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1990 J. Phys.: Condens. Matter 2 3237

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The origin of the γ incommensurate structure in n-propylammonium tetrachlorometallates

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Received 24 November 1989

Abstract. This paper concerns the similar γ incommensurate phases found in bis (n-propylammonium) tetrachloro-manganate and -cuprate. The modulation is driven by the propyl chains. A simple physical picture explains the microscopic origin of these modulated structures in terms of interatomic interactions. The ends of the propyl chains from successive layers interpenetrate at the 'peaks' of the modulation, while at the 'troughs' of the wave the adjacent chains from the same layer are brought closer together. Both effects serve to lower the Van der Waals energy between chains. Some theory and some computer simulation round off the picture and give quantitative support.

1. Introduction and qualitative physical picture

The purpose of this paper is to give a microscopic explanation for the occurrence of the γ phase in the $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4$ and $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{MnCl}_4$ compounds. It is the easiest modulated structure to understand in simple qualitative terms, at least among those known to us. The structure is characterised by a succession of inorganic layers of corner-sharing $\text{Cu}(\text{Mn})\text{Cl}_6$ octahedra. The ammonium ends of the organic chains are connected by hydrogen bonds to the Cl atoms. The chains stand approximately perpendicular to the layers on both sides (figure 1). The structure is modulated in the manner shown in figure 1. The γ phase of the Mn compound was determined qualitatively (Depmeier 1981, Muralt *et al* 1986). The structural investigation of the Cu compound (Doudin and Chapuis 1990b) leads to the same characteristics, summarised in figure 1. Both compounds exhibit a wave vector $q_{1C} = \alpha a^*$, α being approximately equal to 0.18. However, the Jahn–Teller deformation affecting the coordination of the Cu atom induces a decrease of the symmetry with respect to the Mn specimen. This change in the inorganic part of the structure does not affect the stacking of the organic chains, which is similar in the two compounds. The lateral spacing, a_0 , of the chains is also important and is determined (for short chains) by the inorganic 'backbone' layer formed from metal chloride octahedra.

Muralt has already given a suggestive qualitative physical picture of what causes the transition (Muralt 1986, Kind and Muralt 1986). The main point is that the adjacent chains within one layer are much further apart (due to the backbone) than under optimum close packing of such chains; but the spacing is not double the optimum, i.e. not enough for chains from successive layers to interpenetrate. This situation is rather

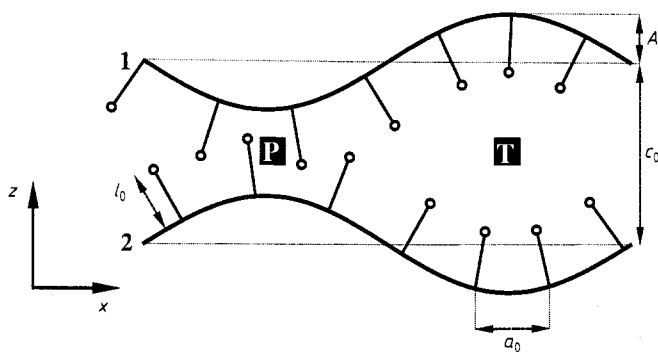


Figure 1. Propyl chains from successive layers 1 and 2, the small circle being their methyl end group. At the 'troughs' T of the modulation of the lower layer, the chains from successive layers draw apart, but adjacent chains from the same layer come close together. At the 'peaks' P the adjacent chains on the same layer are splayed open and allow greater interpenetration by the chains from the next layer. The lines at 1 and 2 denote the metal chloride backbone of the layers.

unsatisfactory from the point of view of the Van der Waals (vdw) interaction energy of the chains. There are two ways of lowering the vdw energy, and the modulated phase achieves both: if we open up the spacing between adjacent chains, we can get more interpenetration and hence lower the energy; similarly, if we close up the spacing between adjacent chains, that also lowers their vdw energy. Figure 1 shows that the first type occurs in the regions P of the modulation and the second type in the region T.

We can make this picture more convincing by using a computer simulation (section 3 and 4). Instead of varying the aperture angle of the adjacent chains, we vary the separation a between adjacent chains in a static model ($T = 0$). We also vary the spacing c between successive layers. The energy $E(a, c)$ per chain is shown in figure 2, where a and c represent the local situation. We see that the energy at the mean spacing (a_0, c_0) corresponds to a saddle point, with two minima close by. The minimum at P has larger a and smaller c spacing, as at P in figure 1; the minimum at T corresponds to the local situation at T in figure 1. Clearly, the modulation makes use of these two minima to lower the energy. We can use the energy from figure 2 to develop a quantitative theory of the modulation in section 2. The energy is expanded in power series and the various terms determine the instability leading to a modulated phase, the magnitude of the wave vector, etc. Of course, the theory is only static and hence cannot do justice to the phase transitions to the two adjacent β and δ phases at higher and lower temperatures respectively. We will give a qualitative discussion in section 4 of what we believe causes these transitions. Note that phase δ is a re-entrant phase of the same symmetry as β .

2. Theory of the modulation

For a modulation wave running along x , we can estimate the local variables $c(x)$ and $a(x)$ expressing the distance separating successive inorganic planes and the separation along x between the methyl ends of two adjacent chains respectively, shown in figure 1,

$$c(x) = c_0 + 2A \cos(2\pi qx) \quad (2.1)$$

$$a(x) = a_0 - 4A\pi^2 q^2 l_0 a_0 \cos(2\pi qx) \quad (2.2)$$

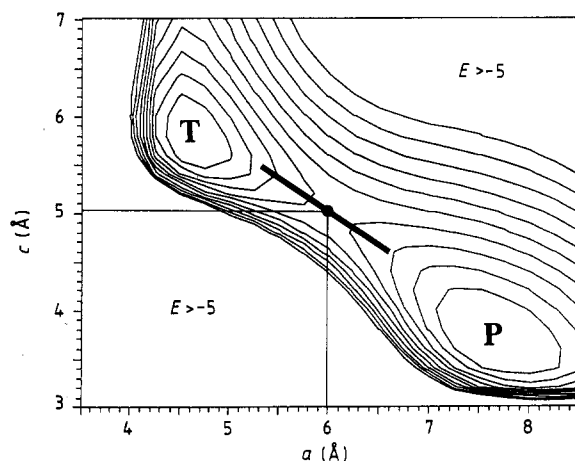


Figure 2. Energy contours from the simulation, showing the local energy $E(a, c)$. The heavy dot is at a_0, c_0 , which are the mean values of the separation between adjacent chains and the vertical separation between successive layers respectively. The low energies at P and T correspond to the situations also labelled P and T in figure 1. The slope of the bold line indicates the ratio of the a and c modulation amplitudes. In producing this plot, we have removed the effect of the first derivative $(\partial E/\partial a)_{a_0}$ at $a_0 = 6.0$ Å which is balanced by the rigidity of the backbone.

where A is the displacement amplitude of the backbone in the z direction, l_0 is the length of the organic chains and q is the modulation wave vector component. The factor 2 in (2.1) comes from the antiphase motion of successive layers. The modulation amplitude in (2.2) is a simple consequence of tilting the propyl chains, keeping them perpendicular to the backbone, in the approximation $qa_0 \ll 1$.

We now evaluate the energy $W_0(a_0, c_0; A, q)$ of the modulated structure centred on the average spacings a_0, c_0 . Let $E(a, c)$ be the local energy per propyl chain for given local separations a and c . Then

$$W_0(a_0, c_0; A, q) = \frac{1}{L} \int_0^L E(a, c) dx \quad (2.3)$$

where L is large compared with a_0 , and a and c vary with x according to (2.1) and (2.2). We expand $E(a, c)$ as a Taylor series about a_0, c_0 :

$$E(a, c) = E(a_0, c_0) + \partial_a(a - a_0) + \frac{1}{2}\partial_{aa}(a - a_0)^2 + \partial_{ac}(a - a_0)(c - c_0) + \frac{1}{2}\partial_{cc}(c - c_0)^2 + \dots \quad (2.4)$$

Here $\partial_a, \partial_{aa}, \partial_{ac}$ are first and second derivatives of E with respect to a and c , evaluated at (a_0, c_0) . There is no ∂_c term in (2.4) because $\partial_c = 0$ by the equilibrium condition with respect to the c -spacing. However, there is a non-zero term in ∂_a which is cancelled by an equal and opposite stress in the backbone, not so far included in E or W_0 . From (2.1) to (2.4) we obtain

$$W_0 = E(a_0, c_0) + (\partial_{cc} - \partial_{ac}Q^2 + \frac{1}{2}\partial_{aa}Q^4)A^2 + O(A^4). \quad (2.5)$$

Here Q^2 is a dimensionless form of the wave vector component q :

$$Q^2 = 4\pi^2 q^2 l_0 a_0. \quad (2.6)$$

The value of Q^2 also expresses the ratio in (2.1), (2.2):

$$\frac{1}{2}Q^2 = \frac{\text{amplitude of } a(x) \text{ modulation}}{\text{amplitude of } c(x) \text{ modulation}}. \quad (2.7)$$

For a modulated phase to be stable, the coefficient of A^2 in (2.5) must be negative. It is clearly being driven negative by $-\partial_{ac}Q^2$ and a necessary condition is

$$\partial_{ac} > 0. \quad (2.8)$$

Minimising the coefficient of A^2 with respect to Q gives the value Q_m at the minimum

$$Q_m^2 = 2\partial_{ac}/\partial_{aa}. \quad (2.9)$$

If we substitute (2.9) into (2.5), we obtain

$$\Delta = \partial_{cc}\partial_{aa} - (\partial_{ac})^2 < 0 \quad (2.10)$$

as the condition for the coefficient of A^2 to be negative. This condition, stronger than (2.8), is necessary and sufficient for a modulated phase to exist. Actually, this algebra is not quite appropriate because we need a global minimum with respect to A and Q . The condition (2.10) is the condition for the energy to have a saddle point at (a_0, c_0) , and the ratio (2.7) is optimised by choosing the direction of steepest descent from the saddle, given by

$$\frac{2}{Q^2} = \tan \left[\frac{1}{2} \tan^{-1} \left(\frac{2\partial_{ac}}{\partial_{aa} - \partial_{cc}} \right) \right] \quad (2.11)$$

instead of (2.9).

We now have to include the contribution W_i to the energy from the inorganic backbone. This has two effects. Firstly, it cancels any linear term from $\partial W_0/\partial a_0$ in the total energy

$$W = W_0 + W_i \quad (2.12)$$

as already explained. Secondly, it adds an energy

$$W_i = \frac{1}{4}CQ^4A^2 \quad (2.13)$$

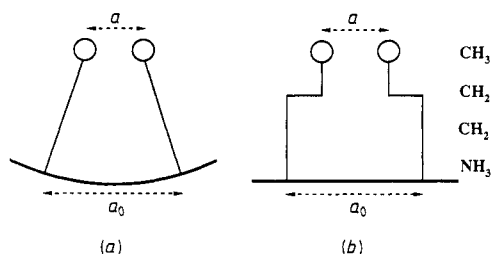
as the elastic energy of buckling the backbone, with $C > 0$ (Landau and Lifshitz 1959). Adding (2.13) to (2.5) simply replaces ∂_{aa} by $\partial_{aa} + C$. The same replacement should be made in the inequality (2.10): if C is too large, it will clearly destroy the saddle point and give a minimum at $A = 0$. Similarly, from (2.9) or (2.11), the same substitution shows that W_i decreases the value of Q_m^2 .

3. The computer simulation

We want to calculate the VDW energy of the interacting propyl chains. Modelling the interaction of organic molecules is a highly developed art and we simply follow the practitioners (Williams and Cox 1984, Price 1986, and references cited therein). Since we treat the organic chains as rigid, only the non-bonding interchain energy is calculated,

Table 1. Potential parameters used for the calculations (taken from Williams and Cox 1984). The notation corresponds to equation (3.1).

| | | |
|---|---------------------------------------|---|
| $A_{CC} = 2439.8 \text{ kJ mol}^{-1} \text{ \AA}^6$ | $B_{CC} = 369743 \text{ kJ mol}^{-1}$ | $C_{CC} = 3.60 \text{ \AA}$ |
| $A_{HH} = 136.4 \text{ kJ mol}^{-1} \text{ \AA}^6$ | $B_{HH} = 11971 \text{ kJ mol}^{-1}$ | $C_{HH} = 3.74 \text{ \AA}$ |
| $A_{CH} = (A_{CC}A_{HH})^{1/2}$ | $B_{CH} = (B_{CC}B_{HH})^{1/2}$ | $C_{CH} = \frac{1}{2}(C_{CC} + C_{HH})$ |

**Figure 3.** A pair of adjacent chains is represented. The case (a) corresponds to a tilting angle given by the bending of the backbone (bold line). The simplification used in our calculations corresponds to the case (b) taking into consideration only the interaction involving the methyl ends and a part of the next $-\text{CH}_2-$ group of the chains.

the interaction between atoms being given by an empirical energy expression of the form (Kitaigorodsky 1973):

$$E_{jk} = B_{jk} \exp(-C_{jk}r_{jk}) - A_{jk}r_{jk}^{-6} + q_jq_kr_{jk}^{-1}. \quad (3.1)$$

Here r_{jk} is the distance separating the two atoms. The exponential term is a short range strong repulsive energy, the r^{-6} term corresponds to a VDW energy, and the last term represents the Coulombic interaction. The parameters A , B , C and q , concerning the carbon and hydrogen atoms have been determined by fitting a large number of azahydrocarbons and saturated hydrocarbons structures. They are summarised in table 1. The Coulombic contribution to the energy is less than one per cent and was neglected (Williams and Cox 1984). The calculations were performed with the help of the program WMIN (Busing 1981).

We want to compute the energy $E(a, c)$ where a is the separation of the tips of the propylammonium chains caused by tilting them as in figure 1. A complete simulation of this would be difficult. We therefore suppose that the tilting brings the top methyl group and, say, half the next $-\text{CH}_2-$ groups closer together to a distance a , the rest of the chain remaining unchanged. That is, we replace the real geometry of figure 3(a) by that of figure 3(b).

The model system for our calculation is therefore that shown in figure 4 consisting of parallel propane molecules with variable spacing a , the three-dimensional arrangement corresponding to that of the real crystal. While the absolute magnitude of our calculated energy will certainly be in error by a factor of order unity, we trust the variation of $E(a, c)$ with a and c will be given satisfactorily. The propane chains have an internal symmetry $mm2$ for the optimal internal energy configuration (figure 4). The C-C bond length value of 1.53 \AA and the C-H bond length of 1.02 \AA were given. The computer model has four propane molecules per orthorhombic unit cell (figure 4). The four molecules were initially given at positions related by glide plane symmetry and b -face centring (figure 4), but were then completely relaxed by independent rotations and translations (only the rotation around the x axis was fixed at a zero value, in order to respect the geometry imposed by the backbone). It turned out that these needed to be non-zero to

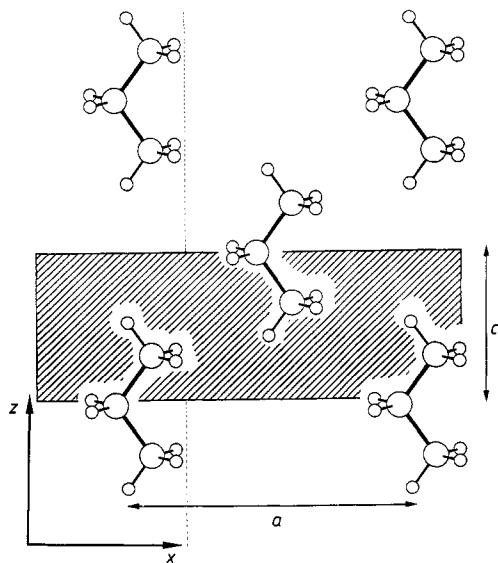


Figure 4. A plot showing a projection along y of the structure used for the calculations. Only the molecules around the plane ($y = 0$) are shown. Two other molecules are generated by a glide plane perpendicular to x , with a translation of $\frac{1}{2}b$ (vertical dotted line in the figure). The shaded region corresponds to the interacting ends of the propylammonium chains. The c is analogous to the c_0 of figure 1, but the dimension of the modelling cell is $2c$.

obtain an improved interpenetration of the molecules, but the effect was to shift $E(a, c)$ by an amount that was almost a constant, independent of a and c . The only parameter significantly different from zero corresponds to a translation of all molecules around $y = \frac{1}{2}$ in the x direction, with a value reaching 1.0 \AA when a is large ($>7.0 \text{ \AA}$), and decreasing to 0.4 \AA for smaller values of a ($<5.5 \text{ \AA}$). The b dimension of the modelling cell was also an *a priori* choice. As the high symmetry phase occurring at high temperature (phase α) showed equal values for a and b , we imposed a value of 7.0 \AA for b (the experiments showed values around 7.5 \AA) corresponding to the critical values found for a in our calculations. For all the conclusions deduced from our calculations, we checked that the variations induced by a change in the value of b can be neglected.

4. Results and discussion

As a first step, we calculated the interaction energy of a single layer by setting c to a very large value in the simulation. The result (figure 5) confirms that our value of a_0 (about 7.0 \AA), set by the backbone, is much larger than that (about 4.5 \AA) for close packing of the molecules, but clearly not twice as large as would be needed for large interpenetration.

The next step was to calculate $E(a, c)$ for many values of a and c . With a fixed value of 0.6 \AA for the shift in the x direction characterising the molecules around $y = \frac{1}{2}$, we calculated a grid of 20×20 values. In order to discuss the expansion (2.4), an approximate representation by a series of Chebyshev polynomials was used. A determination of the second derivatives, with a reliability of a few per cent on changing the grid or the degree of the polynomials, was possible. All these calculations were performed with the help of the mathematical library Nag Fortran. Figure 6 shows the results of the calculation of Δ , expressed using the inequality (2.10). We found negative values over a large region of the parameter space. However, Δ is positive if the value of a corresponds to the observations (around 7.4 \AA). We must not be surprised by this result, the structure being

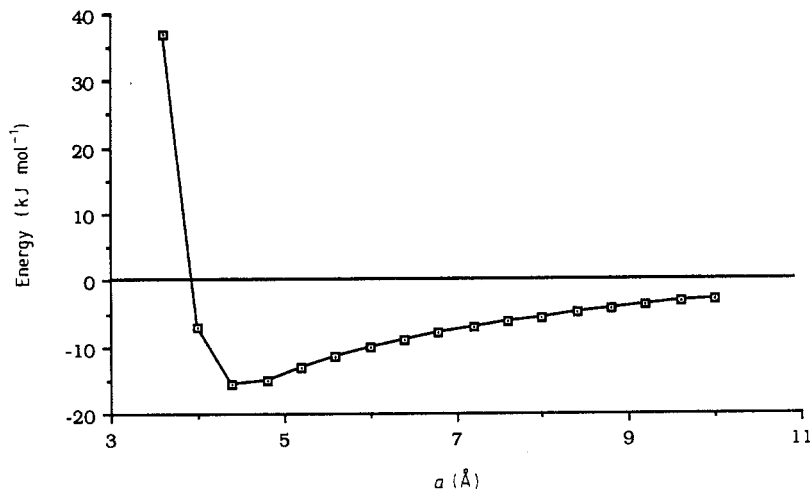


Figure 5. The energy function of the separation between adjacent chains, of a planar packing of propane chains.

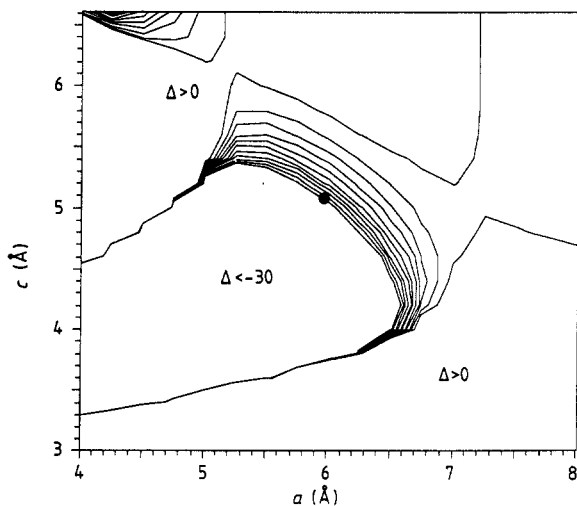


Figure 6. A map showing the calculated values of the second-derivative test Δ concerning the local energy. The contour lines are limited to values between -30 and 0 . The area where $\Delta < -30$ or $\Delta > 0$ are specified without contour lines. If a_0 is greater than 6.9 \AA , a commensurate configuration is preferred.

commensurate at lower temperatures (phase δ). The local energy showed an absolute minimum at $a = 7.96 \text{ \AA}$, with an energy equal to $-27.4 \text{ kJ mol}^{-1}$ of propane chains.

Our static model cannot reproduce a phase at $T > 0$, except in an approximation where the thermal agitation and the entropy will induce a larger effective diameter of the molecule. This effect can be reproduced, not by expanding the molecule, but by choosing an artificially reduced effective value for a_0 . Figure 2 was produced with a value of $a_0 = 6.0 \text{ \AA}$ ($E(a_0, c_0) = -10.9 \text{ kJ mol}^{-1}$). The choice of a_0 also determines the linear

Table 2. Comparisons between the cell parameter a and the parameter ΔZ as regards the phase δ of the Cd, Cu and Mn compounds and the configuration P observed in the local energy. The second part compares the values observed for the β phase of the Cu compound and the configuration T of the local energy.

| Compound | Cd† | Mn‡ | Cu§ | This work |
|----------------------------------|------|------|------|-----------------|
| Phase δ , temperature (K) | 295 | 295 | 360 | Configuration P |
| a (Å) | 7.64 | 7.46 | 7.65 | 7.7 |
| ΔZ (Å) | 0.97 | 1.11 | 1.02 | 1.15 |
| Phase β , temperature (K) | | | 433 | Configuration T |
| a (Å) | | | 7.53 | 4.65 |
| ΔZ (Å) | | | 2.03 | 3.3 |

† Doudin and Chapuis (1988).

‡ Peterson and Willett (1972).

§ Doudin and Chapuis (1990a).

term, expressing the equilibrium condition with the stiffness of the backbone, which cancels the first derivative of E with respect to a (section 2). The effective local energy will be given by

$$E_{\text{eff}}(a, c) = E(a, c) - (a - a_0)\partial_a. \quad (4.1)$$

To avoid the use of another symbol in the following discussion, we will consider the local energy given by E_{eff} .

The use of an effective lower value for a_0 is also supported by the experimental observations. A minimum of the local energy is reached when the value of a_0 is less than approximately 5.0 Å, which we take to model a higher temperature still. The large value of c , obtained in the simulation for this a_0 , corresponds to the separation observed in the β phase of the Cu compound. The phase δ , the fundamental state in our model, also corresponds to an absolute minimum found for the local energy when a_0 is greater than 7.0 Å. Table 2 shows how the experimental values for a and c are analogous to those deduced from the minima P and T of the local energy. The comparison of the interpenetration was done using the quantity ΔZ , defined as the distance along z separating the carbon atoms of the methyl end of the chains. The same quantity was used to exhibit the structural difference between β and δ phases in the Cu compound (Doudin and Chapuis 1990a).

We now return to the modulated phase γ . The value of Q^2 will be given by the direction of the steepest downward slope of figure 2 (indicated by the bold line), corresponding to equation (2.11). From figure 2, we deduce

$$Q_{\text{fig}}^2 \approx 2.2. \quad (4.2)$$

Including the stiffness, C , of the backbone in (2.9) and (2.11) will reduce the value of Q^2 from (4.2) as discussed below (2.13). Alternatively, the value of Q^2 can be related to the observed wave vector of the modulation, leading to

$$Q_m^2 \approx 1.27 l_0/a_0 \quad (4.3)$$

where l_0 is the length of the organic chain and has a value around 6.4 Å for the n-propylammonium. Its effective value can differ slightly: remember that the value Q_m^2 is deduced from a model involving a rigid connection of the chains with the backbone and

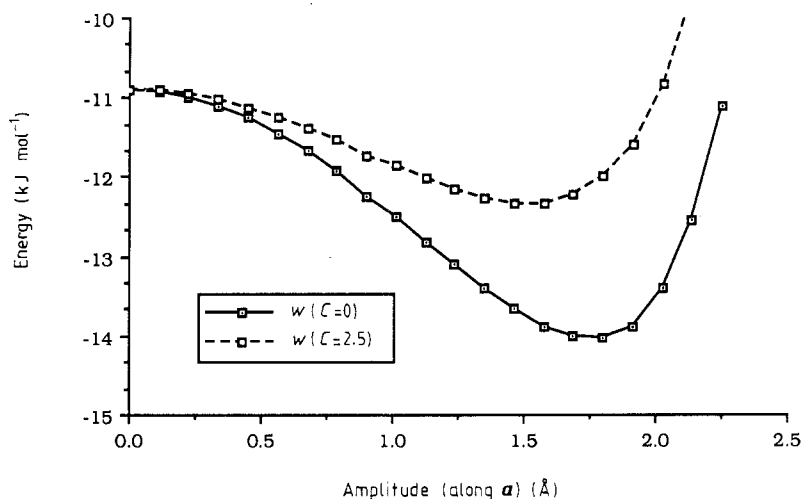


Figure 7. The variation of the energy with the modulation amplitude of the a -displacement. The full curve is the numerical estimation of W_0 , based on the local energy (centred at $a_0 = 6.0$ Å). The broken curve is obtained on adding to W_0 the elastic energy W_i , proportional to A^2 , corresponding to the equation (2.13). Taking, for example, a value of 2.5 for C , the figure shows how the amplitude minimising the energy is decreased.

neglecting the phase difference separating the displacement of two successive organic chains (it corresponds to the hypothesis of $qa_0 \ll 1$ in the deduction of (2.2)). In view of these approximations and the reduction of (4.2) due to C , we regard the agreement between (4.2) and (4.3) as satisfactory.

Figure 2 will also give a direct estimation of the modulation amplitude. The existence of the two minima in the energy map results in a finite value for A_{\min} , and is beyond our energy expansion (2.5). The value of A must be large enough to reach the minima in P and T in figure 2. Figure 7 gives an estimate of the variation of the energy with A , from which we would expect an amplitude A of 1.5 Å. This will also be reduced severely by the effect of C (section 2) since the energy W_i (2.13) is proportional to A^2 (figure 7). It explains why the experimental values for the amplitudes along a and c (a few tenths of Å) are much lower than those deduced from the local energy involving only the organic interactions (more than 1 Å).

So far so good, but we start to run into problems if we try to fit a single value of C to account for all the mentioned effects on A and Q . On the one hand C needs to be large enough to reduce (4.2) sufficiently to (4.3). On the other hand, the value of C is limited by the condition

$$C < -\Delta/\partial_{cc} \quad (4.4)$$

deduced from (2.10), if we want a saddle point in (a_0, c_0) .

So this is the place to stop. The purpose of computational physics is to increase understanding. There are a number of details beyond what can be properly accounted for by our static model. No doubt one could tune the interatomic forces in a dynamic calculation until the computer model becomes identical to experiment: but that is not our objective. Our purpose here has been to demonstrate beyond reasonable doubt that the interaction between the chains can drive an incommensurate instability and to show

how this comes about. What was a nice qualitative suggestion for the origin of the γ phase (Muralt 1986) has been refined and lifted to a convincing semiquantitative explanation.

Acknowledgments

The authors would like to thank Dr Busing for sending his program WMIN and Dr S L Price and S Padlewski for their help. The financial assistance of the Science and Engineering Research Council of the UK and the Fondation Georgine Claraz are gratefully acknowledged, as is the hospitality to Bernard Doudin by Clare College and the Cavendish Laboratory in Cambridge, where much of this work was carried out.

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