Application of the High-Symmetry Superspace-Group Description to the Refinement of the Lock-In Structure of Rb_2ZnCl_4

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Abstract

The advantages of using the high-symmetry superspace-group description for the refinement of modulated commensurate structures are discussed, using the ferroelectric phase of Rb_2ZnCl_4 as an example. It is shown that the refinement process is faster and easier to handle than when the usual low-symmetry description is used. Through the choice of a common superspace group for the incommensurate and the lock-in structures, a natural physical hierarchy between the structural parameters may be established, allowing an appropriate block separation and thus accounting efficiently for correlations.

1. Introduction

The superspace formalism (de Wolff, 1974; Janner & Janssen, 1980; de Wolff, Janssen & Janner, 1981), which was originally developed to describe incommensurate modulated structures, has been shown to be useful for the description of commensurate modulated structures as well: numerous superstructures have been described and refined within this framework.

Experimentally, most modulated phases are observed by changing the temperature of the samples. In these cases, the crystals usually undergo phase transitions following a normal–incommensurate–commensurate phase sequence as the temperature is lowered. The normal phase (*N*) is characterized by one of the 230 space groups; the incommensurate phase (IN) may be looked upon as a distortion of a basic structure that in general coincides with phase *N*; it is described by a superspace group (SSG). The commensurate phase (*C*) appears when the periodicity of the distortion locks in with that of the *N* phase; this structure can be described using either a standard space group or the superspace formalism. In the latter case, the *C* phase is considered as a distortion of a basic structure that has the same periodicity as the *N* structure; however, there are two possible choices for the symmetry of the basic structure, corresponding to that of the superstructure or to that of the *N* phase, provided the first is a subgroup of the second. These two possibilities lead to two different

SSG's called 'low symmetry' (LS) and 'high symmetry' (HS), respectively (Pérez-Mato, Madariaga, Zuñiga & Garcia Arribas, 1987).

The HS description has been advantageously employed to interpret many physical properties of modulated systems involving *C* phases; for instance, Dam & Janner (1986) studied morphological aspects; Janssen (1986) described the complete phase diagram of A_2BX_4 compounds in a unified way, and Meekes, Janner & Jannsen (1988) applied general vibrational selection rules to a series of phases of a compound of the same family. However, up to now the refinement of *C* structures with the superspace formalism has been performed using the LS description; this has been so not because it is intrinsically more convenient but because the usual structure-factor formulae (Yamamoto, 1982*a*) are not compatible with the HS description.

This problem has been addressed recently, and an expression for the structure-factor formulae, valid for both LS and HS descriptions, was given (Parisi, 1994, hereafter referred to as I). Beyond the formal aspect of the question, there are certain advantages in using the HS description for the analysis of *C* structures, which have been theoretically discussed in the literature (Pérez-Mato, Madariaga, Zuñiga & Garcia Arribas, 1987; van Smaalen, 1987; Pérez-Mato, 1991).

The fundamental one stems from the fact that the assignment of the same SSG to the IN and *C* phases formally allows the distortion in both phases to be expressed in terms of modes of the same symmetry in the *N* phase, yielding a natural continuity in the description of the system as its phase evolves with temperature. Obviously, there are characteristics that are specific for each phase: owing to the incommensurability of the modulation vector q_{IN} (for simplicity, we assume a one-dimensional modulation) in the IN phase, the basis of normal modes that describe the distortion is infinite, containing all modes with wavevector nq_{IN} (integer *n*) with the appropriate symmetry. On the other hand, in the *C* phase (modulation vector q_C), the finite basis is limited to those modes of wavevector nq_C of the appropriate symmetry that are not redundant with respect to a translation of a reciprocal-lattice vector of the *N* structure. In practice, this distinction is largely

academic: in the IN phase (at least in the sinusoidal regime), the size of the basis is limited by the order of the observable satellite reflections, and is usually reduced to the principal mode that condenses at the transition temperature and eventually some low-order harmonic term; as a result, both phases have most of their relevant terms in common, and this allows a correspondence to be established between some of the structural parameters of each phase. Experimentally, on the other hand, it is often found that, in materials presenting the N–IN–C phase sequence, the distortion related to the primary mode is practically the same in both modulated phases (Pérez-Mato, Gaztelua, Madariaga & Tello, 1986; Madariaga, Zuñiga, Pérez-Mato & Tello, 1987; Aramburu, Madariaga, Pérez-Mato & Breczewsky, 1996) and the higher-order terms that become relevant in the C phase are small with respect to the primary one. Thus, the HS description allows us to establish a physical hierarchy in the structural parameters for the C phase, leading to an improvement in the refinement strategy.

In this work, we present the first refinement of a C structure using the HS description, made possible by the introduction of the modifications given in I into the program *REMOS* (Yamamoto, 1982*b*). We have used as an example Rb_2ZnCl_4, a well known material presenting the N–IN–C phase sequence. The C-phase structure has been solved using the conventional 3D formalism (Quilichini & Pannetier, 1983); later, Hedoux, Grebille, Jaud & Godefroy (1989, hereafter referred to as II) determined the IN and C structures using the superspace formalism, refining the C structure in the LS description; however, owing to an erroneous choice of the phase of the modulation, their results are not correct. Here we present a refinement using the data of II; the discussion, however, is focused on the comparison of the LS and HS descriptions, pointing out the important advantages inherent to the latter.

2. Superspace formalism for commensurate structures

In the superspace formalism, a one-dimensionally modulated structure is described through a $(3 + 1)$-dimensional space group. A symmetry element of such a space group can be written as $(R_E R_I | \mathbf{v}_E \tau_4)$; $(R_E | \mathbf{v}_E)$ is a 3D operator that acts on the 3D real space and $(R_I | \tau_4)$ $(R_I = \pm 1)$ acts on the fourth coordinate $\bar{x}_4^\nu$ defined, for each atom ν, as

$$\bar{x}_4^\nu = \mathbf{q} \mathbf{r}_0^\nu + t, \tag{1}$$

where $\mathbf{r}_0^\nu$ is the position of an atom ν in the basic structure, t is the initial phase that determines the section of the supercrystal parallel to the three-dimensional space at which atom ν lies, and $\mathbf{q}$ is the modulation wavevector, which is written as

$$\mathbf{q} = (1/M) \sum_i m_i \mathbf{a}_i^*, \tag{2}$$

M and m_i being integers and $\mathbf{a}_i^*$ basic unit reciprocal-lattice vectors.

The condition for the superspace operation $(R_E R_I | \mathbf{v}_E \tau_4)$ to be associated with a 3D space group $(R_E | \mathbf{v}_E)$ is

$$\tau_4 - \mathbf{q} \mathbf{v}_E + (R_I t - t) = 0. \tag{3}$$

If $R_I = 1$, τ_4 is fixed. For $R_I = -1$, the operator will be an element of the 3D space group, for a given value of τ_4, for the sections t fulfilling condition (3). If t_0 is the chosen section with the appropriate symmetry, there exists another independent section $t = t_0 + 1/2M$ that has the same space-group symmetry. The set of symmetry operators that leaves invariant these sections form the low-symmetry SSG $\{G_L\}$.

The possibility of adopting the high-symmetry SSG $\{G_H\}$ is related to the existence of these two invariant sections in the supercrystal; when the HS description is feasible, both sections are linked by the symmetry operations of $\{G_H\}$ that do not correspond to operations of the space group of the superstructure. The real structure is then built up from the independent $(t = t_0)$ atoms by the application of the symmetry operators belonging to $\{G_L\}$, and from the independent $(t = t_0 + 1/2M)$ atoms by the application of the remaining symmetry operators belonging to $\{G_H\}$.

A general expression for the sections t on which the independent atoms must be placed before the application of a symmetry operator, in order to produce non-zero contributions to the structure factors, is $t = R_I(t_0 + \mathbf{q}\mathbf{v}_E - \tau_4) \mathrm{mod}(1/M)$. This fact is taken into account in the structure-factor formulae proposed in I, which were included in the refinement program *REMOS* (Yamamoto, 1982*b*), and used in the redetermination of the structure of the lock-in phase of Rb_2ZnCl_4, which is discussed in the following section.
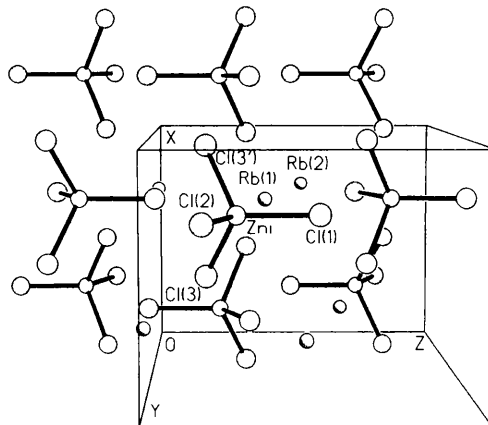

Fig. 1. Representation of the structure of the N phase of Rb_2ZnCl_4 along the *b* axis.

Table 1. *Elements of the superspace groups* $P^{Pmcn}_{\quad s\,s\,\bar1}$ *and*
$P^{P2_1cn}_{\quad\bar1\,s\,\bar1}$

$P^{Pmcn}_{\quad s\,s\,\bar1}$	
$P^{P2_1cn}_{\quad\bar1\,s\,\bar1}$	
$(E, 1\|0, 0, 0, 0)$	$(I, \bar1\|0, 0, 0, \alpha)$
$(C_{2x}, \bar1\|\frac12, 0, 0, \frac12 + \alpha)$	$(\sigma_x, 1\|\frac12, 0, 0, \frac12)$
$(\sigma_y, 1\|0, \frac12, \frac12, \frac12)$	$(C_{2y}, \bar1\|0, \frac12, \frac12, \frac12 + \alpha)$

3. Application to the lock-in phase of Rb_2ZnCl_4

Like other members of the A_2BX_4 family, Rb_2ZnCl_4 exhibits the normal–incommensurate–commensurate phase sequence when the temperature is lowered [see Cummins (1990) for a review of these materials]. The normal structure (Fig. 1) has space-group symmetry *Pmcn* $(Z = 4)$, with all the atoms lying on special positions $4(c)$, except for one chlorine atom [Cl(3)]. The incommensurate phase is characterized by the modulation wavevector $\mathbf{q} = (\frac13 - \delta)\mathbf{c}^*$, δ being a function of temperature. At $T \simeq 191\,\mathrm{K}$, $\delta = 0$ and the threefold commensurate phase, characterized by a triplicate cell along $\mathbf{c}$ and a spontaneous polarization along $\mathbf{a}$, is reached.

The threefold commensurate structure of Rb_2ZnCl_4 has space-group symmetry $P2_1cn$. In the superspace formalism, the two equivalent SSG that may be assigned for this phase are $\{G_H\} = P^{Pmcn}_{\quad s\,s\,\bar1}$ (HS) and $\{G_L\} = P^{P2_1cn}_{\quad\bar1\,s\,\bar1}$ (LS). In the latter case, the basic structure has another independent atom generated by the application of the σ_x operation on the Cl(3) atom. The symmetry elements of these superspace groups are given in Table 1.

For $\alpha = \frac12$, the $t = 0 \bmod(\frac13)$ and the $t = \frac16 \bmod(\frac13)$ sections have space-group symmetry $P2_1cn$. Both sets of sections are invariant with respect to the application of a symmetry operator belonging to $\{G_L\}$ (first column in Table 1) and are connected by the symmetry operators of $\{G_H\}$ that do not belong to $\{G_L\}$ (second column in Table 1). It is worth noting that the values $\alpha = 0$ and $t = 0$ taken in II give space-group symmetry $P1c1$ for the superstructure.

With the basic structure known, the structural parameters needed to describe the structure are the amplitudes involved in the modulation function, which can be expressed as a Fourier series in terms of the internal coordinates $\bar x_4^\nu$:

$$\mathbf{u}^\nu(\bar x_4^\nu) = \sum_{n=0}^{n_{max}} (\mathbf{u}_n \cos 2\pi n\bar x_4^\nu + \mathbf{v}_n \sin 2\pi n\bar x_4^\nu), \quad (4)$$

where n_{max} is the maximum Fourier order consistent with the description (LS or HS) and the multiplicity of the superstructure.

In the LS description, all the atoms are in general positions, and therefore there are no restrictions on the modulation functions. In terms of the symmetry modes

of the basic structure $(P2_1cn)$, the distortion corresponding to each atom is decomposed as $3A_g(\mathbf{k} = 0) + 6\Sigma_2(\mathbf{k} = \frac13\mathbf{c}^*)$ (where Σ_2 is antisymmetric with respect to σ_y). This decomposition is consistent with taking terms with $n = 0$ and 1 in (4), leading to 63 positional parameters to be determined, in agreement with the degrees of freedom in the standard 3D treatment (Pérez-Mato, 1991).

In the HS description, the modulation functions of the atoms in special positions $4(c)$ [Rb(1), Rb(2), Zn, Cl(1) and Cl(2)] are restricted by the presence of the element $(\sigma_x\|\frac12, 0, 0, \frac12)$, giving the rules

$$(u_n^\nu)_x = (v_n^\nu)_x = 0 \quad (n = \text{even}) \quad (5)$$

$$(u_n^\nu)_{y,z} = (v_n^\nu)_{y,z} = 0 \quad (n = \text{odd}). \quad (6)$$

In terms of the symmetry modes of the basic structure $(Pmcn)$, the modulation function corresponding to each atom is decomposed as $2(3)A_{1g}(\mathbf{k} = 0) + 2(6)\Sigma_2(\mathbf{k} = \frac13\mathbf{c}^*) + 4(6)\Sigma_3(\mathbf{k} = \frac13\mathbf{c}^*) + 1(3)B_{2u}(\mathbf{k} = 0)$ (Pérez-Mato et al., 1986). The numbers between parentheses indicate the decomposition of the modulation function for the Cl(3) atom. It can be seen that the Fourier description (4) includes up to $n = 3$ terms. Comparing the expressions for the distortion in the two descriptions, we see that the $n = 0$ $(n = 1)$ terms in LS correspond to the $n = 0$ and 3 $(n = 1$ and 2$)$ ones in HS.

4. Refinements of the structure

The structure was refined in the framework of both descriptions in order to compare the methods; we have used the structure factors, measured at 115 K, given in II (1215 main reflections and 1065 first-order satellite reflections). At that temperature, the unit-cell parameters are: $a = 7.230$, $b = 12.608$ and $c = 9.199\,\text{Å}$. The general minimized function was $R_w = \sum w|\Delta F|^2 / \sum w|F_o|^2$ $(w = 1$ in our refinement). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974); anisotropic displacement parameters were employed for all the atoms; in the first stage, only zero-order Fourier terms were included, leading to 42 of these parameters in the LS description and to 26 in the HS one.

When the refinement is attempted using the LS description, including all structural parameters in a single block, it was observed that the convergence process was extremely slow; furthermore, the minimum thus obtained depended on the starting point and the values of R_w were unreasonably high. In order to get a reasonable convergence to the true structure, it is indispensable to separate the parameters, as usual, in blocks; the definition of these is, in the LS case, non-trivial. Inevitably, one has to refer to the incommensurate phase and establish links between structural parameters of both phases to be able to decide which of these were more relevant in the C phase; but this

Table 2. *Positional* $(\times 10^4)$ *and equivalent isotropic displacement parameters* $(\mathring{A}^2 \times 10^4)$ *of the superstructure*

- parameter fixed at 0 by symmetry;   * fixed to constrain translation along polar axis.

		r_0	u_0	u_1	v_1	u_2	v_2	u_3	U_{eq}†
Rb(1)	x	2500	–	−133 (3)	−143 (2)	–	–	9*	
	y	4067	−8 (1)	–	–	41 (4)	10 (4)	–	289 (6)
	z	6298	−9 (1)	–	–	−10 (4)	−8 (4)	–	
Rb(2)	x	2500	–	−205 (2)	−19 (2)	–	–	39 (6)	
	y	8196	−5 (1)	–	–	2 (3)	−14 (3)	–	129 (5)
	z	4862	14 (1)	–	–	−15 (4)	11 (3)	–	
Zn	x	2500	–	−112 (2)	40 (2)	–	–	−161 (42)	
	y	4217	−2 (1)	–	–	10 (3)	9 (3)	–	78 (5)
	z	2240	−11 (1)	–	–	−17 (4)	10 (4)	–	
Cl(1)	x	2500	–	−516 (7)	78 (8)	–	–	−33 (10)	
	y	4189	17 (2)	–	–	70 (6)	−12 (7)	–	211 (12)
	z	−175	−18 (2)	–	–	4 (8)	45 (7)	–	
Cl(2)	x	2500	–	−87 (11)	623 (7)	–	–	−118 (26)	
	y	5851	−12 (2)	–	–	26 (7)	8 (6)	–	218 (11)
	z	3204	29 (2)	–	–	−16 (11)	1 (7)	–	
Cl(3)	x	10	6 (2)	−59 (4)	−236 (4)	−23 (7)	4 (6)	106 (20)	
	y	3410	−25 (2)	0 (4)	314 (3)	19 (6)	−1 (4)	−116 (10)	235 (10)
	z	3139	−27 (2)	121 (4)	163 (3)	−2 (6)	−42 (5)	−53 (13)	

† $U_{eq} = (U_{11} + U_{22} + U_{33})/3$ was calculated using the zeroth-order Fourier terms.

correlation is not obvious because they do not have a common basis structure; it can be established for some atoms lying on symmetry elements (in our case, those on σ_x in the N phase) but not for those on general positions. Finally, convergence was achieved after 25 cycles. In short, the refinement process using LS was slow, laborious, and required a lot of non-systematic manual intervention, even for our relatively simple structure.
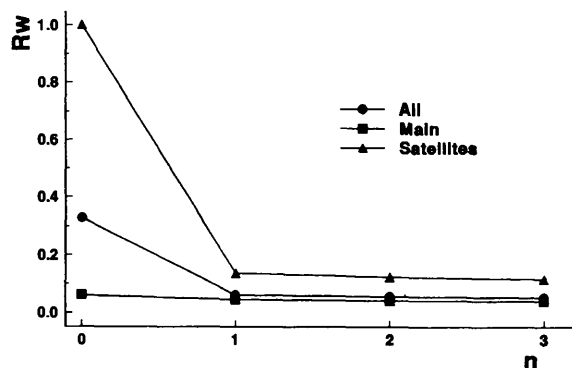
The situation is completely different in the HS description: since IN and C phases are described through a common basis structure, parameters having a common physical meaning are easily identified. In the IN phase, the distortion, in the sinusoidal regime, is characterized essentially by A_g and Σ_2 modes, and it is straightforward to attempt a refinement assuming this distortion will be the leading one in the C phase, and including as a first step only the $n = 0$ and 1 Fourier terms. After a few cycles, the refinement converges to $R_w = 0.061$ for all reflections (0.045 and 0.135 for main

Fig. 2. Evolution of the R_w factors as a function of the Fourier order included in the modulation functions.

and first-order satellite reflections, respectively), although the process was started with all positional parameters set to zero. At this point, the main characteristics of the distortion are already taken into account (see Fig. 2); addition of the successive orders $n = 2, 3$ do not change it much, although they may be important for other reasons: the order $n = 3$, involving a B_{2u} mode, carries the ferroelectrical property. At the final stage, and after 12 cycles, the reliability R_w values obtained with 63 positional and 26 thermal parameters were 0.0533, 0.040 and 0.115 for all, main and first-order satellite reflections, respectively.

It is obvious that, in the end, the only difference between the structures refined using LS and HS may lie in the number of thermal parameters used. To make them coincide, it is necessary to include the $n = 3$ order in the HS description (remembering that $n = 0$ in LS is equivalent to $n = 0$ and $n = 3$ in HS). In this situation, the values R_w obtained were 0.0516, 0.039 and 0.111 for the sets of reflections mentioned, which compare favorably, for obvious reasons, with those reported in II (0.0587, 0.041 and 0.136), especially so for the set of satellite reflections. In Table 2, the final values of the refined structural parameters are shown.

5. Discussion

The structural characteristics of the compounds of the A_2BX_4 family that undergo incommensurate and lock-in phase transitions have been repeatedly described, and the behavior of Rb_2ZnCl_4 in the commensurate phase found here is similar: an almost rigid rotation of the $ZnCl_4$ tetrahedra and a relative displacement of the Rb atoms with respect to the rigid tetrahedra, which gives rise to the ferroelectricity of the material. From the

structural point of view, it is interesting to correlate the measured polarization (Hamano, Ikeda, Fujimoto, Ema & Hirotsu, 1980) with the structural parameters of Table 1 (in particular, those corresponding to the $n = 3$ Fourier term, which are closely related to the spontaneous polarization), as a way to check the theoretical models for the charge distributions of the tetrahedra, a matter that has been the object of special attention for the construction of interatomic potentials (empirical or otherwise) that explain the instabilities that drive the N–IN phase transition (Lu & Hardy, 1992; Extebarria, Pérez-Mato & Madariaga, 1992). With the charge distribution calculated by Lu & Hardy (charge $+0.9508e$ for Zn and $-0.7377e$ for Cl), we obtain for the calculated polarization a value of $0.11\,\mu C\,cm^{-2}$, very close to that measured by Hamano et al. (1980) ($0.12\,\mu C\,cm^{-2}$) for temperatures scarcely below the lock-in transition.

Beyond specific structural questions, the aim of this paper was to show in practice the application of the HS description to the refinement of commensurate modulated structures, and to compare it with the LS one. The main advantage found in the former description lies in its ability to describe the material with the same SSG in the IN and C phases as it evolves, for example, with temperature, thus making possible a direct relation between structural parameters in both phases. In LS, instead, there is a loss of 'memory' of the physical path of the material, preventing, in general, a correlation with the IN distortion; in this sense, we can refer to HS as a 'physical' description, and to LS as a 'structural' one. The structure determination presented above is an example of the great improvement in the refinement process when the physics of the problem is taken into account; the main difference appears in the earlier stages; the HS description allows an effective decrease of structural parameters through the inclusion of only those Fourier terms that are relevant in the IN phase, thereby introducing correlations between otherwise independent atoms without an artificial increase of spatial symmetry. The existence of these correlations is one of the main problems in the refinement of superstructures; the HS formalism appears as most efficient to cope with it. The example presented here may be one of the simplest to deal with; in more complex cases, with large superstructures and/or a high number of independent atoms, the use of the HS description will probably be not only convenient but indispensable.

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