

## Ziegler-Natta Catalysis II. Surface Structure of Layer-Lattice Transition Metal Chlorides

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This article is the second in a series of three which propose a detailed theory of Ziegler-Natta polymerization of  $\alpha$  olefins. It deals exclusively with developing a picture of the surface structure of the crystalline transition metal chloride from principles of inorganic crystal chemistry. It is argued that finite crystals of these chlorides carry chlorine vacancies, i.e. incompletely coordinated titanium ions, at their surface. Their number as a function of crystal size is calculated and it is shown that they will not occur at the usually best developed crystal face of these layer-lattice structures, (0001), but at the other faces forming the sides of crystal platelets.

As an example the structure of the (10 $\bar{1}$ 0) face is discussed. The geometry of the potential active centers formed by the Ti ion and its surrounding five Cl ions and one Cl vacancy is described in detail.

Its steric and chemical consequences and the mechanistic ideas proposed in the first article of this series will be combined in a third article to build a theory of the mechanism of stereospecific polymerization of  $\alpha$  olefins by Ziegler-Natta catalyst systems.

### I. INTRODUCTION

Ziegler-Natta catalyst systems for the stereospecific polymerization of olefins usually contain a transition metal halide as the solid phase at the surface of which the reaction takes place. In the first article of this series (1) it was postulated that the catalytically active center consists of a transition metal ion which is not fully coordinated by chlorine ions but carries an alkyl group and a chlorine vacancy. That the latter may play a role in the catalytic reaction was first suggested by Boor (2).

In the present article we shall investigate whether from the viewpoint of inorganic crystal chemistry a picture of the surface structure can be developed. We shall deal exclusively with titanium chlorides, because their structures are particularly well known, but our considerations may apply generally to transition metal halides with a layer-lattice structure. In particular we shall discuss the occurrence of chlorine vacancies at the crystal surface, their number, and their most probable location. From the theoretical

study of these questions a picture of the structure of the crystal faces will emerge which includes the geometric situation around exposed titanium ions at a crystal face.

In a subsequent article (3) it will be shown how a combination of the present results with the postulates put forward in the first article leads to a consistent theory of the formation of isotactic polymer, which not only describes the mechanism of the polymerization but also the locus of polymerization at the crystal surface.

### II. SURVEY OF THE CRYSTAL STRUCTURE OF TiCl<sub>2</sub> AND TiCl<sub>3</sub>

The  $\alpha$  and  $\gamma$  modifications of TiCl<sub>2</sub> and TiCl<sub>3</sub> consist of stacks of elementary crystal sheets each containing two chlorine layers with one titanium layer in between (4-6). Thus along the principal axis of the crystal two chlorine layers alternate with one titanium layer. The Ti ions in all cases are located in octahedral interstices of the Cl lattice. The Cl ions themselves are either

packed according to a cubic close packing ( $\gamma$  modifications) or according to a hexagonal close packing ( $\alpha$  modifications). In a  $\text{TiCl}_2$  sheet all octahedral interstices are occupied by  $\text{Ti}^{2+}$ . In a  $\text{TiCl}_3$  sheet only two-thirds of the octahedral interstices contain  $\text{Ti}^{3+}$ ; the  $\text{Ti}^{3+}$  are arranged in regular hexagons with an empty Ti site at the center. In a third modification of  $\text{TiCl}_3$  ( $\beta$ ) the Cl ions are also arranged in a h.c.p. but here one titanium layer alternates with one chlorine layer; accordingly in this case the titanium layers contain only half as many Ti ions as those of  $\alpha\text{-TiCl}_3$ . A further difference between the  $\alpha$  and  $\beta$  modifications is the arrangement of the Ti ions along the  $c$ -axis of the crystal. In  $\beta\text{-TiCl}_3$  all octahedral interstices in that direction are either filled or empty so that the crystal may be considered as consisting of threadlike molecules  $(\text{TiCl}_3)_n$ .

In  $\alpha\text{-TiCl}_3$  the Ti ions along the  $c$ -axis are separated alternately by one and three empty octahedral sites, in  $\alpha\text{-TiCl}_2$  always by one. The structures with h.c.p., which we will discuss extensively, are given in Fig. 1.

### III. CHLORINE VACANCIES AND ALTERNATIVE LATTICE DISTURBANCES IN REAL CRYSTALS

In order to illustrate our general line of thought (?) we deal first with an elementary sheet of  $\text{TiCl}_2$ . This should have the composition  $\text{Ti}/2 \text{ Cl}$  and be electroneutral. It is to be expected from the differences in characteristic properties of the ions concerned that the thermodynamically most favorable situation is that in which the Ti ions are fully surrounded by Cl ions. However, this appears not to be possible in an elementary sheet of finite dimensions and, consequently, not in a real crystal built up from a number of such sheets either. Figure 2 shows a rhombus sheet in which all Ti ions are fully coordinated with Cl ions (A and B do not partake in the formation of octahedral interstices). It is easily seen that for the formation of  $(m - 1)^2$  octahedral interstices of  $\text{Ti}^{2+}$  ions,  $2(m^2 - 1)$  Cl ions are needed. Thus the sheet would be electronegative and carry  $2(m^2 - 1) - 2(m - 1)^2 = 4(m - 1)$

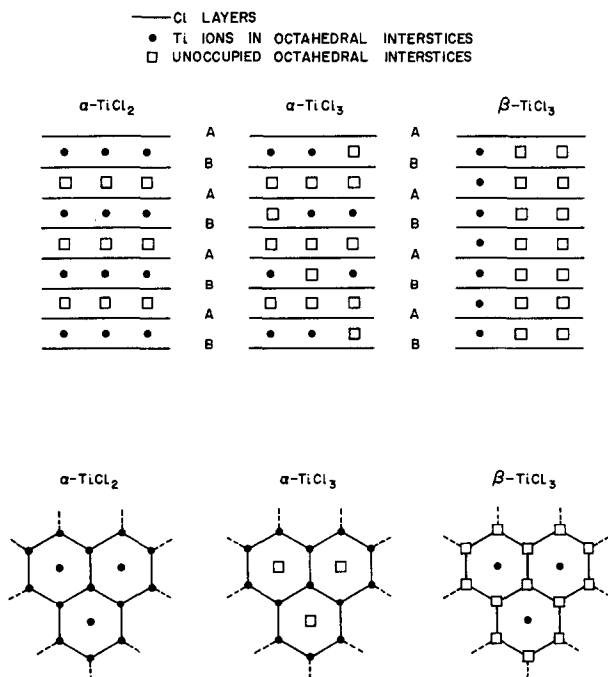


FIG. 1. Schematic representation of the crystal structure of Ti chlorides with hexagonal close packing of Cl ions.

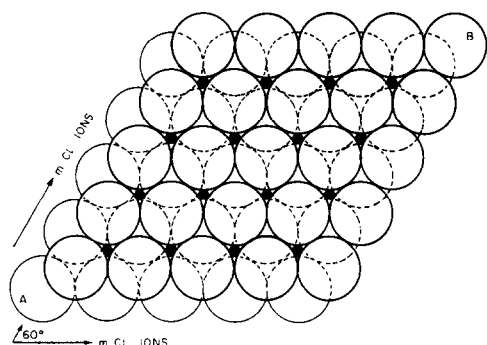


FIG. 2. Sheet consisting of two Cl layers with octahedral interstices.

electronic charges and its composition would be  $\text{TiCl}_{2(m+1)/(m-1)} \approx \text{TiCl}_{2[1+(2/m)]}$ . Starting from the situation of Fig. 2 an electroneutral sheet may be obtained by the introduction of

- Cl vacancies;
- interstitial  $\text{Ti}^{2+}$  ions;
- $\text{Ti}^{3+}$  ions instead of  $\text{Ti}^{2+}$  ions ("positive holes");
- any combination of (a), (b), and (c).

Alternative (a) might be the most simple, the more so because—as will be discussed later—Cl vacancies most probably are located at the edges of the sheets.

For alternative (b), extra Ti ions should be located at the tetrahedral interstices of the sheet or (and) in octahedral interstices between different sheets. This would mean a deviation from the ideal crystal structure, given by X-ray diffraction analysis.

For (c),  $\text{Ti}^{3+}$  ions would have to be substituted for part of the  $\text{Ti}^{2+}$  ions. In this case  $\text{TiCl}_2$  should be assumed to possess a certain content of  $\text{Ti}^{3+}$  which would be the higher the smaller the crystalline particles.

Experimentally it is very difficult to discriminate between the above possibilities. For the purpose of the present discussion it is convenient to assume that electroneutrality is only obtained by Cl vacancies. Their presence would allow of easy accessibility of the transition metal ion for reactants and it is quite conceivable that interstitial ions and positive holes would only operate catalytically after conversion into the equivalent situation involving a Cl vacancy.

#### IV. THE NUMBER OF CL VACANCIES AS A FUNCTION OF CRYSTAL SIZE

From the picture developed in the preceding section the number of Cl vacancies as a function of size and shape of an elementary sheet of  $\alpha\text{-TiCl}_2$  easily follows. The rhombus sheet should carry  $4(m-1)$  Cl vacancies per  $(m-1)^2$  ions  $\text{Ti}^{2+}$  which gives the quantity of Cl vacancies ( $h$ ) in equivalents per mole of  $\alpha\text{-TiCl}_2$ :

$$h = 4(m-1)/(m-1)^2 = 4/(m-1) \approx 4/m \quad (1)$$

If an arbitrary number of sheets is stacked to form the crystal this formula still holds as each sheet contributes equally. Thus only the dimension in the plane of the sheet, i.e. perpendicular to the principal axis of the crystal, influences the magnitude of  $h$ . When this dimension ( $d$ ) is expressed in  $\mu$  ( $10^{-4}$  cm) and the diameter of a Cl ion is taken as  $3.60 \text{ \AA}$ , Eq. (1) is easily converted into

$$h \approx (1.44 \times 10^{-3})/d \quad (2)$$

Equations (1) and (2) apply rigorously only to the case of rhombus sheets but it is easily verified that it gives the correct order of magnitude of  $h$  for crystals of any reasonably compact shape. The formula indicates that for particles of a size well under  $1 \mu$ , as encountered under the conditions of Ziegler-Natta polymerization, the molar amount of Cl vacancies is sufficient to be correlated with the number of active sites.

Also for the case of  $\alpha\text{-TiCl}_3$ —which is of greater practical importance— $h$  may be calculated. As is seen in Fig. 1 only two thirds of the octahedral interstices are filled with  $\text{Ti}^{3+}$  ions. Consequently in a rhombus sheet with large  $m$  there are  $(1/3)(m-1)$  Ti vacancies along an edge and at each of them there is also a Cl vacancy. These vacancies correspond to Cl ions that would not be bound to any Ti ion. It follows that  $2(m^2-1) - (4/3)(m-1)$  Cl ions are necessary for fully coordinating  $(2/3)(m-1)^2$   $\text{Ti}^{3+}$  ions. Consequently the number of Cl vacancies needed for electroneutrality is  $2(m^2-1) - (4/3)(m-1) - 2(m-1)^2 = (8/3)(m-1)$  and therefore

$$h = \frac{(8/3)(m-1)}{(2/3)(m-1)^2} = \frac{4}{(m-1)} \approx \frac{4}{m}$$

Thus (2) also applies for  $\alpha$ -TiCl<sub>3</sub>.

While for the rhombus sheet  $d$  is the length of the side, for crystals of the shape of a regular hexagon  $d$  stands for the diagonal.

It will be clear that considerations of this kind are valid generally for ionic layer lattices. Therefore the above formulae also apply to  $\gamma$ -TiCl<sub>2</sub> and  $\gamma$ -TiCl<sub>3</sub>, in which the Cl ions are arranged according to a cubic close packing. For the case of  $\beta$ -TiCl<sub>3</sub>, which consists of threadlike macromolecules,  $3(n+1)$  Cl ions are necessary for fully coordinating  $n$  Ti<sup>3+</sup> ions giving the number of Cl vacancies per thread as 3. In this case  $h = 3/n$ . Expressing  $h$  in the dimension of the crystal along the  $c$ -axis,  $l$ , one finds  $h = (0.88 \times 10^{-3})/l$ .

In all cases  $h$  only gives the order of magnitude of the number of Cl vacancies and may vary considerably with the shape of the crystal. Of greater importance for the following discussion is the fact that independent of size and shape of crystals the number of Cl vacancies is practically equal to the number of Ti ions situated at the edges of the sheets. This equality is readily demonstrated by the example of Fig. 2, the number of Cl vacancies being  $4(m-1)$  whereas  $4(m-1) - 4$  Ti ions are situated at the edge. However, it follows generally from the fact that in the interior of a perfect crystal the full coordination leads to zero charge; at the exterior uncomplete coordination is necessary for maintaining electroneutrality. Whether in the layer structures under consideration the Cl vacancies actually are located at the Ti ions of the edges will be discussed next.

## V. LOCATION OF CHLORINE VACANCIES

If it is admitted that crystals of transition metal chlorides carry Cl vacancies the question arises whether the vacancies occur preferentially at the surface of the sheet or at its edges. Therefore the energies necessary for removing a Cl ion in both situations should be compared. In order to get an estimate of this energy difference the transition metal chlorides will be considered as completely ionic compounds. Only the

Coulomb part of the energy will be calculated and all other energy terms will be omitted. This seems permitted because not only is the Coulomb part by far the greatest but also because the most important other terms, the Born repulsion and the term due to the polarization of the Cl ions, have opposite sign and partially cancel each other. Moreover the calculations only refer to crystallographically different sites in the same compound and it is only the difference of energy between these sites that is of interest to us.

For the most primitive model of the elementary sheet of TiCl<sub>2</sub>, the hypothetical particle [Ti<sub>4</sub>Cl<sub>16</sub>]<sup>8-</sup>, in which the Ti ions are completely surrounded by Cl ions, it was found that the Cl ions at the edge are more strongly repelled than those at the center. The same result was obtained for the simplest models of TiCl<sub>3</sub>, viz. the particle [Ti<sub>6</sub>Cl<sub>24</sub>]<sup>6-</sup> in which 6 Ti<sup>3+</sup> ions form a regular hexagon with an empty octahedral hole at its center, and [Ti<sub>4</sub>Cl<sub>18</sub>]<sup>6-</sup> in which the center and three alternate corners of a regular hexagon are occupied by a Ti<sup>3+</sup> ion.

These results indicate that Cl ions will be more strongly bound in the middle of a sheet than at its edges and that consequently Cl vacancies most probably will occur at the edges. In order to check this preliminary conclusion more realistic models for TiCl<sub>3</sub> were used. For a Cl ion in the middle of the surface of a sheet the net attraction energy due to all ions in this sheet lying within a certain radius around the Cl ion was calculated. The contributions of the ions lying at the circumference of this spherical segment were taken into account for such a part that the net charge of this segment was zero or +1e, whereas the sheet outside the segment was considered as a neutral continuum. For the Cl ion at the edge of the sheet half a spherical segment was used. In the latter case the calculated energy depends on the model chosen for the edge itself. At the edge of a sheet the Cl ions in both layers and the Ti ions will lie in parallel rows. In the Ti rows pairs of Ti ions alternate with empty octahedral sites. The latter would carry a Cl ion not directly bound to any Ti ion and therefore there must be a Cl vacancy at this site anyway. The Cl ions around the pairs of Ti ions are of two kinds.

Part of them are bound to two Ti ions and part of them are bound directly to one Ti ion. It is obvious that the former will be bound more firmly than the latter, which may thus be more easily removed. Three modes of removing two of these Cl ions from a pair of Ti ions are possible and the resulting situations at the edges (A, B, C) are given in Fig. 3. With mode A, both Cl ions are taken from the outer row, with B from the inner row and with C one from the outer

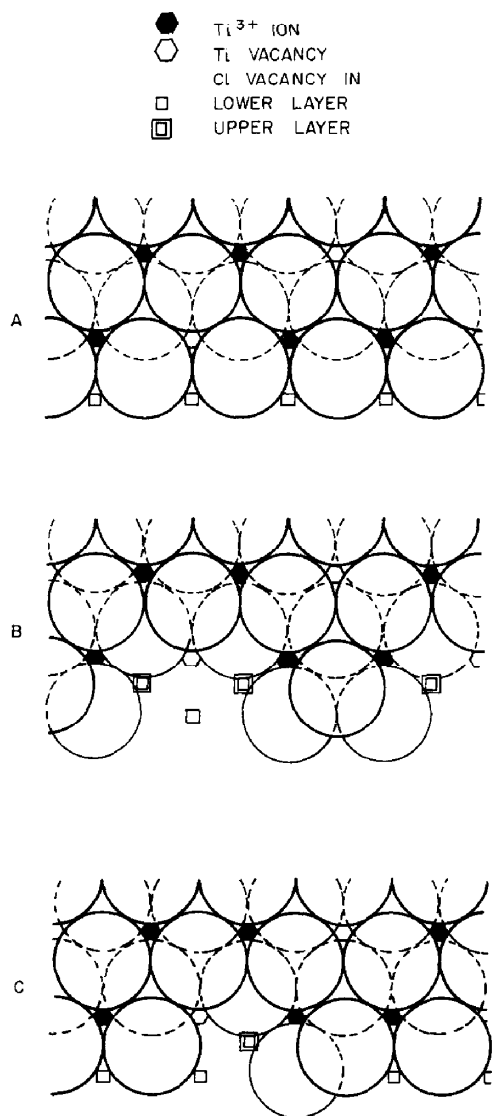


FIG. 3. Possible arrangements of chlorine vacancies at the edge of a  $\text{TiCl}_3$  sheet.

and one from the inner row.\* In Table 1 the attraction energies calculated have been assembled.

It appears that neither extension of the segment to the underlying sheet (cf. I and II) nor variation of the segment radius (cf. III and VI) affects the magnitude of the attraction energy appreciably. This was confirmed by computation of the attraction energy towards the central  $\text{Ti}^{3+}$  ion of a cube-shaped crystal and a square sheet of  $\alpha\text{-TiCl}_3$  for models of varying size. The difference between the energies for models containing 30 and 10 000 Ti ions appeared to be about 10%.

Notwithstanding the disregarding of energy terms other than the coulomb energy the calculated attraction energies are of the right order of magnitude. This follows from a comparison of the calculated Coulomb part of the lattice energy of an  $\alpha\text{-TiCl}_3$  sheet (1036 kcal/mole) with the lattice energy of  $\alpha\text{-TiCl}_3$  (1233 kcal/mole) derived from thermodynamic data (8). Therefore it is felt that appreciable differences in attraction energy found on applying comparable simplifications for different models must be significant.

Thus the most important conclusion from Table 1 is that in the middle of the surface of an  $\alpha\text{-TiCl}_3$  sheet, i.e. at the (0001) face of the crystal, Cl ions are much more strongly bound than at the edges (cf. I, II, with III, etc.). Consequently Cl vacancies will occur preferentially at the edges and hardly, if at all, at the basal plane of the crystal.

Qualitatively this conclusion agrees with the one arrived at by taking into account only the contributions of the directly contacting ions around a Cl ion. At the surface of the sheet every Cl ion is bound directly to two Ti ions whereas at the edge two out of three Cl ions are in contact with only one Ti ion. This effect is only partly compensated for by the greater number of repelling Cl ions around the site at the surface.

Table 1 (cf. III, IV, V) also shows that the arrangement C of Cl ions and vacancies

\* In Fig. 3 the outer row is part of the lower layer and the inner row belongs to the upper layer of Cl ions.

TABLE I  
 ATTRACTION ENERGY OF A CL ION TOWARDS  $\text{TiCl}_3$ 

No.	Form	Radius ( $\times 2r_{\text{Cl}^-}$ )	Characteristics	Charge (e)	Composition	Attraction energy (kcal/mole $\text{Cl}^-$ )
I	Spherical segment	$\sqrt{13}$	Site on 0001	0	$\text{Ti}_{32}\text{Cl}_{96}$	313
				+1	$\text{Ti}_{32}\text{Cl}_{96}$	338
II	Spherical segment <sup>a</sup>	$\sqrt{13}$	Site on 0001	0	$\text{Ti}_{52}\text{Cl}_{156}$	278
				+1	$\text{Ti}_{52}\text{Cl}_{156}$	303
III	Half spherical segment	$\sqrt{13}$	(A) All Cl from outer row	0	$\text{Ti}_{15}\text{Cl}_{45}$	139
				+1	$\text{Ti}_{15}\text{Cl}_{44}$	164
IV	Half spherical segment	$\sqrt{13}$	(B) All Cl from inner row	0	$\text{Ti}_{17}\text{Cl}_{51}$	139
				+1	$\text{Ti}_{17}\text{Cl}_{50}$	165
V	Half spherical segment	$\sqrt{13}$	(C) Cl for $\frac{1}{2}$ from inner, for $\frac{1}{2}$ from outer row	0	$\text{Ti}_{15}\text{Cl}_{45}$	107
				+1	$\text{Ti}_{15}\text{Cl}_{44}$	132
VI	Half spherical segment	$\sqrt{7}$	(A) All Cl from outer row	0	$\text{Ti}_8\text{Cl}_{24}$	143
				+1	$\text{Ti}_8\text{Cl}_{23}$	177

<sup>a</sup> This segment comprises one underlying sheet.

at the edge should be favored above A and B. This is qualitatively in accordance with the fact that in C the loosely bound Cl ions are as far apart as possible whereas in A and B they touch each other. However, the differences in attraction energies (about 20%) are not considered large enough to eliminate A and B, which, therefore, will be included in the further considerations.

The conclusion regarding the location of the Cl vacancies naturally applies also to  $\gamma\text{-TiCl}_2$  and  $\gamma\text{-TiCl}_3$ . Similarly, the three vacancies per threadlike molecule of  $\beta\text{-TiCl}_3$  will not be found somewhere within the thread but at its ends where Cl ions only bound to one  $\text{Ti}^{3+}$  will occur.

#### VI. THE GEOMETRY AT $\text{TiCl}_3$ CRYSTAL FACES OTHER THAN (0001)

When elementary sheets are stacked their combined edges form the crystal faces other than (0001). Quite a few faces that could carry the Cl vacancies may be constructed in this way; which of these faces actually occur at  $\text{TiCl}_3$  crystals is not exactly known.

For the sake of the argument we shall deal especially with one face normal to (0001), viz. (10 $\bar{1}$ 0).

The detailed picture of this face will depend on the arrangements of Cl vacancies supposed to be present at the edges (A, B, or C of Fig. 3). When edges are combined that carry only one of these arrangements, A and B each give one type of 10 $\bar{1}$ 0 face, a (Fig. 4) and b (Fig. 5), respectively whereas C can be combined in two ways,  $c_I$  (Fig. 6) and  $c_{II}$  (Fig. 7). It is seen that—on an atomic scale—(10 $\bar{1}$ 0) is not as smooth as (0001), in which all Cl ions lie in the same plane. This applies also to other faces especially when edges with the arrangement C, which probably is preferred, are combined. In all cases the Ti ions are coordinated with five Cl ions and one Cl vacancy.

Starting from the most regular situation, a (Fig. 4), the other situations may be obtained by systematically shifting loosely bound Cl ions, L, to the vacancy of their own Ti ions. The Cl ions, F, bound to two Ti ions remain fixed. Shifting both L's

around a pair of Ti ions gives situation b (Fig. 5). Shifting one L may be done in two ways: either along a line  $x$ , which gives  $c_I$  (Fig. 6) or along  $y$ , which gives  $c_{II}$  (Fig. 7).

the surface polarization effects will be of greater importance than in the interior; moreover deviations from the exactly octahedral configuration may occur. Apart from

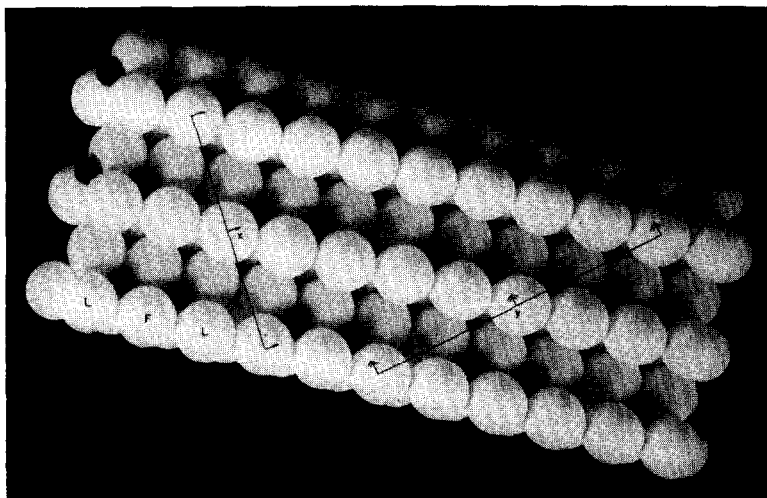


FIG. 4. Structure of face  $(10\bar{1}0)$ . a. Chlorine arrangement A.

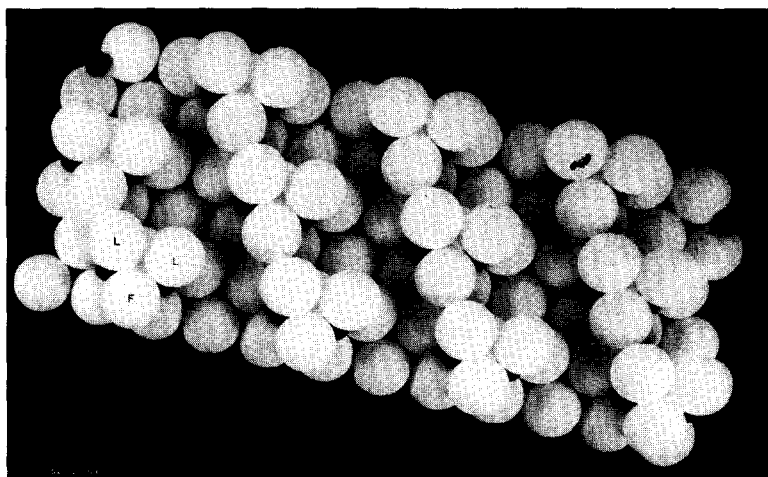


FIG. 5. Structure of face  $(10\bar{1}0)$ . b. Chlorine arrangement B.

It will be obvious how a  $10\bar{1}0$  face can be obtained in which the three arrangements A, B, and C all occur, e.g. in a random distribution.

Naturally the picture of the catalyst surfaces developed here still is primitive, being based upon ions considered as hard spheres and occupying positions derived from the structure of the interior of the crystal. At

these details we believe that the representation is essentially correct and may be applied in the further considerations.

#### VII. THE SITUATION OF EXPOSED TI IONS

Every exposed Ti ion is a potential active center and its situation deserves detailed consideration. Of the five Cl ions surround-

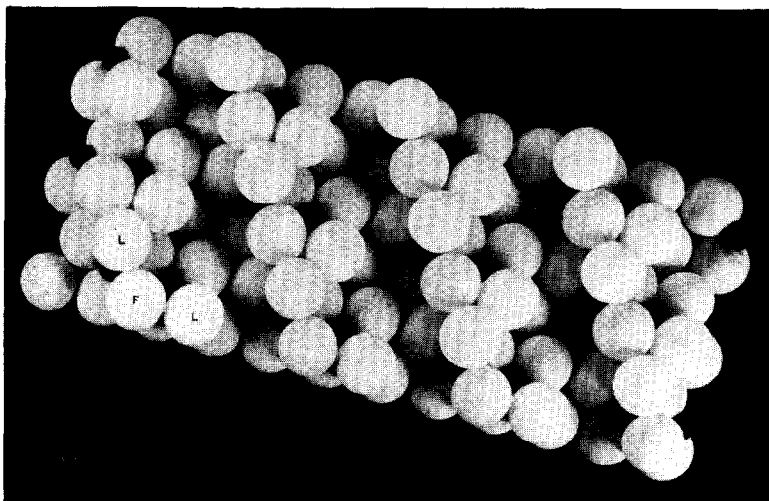


FIG. 6. Structure of face  $(10\bar{1}0)$ . c<sub>I</sub>. Chlorine arrangement C.

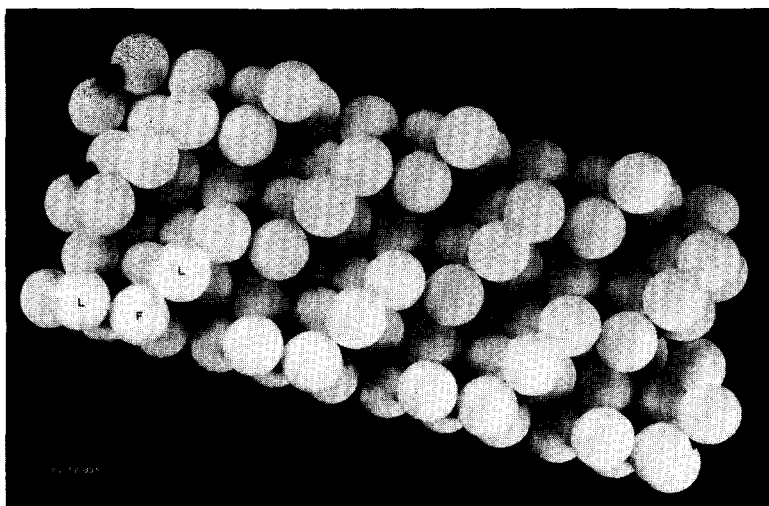


FIG. 7. Structure of face  $(10\bar{1}0)$ . c<sub>II</sub>. Chlorine arrangement C.

ing such a Ti, four are directly bound also to a second Ti ion. Therefore these four Cl ions are fixed and under mild conditions will not enter into chemical reactions. The one Cl ion bound directly only to the exposed Ti ion will be more reactive.

The Cl vacancy is at the apex of a square pyramid the base of which has four Cl ions (among which is the loosely bound one) at its corners and the Ti ion at its center. Opposite the Cl vacancy lies the fifth Cl ion which anchors the center to the crystal. From the geometry of the arrangements A,

B, and C in a sheet (Fig. 3) it follows that the square bases include an angle of  $54^{\circ}44'$  with the basal plane (0001) of the crystal. As in general crystal faces other than (0001) are obtained by stacking of sheets this statement applies to all faces. The square bases are always parallel to one of the axes  $a$ ,  $b$ , or  $d$  of the crystal. Identifying the edge with the  $d$  axis, in Fig. 4 the square bases are parallel to  $d$ , in Fig. 5 to  $a$  and  $b$ , in Fig. 6 to  $d$  and  $a$ , and in Fig. 7 to  $d$  and  $b$ .

From Figs. 4-7 it can be concluded that when the square bases are not parallel to



the edge, they carry the loosely bound Cl ion in the most prominent position possible. It should be noted that if the loosely bound Cl ion and the Cl vacancy were interchanged the same statements would apply. The situation of Fig. 4 would change into that of Fig. 5 and *vice versa*. It is stressed, however, that the sites of the Cl vacancy and the loosely bound Cl ion are not equivalent crystallographically. Comparison of Figs. 4 and 5 shows that in the former the loosely bound Cl ions (L) are in the same plane as the fixed Cl ions (F), whereas in the latter the ions L are situated above the plane of the ions F. From the fact that the square bases always include an angle of  $54^{\circ}44'$  with

the basal plane it follows that only for  $(10\bar{1}1)$  may they lie in the crystal face itself. For all other faces the square bases will be in an oblique position with respect to the crystal face.

The great number of possible situations of square bases, dependent on the choice of the crystal face and the arrangement of Cl ions, forbids their separate discussion. However, a characterization applying to all of them and examples of situations at  $(10\bar{1}0)$  can be given.

Quite generally a square base contains, firstly, two "exposed" Cl ions, the loosely bound Cl ion (L) and the most protruding fixed one of the center (F), and, secondly,

THE SITUATION AROUND A PAIR OF TI IONS FROM FIG. 7

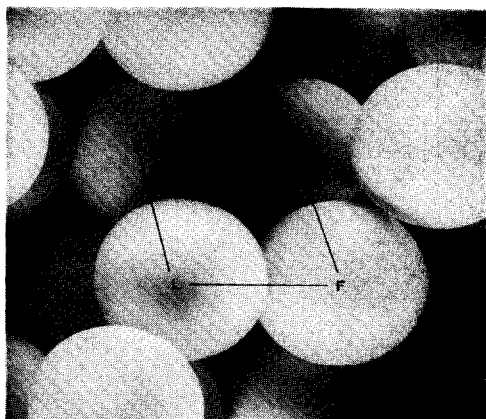


FIG. 8. Square base parallel to  $d$  axis.

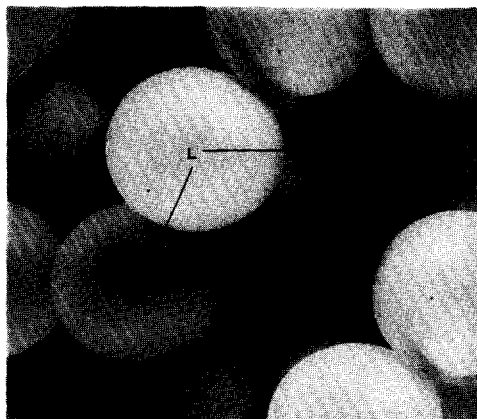


FIG. 9. Square base parallel to  $a$  axis.

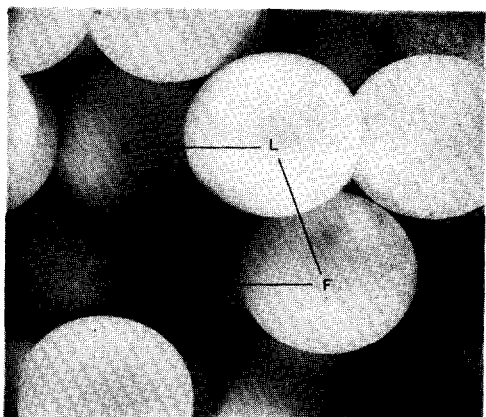


FIG. 10. After interchange of L and Cl vacancy of Fig. 8.

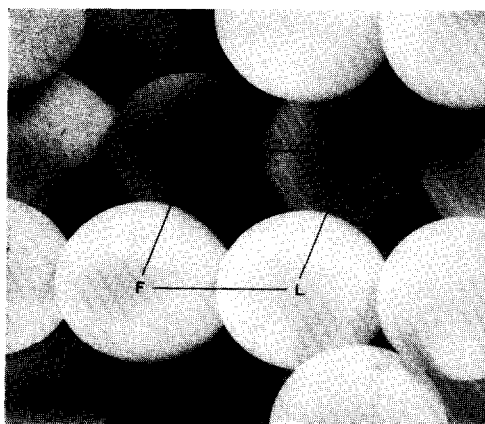


FIG. 11. After interchange of L and Cl vacancy of Fig. 9.

two "blocked" Cl ions (B), which to a certain extent are embedded in the crystal. This is shown in the closeups (Figs. 8-11) of a pair of Ti ions in their surroundings at the  $10\bar{1}0$  surface  $c_{11}$  of Fig. 7.

The general picture of the situation of an exposed Ti ion at the crystal surface developed here forms a necessary element for the theory of stereospecific polymerization of  $\alpha$  olefins, which will be given in a subsequent contribution (3). Especially the following points regarding the geometry of the exposed Ti ions will be used there:

(1) All potential active centers consist of a square base of four Cl ions around a  $Ti^{3+}$  ion, which is in an oblique position with respect to the crystal face [except in the case of the  $(10\bar{1}1)$  face].

(2) The four Cl ions of a square base are not equivalent. Two are sterically blocked (B) and two protrude from the crystal; one of the latter (F) is bound to two  $Ti^{3+}$  ions,

whereas the other (L) is only bound to the  $Ti^{3+}$  of the active center. The ion F is non-reactive, the ion L is reactive and might interchange its site with the Cl vacancy of the active center.

(3) The sites of the loosely bound Cl ion (L) and of the Cl vacancy are not equivalent.

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