{l})$$

(r^* labels U and I for λ_r^*). Note also that

$$\sum_r U_r(hkl) = \sum_{i=1}^{r} \varphi^{\underline{i}^*}(hkl)\, P_{\underline{i}}\, \delta_{ij}\, \varphi^j(hkl) = \sum_{i=1}^{r} P_{\underline{i}}\, \varphi^{\underline{i}^*}(hkl)\, \varphi^i(hkl).$$

In most cases different types of layers have the same $\varphi^{\underline{i}}(hkl)\, \varphi^{\underline{i}^*}(hkl) \equiv \Phi(hkl)$; this is especially the case for stacking faults. Then $\sum_r U_r(hkl) = \Phi(hkl)$ does not depend on the probability transitions.

Decomposition of the diffraction

We sum over m and n in I_r (hkl will be generally omitted); the λ_r are the (diagonal) matrix elements of Λ.

$$\frac{I_r}{U_r} = \sum_{n=1}^{N} \left\{ \sum_{m=1}^{n-1} [\lambda_r \exp(+2i\pi l)]^m + 1 + \sum_{m=1}^{N-n} [\lambda_r \exp(-2i\pi l)]^m \right\}$$

$$= \frac{N}{2} \left\{ \frac{1 + \lambda_r \exp(2i\pi l)}{1 - \lambda_r \exp(+2i\pi l)} + \frac{1 + \lambda_r \exp(-2i\pi l)}{1 - \lambda_r \exp(-2i\pi l)} \right\} + \frac{[\lambda_r \exp(+2i\pi l)]^{N+1} - \lambda_r \exp(+2i\pi l)}{[\lambda_r \exp(+2i\pi l) - 1]^2} + \frac{[\lambda_r \exp(-2i\pi l)]^{N+1} - \lambda_r \exp(-2i\pi l)}{[\lambda_r \exp(-2i\pi l) - 1]^2}.$$

When $|\lambda_r| = 1$, *i.e.* $\lambda_r = \exp(i\theta_r)$, the real part of the first term is zero. The real part of the last terms is

$$\frac{\sin^2(2\pi l + \theta_r)N}{\sin^2(2\pi l + \theta_r)} + \frac{\sin^2(2\pi l - \theta_r)N}{\sin^2(2\pi l - \theta_r)}.$$

We retrieve the shape of spots of a perfect crystal (U_r has to be real). If $|\lambda_r| < 1$ and if $N \gg 1/(1 - |\lambda_r|)$ the last terms can be neglected. If we put $\lambda_r = \rho_r \exp(i\theta_r)$ and $U_r = u_r \exp(i\psi_r)$, the real part of I_r can be split into two parts, say into two spots. The first one is

$$\frac{N}{2} u_r \frac{\cos\lambda_r\{1 - \rho_r^2\} - 2\rho_r \sin\psi_r \sin(\theta_r + 2\pi l)}{1 + \rho_r^2 - 2\rho_r \cos(\theta_r + 2\pi l)}.$$

In the second part l is replaced by $(-l)$. Note that the integrations over l on 2π domains gives $u_r \cos\psi_r = R(U_r)$, which does not depend on λ_r, *i.e.* on the shape of the spot; when $\varphi(hkl)$ does not depend on l (layers without thickness), recalling the sum rule on U_r, we can demonstrate that stacking faults do not change the intensity of diffraction integrated over l.

When λ_r is real the two parts reduce to

$$NU_r \cos\psi_r \frac{1 - \rho_r^2}{1 + \rho_r^2 - 2\rho_r \cos 2\pi l}.$$

If the layers have no thickness, ψ_r does not depend on l; we find spots centered at (h,k,L) if $\lambda_r > 0$, or at $(h, k, L + \frac{1}{2})$ if $\lambda_r < 0$ (L integer); maximum intensity is $2Nu_r \cos\psi_r\ (1 - \rho_r^2)/(1 + \rho_r^2)$ and their full width at mid-height (FWMH) is given by

$$\cos 2\pi l = 1 - \frac{(\rho_r - l)^2}{2\rho_r}.$$

When $\alpha_r = (1 - \rho_r)$ is small a good approximation is

$$\frac{N}{2} u_r \cos\psi_r \frac{2\alpha_r}{\alpha_r^2 + l^2};$$

the FWHM is $2\alpha_r$ and corresponds to the coherence length L_r.

When λ_r is complex two spots arise (but the conjugate eigenvalues give the same spots). In the case of layers without thickness, the extrema are at

$$\tan\left(\pi l \pm \frac{\varphi}{2}\right) = \frac{1 - \rho}{1 + \rho} \frac{(\cos\psi \pm 1)}{\sin\psi}.$$

Such spots are asymmetric. Some parts of some spots may be negative but naturally the sum over all spots is always positive.

Note that when the layers have a thickness the precise shape of the spots can be modified by the dependence of U on l.

Use of group theory

To simplify the diagonalization task with the use of the symmetries in the problem let S be the symmetries which transform any layer into itself or another layer; they build a group $\{S\}$ which leaves Q invariant. The matrices of the transformation of the states by these symmetries build a representation of $\{S\}$. The coordinate transformation which reduces this representation also reduces the matrix Q.

But $\{S\}$ can be very large. It contains the symmetries T which transform any layer into itself and have no effect on the states; they are of no interest in our problem.

Let $\{R\}$ be the quotient of $\{S\}$ divided by $\{T\}$; it is homeomorphic to a group of permutations between the sheets and contains all the information we need (in many cases all the permutations are at work, *i.e.* leave Q invariant). When all successions of ν sheets are allowed, their representation $\mathscr{R}$ on the space of states is the νth power of the regular representation; if some substacks are forbidden it is smaller.

We write the reducing change of base

$$\mathbf{f}_{\Gamma,\alpha,\beta} = \mathbf{e}_i B^i_{\Gamma,\alpha,\beta}.$$

Γ is an irreducible representation of $\{R\}$, α a component of Γ and β another index, necessary when Γ happens more than once.

The B's are analogous to Clebsch–Gordon coefficients.

Considering $\{R\}$ as a group of permutations between the layers, we can show that $\mathscr{R}$ is unitarian; hence the change of base is also unitarian.

To construct the $\mathbf{f}$, we use the Van Vleck projectors

$$\pi(\Gamma,\alpha) = \sum_{REG} \Gamma^{\alpha}_{\alpha}(R) R,$$

with $\Gamma^i_j(R)$ the standard matrix for R in Γ.

The invariant matrix Q is reduced by this coordinate change. The eigenvalue problem is now split into

equations, the degree of which is the number of times a representation occurs (maximum value of index β for Γ). When a representation is of degree y the root has a multiplicity y; this multiplicity does not lead to non-diagonality; non-diagonality arises only when the same representation occurs many times with accidental degeneracy (even then it does not necessarily occur).

Each eigenvalue subproblem leads to a diagonalizing matrix $C(\Gamma,\alpha)$; the combination of this matrix will be called C and the diagonalizing matrix from *ab initio* is

$$A = BC.$$

It will be useful to introduce the vectors

$$V_k = \sum_l \varphi^{l^*} P_{\underline{l}} B^{\underline{l}}_k$$

$$W^k = (B^{-1})^k_j \varphi^j;$$

then the vector U is

$$U_r = V_k C^k_{\underline{r}} (C^{-1})^{\underline{r}}_{\underline{k}'} W^{k'}.$$

Generally, the sheet amplitude diffraction vector φ^l belongs to a component of representation Γ of G; the coordinates of W are zero except for those corresponding to Γ and we need only to calculate

$$W_\beta = (B^{-1})^{\Gamma,\alpha,\beta}_l \varphi^j$$

$$V_\beta = \sum \varphi^{l^*} P_{\underline{l}} B^{\underline{l}}_{\Gamma,\alpha,\beta}$$

and then

$$U_\varrho = V_\beta C(\Gamma,\underline{\alpha})^\beta_{\underline{\varrho}} C^{-1}(\Gamma,\underline{\alpha})^\varrho_{\beta'} W^{\beta'},$$

where the $\lambda\rho$ are the roots for only the representation Γ.

The vector P_l of the stationary distribution of probabilities is also invariant of G and belongs to Γ_1. To find it it is sufficient to diagonalize $C(\Gamma_1)$ and then

$$P_i = C^{-1}(\Gamma_1)^{\lambda_1}_\beta (B^{-1})^{\Gamma,\beta}_l/\sqrt{\tau}.$$

Stacking faults in generalized compact crystals

We described graphite as a stack of layers of three types, A, B and C. The succession of two layers of the same type is forbidden. A compact crystal of hard spheres can be described in the same way if stacking faults are taken into account only in one direction; the perfect crystals made by repetition of AB or ABC are then hexagonal or c.f.c. The cubicity is not needed, the value of C is not relevant and the repetition of ABC may only give a rhombohedral crystal. For the moment nothing has to be known about the structure of the layer as long as the probability of occurrence of a stack is invariant by a permutation of A, B, C.

The permutation group of three objects has six operations in three classes E, C and S.

C is cyclic on the three objects; we choose $C_1(A) = B$ *etc.*, $C_2 = C_1^{-1}$.

S permutes only two objects; we choose that A is invariant in S_1, B in S_2, C in S_3.

The table of characters is

	E	C	S
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	-1

We also need a standard representation for Γ_3:

$$\Gamma_3(C_1) = \begin{pmatrix} j & 0 \\ 0 & j^2 \end{pmatrix}; \quad \Gamma_3(C_2) = \begin{pmatrix} j^2 & 0 \\ 0 & j \end{pmatrix};$$

$$\Gamma_3(S_1) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad \Gamma_3(S_2) = \begin{pmatrix} 0 & j \\ j^2 & 0 \end{pmatrix};$$

$$\Gamma_3(S_3) = \begin{pmatrix} 0 & j^2 \\ j & 0 \end{pmatrix}.$$

With Van Vleck projectors on A, B, C, we find that

$(A + B + C)/\sqrt{3}$ is a base for Γ_1

$(A + jB + Cj^2)/\sqrt{3}$ and $(A + j^2B + jC)/\sqrt{3}$ is a base for Γ_3 in the chosen standard representation.

This permutation group is homeomorphic to C_{3v}.

Now we suppose (as is true in the above examples) that the sheets are crystalline with base vectors **a** and **b** and that B can be deduced from A by the translation $\mathbf{a}/3 + 2\mathbf{b}/3$ and C by the reverse.

If the diffractional amplitude is b for A, then it is $b \exp[2i\pi(h + 2k)/3]$ for B and the conjugate for C (b depends on hkl).

If $h - k = 0$ [3], $\varphi_l \equiv b$ and belongs to Γ_1; it is then straightforward, if tedious, to show that only the eigenvalue Γ_1 is at work and $U_{\lambda 1} = bb^*$. This means that these lines are not altered by the stacking faults, as expected.

If $h - k = 1$ [3], φ is b for stacks beginning with A, bj for stacks beginning with B and bj^2 for the others; it transforms as the first component of Γ_3.

If $h - k = \bar{1}$ [3], the amplitudes are conjugate and transform like the second component of Γ_3.

Interaction with the first neighbors

The invariance of Q means that the successions AB and AC are equiprobable. The probability matrix is

$$\begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}.$$

With the base from the previous paragraph, it becomes

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{pmatrix}.$$

1 belongs to Γ_1 and $-\frac{1}{2}$ to the two components of Γ_3. The stationary distribution is $(\frac{1}{2},\frac{1}{2})$.

For (1,0,l), $U = bb^*$, a fairly widened spot is centered at $1,0,\frac{1}{2} + L$ (L integer); the same result is obtained for (0,1,l). In a pure hexagonal crystal one finds spots $1,0,L$ with intensity $b^2/4$ and spots $1,0,L + \frac{1}{2}$ with intensity $3b^2/4$.

The disorder lets the $1,0,L + \frac{1}{2}$ spots grow at the expense of the $1,I,L$ spots. It must be noted that the disorder is limited to a choice between three positions with the further restriction that neighboring sheets cannot be the same. For more complete disorder the intensity would be constant along the (1,0) reciprocal rod. The growth of the $1,0,\frac{1}{2}$ spot at the expense of the 100 spot was also observed in a Monte-Carlo test. The total intensity of the 101 lines is unchanged. As was foreseeable the lines 111 are not sensitive to disorder.

No rhombohedral spots are to be seen. The same results are obtained for the other *hkl* spots depending on $h + k$ being equal to a multiple of 3 plus 0, 1 or 2.

Interaction with the second neighbors

We take the two-sheet combinations mentioned above as base. We need to construct the results of operations of C_{3v} on this base.

$$\begin{array}{lll} C_1\,\mathbf{e}_1 = \mathbf{e}_2; & C_1\,\mathbf{e}_2 = \mathbf{e}_3; & C_1\,\mathbf{e}_3 = \mathbf{e}_1; \\ C_1\,\mathbf{e}_4 = \mathbf{e}_6; & C_1\,\mathbf{e}_5 = \mathbf{e}_4; & C_1\,\mathbf{e}_6 = \mathbf{e}_5; \end{array}$$

$$\begin{array}{lll} C_2\,\mathbf{e}_1 = \mathbf{e}_3; & C_2\,\mathbf{e}_2 = \mathbf{e}_1; & C_2\,\mathbf{e}_3 = \mathbf{e}_2; \\ C_2\,\mathbf{e}_4 = \mathbf{e}_5; & C_2\,\mathbf{e}_5 = \mathbf{e}_6; & C_2\,\mathbf{e}_6 = \mathbf{e}_4; \end{array}$$

$$\begin{array}{lll} S_1\,\mathbf{e}_1 = \mathbf{e}_4; & S_1\,\mathbf{e}_2 = \mathbf{e}_5; & S_1\,\mathbf{e}_3 = \mathbf{e}_6; \\ S_1\,\mathbf{e}_4 = \mathbf{e}_1; & S_1\,\mathbf{e}_5 = \mathbf{e}_2; & S_1\,\mathbf{e}_6 = \mathbf{e}_3; \end{array}$$

$$\begin{array}{lll} S_2\,\mathbf{e}_1 = \mathbf{e}_5; & S_2\,\mathbf{e}_2 = \mathbf{e}_6; & S_2\,\mathbf{e}_3 = \mathbf{e}_4; \\ S_2\,\mathbf{e}_4 = \mathbf{e}_3; & S_2\,\mathbf{e}_5 = \mathbf{e}_1; & S_2\,\mathbf{e}_6 = \mathbf{e}_2; \end{array}$$

$$\begin{array}{lll} S_3\,\mathbf{e}_1 = \mathbf{e}_6; & S_3\,\mathbf{e}_2 = \mathbf{e}_4; & S_3\,\mathbf{e}_3 = \mathbf{e}_5; \\ S_3\,\mathbf{e}_4 = \mathbf{e}_2; & S_3\,\mathbf{e}_5 = \mathbf{e}_3; & S_3\,\mathbf{e}_6 = \mathbf{e}_1. \end{array}$$

The Van Vleck projectors give the new base

$$\mathbf{f}_1 = (\mathbf{e}_1 + \mathbf{e}_2 + \mathbf{e}_3 + \mathbf{e}_4 + \mathbf{e}_5 + \mathbf{e}_6)/\sqrt{6}$$
$$\mathbf{f}_2 = (\mathbf{e}_1 + \mathbf{e}_2 + \mathbf{e}_3 - \mathbf{e}_4 - \mathbf{e}_5 - \mathbf{e}_6)/\sqrt{6}$$
$$\mathbf{f}_3 = (\mathbf{e}_1 + j\mathbf{e}_2 + j^2\,\mathbf{e}_3)/\sqrt{3}$$
$$\mathbf{f}_4 = (\mathbf{e}_4 + j^2\,\mathbf{e}_5 + j\mathbf{e}_6)\sqrt{3}$$
$$\mathbf{f}_5 = (\mathbf{e}_1 + j^2\,\mathbf{e}_2 + j\mathbf{e}_3)/\sqrt{3}$$
$$\mathbf{f}_6 = (\mathbf{e}_4 + j\mathbf{e}_5 + j^2\,\mathbf{e}_6)/\sqrt{3}.$$

$\mathbf{f}_1$ belongs to Γ_1, $\mathbf{f}_2$ to Γ_2; $\mathbf{f}_3$ and $\mathbf{f}_4$ are transformed like the first component of Γ_3, and $\mathbf{f}_5$ and $\mathbf{f}_6$ like the second. The inverse transformation is readily found as it is unitarian.

The probability transition matrix is

$$\begin{pmatrix} 0 & v & 0 & 0 & 0 & u \\ 0 & 0 & v & 0 & u & 0 \\ v & 0 & 0 & u & 0 & 0 \\ 0 & 0 & u & 0 & v & 0 \\ 0 & u & 0 & 0 & 0 & v \\ u & 0 & 0 & v & 0 & 0 \end{pmatrix},$$

where v is the probability of a rhombohedral stacking fault in the hexagonal stacking ($u + v = 1$).

On the new base it becomes

$$\begin{pmatrix} u+v & & & & & \\ & u-v & & & & \\ & & j^2 v & j^2 u & & \\ & & ju & jv & & \\ & & & & jv & ju \\ & & & & j^2 u & j^2 v \end{pmatrix}.$$

The stationary distribution is readily seen to correspond to equiprobability. In the restricted space ($\mathbf{f}_3$,$\mathbf{f}_4$) we can do all the calculus for the 101 spots. The V and W are

$$b^*/2\sqrt{3}\begin{pmatrix}1\\1\end{pmatrix} \text{ and } b\sqrt{3}\begin{pmatrix}1\\1\end{pmatrix}.$$

The eigenvalues are

$$\lambda\pm = -\frac{v \pm (4u^2 - 3v^2)^{1/2}}{2}$$

$$C(\Gamma_3) = \begin{pmatrix} ju & ju \\ \lambda^+ - j^2 v & \lambda^- - j^2 v \end{pmatrix}$$

$$C^{-1}(\Gamma_3) = \frac{1}{(\lambda^- - \lambda^+)uj}\begin{pmatrix} \lambda^- - j^2 v & -uj \\ -\lambda^+ + j^2 v & uj \end{pmatrix}$$

(neglecting the normalization here), then

$$V_\pm(101) = \frac{1}{2}\left(1 \pm \frac{u}{\lambda^- - \lambda^+}\right).$$

If $u > v\sqrt{3}/2$ the λ are real; in the ($\mathbf{f}_5$,$\mathbf{f}_6$) space, one also finds

$$U_\pm(0,1,1) = U_\pm(1,0,1).$$

For $u > \frac{1}{2}$ the spots are centered on all the pure hexagonal spots but widened; the $1,0,\frac{1}{2} + L$ spots are enhanced at the expense of the $10L$ spots and less widened than the latter. For $u = 1$ the intensities $b^2/4$ and $3b^2/4$ of the pure hexagonal crystal are found as expected.

For $u = \frac{1}{2}$ the $10L$ spots have disappeared: this is the

case of total disorder (case of interaction with the first neighbor).

For u less than $\frac{1}{2}$, but still greater than $v\sqrt{\frac{3}{2}}$, two very large spots are centered on the $1,0,L+\frac{1}{2}$ hexagonal spots.

For $u < v\sqrt{\frac{3}{2}}$ the λ becomes complex; the intensities of U_+ and U_- become equal to $b^2/2$.

For $u = 0$, we find the rhombohedral spots at $l = \frac{1}{3}$ and $l = \frac{2}{3}$. [In a rhombohedral crystal one finds a spot $1,0,\frac{2}{3}$ with intensity b^2 or else a spot $1,0,\frac{4}{3}$; but in the model symmetric stacks are taken into account together.]

When u grows, the spots widen, are displaced in the direction of $1,0,\frac{1}{2}$, symmetrically, but each of them becomes asymmetric.

On the whole an interaction with the second neighbor cannot explain the simultaneous presence of the two systems of spots, hexagonal and rhombohedral.

Interactions with the third neighbor

We choose the base

$$\begin{array}{lll} \mathbf{r}_1 = ABC & \mathbf{r}_2 = BCA & \mathbf{r}_3 = CAB \\ \mathbf{r}'_1 = ACB & \mathbf{r}'_2 = CBA & \mathbf{r}'_3 = BAC \\ \mathbf{h}_1 = ABA & \mathbf{h}_2 = BCB & \mathbf{h}_3 = CAC \\ \mathbf{h}'_1 = ACA & \mathbf{h}'_2 = BAB & \mathbf{h}'_3 = CBC. \end{array}$$

Van Vleck operators give

$$\mathbf{f}_1 = \frac{1}{\sqrt{6}}(\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 + \mathbf{r}'_1 + \mathbf{r}'_2 + \mathbf{r}'_3) \in \Gamma_1$$

$$\mathbf{f}_2 = \frac{1}{\sqrt{6}}(\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 + \mathbf{h}'_1 + \mathbf{h}'_2 + \mathbf{h}'_3) \in \Gamma_1$$

$$\mathbf{f}_3 = \frac{1}{\sqrt{6}}[(\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3) - (\mathbf{r}'_1 + \mathbf{r}'_2 + \mathbf{r}'_3)] \in \Gamma_2$$

$$\mathbf{f}_4 = \frac{1}{\sqrt{6}}[(\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3) - (\mathbf{h}'_1 + \mathbf{h}'_2 + \mathbf{h}'_3)] \in \Gamma_2$$

$$\left.\begin{array}{l} \mathbf{f}_5 = \frac{1}{\sqrt{3}}(\mathbf{r}_1 + j\mathbf{r}_2 + j^2\mathbf{r}_3) \\ \mathbf{f}_6 = \frac{1}{\sqrt{3}}(\mathbf{h}_1 + j\mathbf{h}_2 + j^2\mathbf{h}_3) \\ \mathbf{f}_7 = \frac{1}{\sqrt{3}}(\mathbf{r}'_1 + j^2\mathbf{r}'_2 + j\mathbf{r}'_3) \\ \mathbf{f}_8 = \frac{1}{\sqrt{3}}(\mathbf{h}'_1 + j^2\mathbf{h}'_2 + j\mathbf{h}'_3) \end{array}\right\} \text{first component of } \Gamma_3.$$

$\mathbf{f}_9$ to $\mathbf{f}_{12}$ are $\mathbf{f}_5$ to $\mathbf{f}_8$ with j changed to j^2 and belong to the second component of Γ_3.

A rhombohedral substack $\mathbf{r}$ or $\mathbf{r}'$ is followed by another rhombohedral substack $\mathbf{r}$ or $\mathbf{r}'$ with probability v, and by a hexagonal one $\mathbf{h}$ or $\mathbf{h}'$ with probability $t = 1 - v$. A hexagonal substack $\mathbf{h}$ or $\mathbf{h}'$ is followed by a hexagonal substack $\mathbf{h}'$ or $\mathbf{h}$ with probability u and by a rhombohedral substack $\mathbf{r}'$ or $\mathbf{r}$ with probability $s = 1 - u$.

It is easier to write directly the transition probability matrix on the new base than to make the change of coordinates; in particular we can omit working on $\mathbf{f}_3$ and $\mathbf{f}_4$ as the representation Γ_2 does not show up. On $\mathbf{f}_1$ and $\mathbf{f}_2$, Q becomes

$$\begin{pmatrix} v & t \\ s & u \end{pmatrix}.$$

The eigenvalues 1 and $u - t$; the eigenvalue $\lambda_1 = 1$ gives the stationary distribution: rhombohedral and hexagonal stacks have the probabilities $s/(s+t)$ and $t/(s+t)$:

From $\mathbf{f}_5$ to $\mathbf{f}_9$,

$$V^\beta = \frac{b^*}{2\sqrt{3(s+t)}}(s,t,s,t)$$

and

$$W_\beta = b\sqrt{3}\begin{pmatrix} 1 \\ 1 \\ 1 \\ 1 \end{pmatrix}.$$

Q becomes

$$\begin{pmatrix} vj^2 & tj^2 & 0 & 0 \\ 0 & 0 & sj^2 & uj^2 \\ 0 & 0 & vj & tj \\ sj & uj & 0 & 0 \end{pmatrix}.$$

The eigenvalues are solutions of

$$\lambda^2(\lambda^2 + \lambda v + v^2 - u^2) - \lambda u\varepsilon - \varepsilon^2 = 0,$$

with $\varepsilon = uv - st = v - s$.

When $\varepsilon > 0$ a rhombohedral stack has more chance of being followed by a rhombohedral stack than a hexagonal one has; this is a model somewhat analogous to a long-range ordering which favors the rhombohedral stacking.

$\varepsilon < 0$ corresponds to a long-range favoring of hexagonality.

$\varepsilon = 0$ is equivalent to a second-neighbor interaction.

For small ε, we have two eigenvalues near these and two small eigenvalues

$$\varepsilon\frac{u \pm (4v^2 - 3u^2)^{1/2}}{2(v^2 - u^2)},$$

the corresponding intensities are also of first order in ε: *i.e.* when $u \simeq 1$, small and wide rhombohedral spots

appear together with the hexagonal spots (calculated with the second-neighbor interaction); when $u \simeq 0$, small and wide hexagonal spots appear together with the rhombohedral spots.

Further investigation needs numerical calculation. Some results are shown in Fig. 1. Some remarks can be made:

Two eigenvalues are always real and the two others are complex, *i.e.* spots always appear at hexagonal normal places; the complex eigenvalues give spots near rhombohedral places but always displaced (except for a perfect crystal).

The smaller the modulus of an eigenvalue, the smaller also is the intensity of the corresponding spot.

Disorder always favors the $10\frac{1}{2}$ spot at the expense of the 100.

Comparison with experiment

A 'monocrystalline' ensemble could perhaps be realized by epitaxial growth. But samples with many stacking faults appear mainly as powders. A numerical integration along the rods must be performed as described by Brindley & Méring (1951); our calculation showed that direct multiplication by the Laue–Warren function (Warren, 1941) is not sufficient. Classical factors such as Debye–Waller factors and a polarization factor for X-rays must naturally also be included. We have analysed the 101 lines of papyex, a recompressed ex-foliated graphite from Carbone-Lorraine. In this sample about half of the crystallites are preferentially oriented. The distribution of the c axis has a FWMH of 36°; it was taken as Gaussian and included in the fit. The diameter of the layers is 230 Å from the analysis of the 110 peak.

We found that the propensity to retain hexagonal stacking is $u = 0{\cdot}8 \pm 0{\cdot}02$, but the propensity to stay rhombohedral is not much smaller, $v = 0{\cdot}72 \pm 0{\cdot}02$; the fit is quite sensitive to $u-v = 0{\cdot}08 \pm 0{\cdot}05$; ε is not at all small (~0·5): third-neighbor interaction is very important. The best fit is given in Fig. 1.

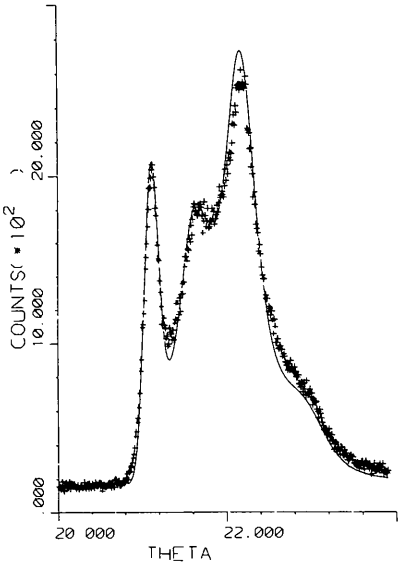

Fig. 1. The 10*l* lines of papyex. + Experimental points obtained with the $K\alpha$ line of copper at 1·5418 Å. —— Calculated curve for $u = 0{\cdot}8$ and $v = 0{\cdot}72$.

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