

forces, and by the different forms of hydration of these crystals.

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Diffuse Scattering and Disorder in Urea Inclusion Compounds $\text{OC}(\text{NH}_2)_2 + \text{C}_n\text{H}_{2n+2}$

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Abstract

Diffuse scattering phenomena in urea inclusion compounds with hexadecane and dodecane adducts were investigated by X-ray and neutron diffraction methods from 380 down to 32 K. In the four different phases of the compound with hexadecane, more than six different kinds of diffuse scattering are found. Most intense are two diffuse layer-line systems perpendicular to the pseudo-hexagonal c^* axis with periods which are incommensurate with the Bragg layers which correspond to the averaged structure. Within these diffuse layers short-range-order maxima were observed. Strong Bragg reflections are accompanied by diffuse wings parallel to c^* . Wavy diffuse streaks parallel to the a^*b^* plane connect the Bragg reflections. A critical increase of diffuse scattering occurs as a precursor of superstructure reflections approaching the phase transition II \rightarrow III from above. A semi-quantitative interpretation of the diffuse layers is given in terms of longitudinal and lateral ordering/disordering of the paraffin chains within the urea framework. The wavy streaking may be understood as interfacial scattering. A complicated satellite pattern in the low-temperature phase (< 120 K) is analysed in terms of a domain structure caused by competing ordering forces within the paraffin-chain system and between host and guest.

I. Introduction

Urea inclusion compounds may be characterized by a framework of urea with open channels along a unique (c) axis exhibiting a honeycomb-like cross section. Within these channels chains consisting of n -alkane molecules $\text{C}_n\text{H}_{2n+2}$ are embedded. There are simple arguments against the naive assumption that the n -alkanes are nothing but weakly bound guests in a practically unaltered host (= urea) structure as in the case of zeolite or clathrate inclusion structures: pure urea crystallizes in a completely different (tetragonal) structure as compared with the adduct compound where it has - on average - a hexagonal symmetry (high-symmetry phase). The hexagonal framework collapses by decomposition several degrees below the melting point of pure urea (McAdie, 1962). The inclusion therefore stabilizes the framework, indicating remarkable interaction forces between host and guest. In addition there are direct interactions between the chain molecules in longitudinal (*i.e.* parallel to c) and lateral (perpendicular to c) directions. These competing temperature-dependent interactions are responsible for the occurrence of different phases and a variety of disorder phenomena which manifest themselves by more or less complicated diffraction patterns (Lenné, 1963; Lenné, Mez & Schlenk, 1970; Forst, 1984).

In the special adduct with hexadecane $C_{16}H_{34}$ as inclusion the chain length of the alkane molecules $c_i = 22.8 \text{ \AA}$ fits approximately with the doubled period of the urea framework $2c_0 = 22.03 \text{ \AA}$. This 'accident' causes some resonance-like structural phenomena. The analysis of the relevant diffraction patterns as a function of temperature shows four different phases (Forst, 1984). The determination and refinement of these structures is the subject of a separate paper (Forst & Jagodzinski, 1987). The high-temperature (hexagonal) phase I which is characteristic of all urea-alkane compounds transforms into a (pseudo-) trigonal phase II with doubling of the c lattice constant at about 360 K.

Phase II transforms by a lateral rearrangement into a phase III at 147.8 K which may be described by using a rhombic unit cell, but probably its real symmetry is monoclinic. Below 120 K this phase is succeeded by a heavily disordered domain structure (phase IV) with a superperiod of about 180 \AA , which is most probably due to the distribution function in the c direction. The true structure is still unknown in detail. This last transformation exhibits a transformation (hysteresis) interval of more than 5 K. A subsequent paper is concerned with the transition mechanisms in context with the results of the structural work (Boysen, Forst, Frey, Jagodzinski & Zeyen, 1986).

The present paper is devoted to the different types of diffuse scattering mainly for the case of hexadecane. As an approximation they will primarily be treated separately although the mutual influence of their physical origins has always to be kept in mind. In the hexadecane adduct the situation is complicated owing to the nearly commensurate, but in fact incommensurate, substructures. None of the phases represents a real superstructure of the urea framework or a commensurate modulated structure, as might be concluded from $c_i = 2c_0$ in $C_{16}H_{34}$. In phases II, III and IV, the formation of domains leads to a splitting of Bragg reflections or the occurrence of very narrowly spaced satellite reflections. A summary of structural data is given in Table 1.

II. Experimental observations

X-ray and neutron experiments were carried out to study the diffuse scattering phenomena. A preliminary account of part of the present work was given by Boysen, Forst, Jagodzinski & Zeyen (1981) and Forst, Jagodzinski, Boysen & Frey (1984). X-ray pictures were taken mostly with conventional normal-beam techniques. A rotating anode with $Cu K\alpha$ radiation was used in most of the experiments, some were made with $Mo K\alpha$ radiation. A bent Ge(111) monochromator provided a variable monochromatic focusing geometry to focus the beam on the film or on the sample. Other experimental details are given in the

Table 1. Summary of structural data

Phase	Average structure	Order/disorder
Dec	Tetragonal urea + paraffin	
380 K I	Hexagonal, $P6_122$ $a_0 = 8.2, c_0 = 11 \text{ \AA}$	Longitudinal disorder in adjacent channels; orientational disorder in each channel
365 K II	~Trigonal, $P3_12$ $c = 22 \text{ \AA} = 2c_0$	Longitudinal disorder in adjacent channels; orientational disorder in each channel. Mutual longitudinal deformation (end groups) (microdomains in ab plane)
148 K III	~Rhombic, $P2_12_12_1$ $a = 8.2, b = 14.2 \text{ \AA}$	Lateral orientational order of guests in adjacent channels
120 K IV	Triclinic? Two lattices	Domain structure (host) ~200 $\text{\AA} \parallel c$

figure captions. The neutron experiments were carried out on instruments D10 of the Institut Laue-Langevin, Grenoble and MANII of FRM, Garching.

The typical features of diffuse scattering observed at room temperature are described in the following:

(1) There is a system of periodic diffuse layers which are sharp along the c^* direction (Fig. 1), *i.e.* their widths parallel to c^* are within experimental error as small as those of the Bragg peaks. These diffuse layer lines will be called s layers. There is no s layer of zeroth order [see also (5) below]. In the room-temperature phase II the distance of these s layers in reciprocal space is slightly smaller than 1/2 of the reciprocal coordinate l which corresponds to the c period of the urea host lattice. Obviously, the s system represents an incommensurate structure of the inclusion. This may be concluded from the higher-order layers of even order, $l' = 2n$, which do not coincide with the Bragg layers. The c' period is found to be 22.6 \AA which is close to, but not exactly equal to c_i , the length of $C_{16}H_{34}$ in pure paraffin crystals (Laves, Nicolaides & Peng, 1965). The intensity within the s layers decreases approximately monotonously for all directions in reciprocal space

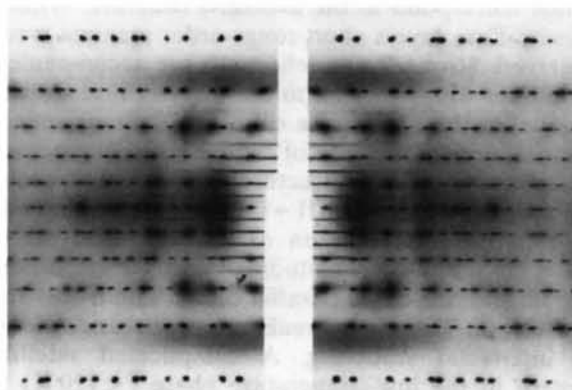


Fig. 1. Oscillation photograph around the c axis ($\pm 30^\circ$) of the hexadecane adduct; normal-beam technique; $Cu K\alpha$ radiation; 5 h exposure time; ambient temperature.

perpendicular to the c^* axis. Obviously, there are no sharp Bragg peaks superimposed exactly on these layers. Weissenberg photographs, however, reveal some modulation within these layers (Fig. 2a). There are weak and broad intensity concentrations centred at positions $h, k = \text{integer}$. This modulation is most prominent in the first two layers close to the meridian. In addition there is a very weak streak system which is observable also in the higher s layers as found by Weissenberg photographs.

Equivalent observations were also made at room temperature in the urea-dodecane compound. There is an equivalent s -layer system (Fig. 3) with a c' period corresponding to the chain length of the $C_{12}H_{26}$ molecule. Within the first s layer modulations are again visible (Fig. 2b) which are quite similar to those mentioned above.

(2) A second periodic diffuse layer system perpendicular to c^* is considerably broadened parallel to c^* in contrast to the s system. This diffuse system will be called d bands hereafter. The first order of these d bands can be seen on Fig. 1, but - as will be discussed in the next section - the strong diffuse background surrounding the zero layer line except the region around the c^* axis could belong to this system, too. With shorter Mo $K\alpha$ radiation this system was observed up to the second order in normal-beam geometry (Fig. 4). By the equi-inclination technique focusing on the 13th Bragg layer was achieved which is fairly close to the third order of the d band. This

was done to confirm the observation that the diffuse d bands of odd order show a kind of extinction, or at least a systematic intensity reduction around the meridian. The distance of the d bands in the c^* direction is approximately 4.3 times c_0^* . Consequently, a distance of $11.05 \text{ \AA} / 4.3 = 2.56 \text{ \AA}$ may be estimated in direct space. Obviously this distance corresponds to the identity period of the nearly periodic alkane molecule. The intensity increases monotonously into all directions perpendicular to the c^* direction (axial symmetry), and decreases after having passed a maximum. Owing to the very low intensity of the higher orders of the d -band system it is hard to decide whether the width of the d bands grows with increasing l' coordinate.

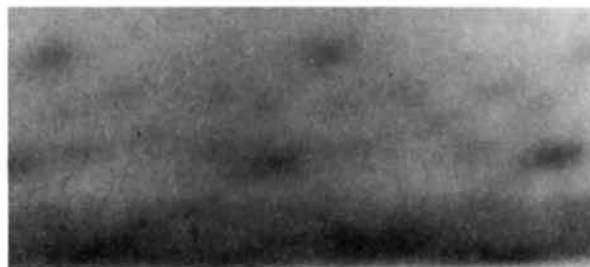
(3) Clearly visible on Fig. 1 is a diffuse scattering accompanying the strong Bragg reflections of the urea host structure. Figs. 1 and 3 both reveal a fanning out along directions parallel to c^* . Although some influence of (the acoustical branches of) thermal diffuse scattering cannot be excluded, there is a major intensity part most probably of static origin. This may be concluded from the temperature dependence discussed below.

(4) Besides the usual diffuse scattering there is a typical diffuse contribution which is distributed nearly continuously in reciprocal space (monotonic Laue scattering), the origin of which is due to fluctuations of atomic positions other than thermal (f scattering). Its static origin may be derived again by the observation of discontinuous changes near the transition temperatures.

(5) On a Weissenberg photograph (Fig. 5a) it is seen that the Bragg peaks are connected by wavy streaks. Mean directions of these streaks are $[\xi 0 0]$ and $[0 \eta 0]$, but close to the Bragg maxima there is a kinking approximately in the $[\xi \xi 0]$ direction. A schematic picture of this behaviour is sketched in Fig. 5(b). These wavy streaks occur in Bragg layers of higher order as well.



(a)



(b)

Fig. 2. Weissenberg photographs of the first diffuse s layer of the hexadecane adduct (a) and dodecane adduct (b); Cu $K\alpha$ radiation, 20 h exposure time, ambient temperature. The weak 'reflections' on top of the diffuse scattering do not belong to this layer but to the neighbouring Bragg sheet (limited resolution).

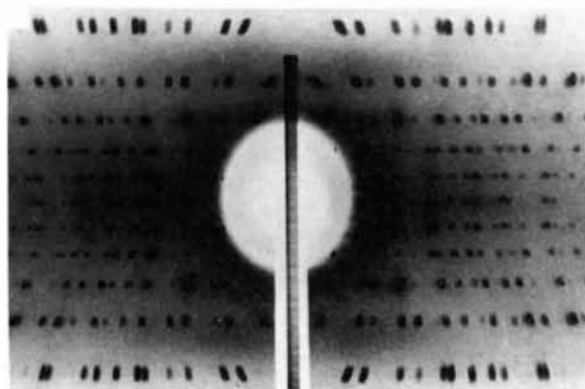


Fig. 3. Oscillation photograph of the dodecane adduct; no focusing on the film; other conditions see Fig. 1.

Temperature dependence

The study of the temperature dependence of the diffuse phenomena is necessary in order to relate the disorder phenomena to the different phases. It will be shown in § III that a semi-quantitative interpretation of important structural elements of the diffuse scattering is possible after carefully studying its behaviour as a function of temperature.

The *s* and *d* layer-line systems are nearly temperature independent in phases I–III. Fig. 6(a) shows a photograph taken at 150 K, *i.e.* close to the transition II → III, and Fig. 6(b) shows an equivalent X-ray pattern taken at 117 K. In the area of the first *d* band the layer lines become more pronounced. Both systems remain still observable in phase IV at low temperatures (Fig. 7), but their integral intensity is reduced considerably. Instead sharp Bragg reflections occur exactly on the *s* layers in phase IV. These are most intense in the area of the first *d* band (*cf.* Fig. 7).

A similar temperature behaviour is found in phases I–III for the diffuse streaking parallel to c^* around the Bragg reflections described above under item (3). Most striking is the rapid disappearance below the transformation III → IV. Instead of these diffuse wings, series of satellite reflections develop which are sharp (along c^*) within the limits of resolution.

Some 50 K above the phase transition II → III (~148 K), a new type of diffuse scattering occurs. Within the Bragg layers (due to the averaged host structure) diffuse peaks (*c* type) develop as a precursor of the lateral ordering process being responsible for this phase transition. Near the transition point there is a critical increase within a range of several degrees. Just at the transition point sharp Bragg reflections grow up at these positions indicating the new structure within the *ab* plane (Fig. 8). Below the transition the diffuse *c* intensity disappears completely, while the Bragg reflections split due to twinning and intergrowth. These new reflections are free from diffuse contributions. A detailed analysis of

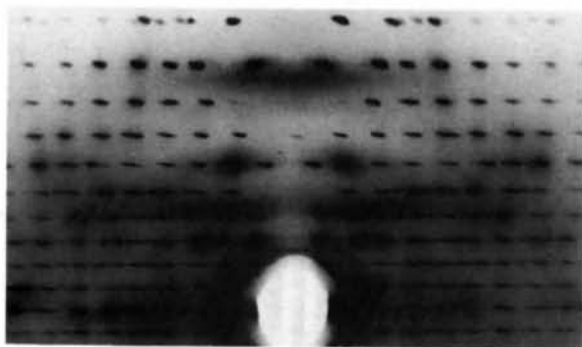
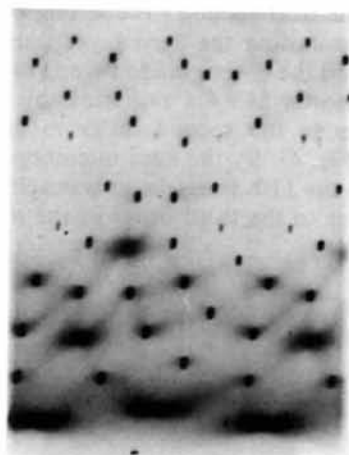


Fig. 4. Oscillation photograph ($\pm 30^\circ$) of the hexadecane adduct; equi-inclination technique, $\mu = 22.7^\circ$ (*i.e.* 13th Bragg layer); Mo $K\alpha$ radiation; 12.5 h; ambient temperature.

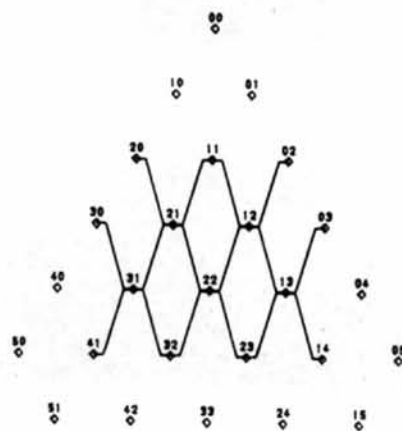
these diffuse intensity contributions is certainly hampered by the overlap with the wavy streaks mentioned above under (5) which also disappear below T_c .

A few additional neutron experiments were carried out for two reasons: (a) some diffuse phenomena might be specifically related to the H ordering and thus hardly visible in X-ray pictures, and (b) the static or dynamic origin of the diffuse scattering can be studied by an energy analysis of the scattering intensity. This may be performed by a simple comparison between an energy-integrating diffractometer measurement and a measurement in a pure elastic configuration of the instrument. We report here the results concerning the *s* and *d* scattering, while the *c* diffuse scattering is discussed more extensively by Boysen *et al.* (1986).

A selection of diffractometer scans parallel to c^* in phase II is shown in Fig. 9. A (00 l') scan (Fig. 9a) shows the *s* layers up to 11th order. Note that all even orders are hidden by the almost superimposed Bragg reflections due to the host structure. A scan at



(a)



(b)

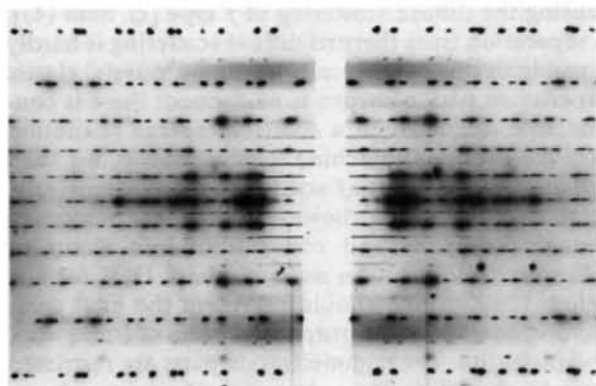
Fig. 5. (a) Weissenberg photograph of the *hk0* layer of hexadecane adduct; Cu $K\alpha$; 90 h; ambient temperature. (b) Schematic rectified picture of the pattern given in (a).

$h = 0.35$, $k = 0$ was performed (Fig. 9b) to reveal all the orders. The question why the first two s layers are not visible in Fig. 9(b) is discussed in the following section. The intensities are strongly diminished and completely unobservable further out in the radial direction (Fig. 9c). This latter figure shows clearly the d bands of zeroth and first order. In Fig. 10 a radial section through the first d band is shown. The general intensity behaviour, in particular the minimum at $h = k = 0$, is in accordance with the X-ray

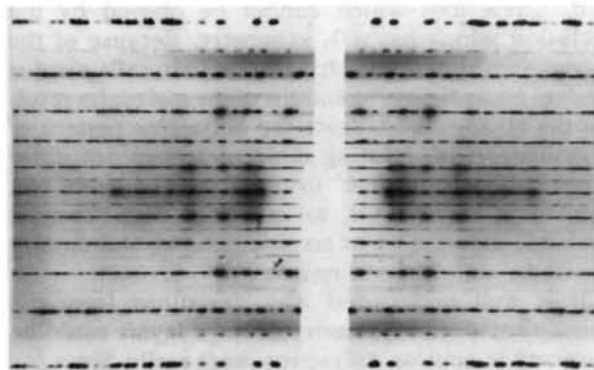
results. In consequence, there is no principal difference between X-ray and neutron data in phases II and III. The comparison of the integral with the elastic neutron measurements reveals no remarkable difference, indicating the static origin of these phenomena (at least within the limits of resolution of the instruments).

III. Interpretation of diffuse scattering

From the analysis of the averaged structure of the urea framework at room temperature (Forst & Jagodzinski, 1987) it is known that there are correlations between the alkane molecules and the framework, because certain low-order reflections other than $hk0$ cannot be explained in terms of the framework alone. In spite of this observation the sharp s layers with a periodicity incommensurate with the framework in the c^* direction show that there is no systematic position of the alkane chains with respect to the framework. On the other hand, it may easily be shown by simple integration of the continuous positions of the atoms that its contributions



(a)



(b)

Fig. 6. Oscillation photographs as in Fig. 1; $T = 150$ K (a) and 117 K (b).

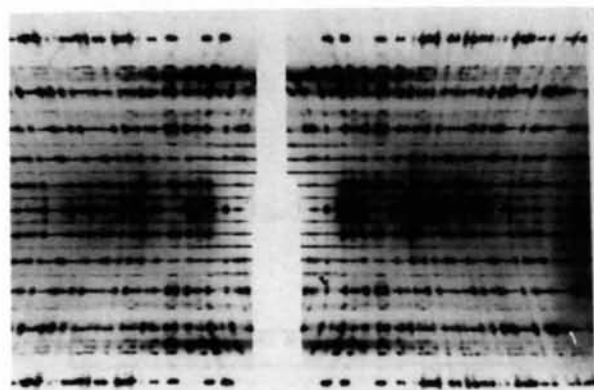


Fig. 7. Oscillation photograph as in Fig. 1; $T = 32$ K.

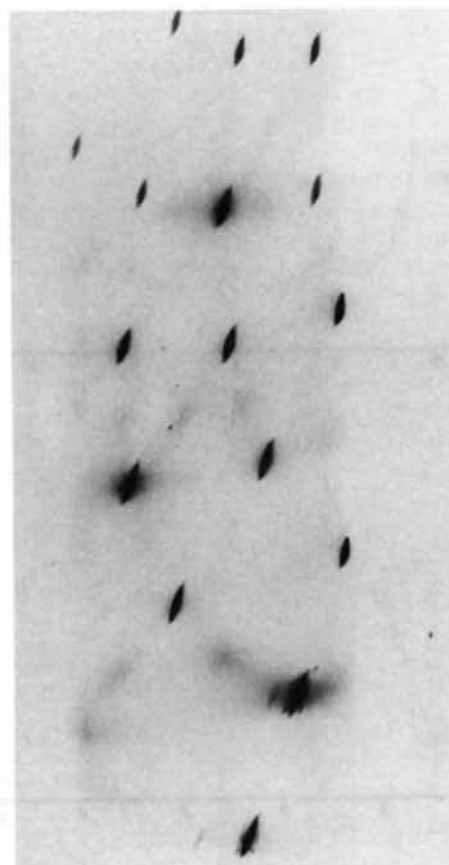


Fig. 8. Section from a Weissenberg photograph of the $hk0$ layer taken at $T = 147.7$ K (phase transition II \rightarrow III).

to the averaged structure must be zero, because

$$f_{\nu} \int_{-1/2}^{+1/2} \exp \{2\pi i(hx_{\nu} + ky_{\nu} + lz)\} dz = 0 \quad (l \neq 0) \quad (1)$$

if all positions have the same probability, as demanded by an independent incommensurate structure. Hence, we may conclude that certain atoms of the inclusion and the framework deviate systematically from their ideal positions such that the periodicity of the partner is taken into account. The positions of the atoms involved in this process are no longer

distributed uniformly along c , c' respectively, in the averaged unit cell of the partner, but show periodicities originating from these systematic displacements. As a consequence, both the framework and the inclusion contribute to sharp reflections of the partner generating the average structure. Since this effect is not periodic in terms of a systematic displacement, a continuous distribution of the displacements of certain atoms has to be introduced, hampering structure analysis of the average structures considerably. This correlation process belongs to a disorder causing the diffuse scattering of f type [*cf.* item (4)]. A separation from thermal diffuse scattering is hardly possible in this case, even if a tedious 'purely' elastic experiment with neutrons is performed: there is considerable doubt about a sufficient energy resolution of a conventional machine. Consequently, we shall not discuss the diffuse f scattering more extensively. It should be added, however, that this scattering should disappear and concentrate into sharp or diffuse reflections, if an ordered phase IV is formed below 120 K which should represent the final commensurate stage of the ordering process of framework and inclusion. The commensurate parts are restricted to small domains.

The idealized structure of the urea framework has a 6_1 screw axis which cannot be obeyed by the inclusion which has a 2_1 symmetry. Because of the incommensurate geometry of the unit cells six (or twelve) equivalent orientations of the molecules result for the alkane chain. Since the diffraction pattern of a structure with rotating molecules does not differ appreciably from that to be expected from six equivalent orientations, we may start with the most probable assumption of six orientations, and modify it without difficulties if necessary.

It is well understood why deviations from the pseudo-rotational symmetry of the s layers could be observed in neutron diffraction more easily. Since the H atoms contribute very little to X-ray diffraction, and the C atoms are not displaced considerably from

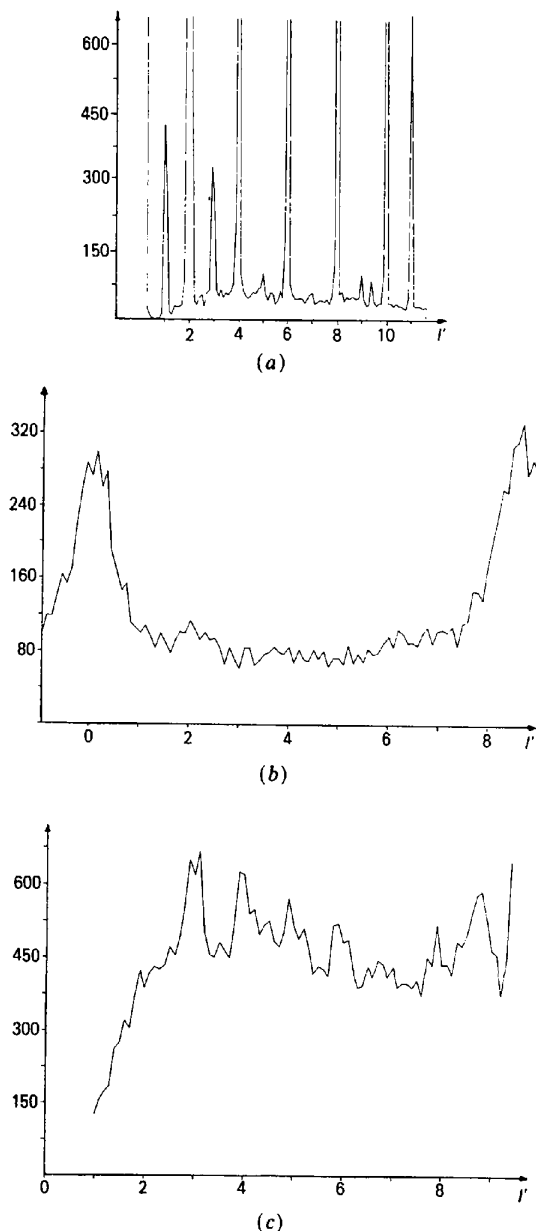


Fig. 9. Purely elastic neutron scans across the diffuse layers parallel to c^* at positions: (a) $h = k = 0$ ($T = 165$ K), (b) $h = 0.35$, $k = 0$ ($T = 165$ K) and (c) $h = 2$, $k = 0.5$ ($T = 205$ K).

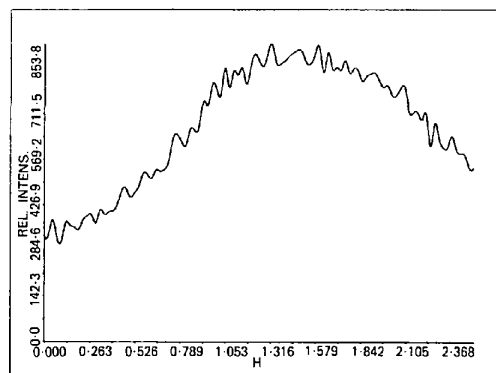


Fig. 10. Neutron diffractometer scan perpendicular to c^* at the position of the first d layer; $T = 200$ K.

the channel axis, the difference between a rotation and a sixfold position of the chain is mainly determined by the H atoms (or deuterons respectively), and only a small contribution to X-ray diffraction results.

Different models may be discussed to explain the diffuse (*s* and *d*) layer-line systems perpendicular to the c^* axis (referring here and in the following always to a (pseudo-) hexagonal setting). To treat the problem in a simplified manner one may separate longitudinal fluctuations of rigid chain links (*i.e.* the paraffin molecules) along one channel from different orientations of the molecules within a channel.

Positional disorder within one chain in a single channel of the urea framework may also originate from fluctuations within one chain molecule like torsional flexure or bending or scissor-like longitudinal fluctuations of the skeleton of a plane (stretched) molecule. Longitudinal and lateral fluctuations may be imagined by orientational disorder within one chain – as mentioned – or fluctuations with respect to the orientational relationship between different chains and/or between single molecules of different chains. The end groups of a paraffin molecule may exhibit, additionally, a different behaviour. All these disorder phenomena may show an individual temperature dependence. Most probably the real behaviour is not correctly described by one or other model, but by a combination, more precisely by a correlation between different mechanisms. The separate discussion of the chain system in the compound does not mean that the inclusion is a free substructure of the compound. On the contrary, the interaction between host and guest is of essential influence for the order-disorder phenomena. This is proven by the results of the structural work and – as will be shown below – by common superperiods of the framework and the inclusion (not commensurate with c_1).

Let us consider in a first step a completely uncorrelated parallel chain system where each chain consists of rigid identical alkane molecules, at least in an averaged sense, and neglect for the moment the internal structure of one alkane molecule. From the observation of a sharp (with respect to the c^* direction) equidistant *s* layer-line system one may conclude there is a well defined unit cell within one chain which corresponds to the length of two alkane molecules. Two neighbouring molecules must occur either in the same orientation (within one channel) or all molecules have approximately rotational symmetry in an averaged sense. The absence of sharp Bragg peaks ($00l'$) superimposed exactly on the diffuse *s* layers indicates that the radial projection of all chains on the *c* axis is not periodic or, in other words, the chains show no long-range interchain correlations with respect to the *z* coordinate.

Longitudinal fluctuations in this simple picture of identical rigid molecules may only occur due to fluctu-

ations of the distance between the end groups of the molecules separated by a mean distance of 2.8 Å. This might be due to different potential minima provided by the surrounding urea matrix, or due to thermal excitation of the whole molecule. Beyond the usual (static or dynamic) Debye-Waller factor reducing the intensity of the corresponding 1-*d* Bragg peaks (= *s* layers) an evaluation of ΔF^2 which is responsible for diffuse scattering yields a contribution which is concentrated symmetrically around the *s* layers (Cowley, 1975). The first *d* layer, however, is not symmetric with respect to the position of the ninth *s* layer. Moreover, from an estimate of the width of a *d* band (measured parallel to c^*) a correlation length comparable with the length of one molecule is found. Correlations between end groups, except adjacent ones, cannot occur.

In the next step this model is extended by inclusion of static or dynamic orientational statistics of the rigid molecules both within one chain or between different chains. The approximate rotational symmetry is now realized by assuming a statistical arrangement of orientations in neighbouring channels. The channels themselves form a perfect ordered array within the *ab* plane. The diffraction pattern of a disordered structure of this type may be described again with the general rule that the sharp maxima are due to the structure factor $\langle F \rangle$ of the averaged arrangement, whereas the diffuse ones are determined by the difference $\Delta F^2 = \langle |F|^2 \rangle - |\langle F \rangle|^2$. Since the average has to be taken for the entity of all cell occupations of the periodic chain, the following results are obtained when – as in the former case – no correlations between the *z* coordinates of the chains in different channels are admitted (*cf.* Fig. 11 for explanation of parameters):

$$\begin{aligned} \langle |F|^2 \rangle &= G^2(h, k) G^2(l') \\ &\times \left\{ \int_{-1/2}^{+1/2} \exp \{ 2\pi i l' z' \} dz' L(l')^2 f_c \right. \\ &\times \left. [\cos 2\pi kx + \cos 2\pi kx + \cos 2\pi(h+k)x] \right\}^2 \\ &= G^2(h, k) G^2(l') \delta(l') L^2(l') \\ &\times \left\{ \frac{2}{3} f_c [\cos 2\pi hx + \cos 2\pi kx \right. \\ &\left. + \cos 2\pi(h+k)x] \right\}^2 \end{aligned} \quad (2a)$$

$$\begin{aligned} \langle |F|^2 \rangle &= G^2(l') L^2(l') (4f_c^2 \{ \cos^2 2\pi l' z' \\ &\times \frac{1}{3} [\cos^2 2\pi hx + \cos^2 2\pi kx + \cos^2 2\pi(h+k)x] \\ &+ \sin^2 2\pi l' z' \frac{1}{3} [\sin^2 2\pi hx + \sin^2 2\pi kx \\ &+ \sin^2 2\pi(h+k)x] \}) \end{aligned} \quad (2b)$$

$$L(l') = \frac{\sin \pi \times 8 \times 0.113 l'}{\sin \pi \times 0.113 l'}$$

In formula (2a) $G^2(h, k)$ represents the Laue factor for the two-dimensional lattice corresponding to the

well defined system of channels projected onto the basal plane and the analogous factor $G^2(l')$ refers to the c' period of the chains defined by the centres of gravity of the molecules. The integral

$$\int_{-1/2}^{+1/2} \exp \{2\pi i l' z'\} dz'$$

takes into account the absence of z correlations between the chains as described above and the factor $L^2(l')$ is nothing but the Laue factor due to one alkane molecule with a period of $c'' = 2.56 \text{ \AA}$, the length of the C-C-C subunit. It takes care of translational symmetry of the zig-zag C-atom arrangement within one alkane molecule (H atoms are neglected). Normalizing c'' to c' gives $2.56/22.6 = 0.113$.

For calculating $\langle F \rangle^2$ and $\langle |F|^2 \rangle$ the following positions of the alkane molecule have been used:

$$\pm x, 0, z'; 0, \pm x, z'; \pm x, \pm x, z';$$

where the parameter z' is given by $\frac{1}{4} \times 2.56/22.6 = 0.028$.

Equation (2a) shows that no sharp reflections on s layers other than $l' = 0$ are to be expected, but the s layer $l' = 0$ should exhibit sharp reflections coinciding with the reflections in the positions of the framework peaks (in agreement with the observations). In contrast to the observation, however, additionally there should be a zeroth-order diffuse s layer as sharp in the l' direction as the higher-order ones. Their intensity is fully described by the difference between equations (2b) and (2a). It should be added that correlations between the origins of chain positions in neighbouring channels would lead automatically to maxima in the s layers, because of the fact that $\langle F \rangle$ is no longer zero if $l' \neq 0$. In fact, Fig. 2 shows within the diffuse s layers broad diffuse maxima indicating a short-range order between these origins. A detailed discussion of these phenomena is beyond the scope of this paper because the situation is even more complicated as there are extremely weak diffuse streaks in addition which connect these short-range-order peaks.

A complete interpretation of the diffuse s and d layers may only be given by consideration of the

positional disorder within one channel, in particular within an alkane molecule. Arguments in favour of this explanation are the observations of a period of the d layer-line system of $8.6c^*$, which corresponds fairly well to the 2.56 \AA of one C-C-C unit, the (pseudo-) extinction rule of a 2_1 screw axis which is characteristic of the zig-zag arrangement of a stretched molecule and the width of the d band of $1/8c^*$, which indicates - as mentioned - a correlation length of exactly one molecule length.

Now we may proceed to elaborate the model in more detail. All positional orientations are occupied statistically with or without correlations. For the sake of simplicity let us first discuss the zero layer line of diffraction, $l' = 0$. Here all displacements of the origins in the various channels are meaningless, see (2a). The reflections $hk0$ generate a projection parallel to c of the structure. In this projection all channel occupations are identical, therefore we get - in agreement with the experimental observations - no diffuse scattering in the zero layer. For the s layers, $l' \neq 0$, we have again $\langle F \rangle = 0$; this is equivalent to the statement that no sharp reflections occur on these layers. The diffuse scattering is fully described by the structure factor of a single chain, if no correlations between neighbouring chains are assumed. The calculation of the scattered intensity of a single chain may now again be done according to the procedure used above. The two equations now describe the sharp s layers and the diffuse d layers which could not be included in (2) as normal disorder scattering. Since the same orientations of alkane molecules have to be used, we get very similar formulae:

$$\begin{aligned} \langle F \rangle^2 &= G^2(l') L^2(l') 4f_C^2 \cos^2 2\pi l' z' \\ &\times [\cos 2\pi hx + \cos 2\pi kx + \cos 2\pi(h+k)x]^2 \end{aligned} \quad (3a)$$

$$\begin{aligned} \langle |F|^2 \rangle &= NL^2(l') 4f_C^2 \{ \cos^2 2\pi l' z' \\ &\times \frac{1}{3} [\cos^2 2\pi hx + \cos^2 2\pi kx \\ &+ \cos^2 2\pi(h+k)x] \\ &+ \sin^2 2\pi l' z' \frac{1}{3} [\sin^2 2\pi hx + \sin^2 2\pi kx \\ &+ \sin^2 2\pi(l+k)x] \}. \end{aligned} \quad (3b)$$

The l' dependence of the intensity of the s layers along a meridian ($00l'$) is therefore due to the product $G^2(l') L^2(l') \cos^2(2\pi l' z')$ (dropping the form factor f_C in the X-ray case). As shown in Fig. 12(a) the first main maximum of $L^2(l')$ is completely cancelled out by the cosine term. The relative intensities of the s layers depend very sensitively on the accurate value of the z' parameter. Note that this calculated intensity behaviour cannot be compared directly with the oscillation photographs because the meridian of these patterns is not a record of the ($00l'$) direction in normal-beam technique: the diffuse layer lines correspond to the annular intersections between the layers

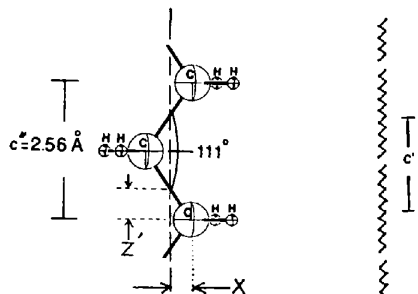


Fig. 11. Schematic sketch of the different chain periods and relevant parameters.

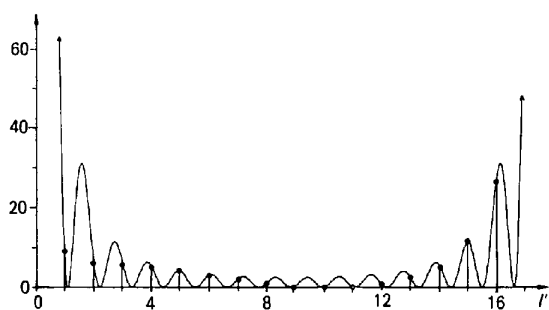
and the Ewald sphere which are away from the c^* axis except at the zeroth layer line.

As stated in § II, the diffuse sheets are not homogeneous, but show short-range-order modulations. These are most pronounced at low Q values leading to a simultaneous reduction of the surrounding diffuse background. This might explain the observation that the scan at $0.35, 0, l'$ performed with neutrons (Fig. 9b) reveals no diffuse intensity in the first and second s -layer positions (this scan was performed at $h = 0.35$ in order to avoid the Bragg peaks hkl_0 due to the averaged structure which are superimposed at all layers $l' = 2n$).

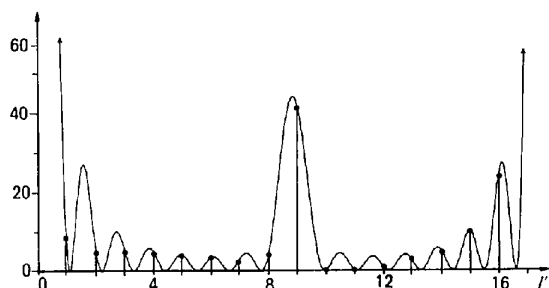
The difference between (3a) and (3b) yields a statistical molecular structure factor which governs the diffuse d -band scattering. The Laue factor $L^2(l')$ in (3b) gives the correct positions of the d bands and the correct width which may be estimated from

$$2(\ln 2/\pi)^{1/2} \lambda / (8c'' \cos \theta) \approx 0.075 \approx 1/13.$$

This value agrees very well with the experimental value taken from Fig. 1. The model explains correctly the other main features of the d -band scattering. Around the zeroth layer line there is diffuse intensity at higher h, k values, at low h, k the difference between $\langle |F|^2 \rangle - |\langle F \rangle|^2$ becomes very small and - in agreement with the observations - the diffuse intensity vanishes. Moving away from $l' = 0$, we have due to $L^2(l')$ a broad maximum between the eighth and ninth s layers and a second maximum at the position $l' = 17$



(a)



(b)

Fig. 12. (a) Plot of the function $L^2(l') \cos^2(2\pi l' z')$ with $z' = 0.113$ versus the s -layer order l' . (b) Functional dependence given in (3b) with $z' = 0.113$, $x = 0.05$, $h = 1.5$, $k = 0$ (form factor f_C neglected).

(roughly). At these positions the influence of $|\langle F \rangle|^2$ is negligible due to $G^2(l)$. On the meridian, however, there is an extinction due to the cosine term which in fact includes the 2_1 pseudo-extinction rule. Further away from the c^* axis the intensity within a d band grows up to a maximum, followed by a decrease due to the atomic form factor and temperature factor. It should again be kept in mind that the maximum intensity of the diffuse d band close to the meridian on the film is a consequence of the technique. Actually the meridian position on the film corresponds to $h \approx 1$. A plot of the theoretical curve at $h = 1.5$, i.e. $1.5, 0, l'$ is shown in Fig. 12(b). The relatively strong intensity of the second d band at $l' \approx 17$ is, of course, damped by the atomic form factor f_C in X-ray scattering. Moreover, the maximum of the first d band is obviously not at $h = 1.5$, but at a higher h value.

The lateral scan within the first d band - performed with neutrons - confirms the pseudo-extinction rule and shows a broad maximum centred at $h = 1.5$, roughly. There is, however, another difficulty in the interpretation of the neutron scans. In the neutron case the deuterium atoms within the paraffin molecule have a considerable scattering power. They were neglected in (3). Because the D atoms have larger x, y parameters - compared with those of the C skeleton - the larger maximum cannot be found in the same position as in an X-ray experiment.

Another approach to evaluate $\langle |F|^2 \rangle$ and $|\langle F \rangle|^2$ relates to the averaged overall cylindrical symmetry of the chain system - at least in the high-temperature phases: the structural parameters (x_i, y_i, z') of the C atoms are replaced by cylindrical coordinates (r, ψ_i, z') . Averaging over the chain orientations means therefore averaging over ψ_i :

$$\begin{aligned} \langle |F|^2 \rangle_\psi &\equiv \Phi_{0l}(l') = \sum_n (A_n + B_n)^2 \\ A_n &= \sum_j f_C J_n(\mathbf{r} \cdot \mathbf{H}_r) \cos [n(\pi/2 - \psi_j) + 2\pi l' z'] \\ B_n &= \sum_j f_C J_n(\mathbf{r} \cdot \mathbf{H}_r) \sin [n(\pi/2 - \psi_j) + 2\pi l' z'] \end{aligned} \quad (4a)$$

$$\langle F \rangle_\psi^2 = |F_{0l}|^2 = |J_0(\mathbf{r} \cdot \mathbf{H}_r) \cos 2\pi l' z'|^2. \quad (4b)$$

The J_n are the cylindrical Bessel functions, \mathbf{H}_r refers to the radial component of the scattering vector in reciprocal space. Equations (4) replace the expressions in wavy brackets in (3) [or in (2)]. Obviously, there is no principal difference in the discussion of the diffuse s and d layers. Consequently a detailed discussion is omitted.

From the model discussed above it is fully understood why the disorder is independent of temperature in a certain temperature range. It follows from the calculations given above that in the case of correlations of molecular orientations within one channel the diffuse d layers should condense into the s layers,

if the same orientation is preferred, or a superstructure of layers, if rational superstructures are realized. This is, however, only true if no other internal disorder process is responsible for the diffuse *d* layers. This might be, for example, a scissor-like movement, or – in a static picture – fluctuations due to partial stretching of the molecules caused by ‘pinning’ of some atoms, *i.e.* due to local potential minima in the channel for only some of the atoms in one molecule.

It is not easy to decide whether or not this model is valid: if remarkable fluctuations within the C–C–C distances of a molecule were to occur, a broadening of the *d*-band scattering along c^* with increasing scattering angle should be observable. There seems to be a small indication of an increased width of the fourth layer (Fig. 4*a*), but the intensity is too low to investigate this model more quantitatively. A detailed quantitative analysis, however (correction for resolution effects), of the line profiles of the first three *d* bands gives an unchanged width. Possibly a superposition of several phenomena occurs.

As pointed out before, the diffuse intensities are of static origin, which is further supported by the observation of a relative insensitivity of the diffuse *d* bands over a wide range of temperature in X-ray and neutron experiments. A kind of sharpening can be seen at the transition temperature from phase II to phase III in the position of the ninth *s* layer, but a careful check reveals also a second parallel layer corresponding to $l' = 8.7$, *i.e.* approximately in the maximum position of $L^2(l')$. If the orientational statistics are responsible for the diffuse *d* band, this would prove that neighbouring molecules cannot have the same orientation even at this temperature.

When we look at the diffraction pattern in the low-temperature phase IV, it becomes clear that the same ordering process continues without reaching perfect order. This ordering of molecules within one channel is also indicated by the geometry of the pseudo-rhombic cell. The *b* axis of this cell is appreciably smaller than $a3^{1/2}$, as demanded by the lateral orientational ordering of the molecules in phase III. Obviously neighbouring positions along *c* should be equivalent from a structural point of view, otherwise the perfect geometry could be violated. In this respect there is no reliable structure determination of the averaged structure of phase III (only the *hk0* projection has been determined until now). This would be necessary to offer a set of solutions in agreement with the statements given above.

A unique interpretation of the *c* diffuse scattering is difficult because there is no clear correlation with the remaining types of diffuse scattering. Owing to the enhanced intensity just at the transition II → III and the observation that a set of split reflections emerges from this diffuse scattering (*cf.* Fig. 8), there is most probably a relationship with the (lateral) structural reordering at this temperature. As reported

the averaged structure of phase II is trigonal, whereas phase III consists of domains with orthorhombic or monoclinic symmetry. Two points seem to be important in this context: the *c* diffuse scattering vanishes completely after the transition II → III, *i.e.* the structural disorder disappears in favour of a well ordered domain structure. Because the corresponding split reflections are as sharp as normal Bragg reflections the domain size exceeds the instrumental limit of resolution. On the other hand, at the high-temperature side pretty far from the transition temperature, *i.e.* in phase II, the *c* diffuse scattering may scarcely be discerned from the diffuse part described as ‘wavy’ streaks in § II.

This wavy streaking has a component close to the Bragg reflections which may be assigned to an averaged lamellar arrangement of microdomains of rhombic or monoclinic structural elements within phase II. The streaking further away from the Bragg points reflects a fine structure of correlated interfaces between these lamellar domains. If these microdomains exist on a very fine scale with congruent interfaces between them, possibly with distortions over some cells, a remarkable diffuse intensity is observable. In this picture the averaged trigonal structure of phase II is due to averaging over these microdomains which develop into the large domains of phase III. Then a remarkable interfacial scattering can no longer occur. Not inconsistent with this qualitative explanation is the increase of the *c* diffuse part as a consequence of large domain-wall fluctuations close to the transition point. In a conventional neutron experiment this scattering will be recorded as elastic within an energy resolution of 0.1 THz which complies with our experimental observation. A more thorough discussion of the *c* diffuse scattering in context with the study of the transition mechanism is found in Boysen *et al.* (1986).

A semi-quantitative interpretation of the diffraction pattern of phase IV (*cf.* Fig. 7) may be found in the following way. Some of the basic reflections are split into series, which sometimes extend from one layer to the next of the framework structure. Hence, an interpretation as a periodic array of domains with a perfect geometry for the urea framework may be excluded. It is well known that a kind of satellite pattern with only one or two pairs of satellites results in this case. The diffuse *s* layers gradually sharpen to peaks in the positions of the urea reflections, *i.e.* there are strong correlations between the paraffin chains with respect to the *z* coordinates [*cf.* (1)]. On the other hand, the diffuse *d* layers begin to resolve into layers corresponding to a superperiod of four cells (22 Å) roughly (Fig. 7). This means that four chain molecules of the inclusion form a kind of superperiod. A more detailed analysis of the urea reflections splitting into a set of satellites reveals the following properties: the central satellite reflection

coincides with the positions of the original framework reflections at all diffraction angles; the general decrease of the intensities of the orders of satellites corresponds to a particle-size effect roughly; some of the reflections are nearly free from satellites, *i.e.* the central satellite has by far the largest intensity. This behaviour in reciprocal space may approximately be described by the equation

$$[G_s(\mathbf{h})P(\mathbf{h})] * [G(\mathbf{h})F(\mathbf{h})] \quad (5)$$

(* denotes the convolution operation), where $G_s(\mathbf{h})$ and $P(\mathbf{h})$ represent the Fourier transform of the superlattice and of a particle size (box function), respectively, while $G(\mathbf{h})$ and $F(\mathbf{h})$ represent the diffraction pattern of the urea framework. Fourier transformation of (5) yields

$$[g_s(\mathbf{r}) * p(\mathbf{r})][g(\mathbf{r}) * f(\mathbf{r})]. \quad (6)$$

The first term in square brackets in (6) describes a periodic array of particles (boxes), while the second term determines the periodic urea framework structure. Since the particle size (Fig. 7) is approximately half of the length of the supercell, the space in between has to be 'empty'. Obviously, this is not really true, but there is only one explanation for this strange result: two sets of domains with a nearly periodic arrangement are rotated away from each other by a (small) angle φ such that their reflections split at least in some parts of reciprocal space. This will generally occur if the change of orientation is accompanied by a symmetry-induced change of lattice constants a' , b' , where the deviation from the condition $b' = a'3^{1/2}$ becomes increasingly important.

In those areas of reciprocal space where they are split, they behave independently ('empty'). In other areas where the splitting is incomplete a more complicated description of the diffraction effects is necessary, in the case of complete coincidence and equal structure factors of the two sets of domains no satellites are observed.

This explanation is in full agreement with the observation that the diffuse d bands show a super-period of four cells (22 Å). This length corresponds roughly to a single domain, which governs the diffraction picture, as disorder destroys the full periodicity of our idealized model. Consequently, one may conclude that the structures of the framework and the inclusion are now commensurate within the small domains. The term commensurate, however, becomes meaningless for the whole structure because of the high degree of disorder which could not be recovered in our experiments.

IV. Concluding remarks

From the discussion of the diffuse phenomena in the hexadecane adduct it becomes clear that the different types of disorder are all more or less directly related to the driving forces for the various structural elements: this is the competition between an ordering force within the chain system to find its own longitudinal and lateral arrangement *and* to fit both the framework and the inclusion (in particular along the channel axis) together. At higher temperatures where both substructures are approximately decoupled, both systems find their appropriate lattice period c and c' , respectively. As the temperature is lowered successively, accompanied by a stepwise freezing of the different chain motions (see Boyden *et al.*, 1986), the mutual influence becomes stronger leading to common disordered superstructures and domain arrangements and, in consequence, to a distinct interfacial structure.

Even the (lateral) transition between phases II and III may be treated as a secondary effect of a rearrangement process of the chains in different channels. At the final lowest-temperature stage the chain system obviously plays the dominant role which becomes evident from the distortion of the framework. Concomitant diffuse scattering, however, at each temperature stage shows that a true commensuration is never achieved. It should become obvious from this paper that a qualitative or semi-quantitative analysis of diffuse scattering is important for a full understanding of the structure of inclusion compounds which cannot be provided by an analysis of Bragg scattering alone.

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