# Determination of Approximate Superstructures in the Urea-Hexadecane Inclusion Compound by Representation Analysis*

H. Boysen and R. Forst
Institut für Kristallographie und Mineralogie der Universität München

Z. Naturforsch. **41 a**, 553–559 (1986); received December 14, 1985

*Herrn Prof. J. Brandmüller zum 65. Geburtstag gewidmet*

The inclusion compound of urea with hexadecane has a superstructure of an ideal hexagonal structure found in other members of the series of urea-n-paraffin adducts consisting essentially of honeycomb-like channels formed by the host into which the long chain molecules are embedded. In order to elucidate the nature of the superstructure, which manifests itself by additonal weaker reflexions ($h\,k\,l/2$) and ($0\,0\,l$) (all $l$ = integer), it is expanded into basis functions transforming as the irreducible representations (IR's) of the average space group $P6_122$. Most of the IR's can be ruled out by exploiting the symmetry of the diffraction pattern. For the remaining sets of basis functions a least squares fit to the measured intensities is performed separately for each IR. Those yielding reliable agreements are then taken as key IR's describing the prevalent modulations. In this way it is possible to obtain valuable information about the main characteristics of the superstructure, even if the true structure cannot be fully determined. In the present case a strong modulation belonging to the $A_3$ IR was found to produce rotations of the urea molecules around axes parallel to the channels as well as slight lateral translations. An additional contribution from $\Gamma_5$ results in a superposition of individual orthorhombic domains with slightly different hydrogen bond angles. A phase transition below 147 K can be attributed to $M_2$ and is connected with an ordering of the guest molecules and a simultaneous orthorhombic deformation of the channels.

## Introduction

Urea ($CO(NH_2)_2$) inclusion compounds are commonly described as a hexagonal framework of hydrogen bonded urea molecules. This host structure contains "infinite" honeycomb-like channels into which long chain guest molecules are embedded with their long axis parallel to the channel axis and with random azimutal orientations. The ideal structure belongs to space group $P6_122$ with six molecules per unit cell ($a = 8.2$ Å, $c = 11.0$ Å) and seems to be realized rigorously in the adduct with dodecane ($C_{12}H_{26}$) [1, 2]. On the other hand the compound with hexadecane ($C_{16}H_{34}$) shows in a diffraction experiment at room temperature additional reflexions ($h\,k\,l/2$) indicating a doubled unit cell as well as ($0\,0\,l$) reflexions with $l = 1, 2, \ldots$ not allowed by the $6_1$-screw axis. This exceptional behaviour of $C_{16}H_{34}$ in the series of n-paraffins may be attributed to the fact that the length of this molecule (22.8 Å) is nearly equal to twice the identity period of the host lattice. Since, however, the intensities of the main strong reflexions are very similar to those in the other adducts, it may be concluded that on an average the same ideal structure applies to the hexadecane adduct, and the slight deviations in the true superstructure are manifested in the weaker superlattice reflexions.

The problem of determining superstructures when the average structure is known has been extensively dealt with in the literature. Rather frequent seems to be the use of difference Patterson functions (e.g. [3, 4, 5]) based upon the superlattice intensities only. A group theoretical analysis of these Patterson data has been given by [6]. The application of direct methods is discussed in [7]. Ito [8] has proposed a minimum residual method by changing each parameter of each atom from its

* This work was supported by funds of the BMFT under project 03-41 E 12.

Reprint requests to Dr. H. Boysen, Institut f. Kristallographie und Mineralogie, Universität München, Theresienstr. 41, D-8000 München 2.

0340-4811 / 86 / 0300-0553 $ 01.30/0. – Please order a reprint rather than making your own copy.

position in the average structure in different directions, calculating the corresponding agreement values ($R$-factors) and attributing the key shifts to the direction of steepest descent. An approximate superstructure can thus be found by least squares methods, which then allows the assignment of approximate phases from which by Fourier and least squares procedures the true superstructure may be determined. This rather simple but possibly cumbersome method of course assumes that only a few important key shifts are responsible. Not only displacive but also substitutional ordering can be handled in exactly the same manner.

We have adopted a similar procedure, but instead of choosing arbitrary shift directions the overall shifts are separated into symmetry adapted coordinates, which transform according to the different irreducible representations (IR's) of the space group $G_0$ of the average structure. Analogous approaches are used in the solution of incommensurate structures (e.g. [9, 10]) also in combination with partial Patterson functions.

## Method and Results

Quite generally the true superstructure may be written as the sum of the average structure plus a difference structure,

$$\varrho(\boldsymbol{r}) = \varrho_0(\boldsymbol{r}) + \delta\varrho(\boldsymbol{r}) , \tag{1}$$

where $\varrho_0(\boldsymbol{r})$ is invariant under the symmetry elements of $G_0$, i.e. transforms according to the identity representation of $G_0$. $\delta\varrho(\boldsymbol{r})$ may then be expanded into the basis functions $\varphi_{l,i}^{(*\boldsymbol{k},m)}$ of all IR's $(*k, m)$ of $G_0$ excluding the identity representation

$$\delta\varrho = \sum_{*\boldsymbol{k}} \sum_{m} \sum_{l} \sum_{i} c_{l,i}^{(*\boldsymbol{k},m)} \varphi_{l,i}^{(*\boldsymbol{k},m)} , \tag{2}$$

where $i = 1, \ldots, d^{(m)}$ runs over the basis functions of one IR $\mathbf{D}^{(m)}$ ($d^{(m)}$ = dimension of $\mathbf{D}^{(m)}$), $l = 1, \ldots, n^{(m)}$ takes into account that $\mathbf{D}^{(m)}$ can occur $n^{(m)}$ times in the expansion, $m$ numbers all the IR's connected with a given star $*\boldsymbol{k}$ and finally the sum over $*\boldsymbol{k}$ runs over all the stars. Since $\delta\varrho(\boldsymbol{r})$ is real, (2) contains only real representations or direct sums of complex conjugate representations. This is fully analogous to the starting point in the Landau theory of phase transitions, where, however, it is then argued that only one particular IR can be responsible (except for accidental situations). This IR then determines the symmetry of the low temperature phase.

Such restrictions may of course not generally be imposed on all substructure-superstructure relationships. Nevertheless, in many cases it should be possible to drastically reduce the number of involved IR's on other physical grounds. First of all it should be remarked that quite often the superstructure has in fact developed by a phase transition from the average structure in which case one may proceed with Landau's theory. In any case the position of the superlattice reflexions immediately defines a modulation with corresponding wave vector $\boldsymbol{k}$, which thus selects a special term in the sum over $*\boldsymbol{k}$. Note, however, that allowance should always be made for a possible admixture of $\boldsymbol{k} = 0$ ($\Gamma$-point) modes.

Further restrictions on the possible IR's may be drawn from observed extinction rules, which cancel the IR's that do not conserve the symmetry elements with corresponding non primitive translations (screw axes, glide planes). On the other hand, the overall symmetry of the reflexion pattern may give hints on those symmetry elements that have to be conserved. With the latter one should, however, be aware of the fact that a possible twinning of the crystal might simulate a higher symmetry. Crystal chemical and physical arguments may occasionally lead to additional restrictions. Thus one is usually left with only a few allowed IR's, each of which may be applied separately (i.e. taking only one term at a time in (2)) in a least squares refinement. Those giving the largest reductions of the R-factors are then considered to be the key IR's. In other words, even if the true superstructure is not solved in this way (e.g. because of too many adjustable parameters and strong correlations between them), the knowledge of the modulations connected with the key IR's may already give valuable informations on the main characteristics of the superstructure.

The occurrence of superlattice reflexions at positions $l/2$ in the $\boldsymbol{c}^*$-direction in our example implies a modulation with wave vector $\boldsymbol{k}_A = (0\ 0\ \pi/c)$, i.e. at the $A$-point of the Brillouin zone, while the $(0\ 0\ l)$ reflexions indicating the absence of any screw axis may be due to a $\Gamma$- and/or $A$-point modulation. Hence we have to consider the group of $\boldsymbol{k}\,G_{\boldsymbol{k}}$ for these two points both having the same point group 622. (The star $*\boldsymbol{k}_A$ contains only one arm, since $-\boldsymbol{k}_A$ is equivalent to $\boldsymbol{k}_A$.) $G_k$ may be de-

composed into the cosets of the invariant subgroup $T$ containing all primitive translations $(C_1 \mid \boldsymbol{t})$,

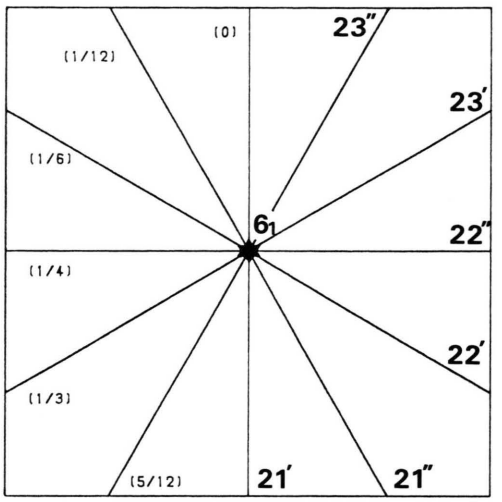
$$\begin{aligned} G_{\boldsymbol{k}} = &(C_1 \mid 000)\,T + (C_6 \mid 00\tfrac{1}{6})\,T \\ &+ (C_3 \mid 00\tfrac{1}{3})\,T + (C_2^z \mid 00\tfrac{1}{2})T \\ &+ (C_3^2 \mid 00\tfrac{2}{3})\,T + (C_6^5 \mid 00\tfrac{5}{6})\,T \\ &+ (C'_{21} \mid 000)\,T + (C''_{21} \mid 00\tfrac{1}{6})\,T \\ &+ (C'_{22} \mid 00\tfrac{1}{3})\,T + (C''_{22} \mid 00\tfrac{1}{2})T \\ &+ (C'_{23} \mid 00\tfrac{2}{3})\,T + (C''_{23} \mid 00\tfrac{5}{6})\,T \\ = &\sum_{i=1}^{12} g_i T\,, \end{aligned} \tag{3}$$

where the second equality defines an abbreviated notation of the representative symmetry elements, which coincides with the choice of [11]. Note that the fractional coordinates associated with the perpendicular twofold rotation axes $C_2'$ and $C_2''$ simply place them at the correct heights $1/2\times$ (fraction) (cf. Fig. 1 a for the orientation of them). At the $\Gamma$-point all relevant IR's of $T$ are equal to $\exp\{-\mathrm{i}\,\boldsymbol{k}\cdot\boldsymbol{t}\} = 1$, while at the $A$-point there are two values $\exp\{-\mathrm{i}\,\boldsymbol{k}\cdot\boldsymbol{t}\} = 1$ for $\boldsymbol{t} = n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c}$ if $n_3$ is even (constituting the invariant subgroup $T_{k_A}$), and $\exp\{-\mathrm{i}\,\boldsymbol{k}\cdot\boldsymbol{t}\} = -1$ if $n_3$ is odd. This of course reflects the fact that the new translation period along the $\boldsymbol{c}$-direction is $2\boldsymbol{c}$ $(T_{k_A})$, i.e. alternating phases $\pm 1$ are associated with subsequent subcells of original height $1\,c$. Therefore at the $A$-point we have to consider 12 additional representative elements

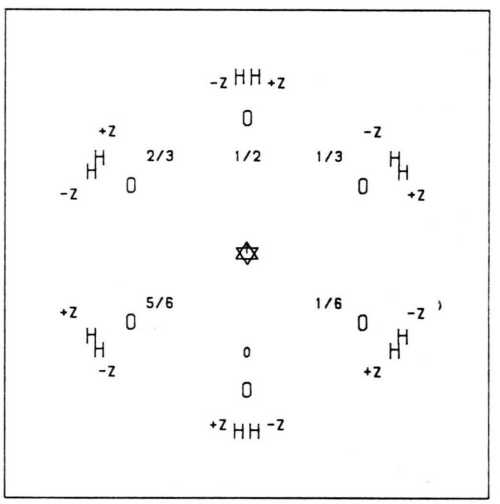
$$g_i' = (C_1 \mid 001)\,g_i \quad \text{and}$$
$$\text{IR's } \mathbf{D}^{(m)}(g_i') = -1 \cdot \mathbf{D}^{(m)}(g_i)\,.$$

Character tables for the IR's at $\Gamma$ and $A$ are given in Tables 1 and 2, respectively. For the two dimensional IR's the matrices are listed in Table 3. They were taken from [11] and converted to real matrices by a unitary transformation $\mathbf{U} = \begin{pmatrix} \varepsilon & i\,\varepsilon \\ \varepsilon & -i\,\varepsilon \end{pmatrix}$ with $\varepsilon = 1/\sqrt{2}$.

Without further information the general problem of solving the true structure would require the determination of $12 \cdot 8 \cdot 3 = 288$ positional parameters as there are 12 molecules in the large cell each containing 8 atoms (the hexadecane molecules are not taken into account here, since they occupy random positions at room temperature). Being aware




(a)




(b)

Fig. 1. Arrangement of principle symmetry elements defined in (2) (a), and location of atoms in special (e.g. O) and general (e.g. H) positions (b) in the unit cell of the average structure.

also of the temperature parameters this is definitely a hopeless problem. The number of parameters corresponding to each IR is given by $l^{(m)} = n^{(m)} d^{(m)}$, where $n^{(m)}$ may be calculated as usual from

$$n^{(m)} = \frac{1}{|g|} \sum_{g \in G} \chi^r(g)\,\chi^{(m)*}(g)\,, \tag{4}$$

where $|g|$ is the order of $G$, $\chi^{(m)}$ the character of the $m$-th IR and $\chi^r$ that of the reducible representation. In establishing the latter we make use of the fact that O and C lie in special positions on perpendic-

ular twofold axes ($x, 2x, 1/4$), while $N$, $H_1$ and $H_2$ occupy general positions ($x, y, z$) in space group $P6_122$ [12] (see Figure 1 b). It is then sufficient to calculate $n^{(m)}$ for these two cases first and multiply by the number of corresponding nonequivalent atoms afterwards to obtain the total number of parameters $l_T$. Resulting values are given in Tables 1 and 2 too.

The worst that can appear are 48 parameters for particular IR's. This number may be further reduced at least in a first step by imposing chemically plausible constraints on some of the intermolecular bonds. A totally rigid molecule would leave at most three translations and three rotations. For the two dimensional IR's symmetry might require a specific combination of its basis vectors also halving the number of free parameters.

From the position of the $l/2$ reflexions exactly on the $c^*$-direction it may be deduced that a principal axis parallel to $c$ is conserved. Since symmetry elements that are conserved must satisfy $\mathbf{D}^{(m)}(g)\,e^{(m)} = e^{(m)}$, where $e^{(m)}$ is a suitable combination of basis functions $\varphi_{l,i}^{(*k,m)}$, the condition $\det(\mathbf{D}^{(m)} - \mathbf{E}) = 0$ has to be fulfilled ($\mathbf{E} = d^{(m)}$-dimensional unit matrix). Hence all elements which are mapped onto unit matrices are always conserved, while for two dimensional IR's those obeying

$$\chi^{(m)}(g) = 1 + \det \mathbf{D}^{(m)}(g)$$

may be conserved. In our case the determinants are $+1$ for elements $g_1$ to $g_6$ and $-1$ for $g_7$ to $g_{12}$. From Table 2 then the only IR that conserves a principal

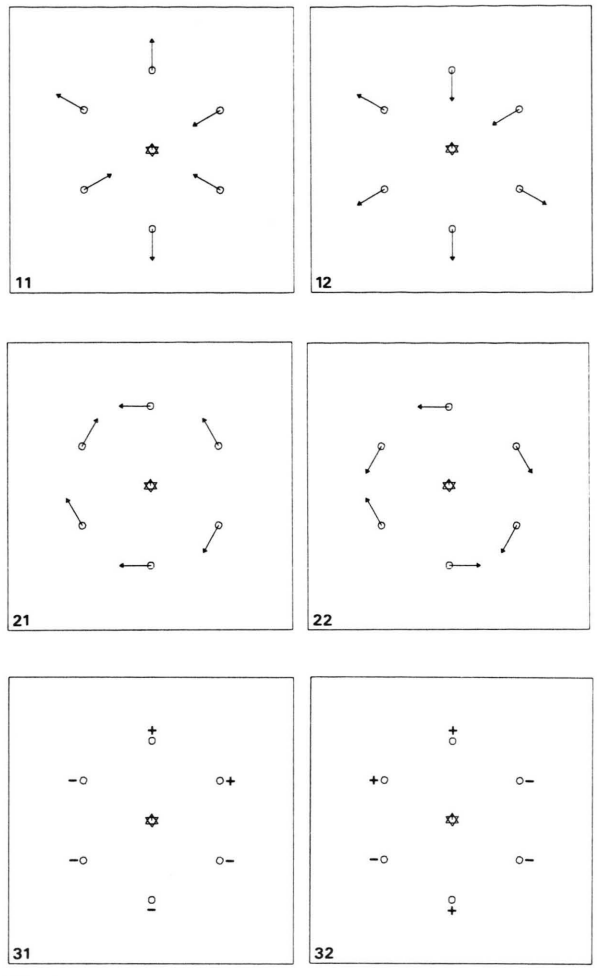


Fig. 2a.

Table 1. Character table at $\Gamma$-point of $P6_122$. Atoms O and H are given as representatives for a special and a general position, respectively, $\chi^r$ is the character of the corresponding reducible representation, $l$ the number of free parameters in each position and $l_T$ the total number of free parameters in the whole urea molecule.

| $P6_122$ | $g_1$ | $g_2, g_6$ | $g_3, g_5$ | $g_4$ | $g_{11}, g_9, g_7$ | $g_{12}, g_{10}, g_8$ | $l$(O) | $l$(H) | $l_T$ |
|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_1$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 3 | 11 |
| $\Gamma_2$ | 1 | 1 | 1 | 1 | −1 | −1 | 2 | 3 | 13 |
| $\Gamma_3$ | 1 | −1 | 1 | −1 | 1 | −1 | 1 | 3 | 11 |
| $\Gamma_4$ | 1 | −1 | 1 | −1 | −1 | 1 | 2 | 3 | 13 |
| $\Gamma_5$ | 2 | −1 | −1 | 2 | 0 | 0 | 6 | 12 | 48 |
| $\Gamma_6$ | 2 | 1 | −1 | −2 | 0 | 0 | 6 | 12 | 48 |
| $\chi^r$(O) | 18 | 0 | 0 | 0 | −2 | 0 | | | |
| $\chi^r$(H) | 36 | 0 | 0 | 0 | 0 | 0 | | | |

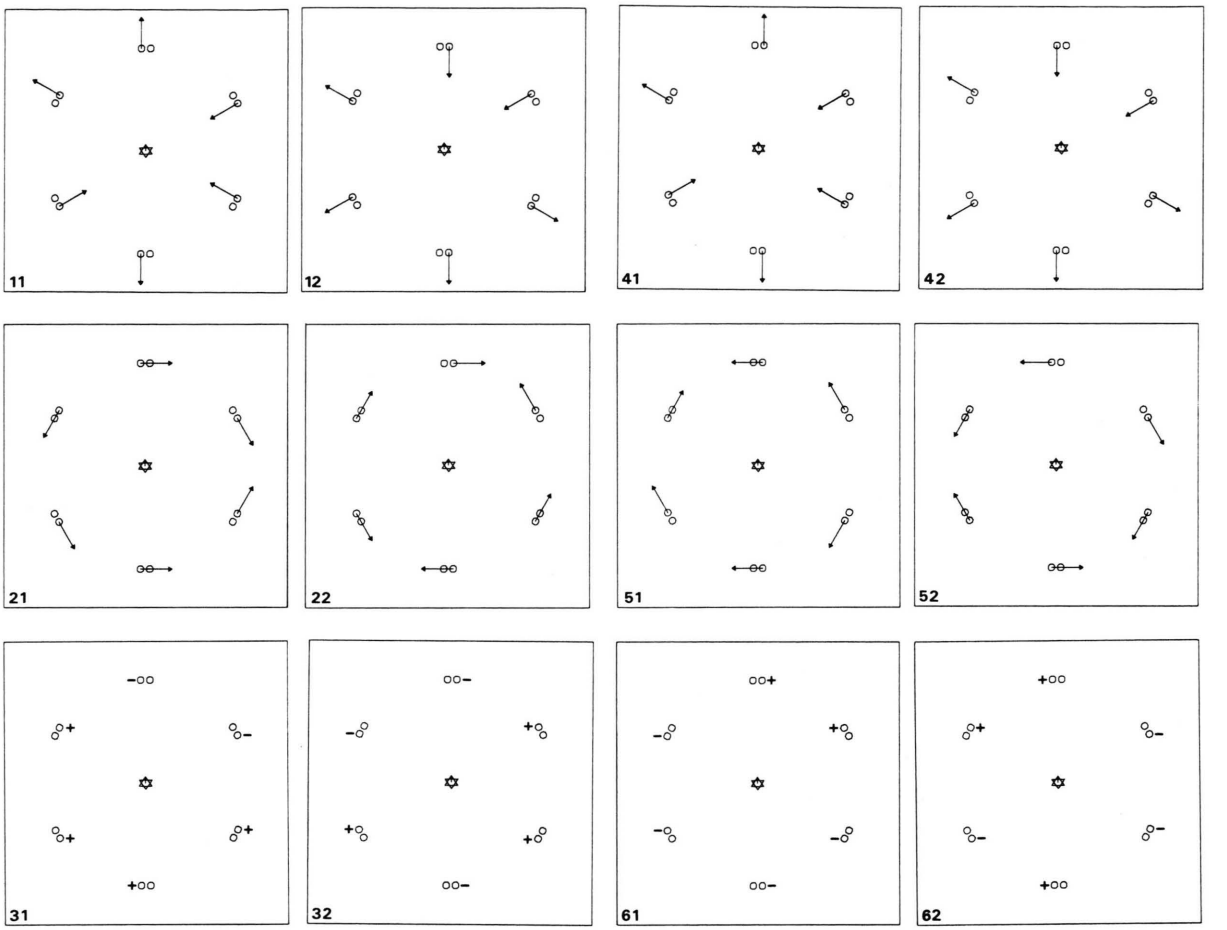



Fig. 2b.

Fig. 2. Schematic basis vectors $\varphi_{l,i}^{(A_3)}$ of the irreducible representation $A_3$ for special (a) and general (b) positions. The displacements shown apply to one subcell (cf. Figure 1 b). In the adjacent subcell (along **c**) all arrows are reversed.

Table 2. Same as Table 1 for $A$-point.

| $P6_122$ | $g_1$ | $g_2$ | $g_6$ | $g_3$ | $g_5$ | $g_4$ | $g_{11}, g_9, g_7$ | $g_{12}, g_{10}, g_8$ | $l$(O) | $l$(H) | $l_T$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_1$ | 2 | $\sqrt{3}$ | $-\sqrt{3}$ | 1 | −1 | 0 | 0 | 0 | 6 | 12 | 48 |
| $A_2$ | 2 | $-\sqrt{3}$ | $\sqrt{3}$ | 1 | −1 | 0 | 0 | 0 | 6 | 12 | 48 |
| $A_3$ | 2 | 0 | 0 | −2 | 2 | 0 | 0 | 0 | 6 | 12 | 48 |
| $\chi^r$(O) | 18 | 0 | 0 | 0 | 0 | 0 | −2 | 0 | | | |
| $\chi^r$(H) | 36 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | | |

axis is $A_3$, for which any combination of basis functions conserves $g_5$ and $g_3'$ (see Table 3). Basis vectors for this IR were calculated with the help of projection operators and are shown in Figure 2. The elements $g_5$ and $g_3'$ become $(C_3^2|00\frac{1}{3})$ and $(C_3|00\frac{2}{3})$ respectively in the large unit cell. Moreover, in $A_3$ it is possible to combine the basis vectors such that also three of the perpendicular twofold axes are conserved (in agreement with the symmetry of the observed diffraction pattern), e.g. $\varphi_{l,1}^{(A_3)} + \varphi_{l,2}^{(A_3)}$ is invariant under $g_7$, $g_{11}$ and $g_9'$ (see Table 3). These elements constitute the group $P3_22$.

The least squares fit to the measured intensities (X-ray and neutron data) converged, but yielded

Table 3. Matrices for the two dimensional irreducible representations of Tables 1 and 2 ($a = 1/2$, $b = \sqrt{3}/2$).

| | $g_1$ | $g_2$ | $g_6$ | $g_3$ | $g_5$ | $g_4$ | $g_7$ | $g_{11}$ | $g_9$ | $g_{10}$ | $g_8$ | $g_{12}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_5$ | 1 0 | $-a\ -b$ | $-a\ \ b$ | $-a\ \ b$ | $-a\ -b$ | 1 0 | 1 0 | $-a\ \ b$ | $-a\ -b$ | 1 0 | $-a\ \ b$ | $-a\ -b$ |
| | 0 1 | $b\ -a$ | $-b\ -a$ | $-b\ -a$ | $b\ -a$ | 0 1 | 0 −1 | $b\ \ a$ | $-b\ \ a$ | 0 −1 | $b\ \ a$ | $-b\ \ a$ |
| $\Gamma_6$ | 1 0 | $a\ -b$ | $a\ \ b$ | $-a\ -b$ | $-a\ \ b$ | −1 0 | 1 0 | $-a\ -b$ | $-a\ \ b$ | −1 0 | $a\ \ b$ | $a\ -b$ |
| | 0 1 | $b\ \ a$ | $-b\ \ a$ | $b\ -a$ | $-b\ -a$ | 0 −1 | 0 −1 | $-b\ \ a$ | $b\ \ a$ | 0 1 | $b\ -a$ | $-b\ -a$ |
| $A_1$ | 1 0 | $b\ -a$ | $-b\ -a$ | $a\ -b$ | $-a\ -b$ | 0 −1 | 0 1 | $-b\ -a$ | $-b\ \ a$ | −1 0 | $-a\ \ b$ | $-a\ -b$ |
| | 0 1 | $a\ \ b$ | $a\ -b$ | $b\ \ a$ | $b\ -a$ | 1 0 | 1 0 | $-a\ \ b$ | $a\ \ b$ | 0 1 | $b\ \ a$ | $-b\ \ a$ |
| $A_2$ | 1 0 | $-b\ -a$ | $b\ -a$ | $a\ \ b$ | $-a\ \ b$ | 0 −1 | 0 1 | $b\ -a$ | $b\ \ a$ | −1 0 | $-a\ -b$ | $-a\ \ b$ |
| | 0 1 | $a\ -b$ | $a\ \ b$ | $-b\ \ a$ | $-b\ -a$ | 1 0 | 1 0 | $-a\ -b$ | $a\ -b$ | 0 1 | $-b\ \ a$ | $b\ \ a$ |
| $A_3$ | 1 0 | 0 −1 | 0 −1 | −1 0 | 1 0 | 0 1 | 0 1 | 0 1 | 0 −1 | 1 0 | −1 0 | −1 0 |
| | 0 1 | 1 0 | 1 0 | 0 −1 | 0 1 | −1 0 | 1 0 | 1 0 | −1 0 | 0 −1 | 0 1 | 0 1 |

| $P6_122$ | $g_1$ | $g_4$ | $g_8$ | $g_{11}$ |
|---|---|---|---|---|
| $M_1$ | 1 | 1 | 1 | 1 |
| $M_2$ | 1 | 1 | −1 | −1 |
| $M_3$ | 1 | −1 | 1 | −1 |
| $M_4$ | 1 | −1 | −1 | 1 |

Table 4. Character table at $M$-point of $P6_122$.

only a slight reduction of the overall weighted $R$-factor. This was of course expected, since the $R$-factor is mainly determined by the strong reflexions pertaining also to the average structure. A better indication on the reliability of the results is achieved by considering only the superlattice intensities. Using only the stronger ones an $R$-factor was obtained similar to that from all reflexions ($\sim 5\%$). This is a good hint that we really have found a key modulation. The refinement showed that the main contributions arise from the basis vectors $\varphi_{2,i}^{(A_3)}$ of the special position and $\varphi_{2,i}^{(A_3)}$ and $\varphi_{5,i}^{(A_3)}$ of the general position (see Fig. 2) meaning a mutual rotation of sets of three molecules each belonging to a $3_2$-spiral. In addition there are minor contributions from $\varphi_{1,i}^{(A_3)}$ and $\varphi_{1,i}^{(A_3)}$, $\varphi_{4,i}^{(A_3)}$, respectively, producing lateral displacements of the molecules. This is an important result, since one might have expected predominant translational displacements along the channel axes in order to better accomodate the included hexadecane molecules.

It is clear, however, that we have not yet fully determined the true structure as there cannot be conserved any screw axis along $\boldsymbol{c}$. From Tables 1 and 2 only $\Gamma_6$, $A_1$ and $A_2$ fulfill this requirement (leaving no principal axis at all) and from Table 3 in each case only one of the perpendicular twofold axes can be conserved. This means that the maximal symmetry is monoclinic. No attempt has been made to determine this additional modulation, since there are too few (0 0 $l$) reflexions, which would provide a reliable indicator.

As pointed out already the pseudo-hexagonal symmetry of the reflexion pattern might also be simulated by a superposition of individual domains of lower symmetry. The only IR, which is compatible with such a model and which still retains rectangular axes is $\Gamma_5$ (conserving e.g. $g_1$, $g_4$, $g_8$ and $g_{11}$, see Table 3) leading to space group $C222_1$. A refinement of this modulation also converged again with only a minor improvement of the $R$-factor. It is mainly associated with a slight change of the O−H ... N hydrogen bond angle. On the other hand the urea-hexadecane adduct undergoes a phase transition below 147 K to a structure with average orthorhombic symmetry. Thus the preformation of domains belonging to $\Gamma_5$ seems to be quite plausible.

In the low temperature phase superlattice reflexions occur at positions $h/2$ and $k/2$ corresponding to the wavevectors of the star of $\boldsymbol{k} = 1/2\,\boldsymbol{a}^*$. Starting in a first approach from the average r.t. structure in space group $P6_122$ (which may be justified because of the orthogonality of the IR's) the principal modulation involved in the phase transition is obtained from the IR's at the $M$-point of the hexagonal Brillouin zone (point group 222). From the characters given in Table 4 $M_1$ and $M_2$ yield an orthorhombic symmetry. However, only $M_2$ leading to space group $P2_12_12_1$ ($g_1$, $g_4$, $g_8'$ and $g_{11}'$ are conserved) is consistent with the observed extinctions. This transition is connected with an order-

ing of the guest molecules in adjacent channels and a simultaneous (orthorhombic) deformation of the host channels. Clearly, this again has to be regarded as an average structure, whereas the true structure is at most monoclinic from similar arguments as above.

Full account of the structural details will be published in a forthcoming paper [13, 2], where also comparisons are made with the results from difference Patterson methods (which support the results given here). It should be remarked that the symmetry aspects of substructure-superstructure problems can also be discussed in terms of ordinary group-subgroup relations [14]. However, we feel that the use of representation theory facilitates an exhaustive consideration of all possibilities, since it prescribes a rather straight-forward systematic approach. It should be added that the method will not be successful when too many IR's are involved at the same time.

*Acknowledgements*

We are greatly indebted to Profs. H. Jagodzinski and F. Frey for many stimulating discussions and critically reading the manuscript. We also thank Prof. J. Brandmüller, who has always stressed the power of representation theory.

[1] A. E. Smith, Acta Cryst. **5,** 224 (1952).
[2] R. Forst, Dissertation München 1985.
[3] M. J. Buerger, Vector Space, John Wiley & Sons, Inc., New York 1959.
[4] M. M. Qurashi, Acta Cryst. **16,** 307 (1963).
[5] Y. Takéuchi, Z. Kristallogr. **135,** 120 (1972).
[6] J. D. C. McConnell and V. Heine, Acta Cryst. **A41,** 382 (1985).
[7] R. Böhme, Acta Cryst. **A38,** 318 (1982); Z. Naturforsch. **38a,** 304 (1983).
[8] T. Ito, Z. Kristallogr. **137,** 399 (1973).
[9] E. Fjaer, Acta Cryst. **B41,** 330 (1985).
[10] J. D. C. McConnell and V. Heine, Acta Cryst. **A40,** 473 (1984).
[11] S. C. Miller and W. F. Love, Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups, Pruett Press, Boulder 1967.
[12] International Tables for X-ray Crystallography, The Knyoch Press, Birmingham 1965.
[13] R. Forst and H. Jagodzinski, in preparation.
[14] M. J. Buerger, J. Chem. Phys. **15,** 1 (1947).