Symmetry of modulated phases in tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ): Four- and five-dimensional superspace groups

Per Bak
Nordita, Blegdamsvej 17, 2100 Copenhagen Ø, Denmark

T. Janssen
Institute for Theoretical Physics, University of Nijmegen, Toernooiveld, The Netherlands
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The three modulated ordered phases in tetrathiafulvalene-tetracyanoquinodimethane are described in terms of four- and five-dimensional superspace groups. The 47-K transition is driven by a soft excitation polarized in the fourth "phase" direction. Extinction rules are derived, and the absence of certain $4k_F$ spots observed by Kagoshima *et al.* are explained. Additional experiments are suggested to completely determine the space groups.

Recently it has been shown by Janner and Janssen[1] and by de Wolff[2] that the symmetry of modulated structures should be described by space groups of dimension higher than three. The additional dimensions are related to internal degrees of freedom associated with relative Euclidean motions of the distortions with respect to the basic lattice. Consider for simplicity a one-dimensional chain with displacement of the n'th atom $u_n = u \sin(qna-2\pi t)$, where t is the relative phase. The distortion is invariant in the x-t plane under a lattice of translations generated by the vectors $\vec{a}_1 = (a, -qa/2\pi)$ and $\vec{a}_2 = (0,1)$. The corresponding reciprocal lattice has a basis with $\vec{a}_1^* = (2\pi/a, 0)$ and $\vec{a}_2^* = (q, 2\pi)$. The projection on position space of this lattice consists of the vectors $k = na_1^* + mq$ (n and m integers). These are the diffraction spots of the modulated crystal. A modulated crystal in n dimensions can in a similar way be imbedded into an $(n+1)$-dimensional superspace. If the modulation is given by a superposition of two incommensurate wave vectors the dimensionality of the superspace group is $n+2$. Like ordinary space groups, superspace groups can be used for the classification of structures, for characterization of excitations, and to explain systematic extinctions in structures not having space-group symmetry.

In this paper we shall analyze the modulated phases in TTF-TCNQ in terms of such superspace groups. The notation used will be that of Ref. 1. X-ray[3] and neutron-diffraction data[4] originally revealed structural phase transformations at $T_1 = 54$ K and $T_3 = 38$ K. Bak and Emery[5] have analyzed these transitions in terms of a Ginzburg-Landau theory and predicted that there should in fact be a *third* transition at $T_2 \simeq 47$ K. The existence of this transition has now been confirmed[6]. The picture that emerges is that at 54 K there is a transition to an ordered state $M_{\rm III}$ characterized by a noncommensurate wave vector $\vec{q} = (\frac{1}{2}, \beta, 0)$, $\beta = 2k_F \sim 0.295$. Between 47 and 38 K the wave vector component in the a^* direction decreases as $(q_a - \frac{1}{2})^2 \propto T_2 - T$. Below 38 K the wave vector remains locked into $\vec{q}_1 = (\frac{1}{4}, \beta, 0)$. The latter two phases are denoted $M_{\rm II}$ and $M_{\rm I}$, respectively. The theory as presented here is fully consistent with the theory of Bak and Emery.[5,7]

The space group of TTF-TCNQ in the nonordered phase is $P2_1/c$.[8] The structure consists of chains of TTF molecules and chains of TCNQ molecules arranged in the b-c plane. The lattice is spanned by the vectors $\vec{a}$, $\vec{b}$, $\vec{c}$. There is inversion symmetry and a twofold screw axis along $\vec{b}$. Figure 1 indicates the positions of molecules in the unit cell.

The $M_{\rm III}$ phase is characterized by a single wave vector and the superspace group is therefore four-dimensional. Figure 2 is an attempt to visualize the nature of this group. The c direction has been left out. The extra "phase" direction is the vertical direction. If we consider a fixed position in real space, a shift of the relative phase of the modulation can be expressed as a shift in this direction. The basis of the four-dimensional (4D) lattice is

$$(\vec{a}, -\tfrac{1}{2}), (\vec{b}, -\beta), (\vec{c}, 0), (0,0,0,1).$$

(This lattice belongs to the Bravais class $C^{P2/m}_{\cdot\bar{1}}$ according to Ref. 1.) The distortions of the jth molecule in the nth unit cell may be written

$$\vec{u}(n,j) = \vec{f}_j(\vec{q}) \exp(i\, \vec{q}\cdot\vec{n}) + \text{c.c.}$$

Since the transition from the nonordered phase to $M_{\rm III}$ is second order, the polarizations should belong to an irreducible representation of $P2_1/c$,[9] with wave vector $\vec{q}$. This means

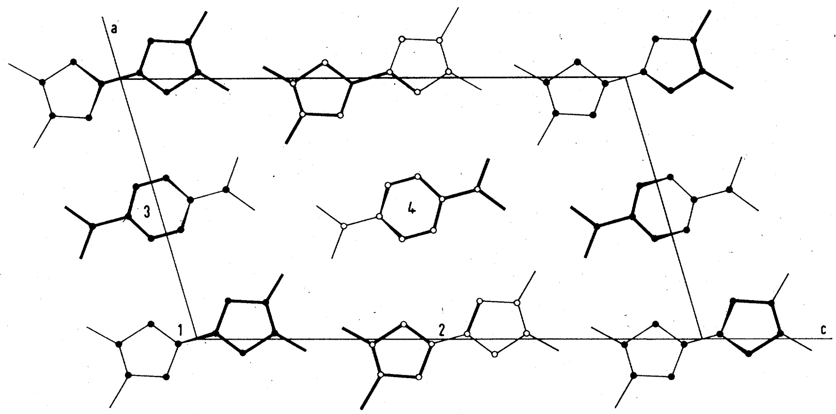

FIG. 1. Positions of molecules within the unit cell of TTF-TCNQ. 1 and 2 are TTF, 3 and 4 TCNQ. The twofold axis may be chosen through 4. The full circles are approximately in the base plane, the open ones are approximately at height $\frac{1}{2}$.

$$f_2(\vec{q}) = \epsilon 2_y f_1(\vec{q}), \quad f_4(\vec{q}) = -\epsilon 2_y f_3(\vec{q}),$$
$$\epsilon = \pm 1,$$

where 2_y is the twofold rotation with axis in the b direction. An extended discussion of these modes is presented in Ref. 11. For the symmetry elements of the superspace group we shall use the notation

$$g = (\{R_E\,|\,\vec{a}_E\}, \{R_I\,|\,\vec{a}_I\}),$$

where R_E and $\vec{a}_E$ are orthogonal transformations and translations, respectively, in position space, and R_I and $\vec{a}_I$ the corresponding operations in internal "phase" space. The possible symmetry elements are the inversion and the twofold screw axis combined with internal operations:

(i)

$$(\{2_y\,|\,0, \tfrac{1}{2}, \tfrac{1}{2}\}, \{1\,|\,a_I\});$$

this element is always present, with $a_I = 0$ if $\epsilon = 1$, and $a_I = \frac{1}{2}a_4$ if $\epsilon = -1$.

(ii)

$$(\{\bar{1}\,|\,0\}, \{\bar{1}\,|\,a_I\});$$

this element is present if $\arg(f_1) = \arg(f_3) \pm \pi\frac{1}{2}$. Now, let us consider the possibility of having systematic extinctions. The diffraction spots are at $h\vec{a}^* + k\vec{b}^* + l\vec{c}^* + m\vec{q}$. We note that the $4d$ wave vector $Q = (0, k, 0, m)$ is invariant under (i), and $Q \cdot (\vec{a}_E, \vec{a}_I)/2\pi = \frac{1}{2}k$ is noninteger for k odd. *We therefore predict that the satellites $k\vec{b}^* + m\vec{q}$ should vanish for k odd.* We suggest that this be checked in an x-ray or neutron-scattering experiment. In addition, the satellites $(h, 0, l, 0) = Q'$ are invariant under the combined operations (i) and (ii), and $Q' \cdot (0, \frac{1}{2}, \frac{1}{2}, 0)/2\pi = \frac{1}{2}l$. The main Bragg peaks $(h, 0, l, 0)$, l odd, should therefore be present in the M_{III} phase *only* if the inversion symmetry (ii) is absent. This could easily be checked in an experiment. For the very dedicated reader we note that the superspace group of M_{III} is

$C^{P2_1/c}_{\cdot 1\bar{1}}$ if inversion present,

$C^{P2_1}_{\cdot 1}$ otherwise.

These space groups are both *monoclinic*, i.e., the action on position space is a monoclinic space group.

The modulation vector of the M_{II} phase is $\vec{q} = (\alpha, \beta, \gamma)$, $\gamma \sim 0$, $\frac{1}{4} < \alpha < \frac{1}{2}$. The lattice of the space group is formed by the vectors $(\vec{a}, -\alpha)$, $(\vec{b}, -\beta)$, $(\vec{c}, -\gamma)$, $(0, 0, 0, 1)$. This lattice belongs to the (tri-

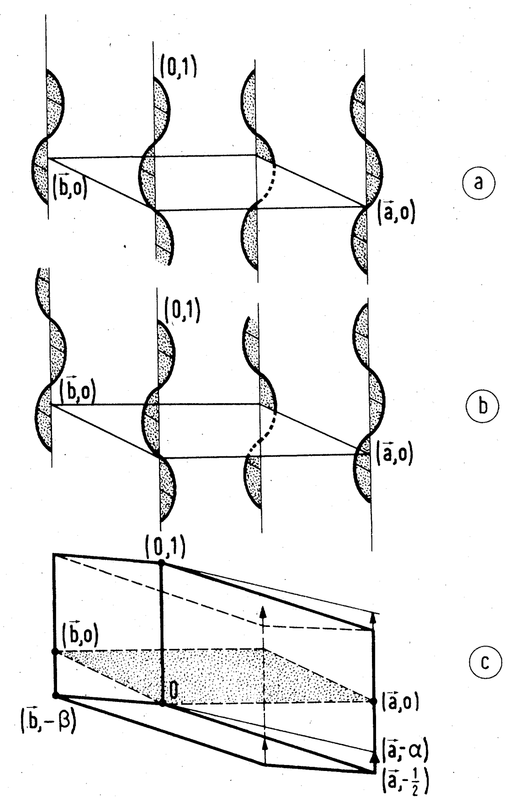

FIG. 2. Schematic representations of the modulated structures. (a) and (b): Four-dimensional lattices of the phases M_{III} and M_{II}, respectively. The sine waves indicate the distortions in superspace. (c) Four-dimensional lattice distortions at the 47-K transition.

clinic) Bravais class $P^{P\bar{1}}_{\cdot\bar{1}}$. The only possible symmetry element besides the primitive translations is $(\{\bar{1}|0\},\{\bar{1}|a_I\})$. If this element is present the superspace group is $P^{P\bar{1}}_{\cdot\bar{1}}$, otherwise $P^{P1}_{\cdot 1}$. Both these groups are *triclinic*, and there are no systematic extinctions in this phase. The space groups are subgroups of the groups of the M_{III} phase, consistent with the transition at 47 K being second order.

M_I ($T<38$ K) is characterized by the *two* vectors $\vec{q}_1=(\frac{1}{4},\beta,\gamma)$ and $\vec{q}_2=(-\frac{1}{4},\beta,-\gamma)$, $\gamma\sim 0$.[7,12] The dimensionality of the superspace group is therefore *five*. The lattice vectors are $(\vec{a},\frac{1}{4},-\frac{1}{4}),(\vec{b},-\beta,-\beta)$, $(\vec{c},\gamma,-\gamma)$, $(0,0,0,1,0)$, and $(0,0,0,0,1)$.

The possible symmetry elements are

(i)

$$(\{2\,|0,\tfrac{1}{2},\tfrac{1}{2}\},\{m\,|0\}).$$

Recall that m is a mirror line in the $2d$ internal space. This element is present if

$$f_2(\vec{q}_2)=2_y f_1(\vec{q}_1),$$
$$f_2(\vec{q}_1)=2_y f_1(\vec{q}_2),$$
$$f_4(\vec{q}_2)=2_y f_3(\vec{q}_1)\exp(-\tfrac{1}{2}\pi i),$$
$$f_4(\vec{q}_1)=2_y f_3(\vec{q}_1)\exp(\tfrac{1}{2}\pi i);$$

(ii)

$$(\{m_y\,|0,\tfrac{1}{2},\tfrac{1}{2}\},\{m\,|0\}),$$

if

$$f_2(\vec{q}_l)=m_y f_1(\vec{q}_l),$$
$$f_4(\vec{q}_l)=m_y f_3(\vec{q}_l);$$

(iii)

$$(\{\bar{1}\,|0\},\{\bar{1}\,|0\}),$$

if

$$\arg[f_1(\vec{q}_1)]=0,\ \pm\tfrac{1}{2}\pi,\pi$$

and

$$\arg[f_3(\vec{q}_1)]=\pm\tfrac{1}{4}\pi.$$

The diffraction spots are labeled $(hklmp)$. The symmetry element (i) leaves the vectors $Q=(0,k,0,m,m)$ invariant, and $Q\cdot(0,\frac{1}{2},\frac{1}{2},0,0)/2\pi=\frac{1}{2}k$. This implies that there are extinctions for k odd. The positions of the corresponding peaks are $\pm(0,2m\beta(=m4k_F),0)$ around $(0,k,0)$. *These extinctions have already been observed by Kagoshima et al.*[10] The peak at $(0,3-0.59,0)$ vanishes completely, whereas the peaks at $(0,3-0.59,l)$ $(l\neq 0)$ are clearly present (Ref. 10, Figs. 2–5). We may therefore conclude that the element (i) is present. Note that there exist two different types of "$4k_F$" spots, namely $(hkl20)$ and $(hkl11)$. The corresponding satellites are situated at $(\frac{1}{2},4k_F,0)$ and $(0,4k_F,0)$, respectively. This is also in agreement with the observations of Kagoshima *et al.* The $(hkl11)$ peaks disappear abruptly at 38 K as they should. The extinctions as derived here are in agreement with those derived in Ref. 11 from a different point of view. The vectors $Q'=(h,0,l,m,-m)$ are invariant under (ii). The corresponding extinctions are at $(h+\frac{1}{2}m,0,l+2m\gamma)$. The superspace group is

$P^{P2_1/c}_{cmm}$ if (iii) is present,

$P^{P2_1}_{cm}$ otherwise.

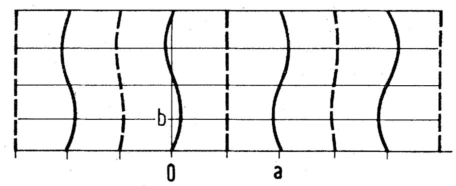

FIG. 3. Periodic distortions in M_I phase projected onto the a-b plane. Drawn lines, TTF; broken lines, TCNQ.

These groups are both *monoclinic*. Figure 3 illustrates the modulation in the a-b plane in the case where all the symmetry elements are present. We note that the space group of this phase is not a subgroup of the space group of M_{II} (or vice versa). The 38-K transition must therefore be first order.

At the 47-K transition one of the basis vectors changes from $(\vec{a},\frac{1}{2})$ to $(\vec{a},\frac{1}{2}+\delta)$. In analogy with a uniform structural phase transition in a normal $3d$ lattice, this transition can be accomplished by an excitation with wave vector $k=(\epsilon,0,0,0)$, $\epsilon\to 0$, and polarization $(0,0,0,p)$ [see Fig. 2(c)]. The displacement in 4D space corresponding to this excitation is

$$[\vec{u}(n,j)]_t=\vec{f}_j(\vec{q})\exp[i(\vec{q}\cdot\vec{n}-2\pi t+p\cos(\vec{k}\cdot\vec{n})]+\text{c.c.},$$

This is the soft phason introduced in Ref. 7. The phason belongs to an irreducible representation of $C^{P2_1/c}_{\cdot 1\bar{1}}$. The only rotational symmetry element which leaves k invariant is $\{m,\bar{1}\}$. The phason transforms as Γ_- with respect to the little group of this k. The inversion $\{\bar{1},\bar{1}\}$ leaves the phason invariant. This element is therefore either absent or present in both the phases M_{III} and M_{II}. To the same irreducible representation belongs *another* excitation given by the wave vector k and polarization $(0,p,0,0)$, which is an acoustical phonon. This means that there is a linear coupling between the (soft) phason and an irreducible strain of the M_I phase, and there is a distortion of the monoclinic lattice to a triclinic one; the angle γ between $\vec{a}$ and $\vec{b}$ axis should differ from 90° in M_{II} only!

[1](a) A. Janner and T. Janssen, Phys. Rev. B 15, 643 (1977); (b) T. Janssen, in Proceedings of NATO Advanced Study Institute, Geilo, Norway, 1977 (unpublished).

[2]P. M. de Wolff, Acta Crystallogr. A 30, 777 (1974); and in Ref. 1a.

[3]F. Denoyer, R. Comês, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 35, 445 (1975).

[4]R. Comês, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 35, 1518 (1975); Phys. Rev. B 14, 2376 (1976).

[5]Per Bak and V. J. Emery, Phys. Rev. Lett. 36, 978 (1976).

[6]W. D. Ellenson, R. Comês, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, Solid State Commun. 20, 53 (1976).

[7]Per Bak, Phys. Rev. Lett. 37, 1071 (1976).

[8]B. T. Kistenmacher, T. E. Phillips, and D. O. Cowan, Acta Crystallogr. B 30, 763 (1974).

[9]L. D. Landau and M. E. Lifshitz, *Statistical Physics*, 2nd ed. (Pergamon, New York, 1968), Chap. XIV.

[10]S. Kagoshima, T. Ishiguru, and H. Anzai, J. Phys. Soc. Jpn. 41, 2061 (1976).

[11]Per Bak and V. J. Emery (unpublished).

[12]A. Bjelis and S. Barisic, Phys. Rev. Lett. 37, 1515 (1976).