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Theoretical Study on the Stacking Faults Type Disorder in Crystals of Finite Size

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A disorder function has been developed for triple-layer structures containing stacking faults. The mathematical model includes the effect of the finite size of crystallites. The application of the method to the elucidation of the structure of δ-$TiCl_3$ is discussed.

Introduction

Several examples of triple-layer structures set up by a metal layer between two chlorine layers are known (Klemm and Krose, 1947). At least in one case, that is $TiCl_3$, (Guidetti *et al.*, in preparation) three polymorphic forms, labelled α, γ and δ are described. They are characterized by different mutual positions of the triple layers, within which the titanium atoms are placed in two thirds of the interstitial octahedral sites.

In α-$TiCl_3$ the layer succession along the direction of the $\underset{c}{}$ axis leads to a hexagonal close packing of chlorine atoms (G. Natta *et al.*, 1961). Conversely, in γ-$TiCl_3$ the mutual position of the triple layer leads to a cubic close packing of chlorine atoms (G. Natta *et al.*, 1961).

The term δ-$TiCl_3$ indicates the activated forms of α- and γ-$TiCl_3$ (G. Natta *et al.*, 1961, G. Allegra, 1962); the activation consists of vigorous and prolonged grinding.

The X-ray diffraction pattern of crystalline powder of δ-$TiCl_3$, obtained by grinding γ-$TiCl_3$ for 24 hr exhibits considerable structural modifications with respect to γ-$TiCl_3$. The peaks of γ-$TiCl_3$ at $2\theta = 15.28°$ and $2\theta = 51.64°$ (G. Natta *et al.*, 1959), though less sharp, are still evident. However, in the angular range 28–38°, all the peaks of γ-$TiCl_3$ disappear and are replaced by an asymmetric halo.

Allegra formulated at hypothesis about the crystalline structure of δ-$TiCl_3$ (G. Allegra, 1962), which can be summarized as follows:

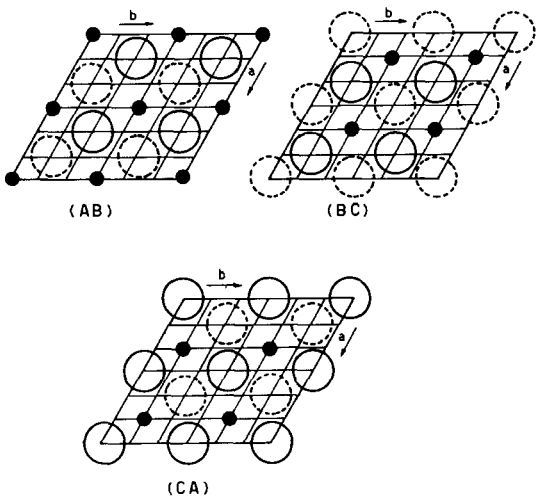

Fig. 1. Partial view (four reduced cells) of the three types of layers which give rise to the close packing of chlorine atoms.

a) the rather sharp peaks of the diffraction pattern of δ-$TiCl_3$ are related to the close packing of the chlorine atoms within the structural layers, which is unaffected by the disorder produced by the grinding;

b) in order to reproduce the angular position of the maximum of the halo which lies at $2\theta = 33.8°$, intermediate between the sharp peaks at $2\theta = 32.97°$ (R. Zannetti, 1967), characteristic of the hexagonal close packing in α-$TiCl_3$, and $2\theta = 35.77°$ (G. Natta *et al.*, 1959), peculiar to cubic close packing of γ-$TiCl_3$, Allegra proposed a mixed cubic-hexagonal structure, in which stacking faults occur in the succession of the structural layers. For this purpose the approximation of 'infinite crystal' was sufficient.

However, our purpose of reproducing the complete X-ray diffraction pattern of δ-$TiCl_3$ powder, does not allow us to neglect the finite size of crystallites.

Mathematical Model

In the present work we will use the reduced cell, space group $P\bar{3}m1$, adopted by Allegra (1962) By translation of the reduced cell along the $\underset{\sim}{a}$ and $\underset{\sim}{b}$ axes with respect to a fixed space origin (G Allegra, 1962), only three different types of structural layers can be obtained (*i e* (AB), (BC) and (CA), differing only in the position relative to the common origin) whose succession gives rise to a close packing of chlorine atoms (Fig 1)

A layout of the structure factors of the three types of cell is straightforward

$$F_{AB} \equiv F_1$$

$$F_{BC} \equiv F_{AB} \exp[-2\pi i(\tfrac{1}{3}h + \tfrac{2}{3}k)] \equiv F_{AB}\exp(-2\pi i\phi) \equiv F_2 \qquad (1)$$

$$F_{CA} \equiv F_{AB} \exp[2\pi i(\tfrac{1}{3}h + \tfrac{2}{3}k)] \equiv F_{AB}\exp(2\pi i\phi) \equiv F_3$$

It is possible to build up the matrix $P^{(1)}$ whose element $P^{(1)}_{rs}$ (r, s = 1, 2, 3) represents the probability that the layer one forward step ahead of an r-type layer is an s-type layer The successions (AB)–(BC), (BC)–(CA) and (CA)–(AB) are forbidden, because they do not give rise to close packing, so that the matrix $P^{(1)}$ is

$$P^{(1)} = \begin{vmatrix} \Pi & 0 & (1-\Pi) \\ (1-\Pi) & \Pi & 0 \\ 0 & (1-\Pi) & \Pi \end{vmatrix} \qquad (2)$$

The element $P^{(2)}_{rs}$ of the matrix $P^{(2)} = P^{(1)}.P^{(1)}$ represents the probability that the layer two forward steps ahead of an r-type layer is an s-type layer

Analogously it is possible to define $P^{(j)}$ (j = 1, 2, ∞) Finally, let us define $P^{(0)}$

$$P^{(0)} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \qquad (3)$$

It follows immediately

$$P^{(m)}_{11} = P^{(m)}_{22} = P^{(m)}_{33}$$

$$P^{(m)}_{12} = P^{(m)}_{23} = P^{(m)}_{31} \qquad (4)$$

$$P^{(m)}_{13} = P^{(m)}_{32} = P^{(m)}_{21}$$

The elements $P^{(-1)}_{rs}$ of the matrix $P^{(-1)}$ define the probability that the layer one backward step before an r-type layer is an s-type layer,

$$P^{(-1)} = \begin{vmatrix} \Pi & (1-\Pi) & 0 \\ 0 & \Pi & (1-\Pi) \\ (1-\Pi) & 0 & \Pi \end{vmatrix} \qquad (5)$$

The definition of the matrix $P^{(-m)}$ (m > 0) is now obvious, its elements $P^{(-m)}_{rs}$ satisfy the relationship

$$P^{(-m)}_{rs} = P^{(m)}_{sr} \qquad (6)$$

Relationships (4) are still valid

The diffracted intensity from a disordered layer structure will be calculated by using the above matrices

The intensity diffracted from a crystal constituted by N_1, N_2, N_3 cells along the crystallographic axes ($\underset{\sim}{a}$, $\underset{\sim}{b}$, $\underset{\sim}{c}$ respectively) is

$$I = \sum_{j_1=0}^{N_1-1} \sum_{j_2=0}^{N_2-1} \sum_{j_3=0}^{N_3-1} \sum_{j'_1=0}^{N_1-1} \sum_{j'_2=0}^{N_2-1} \sum_{j'_3=0}^{N_3-1} \{F_{j_1j_2j_3} F^*_{j'_1j'_2j'_3} \exp[-2\pi i(\underset{\sim}{r}_j - \underset{\sim}{r}_{j'})\cdot\underset{\sim}{S}]\} \qquad (7)$$

where $F_{j_1j_2j_3}$ is the structure factor of the cell whose position relative to the origin is

$$\underset{\sim}{r}_j = j_1\underset{\sim}{a} + j_2\underset{\sim}{b} + j_3\underset{\sim}{c} \qquad (8)$$

and S is the radius vector in the reciprocal space

$$\underset{\sim}{S} = h\underset{\sim}{a}^* + k\underset{\sim}{b}^* + l\underset{\sim}{c}^* \qquad (9)$$

$$|\underset{\sim}{S}| = (2 \sin\theta)/\lambda \qquad (10)$$

In a layer structure containing stacking faults between layers perpendicular to the $\underset{\sim}{c}$ axis, for a fixed index j_3, the structure factor does not depend on j_1 and j_2 anymore, so that it is possible to replace $F_{j_1j_2j_3}$ by F_{j_3} Therefore the expression (7) can be simplified by

$$I = \frac{\sin^2 N_1\pi h}{\sin^2\pi h} \frac{\sin^2 N_2\pi k}{\sin^2\pi k} \sum_{j_3=0}^{N_3-1} \sum_{j'_3=0}^{N_3-1} \{F_{j_3} F^*_{j'_3} \exp[-2\pi i(j_3 - j'_3)l]\} \qquad (11)$$

The substitution $j'_3 = j_3 + m$ gives

$$I = \frac{\sin^2 N_1\pi h}{\sin^2\pi h} \frac{\sin^2 N_2\pi k}{\sin^2\pi k} \left\{ \sum_{m=-(N_3-1)}^{0} \sum_{j_3=-m}^{N_3-1} [F_{j_3} F^*_{j_3+m} \exp(2\pi i m l)] + \right.$$

$$+ \sum_{m=1}^{N_3-1} \sum_{j_3=0}^{N_3-m-1} [F_{j_3} F^*_{j_3+m} \exp(2\pi i m l)] \Bigg\} \quad (12)$$

Since the structure is disordered, it is profitable to introduce the mean value J_m of $F_{j_3} F^*_{j_3+m}$, so that the double sum is reduced to a simple sum:

$$I = \frac{\sin^2 N_1 \pi h}{\sin^2 \pi h} \frac{\sin^2 N_2 \pi k}{\sin^2 \pi k} \sum_{m=-(N_3-1)}^{N_3-1} [(N - |m|) J_m \exp(2\pi i m l)] \quad (13)$$

where

$$J_m = \frac{1}{3}(F_1 F_1^* P_{11}^{(m)} + F_1 F_2^* P_{12}^{(m)} + F_1 F_3^* P_{13}^{(m)}) + \frac{1}{3}(F_2 F_1^* P_{21}^{(m)} + F_2 F_2^* P_{22}^{(m)} + F_2 F_3^* P_{23}^{(m)}) + \frac{1}{3}(F_3 F_1^* P_{31}^{(m)} + F_3 F_2^* P_{32}^{(m)} + F_3 F_3^* P_{33}^{(m)}) \quad (14)$$

Referring to (1) and (4) gives:

$$J_m = |F_1|^2 P_{11}^{(m)} + 1/3\, P_{12}^{(m)} (F_1 F_2^* + F_2 F_3^* + F_3 F_1^*) + \frac{1}{3} P_{13}^{(m)} (F_1 F_3^* + F_3 F_2^* + F_2 F_1^*) \quad (15)$$

and:

$$J_m = |F_1|^2 \{P_{11}^{(m)} + \frac{1}{3} P_{12}^{(m)} [2\exp(2\pi i\phi) + \exp(-4\pi i\phi)] + \frac{1}{3} P_{13}^{(m)} \times [2\exp(-2\pi i\phi) + \exp(4\pi i\phi)]\} \quad (16)$$

Introducing (16) into (13) gives:

$$I = |F_1|^2 \frac{\sin^2 N_1 \pi h}{\sin^2 \pi h} \frac{\sin^2 N_2 \pi k}{\sin^2 \pi k} \sum_{m=-(N_3-1)}^{N_3-1} (N_3 - |m|) \{P_{11}^{(m)} \exp(2\pi i m l) + \frac{1}{3} P_{12}^{(m)} \times [2\exp[2\pi i(ml + \phi)] + \exp[2\pi i(ml - 2\phi)]] + \frac{1}{3} P_{13}^{(m)} [2\exp[2\pi i(ml - \phi)] + \exp[2\pi i(ml + 2\phi)]]\} \quad (17)$$

Summing the terms corresponding to the same m absolute value (keeping in mind (4) and (6)) gives:

$$I = |F_1|^2 \frac{\sin^2 N_1 \pi k}{\sin^2 \pi k} \frac{\sin^2 N_2 \pi k}{\sin^2 \pi k} \Bigg\{ N_3 + \sum_{m=1}^{N_3-1} (N_3 - m) \times [2P_{11}^{(m)} \cos(2\pi m l) + \frac{2}{3} P_{12}^{(m)} [2\cos(2\pi(ml + \phi)) + \cos(2\pi(ml - 2\phi))] + \frac{2}{3} P_{13}^{(m)} \times [2\cos(2\pi(ml - \phi)) + \cos(2\pi(ml + 2\phi))]] \} \quad (18)$$

Finally, applying the cosine addition formulae and separating cosiny and sine terms gives:

$$I = |F_1|^2 \frac{\sin^2 N_1 \pi h}{\sin^2 \pi h} \frac{\sin^2 N_2 \pi k}{\sin^2 \pi k} \Bigg\{ N_3 + \sum_{m=1}^{N_3-1} (N_3 - m) \times \cos(2\pi m l)[2P_{11}^{(m)} + \frac{2}{3}(1 - P_{11}^{(m)})(2\cos(2\pi\phi) + \cos(4\pi\phi))] + \sum_{m=1}^{N_3-1} (N_3 - m) \sin(2\pi m l) \times [\frac{2}{3}(P_{13}^{(m)} - P_{12}^{(m)})(2\sin(2\pi\phi) + \sin(4\pi\phi))] \} \quad (19)$$

The expression (19) can be written as:

$$I = |F_1|^2 \frac{\sin^2 N_1 \pi h}{\sin^2 \pi h} \frac{\sin^2 N_2 \pi k}{\sin^2 \pi k} F_D \quad (20)$$

The disorder function F_D depends on N_3, Π (through the matrices $P^{(m)}$), h and k (through ϕ) and l. In particular, when Π = 1 (hexagonal successions only), the expression (20) becomes:

$$I = |F_1|^2 \frac{\sin^2 N_1 \pi h}{\sin^2 \pi h} \frac{\sin^2 N_2 \pi k}{\sin^2 \pi k} \left[N_3 + 2 \sum_{m=1}^{N_3-1} (N_3 - m)\cos(2\pi m l) \right] \quad (21)$$

whence immediately:

$$I = |F_1|^2 \frac{\sin^2 N_1 \pi h}{\sin^2 \pi h} \frac{\sin^2 N_2 \pi k}{\sin^2 \pi k} \frac{\sin^2 N_3 \pi l}{\sin^2 \pi l} \quad (22)$$

The same result is obtained when ϕ = integer, independently of Π values.

The (22) is the expression of the intensity diffracted from a tridimensionally ordered crystal.

The function F_D (in which Π = 0.6, h = 1, k = 0) and the interference function, both calculated for N_3 = 20, are plotted in Fig. 2 as functions of l.

The function F_D satisfies the requirement of being definite positive; its maximum, for non-integer Π values, corresponds to non-integer l values. The F_D peaks appear broadened in comparison with those of the interference function.

The treatment developed in the present work and Allegra's theory are analogous; however, whereas the p parameter refers to the probabilistic event: "the translation between the j-th and j + 1-th structural layer is...", our parameter Π refers to the event: "the next jth structural layer following the first is...". One further, more substantial, difference, is that

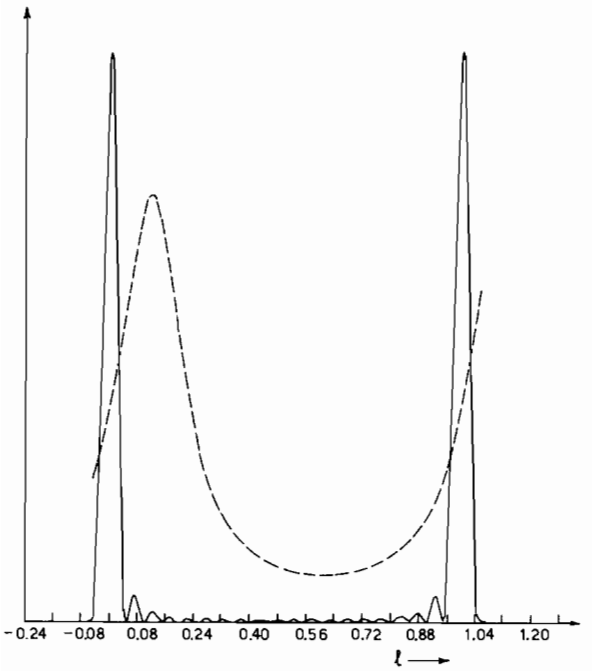

Fig. 2. Solid line: interference function (N_3 = 20); dashed line; disorder function (N_3 = 20, Π = 0.6). The calculations are carried out along the 10*l* reciprocal line. The disorder function is drawn with a multiplicative factor of 5 with respect to the interference function.

whereas Allegra's formula is developed in the "infinite crystal" approximation, we have taken into account the finite size of crystallites. Therefore, our treatment is suited for a complete reproduction of an experimental pattern.

Calculation Method

In order to reproduce the experimental powder spectra, the expression (19) must be converted into a function of 2θ:

$$I(2\theta) = \frac{1}{4\pi |\underset{\sim}{S}|^2} \int_{\Sigma} I \, d\sigma \qquad (23)$$

extended to the surface Σ of the sphere with radius $\underset{\sim}{S}$. The integration is carried out numerically; the sample of points selected for the calculation of (19) must include points from the intervals in which the interference functions attain their absolute maxima. Achieving this goal by constant steps (little areas of constant size on the sphere) would require the sampling of a great number of points and, as a consequence, exceedingly long computing time. Therefore we have adopted in the regions around the absolute maxima of the interference functions a smaller integration step with respect to the other zones. Actually, the predominant contribution to the integral is due to the maximum zones.

In setting up the computer program for surface integration (23), it proved rather difficult to follow the course of the interference functions on the spherical surface; therefore we preferred to convert the integral (23) into a double integral and carry out the calculations in the *hk* plane, by the Simpson procedure:

$$I(2\theta) = \frac{A}{4\pi |\underset{\sim}{S}|} \iint I(h, k, l(h, k)) \frac{dh \, dk}{l} \qquad (24)$$

A is a constant multiplicative factor for all points of a given spectrum whereas the polarization factor is a function of 2θ. Hence, the prospective relationship for the fitting of experimental patterns should be:

$$I'(2\theta) = \tfrac{1}{2}(1 + \cos^2 2\theta) \, I(2\theta) \qquad (25)$$

Applications to $TiCl_3$ and Results

The experimental pattern we intended to reproduce is that of δ-$TiCl_3$ obtained after 24 hr of activation, *i.e.* of the basic component of the Ziegler–Natta catalyst that is widely employed in the polymerization of olefins, in particular to produce isotactic polypropylene.

The atomic factors have been derived from the International Tables for X-Ray Crystallography (1974). As regards the fractional coordinates, Allegra's reduced cell (1962) has been employed, but for the parameter *z* of chlorine atoms a value of 0.2370 has been used. This corresponds to three times the value of 0.079, as reported by Klemm (1947) for the cell constituted by three structural layers and is not very different from Allegra's 0.250 figure.

The radiation wavelength employed in the calculations is obviously the same employed in the recording of the experimental diffraction pattern (λ = 1.54184 Å; Klug and Alexander, 1974). The best fit with the experimental diffraction pattern of δ-$TiCl_3$ has been achieved by superimposing two computed spectra: 1) the spectrum of a disordered structure, named ϵ_1, characterized by Π = 0.6, in which therefore hexagonal successions prevail; 2) the spectrum of a disordered structure, named ϵ_2, characterized by Π = 0.2, in which therefore cubic successions prevail. Following this interpretation of the experimental data the values of some parameters have been refined subsequently as follows:

I) the best values for the reduced cell parameters are:

ϵ_1: $|\underset{\sim}{a}| = |\underset{\sim}{b}| = 3.545$ Å; $|\underset{\sim}{c}| = 5.88$ Å;

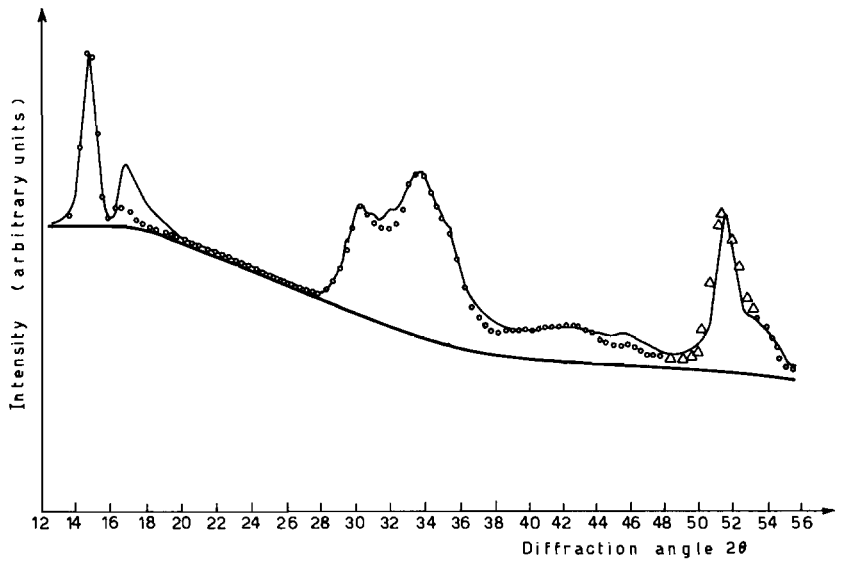

Fig. 3. Comparison between the calculated and the observed patterns for δ-$TiCl_3$; ———— = observed pattern; ———— = background; ooooo = calculated pattern (Method I); ΔΔΔΔΔΔ = calculated pattern (Method II).

ϵ_2: $|\underset{\sim}{a}| = |\underset{\sim}{b}| = 3.545$ Å; $|\underset{\sim}{c}| = 5.80$ Å;

II) as regards the size of the crystallites, N_1, N_2 and N_3 were allowed to change, in the initial step, independently of one another. However, the best results have been obtained for:

$$aN_1 = bN_2 \cong cN_3$$

In particular the final values for N_1, N_2 and N_3 are: $N_1 = N_2 = 20$, $N_3 = 12$. These values correspond to a size of about 70 Å along each crystallographic axis, in good agreement with that determined by Wilchinsky (1973).

III) Several tests were carried out to determine the best integration steps. For a wide range of crystallite sizes, good results have been achieved with 16 steps in the absolute maximum regions of the interference function and with 4 steps elsewhere. If we assume the final values of N_1, N_2, N_3 this corresponds to $\Delta h = \Delta k = 1/160$ in the absolute maximum regions and $\Delta h = \Delta k = 18/80$ in the other regions.

IV) The best fit with the experimental pattern has been obtained by the two calculated spectra in the ratio $\epsilon_2/\epsilon_1 = 0.39$ (Guidetti *et al.*, in preparation). In Fig. 3, along with the experimental pattern of δ-$TiCl_3$, we have drawn the best fitting one. However, it should be noted that the calculations have been carried out according to the above described procedure only in the regions $2\theta \leqslant 48°$ and $2\theta > 53°$. The former region includes the angular range $28° \leqslant 2\theta \leqslant 48°$, which reflects mostly the disorder effects on the diffracted intensity. Actually the above described procedure (first method) does not allow a reliable calculation in the regions around $l = 0$. In particular, the peak at $2\theta \cong 51.5°$ is not reproduced and that at $2\theta \cong 17.2°$ exhibits a markedly reduced intensity with respect to the observed one. Therefore, in these regions we had to resort to the integration procedure on the surface of the sphere (second method) according to (23), although this method is less simple and slower to execute than Eqn. (24).

The good agreement for the peak at $2\theta \cong 51.5°$ (Fig. 3) confirms the validity of the proposed approach to the study of structures affected by stacking faults.

Conclusions

The mathematical model described in the present work is a powerful tool in investigating the disorder in triple-layer structures. The application to the study of δ-$TiCl_3$ allowed us to check and develop Allegra's structural hypothesis and to obtain for the first time a complete reproduction of the experimental diffraction pattern.

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