departure from this geometry complicates the execution and operation of the camera, so that an unconventional camera design can be justified only by the special advantages it offers. Cameras linear in $\sin\theta$ or $\sin^2\theta$ have the important advantage of making possible, at least in principle, indexing by inspection, but this advantage is gained at the expense of simplicity of design and is counteracted by certain unfavourable factors. In circumstances where the Debye–Scherrer camera is not completely satisfactory the non-standard

camera could be a desirable alternative. However, one should always consider the desirable special features of non-standard cameras in conjunction with the extent of normal incidence, film utilization and coverage, the F^{-2} factor, and the extent and location of the range of maximum resolution in θ.

Reference

KAMKE, E. (1961). *Differentialgleichungen.* Leipzig: Akademische Verlagsgesellschaft.

The Intensity of X-rays Diffracted by Monodimensionally Disordered Structures. Case of Identical Layers and Three Different Translation Vectors

BY M. CESARI

Società Nazionale Anonima Metanodotti, Div. LRSR, San Donato, Milano, Italy

AND G. ALLEGRA

Istituto di Chimica Industriale del Politecnico, Milano, and Centro Nazionale di Chimica delle Macromolecole del C.N.R., Sez. I, Milano, Italy

The intensity of X-rays diffracted by a disordered structure in which identical layers are connected by three different translation vectors has been calculated as a function of the reciprocal vector s. The relative positions of two neighbouring layers have been supposed to exert a probabilistic influence upon the position of a third vector ($s=2$). The resulting formula may be applied to cases in which the vectors point perpendicular to the layers, as well as when the vectors have non-zero components parallel to the layers themselves. Intensity fields have been calculated and discussed for structural models related to some three-component mixed layer clay minerals. The results show that the third-component effect begins to be detectable only when the corresponding percentage is about 15–20%, and that it is more evident the greater the alternation of the various interlayer vectors amongst themselves.

1. Introduction

In the study of several layer-type structures affected by monodimensional disorder, it is generally assumed, and often proved, that only two main interlayer (or translation) vectors are present in the stacking.

There are some cases, however, for which three different vectors must be taken into account: here, we wish to recall particularly the three-component interstratified clay minerals which are rather widely distributed in sedimentary rocks (Weawer, 1956; Jonas & Brown, 1959; MacEwan, Ruiz Amil & Brown, 1961). In other cases, when the interpretation of the X-ray diffracted intensity is not completely satisfied by models of structures built up by two vectors only, the presence of a third interlayer vector should be considered at least as probable.

Owing to the lack of an adequate development of theoretical calculations, the effect of a third translation vector, besides the main two, on the X-ray intensity distribution has until now not been investigated to any extent.

A general theory recently developed by one of the authors (Allegra, 1961, 1964) seems to be particularly suitable for this purpose. In fact, it differs from other general treatments (Wilson, 1942; Hendricks & Teller, 1942; Jagodzinski, 1949a,b; Kakinoki & Komura, 1954a,b) in the sense that the physico-mathematical description of a layered disordered structure is given in terms of the statistical succession of the interlayer vectors, instead of their positions in space with reference to a fixed frame. Starting from the general results of the matrix formulation of this theory, some calculations have been carried out in order to establish a formula suitable for direct numerical computation, which allows the above mentioned effect to be explored. In particular, in the present paper, the general problem of a monodimensionally disordered structure, constituted by a large number of parallel layers with the same internal structure (*i.e.* with the same layer form factor) connected by three different translation vectors, has been investigated. Furthermore, the relative positions of two adjacent layers have been assumed to exert a probabilistic influence on the relative position of the

third one ($s=2$). In § 2, the general relationships between the probability parameters, which allow the structure to be described from a statistical point of view, are developed. In § 3, the derivation of the average X-ray intensity as a function of the parameters already established is reported. In § 4, some interference functions, calculated for different models of statistical structures, whose main interest is related to the field of clay minerals, are given and discussed.

2. Correlations among the probability parameters

Let f_1, f_2 and f_3 be the relative frequencies of occurrence of the three translation vectors t_1, t_2 and t_3. If p_{jk} is the probability that the t_k vector follows t_j, the general relationships among f's and p's are:

$$f_k = \sum_{j=1}^{3} f_j p_{jk} \quad (k=1, 2, 3).$$ (1)

The linear system (1) may also be expressed in the matrix form:

$$\mathbf{f} = \mathbf{f} \cdot \mathbf{P}$$ (2)

where

$$\mathbf{f} = |f_1 f_2 f_3|,$$

$$\mathbf{P} = \begin{vmatrix} p_{11} p_{12} p_{13} \\ p_{21} p_{22} p_{23} \\ p_{31} p_{32} p_{33} \end{vmatrix}.$$

The normalization conditions for f_j and p_{jk} are:

$$\sum_{j=1}^{3} f_j = 1; \quad \sum_{k=1}^{3} p_{jk} = 1 \quad (j=1, 2, 3).$$ (3)

If the whole set of p_{jk} is given a priori, then the homogeneous system (2) in the f_j unknowns may be easily solved with the aid of (3), and consistent values of the frequencies of occurrence may be obtained.

Let us now suppose the reverse case: the f_j values are fixed, and a consistent set of p_{jk} must be derived. Then (2) and (3) furnish 6 linear equations in the 9 unknowns p_{jk}; however, it can be easily checked that the rank of the matrix of the coefficients of p_{jk} is only 5, so that there are only 5 independent relationships among p_{jk}. Therefore, four independent values of p_{jk} may be arbitrarily fixed, under the limitation given by the normalization conditions (3), and then the remaining unknowns obtained from (2) and (3).

We will discuss in the following some particular cases of physical interest, which correspond to some specific limitations imposed to the p_{jk} values.

Symmetrical case

If the condition is imposed that, moving in a defined direction, the relative frequencies of occurrence of the vector pairs ($t_j t_k$) and ($t_k t_j$) are the same, we define a symmetrically statistical structure. This condition seems particularly likely to be fulfilled in practice when both sides of every layer are symmetrically equivalent; in such a case, both directions normal to the layer are equivalent with respect to the layer itself, and therefore it seems a priori reasonable that such equivalence is maintained throughout the whole stacking.

The above condition may be expressed by the following equations:

$$f_j p_{jk} = f_k p_{kj} \quad (j, k = 1, 2, 3),$$ (4)

since the frequency of occurrence of the pair ($t_j t_k$) is obviously given by $f_j \cdot p_{jk}$. In (4), three more equations in the p_{jk} unknowns are contained, which, for reasons analogous to those discussed at the beginning of this section, reduce to 3 the number of the independent p_{jk} parameters, once the f_j frequencies are fixed.

Random case

If the translation vectors are distributed completely at random within the structure, then

$$p_{jk} = f_k,$$ (5)

since the probability of finding the t_k translation vector must be always equal to its frequency of occurrence, no matter which is the preceding vector. It is obvious that, once the f_j parameters are fixed, all the p_{jk} are immediately given.

Case of the maximum degree of alternation among the t_j translation vectors

This is one of the most frequent cases in the two-component mixed-layer clay minerals; it is characterized by the lowest possible values of the p_{jj} probabilities. In the present case, in which three translation vectors are considered, it may be proved that the lowest possible values are $p_{jj} = 0$ for every j, provided that no f_j exceeds $\frac{1}{2}$.

(i) If the latter condition is fulfilled, then only one free parameter for the determination of the p_{jk} set remains, since three parameters are fixed by the conditions:

$$p_{11} = p_{22} = p_{33} = 0.$$ (6)

By choosing, for instance, p_{23} as the arbitrary parameter, the solution of the system (2) in the p_{jk} unknowns is represented by the following matrix:

$$\mathbf{P} = \begin{vmatrix} 0 & \dfrac{f_2 - f_3 \lambda}{f_1} & 1 - \dfrac{f_2 - f_3 \lambda}{f_1} \\ \dfrac{f_1 - f_3(1-\lambda)}{f_2} & 0 & 1 - \dfrac{f_1 - f_3(1-\lambda)}{f_2} \\ 1 - \lambda & \lambda & 0 \end{vmatrix}.$$ (7)

Of course, the value of λ must be chosen in such a range of values that the condition $0 \leq p_{jk} \leq 1$ will be fulfilled for every (j, k) pair. Furthermore, if symmetrical conditions are imposed, all p_{jk} parameters are at once fixed. In fact by combining the identities (4) with the system (2), we find:

$$f_2 p_{21} = f_1 p_{12} = \frac{f_1 + f_2 - f_3}{2}$$

$$f_3 p_{31} = f_1 p_{13} = \frac{f_1 - f_2 + f_3}{2}$$

$$f_3 p_{32} = f_2 p_{23} = \frac{-f_1 + f_2 + f_3}{2}.$$ (8)

From (8) all p_{jk} (for $j \neq k$) unknowns may be easily obtained, when the f_j coefficients are established.

(ii) If one of the f_j values, say f_1, is $> \frac{1}{2}$, the lowest values of p_{jj} are:

$$p_{11} = \frac{f_1 - f_2 - f_3}{f_1} \; ; \; p_{22} = p_{33} = 0 \; . \tag{9}$$

In fact, the maximum possible values of the frequencies of occurrence of the $(t_1 t_2)$ and $(t_1 t_3)$ pairs are f_2 and f_3 respectively; this leaves a residual frequency $(f_1 - f_2 - f_3) = f_1 p_{11}$ for the $(t_1 t_1)$ pairs. Moreover, both p_{23} and p_{32} must be equal to zero, since the presence of vector sequences $(t_2 t_3)$ and/or $(t_3 t_2)$ would result in an increase of the number of sequences $(t_1 t_1)$. Therefore, in the present case all the p_{jk} parameters are uniquely fixed; it also results that the statistical configuration is of the symmetrical type. The complete set of p_{jk} probabilities is then given by the following matrix:

$$\mathbf{P} = \begin{vmatrix} \dfrac{f_1 - f_2 - f_3}{f_1} & \dfrac{f_2}{f_1} & \dfrac{f_3}{f_1} \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix} . \tag{10}$$

3. The calculation of the interference function

Let us recall briefly some fundamental results previously achieved by one of us (Allegra, 1964) in the formulation of the general theory.

The statistical distribution in space of a set of parallel layers is completely described by a set of interlayer vectors, t_j. In many cases, and particularly in X-ray studies on the clay minerals, t_j is assumed to be coincident with the vector perpendicular to the layer, c_j; in these cases, the reciprocal vector s is also assumed to point perpendicularly to the layers. However, in the most general case, t_j is allowed to have a non-zero

component in a direction parallel to the layers. The statistical correlation of order s between layer positions may be reduced to a statistical correlation of order $(s-1)$ between consecutive vectors. This means that, if the set of space positions (complexions) of s neighbouring layers have a probabilistic influence on the position of the $(s+1)$th layer, this is the same as to say that $(s-1)$ neighbouring vectors influence the nature of the sth vector.

A disordered structure constituted by layers of the same type which may follow one to another by three possible translation vectors (t_1, t_2 and t_3) with order of influence $s = 2$ has so far not been considered; in this case the complexions of $(s-1)$ neighbouring translations reduce to the translations themselves.

Let us now consider the general expression for the average diffracted intensity per layer I_{Av}, given in the above mentioned paper [Allegra, 1964, equation (18)]:

$$I_{Av} = V V^* . \; \Phi(s) =$$
$$V V^* \{ 1 F [-\tfrac{1}{2} E_{\mathscr{N}} + (E_{\mathscr{N}} - Q)^{-1}] \tilde{1} + \text{conjug.} \} . \tag{11}$$

Under the above established conditions $V = V(s)$ is the layer form factor referred to a proper origin intrinsic to the layer;

$\Phi(s)$ is the interference function;

$\mathscr{N}$ is the total number of distinct interlayer vectors, i.e. $\mathscr{N} = 3$;

1 and $\tilde{1}$ are unit row and column vectors of order 3;

$E_{\mathscr{N}}$ is the unit matrix of order 3;

F is a diagonal matrix of order 3, whose (jj) element is given by f_j;

Q is a square matrix of order 3, whose (jk) element is given by the product: $p_{jk} \exp(-2i\pi . t_k . s) = p_{jk} \exp(-i\varphi_k)$.

Developing the calculations, the following expression is obtained from (11):

$$\Phi(s) = 1 + \cfrac{2 \left\{ \begin{array}{l} -f_1 p_{11} - f_2 p_{22} - f_3 p_{33} + SA + TB + UC + VD + (f_1 + f_2 A + f_3 B - p_{22}S - p_{33}T + UD + ZC) \cos\varphi_1 + (f_2 + f_1 A + f_3 C - p_{11}S - p_{33}U + UD + ZB) \cos\varphi_2 \\ + (f_3 + f_1 B + f_2 C - p_{11}T - p_{22}U + SD + ZA) \cos\varphi_3 + (S + f_3 D - p_{33}Z) \cos(\varphi_1 + \varphi_2) + (-f_1 p_{22} - f_2 p_{11} + TC + UB) \cos(\varphi_2 - \varphi_1) + (T + f_2 D - p_{22}Z) \cos(\varphi_1 + \varphi_3) \\ + (- f_1 p_{33} - f_3 p_{11} + SC + UA) \cos(\varphi_3 - \varphi_1) + (U + f_1 D - p_{11}Z) \cos(\varphi_2 + \varphi_3) + (- f_2 p_{33} - f_3 p_{22} + SB + TA) \cos(\varphi_3 - \varphi_2) + (f_1 C - p_{11}U) \cos(\varphi_2 - \varphi_1 + \varphi_3) \\ + (f_3 A - p_{33}S) \cos(\varphi_1 + \varphi_2 - \varphi_3) + (f_2 B - p_{22}T) \cos(\varphi_1 - \varphi_2 + \varphi_3) + Z \cos(\varphi_1 + \varphi_2 + \varphi_3) \end{array} \right\}}{1 + p_{11}^2 + p_{22}^2 + p_{33}^2 + A^2 + B^2 + C^2 + D^2 + 2 \left\{ \begin{array}{l} (CD - p_{11} - p_{22}A - p_{33}B) \cos\varphi_1 + (BD - p_{22} - p_{11}A - p_{33}C) \cos\varphi_2 + (AD - p_{33} - p_{11}B - p_{22}C) \cos\varphi_3 \\ + (A - p_{33}D) \cos(\varphi_1 + \varphi_2) + (BC + p_{11}p_{22}) \cos(\varphi_2 - \varphi_1) + (B - p_{22}D) \cos(\varphi_1 + \varphi_3) + (AC + p_{11}p_{33}) \cos(\varphi_3 - \varphi_1) + (C - p_{11}D) \cos(\varphi_2 + \varphi_3) \\ + (AB + p_{22}p_{33}) \cos(\varphi_3 - \varphi_2) + p_{11}C \cos(\varphi_2 - \varphi_1 + \varphi_3) + p_{33}A \cos(\varphi_1 + \varphi_2 - \varphi_3) + p_{22}B \cos(\varphi_1 - \varphi_2 + \varphi_3) + D \cos(\varphi_1 + \varphi_2 + \varphi_3) \end{array} \right\}}$$

$$\tag{12}$$

where :

$$\varphi_1 = 2\pi t_1 . s \; ; \quad \varphi_2 = 2\pi t_2 . s \; ; \quad \varphi_3 = 2\pi t_3 . s \; ; \quad s = (2\sin\vartheta)/\lambda \; ;$$

$A = p_{11}p_{22} - p_{12}p_{21}$	$G = p_{21}p_{32} - p_{22}p_{31}$	$S = f_1 p_{12} - f_1 p_{22} + f_2 p_{21} - f_2 p_{11}$
$B = p_{11}p_{33} - p_{13}p_{31}$	$H = p_{12}p_{33} - p_{13}p_{32}$	$T = f_2 p_{23} - f_2 p_{22} + f_3 p_{32} - f_3 p_{22}$
$C = p_{22}p_{33} - p_{32}p_{23}$	$L = p_{12}p_{23} - p_{13}p_{22}$	$U = f_1 p_{13} - f_1 p_{33} + f_3 p_{31} - f_3 p_{11}$
$D = p_{32}K + p_{12}F - p_{22}B$		$Z = f_1(G - H - L) + f_2(B - F - M) + f_3(G - G + A)$
$F = p_{21}p_{33} - p_{23}p_{31}$	$M = p_{11}p_{23} - p_{13}p_{21}$	
	$O = p_{11}p_{32} - p_{12}p_{31}$	

For the random case alone, all terms $A, B, C \ldots Z$ reduce to zero; in such a case, (12) reduces to the following simpler formula:

$$\Phi(s) = \frac{1 - t_1^2 - t_2^2 - t_3^2 - 2\,t_1 t_2 \cos(\varphi_2 - \varphi_1) - 2\,t_1 t_3 \cos(\varphi_3 - \varphi_1) - 2\,t_2 t_3 \cos(\varphi_3 - \varphi_2)}{1 + t_1^2 + t_2^2 + t_3^2 - 2\left\{ t_1 \cos\varphi_1 + t_2 \cos\varphi_2 + t_3 \cos\varphi_3 - t_1 t_2 \cos(\varphi_2 - \varphi_1) - t_1 t_3 \cos(\varphi_3 - \varphi_1) - t_2 t_3 \cos(\varphi_3 - \varphi_2) \right\}} \tag{13}$$

It should be remembered that both (12) and (13) may be applied only if the X-ray intensity is a continuous function of the s reciprocal vector. In particular the above formulae fail for those s values which satisfy the joint conditions:

$$s \cdot t_1 = m;\ s \cdot t_2 = n;\ s \cdot t_3 = p, \tag{14}$$

where m, n and p are integral numbers, including zero. At these points of reciprocal space, the X-ray intensity takes the form of infinitely sharp peaks, corresponding to the true Bragg reflexions. It may be shown that, when $f_3, p_{j3}, p_{3k} = 0$, (12) reduces to formula (37) of Allegra (1964), which refers to the case of only 2 possible translations, and that (13) reduces to the well-known Hendricks & Teller (1942) formula.

4. Calculation of the $\Phi(s)$ function for some models of statistical structures

Formula (12) may be used to calculate interference functions for any statistical model of stacking of the kind already discussed. It must be remarked that this rather forbidding-looking formula may be very easily utilized in all practical cases with the aid even of a small electronic computer.

In order to investigate the modulating effect of a third translation vector on the X-ray intensity distribution, we have chosen some structural models, which, although they are of a hypothetical kind, are related to some actual structures occurring in three-component mixed layer clay minerals, such as those of mica–montmorillonite–chlorite type. The statistical structure of these minerals (when treated with glycerol) may be interpreted as a stacking of parallel layers whose reciprocal positions, in the direction perpendicular to them, are given by three translation vectors, whose moduli are:

$|t_1| = 10.0$ Å (for mica layers),

$|t_2| = 17.8$ Å (for expanded montmorillonite layers),

$|t_3| = 14.0$ Å (for chlorite layers).

Since the most frequent two-component minerals are of the mica–montmorillonite type, we have calculated some $\Phi(s)$ functions for statistical models in which the f_1/f_2 ratio is approximately constant and equal to the value observed in several practical cases of two-component clay minerals (MacEwan, 1956; Cesari, Morelli & Favretto, 1961); f_3 is allowed to assume increasing values. In spite of the fact that the layer form factor of the chlorite layers shows some significant differences from those of the mica and montmorillonite layers,

we have assumed, as a first approximation, complete identity among the layer structures, in order to obey the preliminary defined condition.

In Fig. 1 two sets of $\Phi(s)$ functions are plotted; the set labelled A refers to statistical configurations of a random type, while set B refers to statistical configurations with a maximum degree of alternation of the layers (symmetrical case). The functions $1A$ and $1B$ have been previously calculated (Cesari, Morelli & Favretto, 1965) for structural models involving only two vectors, viz. t_1 and t_2. Table 1 gives the f_j coefficients for the two sets.

Table 1. *Relative frequencies of three interlayer translation vectors*

	f_1	f_2	f_3
$1A$, $1B$	0.70	0.30	—
$2A$, $2B$	0.65	0.28	0.07
$3A$, $3B$	0.60	0.25	0.15
$4A$, $4B$	0.45	0.20	0.35

The probabilities of sequence p_{jk} for the A set of functions are immediately derived from the f_j frequencies, by means of the relationships (5). For the B set, the p_{jk} values, obtained by using (8) and (10), are given by the following matrices:

$$\begin{matrix}(2B)\\ \begin{vmatrix} 0.462 & 0.431 & 0.107 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix}\end{matrix} ; \quad \begin{matrix}(3B)\\ \begin{vmatrix} 0.333 & 0.417 & 0.250 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix}\end{matrix} ;$$

$$\begin{matrix}(4B)\\ \begin{vmatrix} 0 & 0.333 & 0.667 \\ 0.750 & 0 & 0.250 \\ 0.857 & 0.143 & 0 \end{vmatrix}\end{matrix} .$$

It can be seen from Fig. 1 that the interference function plots, in the case under examination, do not show very significant differences, at least not unless the f_3 value exceeds about 15–20%. If the frequency of the third translation vector increases above these values, it is possible to observe not only significant changes in the relative intensities of the different peaks, but also the appearance of new peaks, especially in the case of maximum alternation among translation vectors (B set of functions).

5. Conclusion

Formula (12) may be utilized to calculate exactly, by means of (11), the average X-ray intensity diffracted by monodimensionally disordered structures with iden-

tical layers, connected by three types of translation vector, assuming $s = 2$. In several cases, however, as in the field of clay minerals, the condition of identity amongst the intrinsic form factors, V_j, is not generally satisfied. In such cases, a reasonable approximation should be expected when the VV^* factor in (11) is expressed as the average of the $V_j V_j^*$ values corresponding to the three types of layer:

$$VV^* = f_1 V_1 V_1^* + f_2 V_2 V_2^* + f_3 V_3 V_3^* \ .$$

Since the resolution of a pattern of a particular sample of a clay mineral was not the aim of this research, no complete calculation of I_{Av} functions has been carried out. However, owing to the fact that the main features of an X-ray pattern (*i.e.* the number and the positions of the peaks) depend chiefly on the values of the interlayer vectors and of the probability parameters, the calculation of $\Phi(s)$ for some structural models related to clay minerals allows the general trends of the X-ray spectra, with increasing percentages of a third component, to be appreciated.

From a qualitative examination of our results, the third-component effect appears to become evident particularly when the structural disorder corresponds to a large degree of alternation between the layers: on these patterns, we may observe the appearance of some new peaks, together with the disappearance of others, when the percentages of the third component reaches 15–20%. When the structural disorder is of a random type, however, it appears to be rather difficult to detect the third component, even when the above mentioned percentage is exceeded.

Finally, examination of the results reported above seems to discourage any further attempt towards accounting for the presence of 4th or higher translation vectors between the layers: any related effect would in any case be very difficult to detect from actual X-ray patterns.
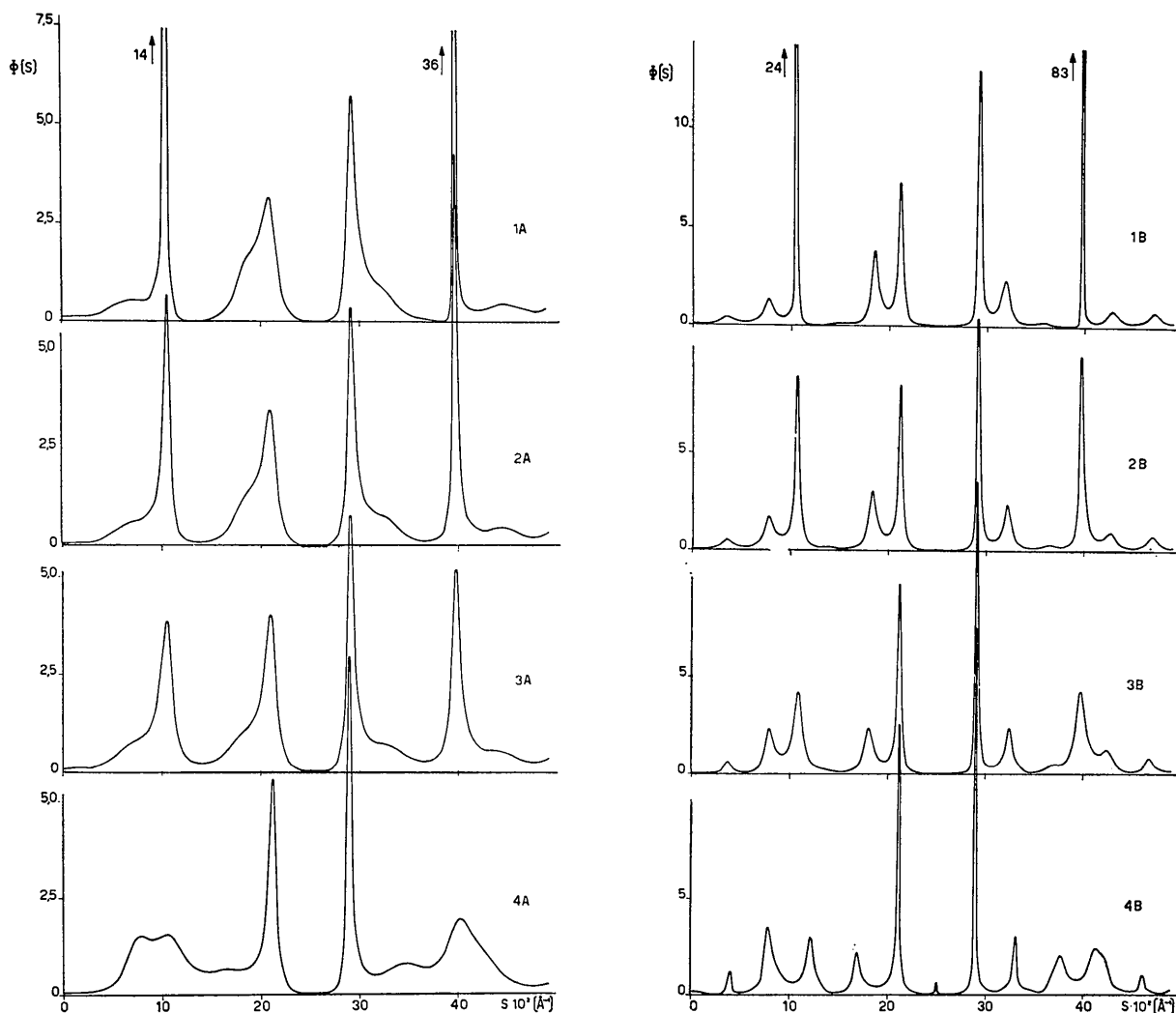

Fig. 1. Plot of a set of $\Phi(s)$ interference functions calculated for different models of monodimensionally disordered structures with three interlayer translation vectors (see text).

References

ALLEGRA, G. (1961). *Acta Cryst.* **14**, 535.
ALLEGRA, G. (1964). *Acta Cryst.* **17**, 579.
CESARI, M., MORELLI, G. L. & FAVRETTO, L. (1961). *Acta Universitatis Carolinae, Serie Geologica, Supplementum,* **1**, 257.
CESARI, M., MORELLI, G. L. & FAVRETTO, L. (1965). *Acta Cryst.* **18**, 189.
HENDRICKS, S. B. & TELLER, E. (1942). *J. Chem. Phys.* **10**, 147.
JAGODZINSKI, H. (1949a). *Acta Cryst.* **2**, 201.
JAGODZINSKI, H. (1949b). *Acta Cryst.* **2**, 208.
JONAS, E. C. & BROWN, T. E. (1959). *J. Sediment. Petrol.* **29**, 77.

KAKINOKI, J. & KOMURA, Y. (1954a). *J. Phys. Soc. Japan,* **9**, 169.
KAKINOKI, J. & KOMURA, Y. (1954b). *J. Phys. Soc. Japan,* **9**, 177.
MACEWAN, D. M. C. (1956). In *Clays and Clay Minerals* (A. Swineford, Editor). p. 166. Washington Nat. Acad. Sci. Nat. Res. Council, publication 456.
MACEWAN, D. M. C., RUIZ AMIL, A. & BROWN, G. (1961). In *The X-ray Identification and Crystal Structure of Clay Minerals* (G. Brown, Editor). p. 393. London: Mineralogical Society.
WEAVER, E. (1956). In *Clays and Clay Minerals* (A. Swineford, Editor). p. 202. Washington Nat. Acad. Sci. Nat. Res. Council, publication 456.
WILSON, A. J. C. (1942). *Proc. Roy. Soc.* A, **180**, 277.

Optical Properties of p-Dichlorobenzene

BY E. MANGHI, C. A. DE CARONI, M. R. DE BENYACAR AND M. J. DE ABELEDO

Comisión Nacional de Energía Atómica, Buenos Aires, Argentina

The optical properties of two polymorphic forms of p-dichlorobenzene have been determined, and a correlation between those properties and the known crystal structures established. From the values of the principal polarizabilities for the p-dichlorobenzene molecule, and taking into account the orientation of the molecule in the crystal cell, the refractive indices α, β, γ, have been calculated for both crystal forms, and their values compared with those measured experimentally. An interpretation of the magnitude and sign of the birefringence is offered. The calculated values of the extinction angles and the orientation of the indicatrix agree with the experimental results.

To study the optical properties of p-dichlorobenzene, suitable crystals were obtained from technical grade British Drug Houses material by slow sublimation on glass surfaces kept at 24°C. Under these conditions two polymorphic forms were obtained: a monoclinic phase as thin (100) plates, and a triclinic phase as prismatic crystals elongated along c. Both crystal forms have been studied by several authors (Frasson, Garbuglio & Bezzi, 1959; Hendricks, 1933; Jeffrey & McVeagh, 1955; Kitaigorodskii, Mnyukh & Asadov, 1963; McCrone, 1957) and their crystal structures are well known.

The monoclinic plates have rectangular outline and show parallel extinction. The triclinic crystals are four-sided prisms showing oblique extinction; according to which face the prism is lying on, the extinction angle observed, referred to the c axis, is 14° or 26°.

For X-ray diffraction study, Weissenberg and precession patterns were taken. The crystals had to be sealed in glass capillaries filled with glycerol to avoid evaporation during exposure.

The optical constants were determined in a Leitz–Wetzlar petrographic microscope, fitted with a four-axis universal stage; a sodium lamp was used as light source ($\lambda = 5\cdot890$ Å). Refractive indices were measured by the Becke line method.

When dissolution of the crystal in the immersion medium was observed, care was taken to saturate the liquid with p-dichlorobenzene beforehand. The refractive indices of the immersion media were measured in an Abbe refractometer. The liquids employed were:

	μ
Sodium iodide + glycerol	1·532
Methylene iodide	1·740
Methylene iodide saturated with p-dichlorobenzene	1·674
Methylene iodide saturated with sulphur	1·778
Methylene iodide saturated with sulphur and p-dichlorobenzene	1·72

For better accuracy in the measurements on the universal stage, the segments with index $\mu = 1\cdot516$ were employed. Their index being very similar to the indices of the other glass surfaces (glass slides $\mu = 1\cdot514$, cover glass $\mu = 1\cdot52$), refraction in the central area of the mounting was avoided (Munro, 1963).

Monoclinic crystals

Weissenberg and precession patterns showed that the plates belonged to the known monoclinic form of p-dichlorobenzene.