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Superspace symmetry and unconventional Landau models with several symmetry-breaking modes: thiourea and betaine calcium chloride dihydrate

J M Pérez-Mato
Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del Pais Vasco, Apdo 644, Bilbao, Spain

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Abstract. The models recently proposed for thiourea and betaine calcium chloride dihydrate, which consider the symmetry break at the normal–incommensurate transition as the result of the condensation of more than one symmetry-breaking normal mode, are discussed in the framework of superspace symmetry and alternatively using the Landau theory. The power and simplicity of the superspace approach for describing the modulation are explicitly shown. As in more conventional cases, the superspace symmetry introduces without further physical arguments restrictions on the form of the incommensurate modulation equivalent to those obtained through a Landau analysis where all possible secondary modes triggered at the transition are calculated, including those induced by high-order coupling terms.

1. Introduction

In the conventional Landau theory of a structural phase transition the symmetry breaking at the transition is determined by the symmetry of the order parameter. This symmetry is described by an irreducible representation of the space group of the high-symmetry phase. If the order parameter is multidimensional, the actual symmetry of the low-symmetry group also depends on the direction taken by the order parameter in the representation space [1].

Thus, in the case of a second-order commensurate–commensurate transition, the space group of the distorted structure is completely determined by the symmetry properties of the order parameter. All other modes or degrees of freedom which may be triggered and become spontaneous at the transition (secondary modes) have a symmetry higher than or equal to that of the order parameter. They cannot further lower the symmetry of the system. Any additional symmetry break can only be associated with a new phase transition. Also, any mode compatible with the space group of the distorted phase can be considered a secondary mode and takes non-zero values after the transition.

In principle, it would be possible to describe the distorted phase in terms of the superposition of the order parameter primary mode and the secondary modes, without making use of its space group. An enumeration of the allowed secondary modes using Landau theory would confirm that the number of parameters to be determined (complex amplitudes of the different modes and their polarization vectors) coincides with that necessary if the more usual and simple description is used in terms of atomic positions

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restricted by the space group. In this sense, the space group associated with the low-symmetry phase and determined solely by the order parameter is an effective way of enumerating all the degrees of freedom of the distorted structure.

The superspace group [2–4] describing the symmetry of an incommensurate (IC) phase plays an analogous role in the case of a commensurate–IC transition. Similarly to the commensurate space groups, the superspace group of an IC phase is completely determined by the symmetry of the order parameter [5, 6]. For order parameters corresponding to two-dimensional irreducible representations there is even a one-to-one correspondence between the superspace group and the irreducible representation of the order parameter [5, 7]. This has led in some cases to the erroneous belief that the superspace group of an IC phase is a concept totally equivalent to the irreducible representation associated with the order parameter. Both concepts play different roles, however. For instance, when the structure of the IC phase of K_2SeO_4 is restricted to conform to the superspace group $P(Pnam):(-1ss)$, the modulation is automatically forced to be the superposition of symmetry modes of wavevector $\boldsymbol{q}_n = n\boldsymbol{q}_i (\boldsymbol{q}_i = (\frac{1}{3} - \delta)\boldsymbol{a}^*$ being the IC modulation wavevector; $n = 1, 2, \ldots$) with symmetries Σ_2, Σ_3, Σ_4 and Σ_1, for $n = 6m \pm 1, n = 6m \pm 2, n = 6m + 3$ and $n = 6m$ ($m = 0, 1, 2, \ldots$), respectively [8]. The modes are also constrained to satisfy specific phase relations between them. An identical restriction on the secondary harmonics participating in the structural modulation of K_2SeO_4 can be obtained from a Landau analysis of the transition, taking $\Sigma_2(\boldsymbol{q}_i)$ as the symmetry of the order parameter. Hence, the superspace group identifies not only the symmetry of the primary distortion associated with the order parameter but also those corresponding to all possible secondary modes and eventual additional restrictions on their superposition.

Similarly, in the case of thiourea, the associated superspace group $P(Pnma):s-11)$ with $\boldsymbol{q}_i = \delta\boldsymbol{b}^*$ automatically implies that the first harmonic in the structural modulation as well as all other odd harmonics in the modulation, have τ_4 symmetry, while even harmonics correspond to the irreducible representation τ_1. In addition, the global phase of the nth harmonic Φ_n is restricted to satisfy $\Phi_n = n\Phi_1 \pmod{\pi}$, where Φ_1 is the free phase of the first harmonic [9]. Again, these symmetry restrictions can also be obtained from the Landau analysis of the transition from the *Pnma* phase with a $\tau_4(\boldsymbol{q} = \delta\boldsymbol{b}^*)$ order parameter [10].

The superspace symmetry associated with an IC structure is therefore fully equivalent to a description of the IC modulation in terms of modes triggered through their coupling with the order parameter in a generalized Landau potential. The use of superspace symmetry constitutes, however, a much simpler method as it automatically introduces, without further physical arguments, the structural consequences of these restrictions, as happens with space groups in the case of a commensurate structure.

The power of the superspace approach and the particular role played by the superspace group concept becomes clearer when we consider unconventional IC phases (real or hypothetical) which have more than one order parameter, i.e. the symmetry breaking is caused by two or more modes. In these cases, the superspace group of the IC structure is not directly related to a single irreducible representation and the advantages of the superspace description compared with a mode description become more significant. We analyse here from this viewpoint two rather different models recently proposed for thiourea and betaine calcium chloride dihydrate (BCCD).

In the case of thiourea, it has been suggested that the relative phase shift of the second- and third-order harmonics with respect to the main distortion (order parameter) may have general values not satisfying the constraint indicated above [10, 11]. Although

this model is discarded by the experimental evidence and physical arguments [9, 12], it is interesting to see its consequences in terms of superspace symmetry. In principle, it implies a reduction in the crystal superspace group determined by the main distortion to a smaller subgroup. The model requires, however, a smaller number of structural parameters than those resulting from the associated superspace group [9]. Hence, a description in terms of normal modes is apparently more effective than the superspace description. Here we prove that in fact this is not the case and the stronger restrictions on the IC structure coming from the mode description disappear when additional secondary modes are considered in the Landau analysis. Hence, the superspace group description is also in this hypothetical case an effective and simple way to introduce all physically acceptable restrictions on the IC modulation.

For BCCD, it was proposed [13, 14] that the IC primary modulation over the *Pnma* structure is the superposition of two modes of symmetries Λ_3 and Λ_2 (for notation see [15]). We shall show that the superspace group of such IC distortion is given by the intersection of the superspace symmetries associated with each of the modes. For special values of the phase shift between the two modes the resulting superspace group is maximal. It can be shown that these special phase relations are energetically favourable in a general Landau potential. As happens with more conventional models, the assigned superspace group automatically introduces the same symmetry structural restrictions which can be derived from a complex Landau analysis, where all coupled secondary modes are considered.

2. Thiourea

The order parameter symmetry at the normal–IC phase transition in thiourea is τ_4 in the notation of [8] (antisymmetric for σ_x and C_{2y}). Consequently, the superspace group associated with the IC phase is $P(Pnma):(s-11)$ [7]. The representative elements of the superspace group $P(Pnma):(s-11)$ are in the usual notation [7, 9]

$$\{E|000, 0\}, \{\sigma_x|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}, -\delta/2 + \tfrac{1}{2}\}, \{C_{2y}|0\tfrac{1}{2}0, -\delta/2 + \tfrac{1}{2}\}, \{\sigma_z|\tfrac{1}{2}0\tfrac{1}{2}, 0\}$$

$$\{I|000, \Phi_1/\pi\}, \{C_{2x}|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}, -\delta/2 + \tfrac{1}{2} + \Phi_1/\pi\}$$

$$\{\sigma_y|0\tfrac{1}{2}0, -\delta/2 + \tfrac{1}{2} + \Phi_1/\pi\}, \{C_{2z}|\tfrac{1}{2}0\tfrac{1}{2}, \Phi_1/\pi\}$$

where Φ_1 is the global phase of the first harmonic, while the superlattice generators are

$$\{E|100, 0\}, \{E|010, -\delta\}, \{E|001, 0\}, \{E|000, 1\}.$$

Under this superspace symmetry, odd and even harmonics in the IC modulation with wavevector $\boldsymbol{q}_n = n\boldsymbol{q}_i$ are forced to have, respectively, τ_4 and τ_1 symmetries while their phases Φ_n are constrained by the relation $\Phi_n = n\Phi_1 \pmod{\pi}$. Indeed, the modulated structure has been successfully refined using this superspace group [9]. (τ_1 is the fully symmetric representation for the point group of the wavevector.)

The model in [10, 11] considers that this constraint between the global phases of the first, second and third harmonics of the IC modulation can be eventually broken, while the harmonics maintain their symmetries τ_4, τ_1 and τ_4, respectively.

The superspace group, under which an nth secondary mode with global phase Φ_n (of symmetry τ_4 for n odd and τ_1 for n even) is invariant, is given by the elements (see [5] for a similar derivation)

$$\{E|000, 0\}, \{\sigma_x|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}, -\delta/2 + m/2\}, \{C_{2y}|0\tfrac{1}{2}0, -\delta/2 + m/2\}, \{\sigma_z|\tfrac{1}{2}0\tfrac{1}{2}, 0\}$$

$$\{I|000, \Phi_n/n\pi\}, \{C_{2x}|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}, -\delta/2 + m/2 + \Phi_n/n\pi\},$$

$$\{\sigma_y|0\tfrac{1}{2}0, -\delta/2 + m/2 + \Phi_n/n\pi\}, \{C_{2z}|\tfrac{1}{2}0\tfrac{1}{2}, \Phi_n/n\pi\}$$

where m is 0 and 1 for n even and odd, respectively, and the superlattice generators are

$$\{E|100, 0\}, \{E|010, -\delta\}, \{E|001, 0\}, \{E|000, 1/n\}.$$

It is easy to see now that, if the phase relationship $\Phi_n = n\Phi_1 \pmod{\pi}$ is fulfilled, the common superspace symmetry of the modulation, given by the intersection of all these groups, coincides with the superspace group $P(Pnma):(s-1\,1)$ associated with the primary distortion. If the phase relation is violated, the superspace symmetry is reduced to a lower subgroup given by the elements of $P(Pnma):(s-1\,1)$ not depending on the mode phase. This superspace group is labelled as $P(Pn2_1a):(ss\,1)$. It should be stressed at this point that this superspace group has been incorrectly labelled in previous literature [9, 10].

Not only does the new symmetry introduce, as new degrees of freedom, the free global phases of the different harmonics, but also the element $\{\sigma_y|0\tfrac{1}{2}0, -\delta/2 + \tfrac{1}{2} + \Phi_1/\pi\}$, which in the centrosymmetric group keeps the thiourea molecules invariant, is absent in this subgroup. As a consequence, some restrictions on the form of the atomic modulations disappear, and the harmonics are no longer forced to satisfy the τ_4 and τ_1 symmetries. In particular, the phases of the atomic modulations can take general values, different for each atom in the asymmetrical unit [9].

Summarizing, a hypothetical model which only lifts the constraints between the phases of the harmonics of the IC modulation while keeping their symmetry reduces the superspace symmetry to a non-centrosymmetric subgroup. However, the description of the structure in terms of this new superspace group implies automatically the introduction into the modulation of many additional degrees of freedom, so that its description in terms of the superposition of odd τ_4 and even τ_1 harmonics is no longer valid. The question is then whether such a model with stronger restrictions on the modulation than those coming from the corresponding superspace group is physically acceptable.

We shall show immediately by a simple Landau analysis that the answer is negative, and the additional degrees of freedom associated to the lower superspace group are physically relevant and are effectively triggered if the phase constraint is lifted.

Let us consider for instance a normal mode with $q = 2q_r$, symmetry τ_1 and coordinate Q_{2q_r,τ_1}. In general, its lowest coupling with the order parameter $Q_{q_r,\mathrm{op}}$ is given by a term in the Landau potential of the form

$$\tfrac{1}{2}V_4(Q^2_{q_r,\mathrm{op}}Q^*_{2q_r,\tau_1} + \mathrm{cc}) \tag{1}$$

or in polar coordinates

$$V_4\rho^2_{\mathrm{op}}\rho_{2q_r,\tau_1}\cos(2\Phi_{\mathrm{op}} - \Phi_{2q_r,\tau 1}) \tag{2}$$

where $(\rho_{\mathrm{op}}, \Phi_{\mathrm{op}})$, $(\rho_{2q_r,\tau_1}, \Phi_{2q_r,\tau_1})$ are the amplitudes and phases of the order parameter and the coupled mode, respectively.

A term such as (2), linear in the coupling variable, is sufficient to make the corresponding mode $2\boldsymbol{q}_i, \tau_1$ spontaneous at the transition, thus acting as a secondary mode or secondary order parameter. In the case of a continuous transition, the cosine function will also force the phase of the secondary mode to satisfy $\Phi_{2\boldsymbol{q}_i,\tau_1} = 2\Phi_{\rm op} \pmod{\pi}$.

The essential point not considered in previous work is that there exist in the structure not only one but several normal modes of symmetry $2\boldsymbol{q}_i, \tau_1$ and all of them will be coupled with the order parameter by terms of the type (2), with different coefficients V_4. Therefore, all of them will be spontaneous in the IC phase and the total second-order harmonic with wavevector $2\boldsymbol{q}_i$ will be the result of their superposition. If the phase constraint is satisfied by all the modes, their superposition, for which all the terms have the same phase, will keep the symmetry τ_1. In this case we can speak in practical terms of a single secondary $2\boldsymbol{q}_i, \tau_1$ mode. On the other hand, the presence in the second harmonic of a single mode $2\boldsymbol{q}_i, \tau_1$ with a phase violating the phase constraint is enough to break the global symmetry of the harmonic. As a result, the phases of the atomic modulations will no longer be fixed by symmetry (as predicted by the superspace group description) and will depend for each atom on the relative amplitudes and relative phases of the superposing modes.

A similar mechanism also exists for the first harmonic. Modes with the same symmetry and same wavevector as the order parameter are coupled with the second-order τ_1 modes by terms of the type

$$V_6\rho_{\rm op}\rho_{\boldsymbol{q}_i,\tau_4}\rho_{2\boldsymbol{q}_i,\tau_1}\cos(\Phi_{\rm op} + \Phi_{\boldsymbol{q}_i,\tau_4} - \Phi_{2\boldsymbol{q}_i,\tau_1}). \tag{3}$$

If a single mode $2\boldsymbol{q}_i, \tau_1$ does not fulfil the above-mentioned phase constraint, a term such as (3) will induce the presence in the first harmonic of secondary $\tau_4(\boldsymbol{q}_i)$ distortions with no fixed phase relation with the τ_4 primary distortion. Consequently, the modulation first harmonic will also lose its τ_4 symmetry.

It is also interesting to analyse the mechanism which reduces the symmetry of the average structure to the non-centrosymmetric subgroup $Pn2_1a$, as given by the superspace group. Homogeneous (zero-wavevector) modes of B_{2u} symmetry (antisymmetric for I, C_{2x}, C_{2z} and σ_y) are coupled to the order parameter and other $\tau_4(\boldsymbol{q}_i)$ modes by terms of the form

$$(\mathrm{i}/2)V_8\rho_{B_{2u}}(Q_{\boldsymbol{q}i,\rm op}Q^*_{\boldsymbol{q}_i,\tau_4} - \text{cc}) = V_8\rho_{B_{2u}}\rho_{\rm op}\rho_{\boldsymbol{q}_i,\tau_4}\sin(\Phi_{\rm op} - \Phi_{\boldsymbol{q}_i,\tau_4}). \tag{4}$$

These terms, as those presented previously, are always present in a full Landau potential of the transition. In a conventional Landau model the phase constraint at the free-energy minimum resulting from terms such as (3) makes the sine function in (4) take a zero value and the terms (4) become irrelevant. In the present hypothetical model, however, the violation of the phase constraint makes the terms active, so that they will induce the spontaneous condensation of the B_{2u} modes, which break the centre of symmetry of the average structure in the form expected from the superspace group description.

It is important to note that the coupling terms (2), (3) and (4) considered above are of relative low order in the order parameter (4, 6 and 8, respectively). Therefore the consequences of this (in particular those resulting from the first two coupling terms) cannot be ignored in a realistic model.

3. Betaine calcium chloride dihydrate

In this case, the basic structure of *Pnma* symmetry is proposed to be modulated by the action of two main modes with wavevector $\boldsymbol{q}_i = \delta\boldsymbol{c}^*$ and symmetries Λ_3 and Λ_2 [14]. The

superspace symmetry corresponding to a mode $\Lambda_3(q_i)$ (antisymmetric for σ_y and C_{2z}) is $P(Pnma):(1s-1)$, while it is $P(Pnma):(ss-1)$ in the case of a mode $\Lambda_2(q_i)$ (antisymmetric for σ_x and σ_y) [15]. The representative elements of the superspace group are in the two cases as follows: for $P(Pnma):(1s-1)$

$$\{E|000,0\},\{\sigma_x|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2},-\delta/2\},\{\sigma_y|0\tfrac{1}{2}0,\tfrac{1}{2}\},\{C_{2z}|\tfrac{1}{2}0\tfrac{1}{2},-\delta/2+\tfrac{1}{2}\}$$
$$\{I|000,\Psi/\pi\},\{C_{2x}|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2},-\delta/2+\Psi/\pi\},\{C_{2y}|0\tfrac{1}{2}0,\tfrac{1}{2}+\Psi/\pi\}$$
$$\{\sigma_z|\tfrac{1}{2}0\tfrac{1}{2},-\delta/2+\tfrac{1}{2}+\Psi/\pi\}$$

and, for $P(Pnma):(ss-1)$

$$\{E|000,0\},\{\sigma_x|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2},-\delta/2+\tfrac{1}{2}\},\{\sigma_y|0\tfrac{1}{2}0,\tfrac{1}{2}\},\{C_{2x}|\tfrac{1}{2}0\tfrac{1}{2},-\delta/2\}$$
$$\{I|000,\Phi/\pi\},\{C_{2x}|\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2},-\delta/2+\tfrac{1}{2}+\Phi/\pi\},\{C_{2y}|0\tfrac{1}{2}0,\tfrac{1}{2}+\Phi/\pi\},$$
$$\{\sigma_z|\tfrac{1}{2}0\tfrac{1}{2},-\delta/2+\Phi/\pi\}$$

where Ψ and Φ are the global phases of the modes Λ_3 and Λ_2, respectively, while the superlattice generators are

$$\{E|100,0\},\{E|010,0\},\{E|001,-\delta\},\{E|000,1\}.$$

Although, the IC structure of BCCD has been determined successfully under the superspace group $P(Pnma):(1s-1)$ [16], thus implying a single Λ_3 primary mode, it is again interesting to analyse the implications of this alternative model in the frame of superspace symmetry.

The superspace symmetry corresponding to the superposition of both modes is given by the intersection between both superspace groups. It is easy to see that the resulting group depends on the phase shift between both modes, so that

$$\begin{aligned}
&\Psi-\Phi=\text{arbitrary} && P(P1m1):(1s1)\\
&\Psi-\Phi=0\,(\text{mod}\,\pi) && P(P1\,2_1/m\,1):(1-1/s1)\\
&\Psi-\Phi=\pi/2\,(\text{mod}\,\pi) && P(P2_1ma):(-1s-1).
\end{aligned} \tag{5}$$

For any of these groups, the extinction rule in the diffraction diagram for diffraction vectors of type $(0,k,l,m)$, which exist for the intersecting superspace groups, disappear.

As in more conventional cases, it can be shown that the phase relations in (5) corresponding to the maximal superspace symmetry are physically favoured. If we call (Q_{q_i},Q_{-q_i}) and (P_{q_i},P_{-q_i}) the complex coordinates corresponding to the modes Λ_3 and Λ_2, their lowest-order coupling terms in a generalized Landau potential are

$$Q_{q_i}Q_{-q_i}P_{q_i}P_{-q_i}=\rho^2_{\Lambda_3}\rho^2_{\Lambda_2} \tag{6}$$

and

$$Q^2_{q_i}P^2_{-q_i}+Q^2_{-q_i}P^2_{q_i}=2\rho^2_{\Lambda_3}\rho^2_{\Lambda_2}\cos[2(\Psi-\Phi)]. \tag{7}$$

The first term is isotropic, but the second favours configurations with $\Psi-\Phi=0$ or $\pi/2$ (mod π) corresponding to the maximal superspace groups.

Another significant question is how the superspace group associated with the modulation $\Lambda_3+\Lambda_2$ allows an average structure of lower symmetry than *Pnma*, if in fact the average structure of both Λ_3 and Λ_2 modulations has *Pnma* symmetry.

Again in this case, the assigned superspace group is taking into account implicitly and without using any physical argument the consequences of the triggering of additional degrees of freedom through their coupling with the primary modes. For instance, if we consider the symmetry properties of the modes it is easy to see that homogeneous modes of symmetry B_{2g} (antisymmetric for C_{2x}, C_{2z}, σ_x and σ_z) and B_{3u} (antisymmetric for C_{2y}, C_{2z}, I and σ_x) will be coupled to the primary modes by terms of the type

$$\rho_{B_{2g}}(Q_{q_i}P_{-q_i} + Q_{-q_i}P_{q_i}) = 2\rho_{B_{2g}}\rho_{\Lambda_3}\rho_{\Lambda_2}\cos(\Psi - \Phi) \tag{8}$$

$$i\rho_{B_{3u}}(Q_{q_i}P_{-q_i} - Q_{-q_i}P_{q_i}) = 2\rho_{B_{3u}}\rho_{\Lambda_3}\rho_{\Lambda_2}\sin(\Psi - \Phi). \tag{9}$$

The B_{2g} modes reduce the *Pnma* symmetry of the average structure to its subgroup $P12_1/m1$, while modes of symmetry B_{3u} induce an average structure of $P2_1ma$ symmetry. Terms of the type (8) and (9) are responsible for the symmetry of the average structure, as predicted by the assigned superspace groups. The minimization of the free energy leads to the condensation of one of these types of mode depending on the actual value (0 or $\pi/2$) of the phase shift $\Psi - \Phi$. If this latter takes a general value, both terms are non-zero and both types of homogeneous mode become spontaneous, reducing the symmetry of the average to $P1m1$, as expected from the superspace group assignment.

4. Conclusions

It has been shown using two hypothetical examples corresponding to IC phases whose symmetry cannot be described by a single order parameter that, even in these unconventional cases, the use of superspace symmetry in the structural description of the IC phase introduces without requiring any physical reasoning the same restrictions on the structural modulation as those derived by a complete Landau analysis, which has to include all eventual spontaneous coupled modes. As both approaches are equivalent, it may be a question of taste, background or personal preference to use one or the other. However, a Landau description without a full consideration of all possible coupled modes, as often done, can lead to erroneous structural models, as has happened in the literature for thiourea. In the superspace approach, the symmetry-breaking modes determine the structure superspace group, and this latter automatically includes in a standard crystallographic form all physically meaningful restrictions on the structural model.

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