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Interaction Energy and Growth Mechanisms on Twinned and Polytypic Crystals of Long-Chain Even *n*-Alkanes. I. Interaction-Energy Calculations

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The energies of interaction between paraffinic layers stacked in different twin or polytypic positions have been calculated with the Lennard-Jones (6–12) potential function. All twins have in common the same contact plane (001) so that the individuals of each twin are only rotated with respect to each other by different angles φ around the normal to (001). The calculations show that, for every observed rotation angle φ_o, there is a potential minimum at a calculated rotation angle $\varphi_c \sim \varphi_o$. The possibility that the (001) contact plane may be the original composition plane for all the twins is discussed.

I. Introduction

The two-dimensional common lattices (2D-CL) which appear at the interface of two identical three-dimensional crystalline lattices, superimposed on the same crystallographic plane, have been studied from different points of view.

Geometrical approach. The mutual orientations of crystallites superimposed on the same plane have been studied for different layered structures such as talc, kaolinite, pyrophyllite, silicon carbide (Sueno, Takeda & Sadanaga, 1971) or cryolite, klockmannite, benstonite (Takeda & Donnay, 1965). The results have been interpreted in terms of compound or pseudocompound tessellation, according to the concept of Coxeter (1961, 1964) which was introduced into crystallography by Donnay & Takeda (1963). Other geometrical theories were proposed in order to describe the interface of two reticular planes belonging to the same structure and having equal or different indices: the coincidence-site lattice theory by Ranganathan (1966) and the *O*-lattice theory by Bollmann (1962). Among these theories, developed for interfaces of high symmetry (tetragonal, hexagonal) it seems that the more elaborated one is that of Bollmann (1962) valid for any crystalline lattice. It was successfully applied to the interpretation of phase boundary problems in cryptoperthites (Bollmann & Nissen, 1968). The stability of the different twin laws has been calculated from geometrical data only, such as reticular constants. Takeuchi, Sadanaga & Aikawa (1972) have interpreted their observations of superimposed biotite lamellae in terms of common lattices and image sets of hexagonal lattices. This interpretation is nearly equivalent to that which can be drawn from the coincidence-lattice theory.

Physical approach. A more physical approach has been made by Gillet (1962) who studied all the mutual possible orientations between two (or more) MoS_2 crystals in contact by their (0001) plane. The polycrystalline aggregates which appear by superimposition or by plastic deformation are here interpreted in terms of rotational gliding with coincidence or pseudo-coincidence on the contact planes.

The final position of the two identical lattices which are superimposed is considered here as the result of a rotation followed by a glide parallel to the contact plane. These operations are both necessary in order to attain the highest interaction energy between the individuals forming the aggregate.

Recently, in studies of growth kinetics (Simon, Grassi & Boistelle, 1974) and of polytypism and periodic polysynthetic twins of long-chain even *n*-alkanes (Boistelle, Simon & Pèpe, 1976; Aquilano, 1977), the twin boundary between two individuals belonging to the same polytypic structure has been described in terms of 2D-CL, in the sense of Takeuchi, Sadanaga & Aikawa (1972). Nevertheless, the geometrical properties of the interfaces are not sufficient to explain the occurrence frequency of the different twins, nor to determine the original composition plane of each twin. This problem would be greatly simplified if the interaction energies between the crystals in twin position were known. Consequently it would also be possible to choose the most probable growth mechanism leading to the formation of a given twin.

This study is a first attempt to explain by physical considerations the experimental results obtained in the works quoted above, for octacosane (n-$C_{28}H_{58}$) or hexatriacontane (n-$C_{36}H_{74}$) crystals. The first step will be the calculation of the interaction energies between two crystals stacked one upon another parallel to the (001) plane, with mutual orientations ranging from 0 to 360°. In a second step the occurrence frequency of these different twins will be discussed in relation to the calculated interaction energies.

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II. Structural features

According to the conditions of crystallization (solvents, temperature, supersaturation, purity of the materials) and the number n_C of C atoms in the paraffinic chains, the even *n*-alkanes crystallize in three different polymorphous forms (Müller, 1928, 1930, 1932; Müller & Lonsdale, 1948; Mazee, 1948; Smith, 1953; Ubbelhode, 1938). Under the experimental conditions which have been used to grow the crystals (Aquilano, 1977) and with $28 < n_C < 36$ we are concerned with the monoclinic series only. The three-dimensional structure of all members of the series can be found by the method of Nyburg & Potworowski (1973) which was built up from the key structure of hexatriacontane determined by Shearer & Vand (1956). In short, a monoclinic crystal is made up of molecular layers, stacked one upon another and parallel to the (001) planes. Inside a layer the paraffinic chains are nearly parallel to **c**. Whatever the value of n_C, the space group is $P2_1/a$ with $Z=2$, $a=5{\cdot}58$ (1), $b=7{\cdot}42$ (1) Å. β is slightly dependent on n_C. In octacosane crystals, the structure of which we have used in the energy calculations, $\beta \sim 119{\cdot}5°$ and $c=38{\cdot}20$ (3) Å (Boistelle, Simon & Pepe, 1976). The molecules are centred at the origin of the cell.

Fig. 1 is a schematic representation of such a monoclinic crystal, reduced to two adjacent layers *A* and *B*. The zigzag chains have been shortened and substituted by straight lines. The C atoms of the chains can be numbered from 1 to n_C, but, for simplicity, only the C atoms of the terminal methyl groups have been drawn. Fig. 2, which is a projection perpendicular to the interfacial (001) plane, shows the position of the atoms A_1 and B_1 directly located at the interface of the layers *A* and *B* (Fig. 1). The **ab**, and the **a′b′** cells refer to the projection of the centres of gravity of the molecules belonging respectively to the layers *A* and *B*. The reciprocal **c** axis, (**n**), passes through the origin of the **ab**, cell.

III. Rotation angles

The long-chain even *n*-alkanes crystallize as rhombic platelets with well developed (001) faces often exhibiting polygonized growth spirals. In most cases these spirals are simple and their steps are parallel to the ⟨110⟩ directions of the monocrystal. In other cases there are two (or more) interlaced spirals which originate from the same core. If the steps of these spirals remain parallel to the ⟨110⟩ directions of the crystal, they lead to a polytypic structure. On the other hand, if the steps of one spiral are rotated with respect to the steps of the second spiral by a well defined angle φ, the two spirals lead to a periodic polysynthetic twin where each individual has been generated by its own spiral. Many kinds of twins, all having in common the same contact plane (001), have been observed. The twin axis and the 2D-CL have already been described (Aquilano, 1977). Here, we summarize only (Table 1) the observed rotation angle φ_o, mainly for $0 < \varphi_o < 90°$, as well as the number of twins observed n_o.

Figs. 3, 4 and 5 are examples of twinned crystals where the rotation angles between the growth spirals are $\varphi_o = 28$, 106 and 180° respectively. With reference to Fig. 1, all these twins could be partially described, from a structural point of view, and in a very simple way, if we consider that the layer *A* is turned with respect to layer *B* by a rotation of the angle φ around the normal to the layer, *i.e.* around an axis parallel to **n**.

It is important to notice, taking into account the spacings between the steps of a simple growth spiral, that the steps have different velocities *V*, but because of the symmetry line *m* in (001) they are equal two by two (Fig. 6). The origin of these different step velocities is due to the inclination of the steps with respect to the (001) face on which they spread out. If these velocities were not anisotropic (case of spirals having *mm* symmetry) it would be impossible to know if the rotation

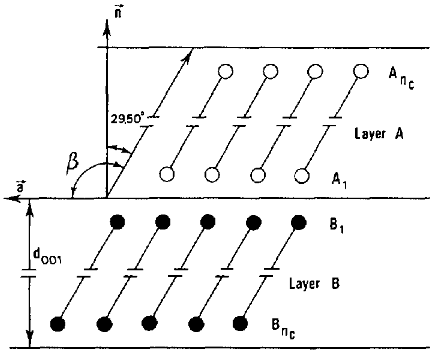

Fig. 1. Schematic drawing of the monoclinic structure of an even *n*-alkane projected along the [010] direction. The value of β (29·5°) relates to n-$C_{28}H_{58}$.

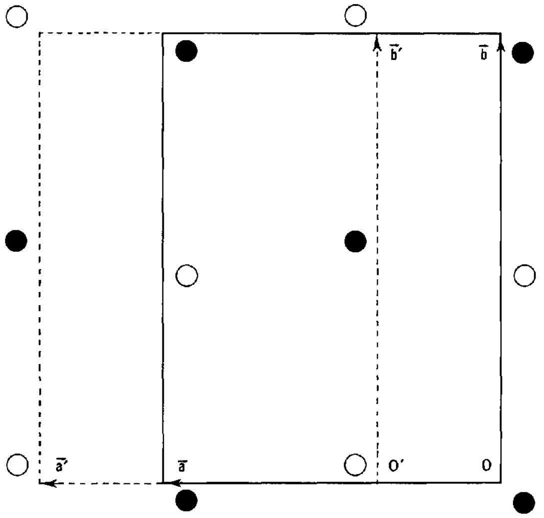

Fig. 2. (001) projection of the carbon atoms located near the interface of the layers *A* and *B* in Fig. 1 (○ atoms A_1; ● atoms B_1).

Table 1. *Number of twins observed n_o at the angular positions φ_o and positions of the rotation axes $\mathbf{n}(x,y)$ giving minima of the potential energy (U^0_p/ε) at the calculated angular positions φ_c*

φ_o (°)	0	15·5 16·0	21	27·5 29·0	42	53·5	59	74 106	87	180
n_o	high	2	2	5	2	1	2	24	13	high
$\mathbf{n}(x,y)$	0, 0	0·250 0·250	0·500 0·050	0·250 0·250	0·250 0·230	0·539 0·365	0·280 0·720	0, 0 0·365 0·500	0·500 0·050	0·365 0·500
φ_c (°)	0	14–15	21	30	42	51	57	74 106	87	180
U^0_p/ε	−25·12	34·96	34·47	32·78	36·15	29·47	29·18	−13·47 −13·44	38·25	−24·75

of the *A* layer (Fig. 1) is clockwise or anticlockwise with respect to the *B* layer. Consequently, it would be impossible to distinguish between the angles φ, $180+\varphi$, $180-\varphi$ and $-\varphi$. In order to avoid any ambiguity, we have always taken as reference the vector which, starting from the core of the spiral, bisects the obtuse angle formed by the two fastest steps of the spiral. The angle φ between the two vectors associated with the interlaced spirals of a twinned crystal has always been taken anticlockwise. The origin of the angles corresponds to the vector associated with the lower observed spiral. Thus if the fast and slow growing steps are respectively schematized by thin and broad lines as in Fig. 7, it is obvious that no ambiguity is left for the determination of the rotation angle. With different angles φ, Fig. 7(*b*), (*c*) and (*d*) could respectively correspond to Figs. 3, 4 and 5.

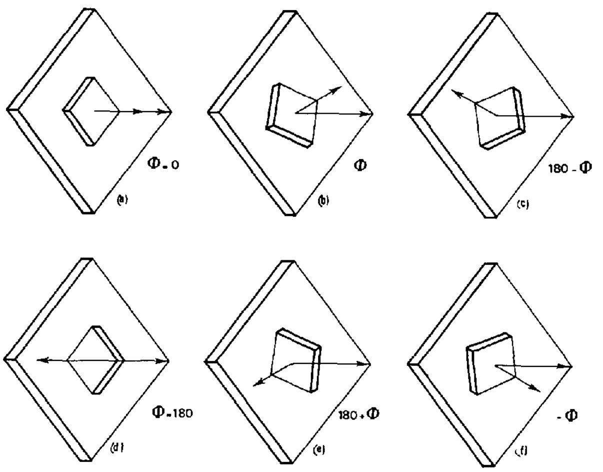

Fig. 7. Schematic representation of two (001) layers superimposed on their contact plane (001) and mutually rotated through a variable angle φ around their normal.

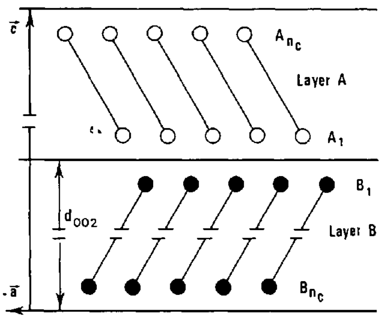

Fig. 8. Projection along the [010] direction of the schematic polytypic structure 2*O*[180].

IV. Positions of the rotation axes

In order to describe structurally the twins corresponding to each rotation angle φ_o, the position of the paraffinic layers close to the interface of the twinned crystals must be known exactly. This means that the twins must be described as being the consequence of two operations: a translation of the origin of the **ab** cell (layer *A*) followed by a rotation φ around the normal to (001) passing through the origin of this cell (**n**); the **a**′**b**′ cell (layer *B*) remains fixed (Figs. 1, 2). As the φ angles are known from experiment, the problem therefore consists only in finding the positions of the rotation axis **n**. Let us call $(\varphi)\mathbf{n}(x,y)$ the position of the rotation axis giving a twinned crystal after a rotation φ and a translation x,y in fractional coordinates along **a** and **b**. Thus, $(0)\mathbf{n}(0,0)$, *i.e.* neither rotation nor translation, corresponds to a usual monoclinic crystal 1*M*[0] (Figs. 1, 2) whereas $(180)\mathbf{n}(0{\cdot}365, 0{\cdot}500)$ corresponds to the polytype 2*O*[180], space group *Pcab*, which is simply made up of monoclinic monolayers turned one to the other by 180° (Boistelle, Simon & Pèpe, 1976).

The orientation of the molecules of this polytype is given in Fig. 8. The interface of the adjacent paraffinic layers is given in Fig. 9. We have kept here the same projection planes and the same conventions as for Figs. 1 and 2. For these two kinds of crystal, the second of which could also be considered as a twin, the position x,y of **n** is found without difficulty since their three-dimensional structures are known. In order to find the position of **n** for all the other twins we could only compute the potential energy between adjacent layers. If calculations of this type are meaningful, this potential energy must have relative minima for each angle φ_o when the corresponding **n** axis is well positioned, *i.e.* when the layer *A* of Fig. 1 after a rotation of φ has been properly shifted in regard to the layer *B*. It could be said that, if for each angle φ_o the calculation gave a

Fig. 3. Growth-polysynthetic twins revealed by two interlaced growth spirals; the rotation angle between the two spirals is $\varphi=28°$.

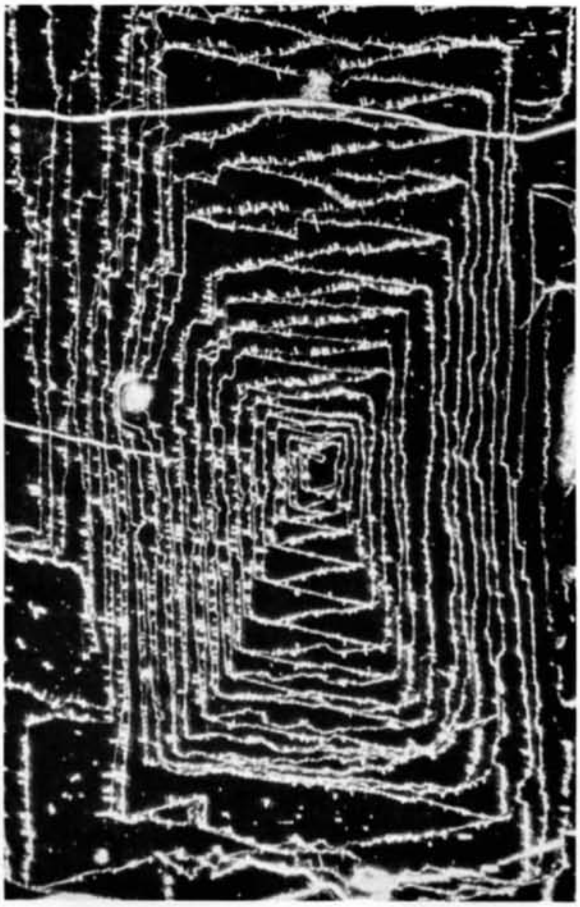

Fig. 4. Growth polysynthetic twins revealed by two interlaced growth spirals; the rotation angle between the two spirals is $\varphi=106°$.

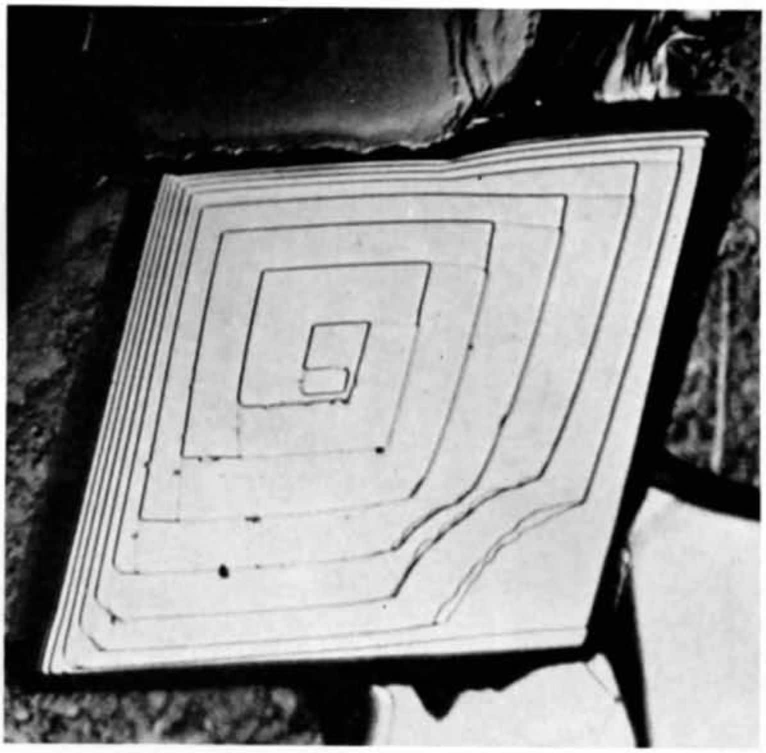

Fig. 5. Complex-growth polytype $(p+q)M[(0)_{p-1}\ 180(0)_{q-1}\ 180]$ revealed by two interlaced growth spirals mutually rotated through an angle $\varphi=180°$.

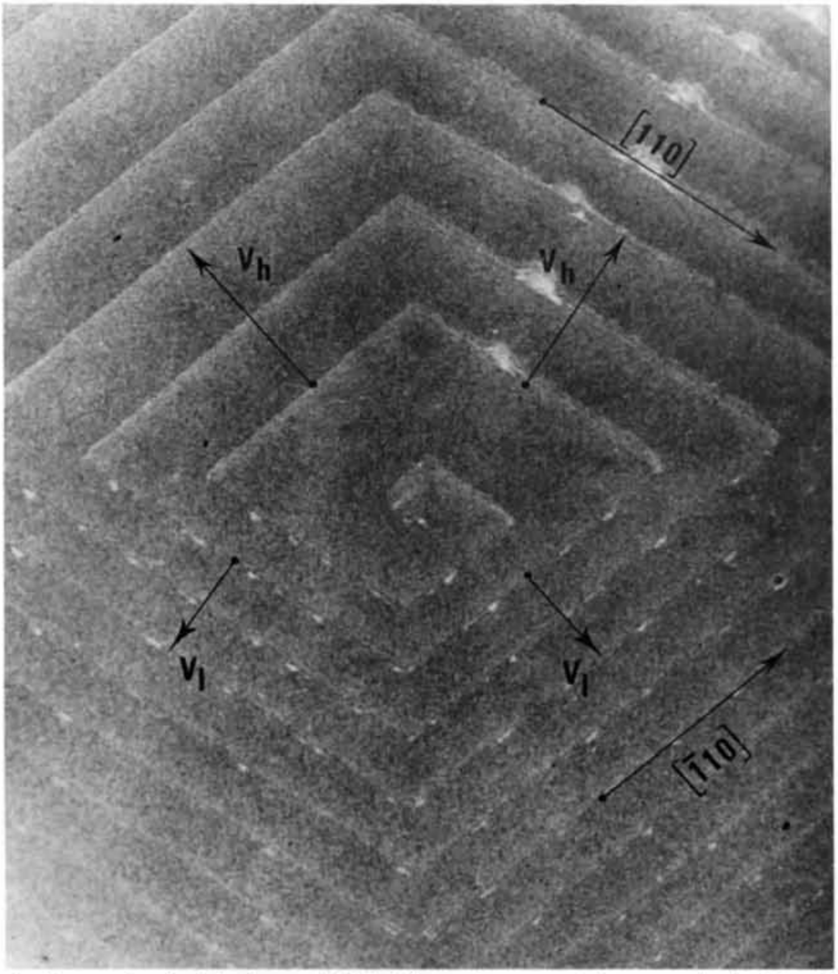

Fig. 6. Simple polygonized growth spiral (polytype $1M[0]$). The anisotropy of the normal velocities of the steps ($V_h > V_l$) is due to the tilt of the paraffinic chains (V_h = higher velocity; V_l = lower velocity).

unique solution for the position x, y of the corresponding **n** axis, the method would lead to an *a priori* knowledge of the three-dimensional structure of the twinned crystals, in the limit of the model used.

V. Calculation method

The Lennard-Jones 6–12 potential function which works well for the non-polar paraffin molecules has been used to calculate the interaction energy between the molecules belonging to two adjacent paraffinic layers. Each C atom of the chains is considered as an interaction centre, and the interaction between two molecules is thus the sum of n_C^2 interactions. If we refer to Fig. 1, with k and l molecules respectively in the layers A and B, the interaction energy between the two layers is:

$$U_p^0=\varepsilon\sum_k\sum_l\sum_{i,j}\left[\frac{(r^*)^{12}}{r_{i,j,k,l}^{12}}-\frac{2(r^*)^6}{r_{i,j,k,l}^6}\right] \qquad (1)$$

where i and j are the numbers of C atoms in the molecules of the layers A and B $(1<i,j<n_C)$.

Since for long-chain paraffins, r^* depends essentially on the distances between molecules belonging to the same layer, we have used in all our calculations the value $r^*=4\cdot6819$ Å calculated previously for a molecule situated in a kink of the crystal (Madsen & Boistelle, 1976). It would be possible (but of no special interest for our purpose) to give the real value of U_p^0 by use of the previously calculated value of the force constant ε $(\varepsilon/k=55\cdot26$ K). Furthermore, in order to obtain the total interaction energy at room temperature between the layers A and B, it would be necessary to take into account the kinetic energy of lattice modes. But as this energy would introduce only a correction by a constant term (Madsen & Boistelle, 1976) we prefer in the sequel, and for the sake of simplicity, to give all the numerical values in terms of the dimensionless quantity U_p^0/ε.

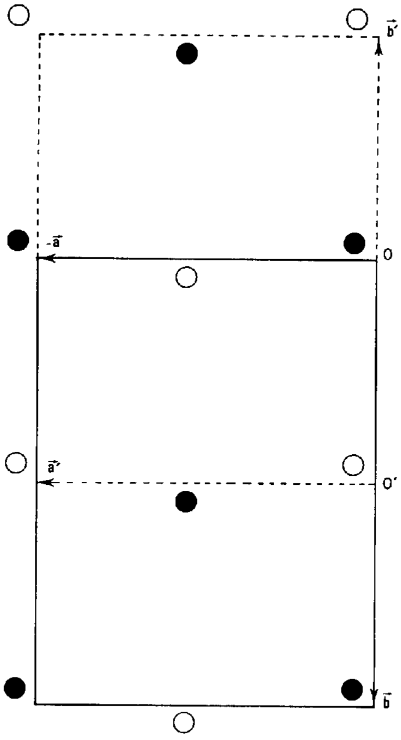

Fig. 9. (001) projection of the carbon atoms located near the interface of the layers A and B in Fig. 8. (○ atoms A_1; ● atoms B_1).

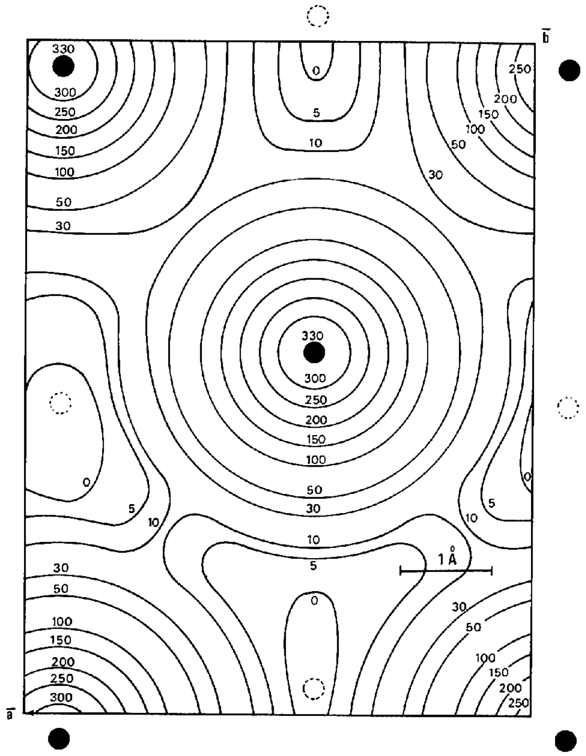

Fig. 10. (001) projection for both carbon atoms and equipotential curves U_p^0/ε as a function of the distances between an atom A_1 and the underlying atoms B_1.

As a reference, let us consider now a normal monoclinic stacking of the paraffinic layers (Figs. 1, 2). Since all the molecules in layer A are crystallographically equivalent with regard to the whole of the molecules in the layer B, the potential energy is the same for each of these molecules.

If in (1), $i=j=n_C$, $k=1$ and $l\to\infty$ one then obtains per molecule $U_p^0/\varepsilon\sim-27$. As a comparison, a molecule situated in a kink of the crystal has the value $U_p^0/\varepsilon\sim-16\cdot11n_C-27$ (Madsen & Boistelle, 1976). The end-group packing energy (between two adjacent layers) is very low compared with the side packing energy (within a layer). In order to be compared with the standard value given by a normal monoclinic stacking, all the values of U_p^0/ε given in the sequel will be given per molecule.

VI. Results

Let us consider now a layer B (Fig. 1) of large lateral extension but reduced to the C atoms B_1, parallel to which moves an atom A_1. In this case the parameters involved in (1) are $i=j=k=1$ and $l \to \infty$. If U_p^0/ε is calculated for all the positions of A_1 one obtains equipotential curves as indicated in Fig. 10, which is a projection normal to (001) for the curves as well as for the C atoms. The dashed white circles are the positions of A_1 in a normal monoclinic crystal. Obviously, it is only for these positions that the values of U_p^0/ε are minima and consequently the interaction energies maxima. Conversely, when A_1 comes close to an atom B_1, the repulsive term in (1) becomes very high and it will never be possible to compensate for it even by introducing all the other C atoms in the paraffinic chains since the best value of their contribution is $U_p^0/\varepsilon \sim -27$. By extension, this means also that a paraffinic layer can be rotated by an angle φ with respect to an adjacent layer only if it is placed in such a way that near the interface the C atoms of the two layers are far enough from one another.

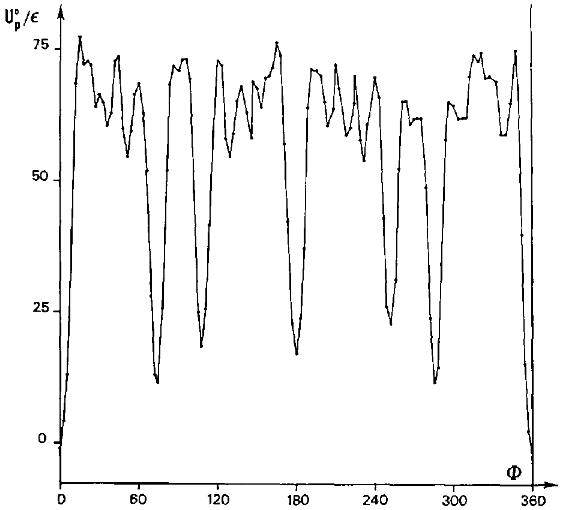

Fig. 11. Values U_p^0/ε *vs* rotation angle φ; the curve is referred to the rotation axis $\mathbf{n}(0,0)$.

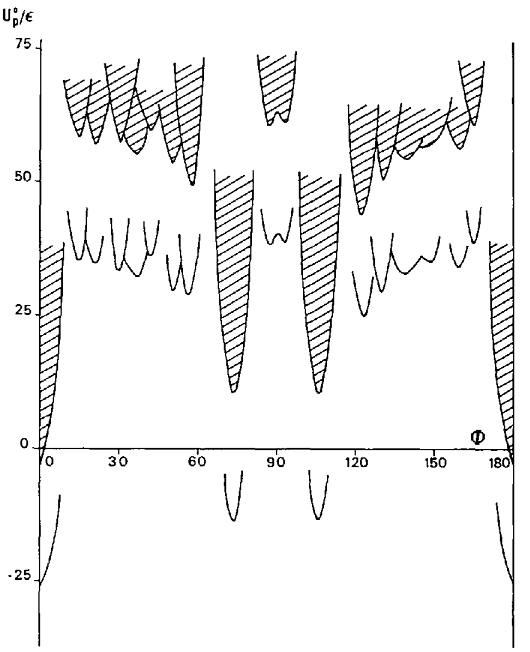

Fig. 12. Synthesis of the calculated values of U_p^0/ε for different rotation axes $\mathbf{n}(x,y)$. Dashed minima: values corresponding to the interactions limited to the interface carbon atoms. Full-line minima: values corresponding to the interaction between two layers with complete paraffinic chains.

First step. Taking into account this result it was interesting as a first step of the calculation to deduce the forbidden values of φ, for a given rotation axis $\mathbf{n}(x,y)$. For this purpose, the calculation of (1) has been limited by considering only the atoms directly situated at the interface of the twinned crystals, under the following conditions. The layer A (Fig. 1) made up of 32 molecules, limited to the A_1 atoms, is rotated anticlockwise on the layer B made up of 155 molecules, also limited to the B_1 atoms. The layer B, circular, is broad enough so that, whatever the orientation of the layer A may be, the interactions at larger distances are negligible. The molecules of the layer A form a nearly square lattice ($4\mathbf{a} \times 3\mathbf{b}$) and rotate at the centre of the layer B. The number of molecules involved in the calculation is sufficiently high to be representative of the phenomena. Numerous rotation axes $\mathbf{n}(x,y)$ have been tested by the calculation of (1) where this time, $i=j=1$, $k=32$ and $l=155$. The φ angles ranged mainly from 0 to 180°, sometimes from 0 to 360°. The increment on φ was 3°.

In Fig. 11 are plotted the results obtained by use of the rotation axis $\mathbf{n}(0,0)$, the A layer rotating from 0 to 360° on the B layer. Obviously there is a background, where the repulsion between layers is high, from which stand out some potential minima. The angular position φ_c of these minima can be shifted up to 2 or 3° in regard to the position φ_o of the twinned crystals (Table 1). This is due on the one hand to the rotation axis which is not the best for all potential wells and on the other to the uncertainty due to the increment of 3° in the angles. Fig. 12 (dashed minima) is a synthesis of the best potential wells obtained between 0 and 180° with different rotation axes $\mathbf{n}(x,y)$.

From these simplified calculations we may infer the following points. (i) Potential minima appear at all the φ angles for which a twin has been observed. Furthermore it seems that the potential wells exist only for angular positions $\varphi_c \sim \varphi_o$. Nevertheless there is one exception (Fig. 12) since a minimum appears at $\varphi_c = 36$–$37°$ for the rotation axis $\mathbf{n}(0{\cdot}064, 0{\cdot}875)$. The question remains open whether a twin can exist at this angular position, since it has not been observed so far.

(ii) The depth of the potential well for a given φ depends greatly on the position of the rotation axis $\mathbf{n}(x,y)$. It disappears if $\mathbf{n}(x,y)$ is not in the right position. (iii) If there is a potential minimum for the conditions $(\varphi)\mathbf{n}(x,y)$, with $0° < \varphi < 90°$, there exist also three other minima, not exactly equivalent, for the conditions:

$$\begin{array}{ll} \text{if } 0<\varphi<90° & \rightarrow x, y \\ 180-\varphi & \rightarrow \bar{x}, y \\ 180+\varphi & \rightarrow x+0{\cdot}365, y+\frac{1}{2} \\ 360-\varphi & \rightarrow \bar{x}+0{\cdot}365, y+\frac{1}{2}. \end{array}$$

The translation 0·365 on x and $\frac{1}{2}$ on y appears readily by comparison of Figs. 1, 2 and Figs. 8, 9. [3·365, *i.e.* 0·365 on x corresponds to $d_{(001)} \times \tan(29{\cdot}5°)/a$].

Second step. As the best rotation axes, for each angle φ, have been found by the simplified calculation described above, it suffices now for obtaining the real value of U_p^0/ε to extend the calculation, taking into account all the C atoms of the paraffinic chains. Actually we have limited the calculation to the first seven atoms of the chains directly located near the interface of the A and B layers. The reason for this limitation is merely a question of computing time which is proportional to the square of the number of atoms considered. This is of no importance for the results, since the error is only of a few percent. As a comparison let us calculate for the position $(0)\mathbf{n}(0,0)$ the values U_p^0/ε per molecule as a function of the number n of atoms in the paraffinic chains. For $n = 1$, 5, 7, and 28 (n_C) we have respectively $U_p^0/\varepsilon = -1$, $-22{\cdot}9$, $-25{\cdot}7$ and -27. Obviously only the first atoms near the interface are of importance. In order to find better angular positions of the potential minima the increment in φ was 1°. The final values of U_p^0/ε, per molecule, calculated with (1) where $i = j = 7$, $k = 32$ and $l = 155$ are given in Table 1. The values (x,y) of the rotation axes $\mathbf{n}$ and the corresponding calculated rotation angles φ_c where the potential minima appear are also indicated. The agreement between φ_o and φ_c is good. In Fig. 12 (full-line minima) we show the shape of the potential wells, between 0 and 180°, close to their minima. Only the minima at $\varphi = 0$, 74, 106 and 180° are negative. For the other values of φ, minima exist but have positive values.

VII. Discussion

(A) The results obtained from our calculations agree well with the observed phenomena, since the relative minima of the potential energy have been obtained by the calculation for all the values φ_o between the twinned crystals, and only for these values (except for $\varphi_c = 36°$). Nevertheless some remarks must be made about the minima having positive U_p^0/ε values.

In our opinion, this is not due to the potential function we have used. It yielded good results previously (Madsen & Boistelle, 1976) and is known to provide a good representation of forces between non-polar molecules. On the other hand, our model of rotation of the paraffinic layers is more open to criticism, since the molecules inside the layers are supposed to remain perfectly rigid as they rotate. It is clear that a whole molecule cannot move easily from its equilibrium position but it is also certain that the end-chain C atoms (methyl groups) are not well located since even at room temperature they have high thermal motion. This has been made evident in different structure determinations (Nyburg & Lüth, 1972; Boistelle, Simon & Pèpe, 1976). If we look at the equipotential curves of Fig. 10 it is obvious that small displacements of the atoms near the interface can decrease drastically the value of U_p^0/ε. A verification of this will be made later with a model taking into account the relaxation of the lattices. Nevertheless, the calculations made with the rigid model described above were necessary, since the most probable two-dimensional common lattices are those which need the weakest relaxations.

Another possible cause of the positive values of some U_p^0/ε is that we have always used the parameters $\mathbf{a}$ and $\mathbf{b}$ of the monoclinic cell determined at 20 °C, whereas experiment shows that the occurrence frequency of twins increases with the temperature (Aquilano, 1977; Aquilano & Boistelle, 1977). To our knowledge, the variation of $\mathbf{a}$ and $\mathbf{b}$, and consequently the variation of the atomic positions in the structures, have not been measured for the monoclinic crystals. For the orthorhombic crystals (Müller, 1928, 1930) for which $a = 7{\cdot}44$ and $b = 4{\cdot}95$ Å, the variations of $\mathbf{a}$ and $\mathbf{b}$ are 2 and 1% between room temperature and the melting point respectively (61 °C for the crystals of octacosane considered here). But the temperature effect is probably of less importance than the relaxation of the lattices.

(B) The difference between the values of U_p^0/ε corresponding to $\varphi = 0$ and 180° is only about 1% (Table 1, Fig. 12) and accounts rather well for the fact that the occurrence frequency of the basic polytype $2O[180]$ or of the complex polytype $(p+q)M[(0)_{p-1}180(0)_{q-1}180]$ is almost as high as that of the normal monoclinic crystal $1M[0]$. [For the notation of the polytypes, see Aquilano (1977).] From a crystal-growth point of view, it could be said that, on the (001) face of a $1M[0]$ crystal, the nucleation of a new layer rotated by 180° around $\mathbf{n}(0{\cdot}365, 0{\cdot}500)$ has almost the same probability as the nucleation of a new layer stacked in a normal orientation.

(C) The depth of the potential wells for the angles $\varphi = 74$ and 106°, even if not so important as those for $\varphi = 0$ or 180°, allows the following deductions. Firstly, these two minima correspond to real twins and not to polytypes since in order to obtain the same minima as for the polytypes we ought to introduce a certain relaxation of the lattices, *i.e.* a change of the distances between the first neighbours at the interface. Secondly, the (001) plane of the crystal can easily become the original composition plane for these twins. Experiment shows indeed some cases where these twins, originated by three-dimensional nucleation or by syneusis, have the (001) plane as the original composition plane. Actually, this occurs even if energetically the (110) planes are more favoured as the original composition planes,

(*D*) About the occurrence frequency of a given twin and the corresponding values U_p^0/ε we can make the following remarks. If the potential minima are negative, the higher the observation frequency of a given stacking, the higher the negative value of the corresponding potential energy. If the potential minima are positive this connexion is no longer valid. As an example we can choose the cases of the minima associated with $\varphi = 87$ and 93°. The relative minima for these angles are not sharp, whereas the occurrence frequency of the corresponding twins is high (Table 1, Fig. 12). We think that for these two cases, even after relaxation of the lattices, we cannot expect very deep potential wells which could allow the nucleation of a new layer or the syneusis of a small crystallite in twin position on (001). On the other hand, experiment shows that the edgewise encounters of two crystallites during their growth can play a fundamental role for the appearance of all the secondary twins (*i.e.* the twins for which we have calculated high positive values of the potential energy). For this kind of twin, the (*hk*0) or (*hkl*) planes can be the original composition planes whereas the (001) plane is only a contact plane on which the exposed ledges of the two individuals in twin position develop, giving rise to the interlaced growth spirals characteristic of the twin.

A study of a model taking into account the relaxation of the lattices at the (001) interface of the twinned crystals, as well as a study of the influence of the growth mechanisms on the twin formation is in progress. The results will be published later.

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