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Ferroelectric–paraelectric phase transitions with no group–supergroup relation between the space groups of both phases?

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The structures of $Sr_3(FeF_6)_2$, β-NbO_2, $TlBO_2$ and $CrOF_3$, previously reported as possible ferroelectrics with no group–supergroup relation between the ferroelectric and the paraelectric symmetries, have been carefully studied. We could not confirm any structural pseudosymmetry with respect to a space group which is not a supergroup of their room-temperature polar space group. In all cases, pseudosymmetry was indeed detected, but only for non-polar supergroups of the actual space groups of the structures. In this sense, the four compounds are possible ferroelectrics, but fulfilling the usual group–supergroup relation between the phase symmetries.

1. Introduction

In the last decade a method for the search of new ferroelectrics based on the detection of structural pseudosymmetry has been developed and applied with great success (see *e.g.* Abrahams, 1994, and references therein). Polar structures having displacements smaller than 1 Å with respect to a hypothetical non-polar configuration were considered as materials with a high probability of having a phase transition into this configuration, *i.e.* as possible ferroelectrics.

Recently, the search of new ferroelectrics among the structures listed in the Inorganic Crystal Structure Database (ICSD; Bergerhoff & Brown, 1987) with point group symmetry 4 has been reported (Abrahams, 1999) with more than 22 new potential ferroelectrics predicted. As expected, in most cases the symmetry of the predicted paraelectric phases achieved by phase transitions is characterized by a space group which is a supergroup of the initial polar space group. However, the author also claims to have discovered four structures whose pseudosymmetry is indicative of transitions from the paraelectric to the ferroelectric phase, which are not subject to a group–supergroup relationship. The reported cases are $Sr_3(FeF_6)_2$, β-NbO_2, with $I4_1$ polar symmetry and pseudosymmetry characterized by the group $I4/m$, and $TlBO_2$, with predicted transitions from $P4_1$ to $P4/m$. As a fourth case, the $CrOF_3$ is attributed a ferroelectric to paraelectric phase transition without a symmetry change.

The aim of this short communication is a careful study of the reported four exceptional cases. The reason is obvious: the existence of a paraelectric ferroelectric phase transition without a group–subgroup symmetry relation between the two structures would be inconsistent with the symmetry-breaking principle which is on the basis of the accepted models or mechanisms of ferroelectricity. In principle, ferroelectricity requires the possibility of polarization reversal through the existence of equivalent domains related by 'lost' symmetry operations. The polarization or polar distortion should act as a symmetry-breaking order parameter, whose null value becomes unstable at the transition. There is no fundamental principle denying the possibility of a first-order polar–nonpolar phase transition without group–subgroup relation, but it is clear that this type of transition would not comply with the features usually associated with ferroelectric phase transitions.

We apply two alternative methods for the study of the pseudosymmetries of each of the above-mentioned structures:

(i) A pseudosymmetry search procedure based on the assumption that the high-symmetry (prototype) structure is described by a supergroup of the structure space group (Igartua *et al.*, 1996). The procedure has already been successfully applied to the pseudosymmetry search and prediction of possible ferroelectrics for the ICSD structures with space groups *Pba*2 (Kroumova *et al.*, 2000*a*) and $Pmc2_1$ (Kroumova *et al.*, 2001). The algorithmization of the generalized pseudosymmetry procedure serves as a basis for the computer program *PSEUDO*[1] (Kroumova *et al.*, 2000*b*), which forms part of the Bilbao Crystallographic Server (Kroumova *et al.*, 1998).

(ii) We apply a completely independent method for the search of pseudosymmetries characterized by a group which is not a supergroup of the initial structure. In our trials to reproduce the results claimed in Abrahams (1999), we use a type of 'direct' method: after generating the structure from the data available, the atomic coordinates were checked against the proposed pseudosymmetries without imposing any group–subgroup constraints. In addition, the structures were tested by the program *KPLOT/RGS* (Hundt, 1979; Hannemann *et al.*, 1998).

2. Results

2.1. $Sr_3(FeF_6)_2$

The tetragonal unit cell of $Sr_3(FeF_6)_2$, with $a = 20.338$ and $c = 14.668$ Å, contains 24 formula units in the space group $I4_1$ with atomic coordinates given in Abrahams *et al.* (1984). The authors have determined additional pseudosymmetry relations between the atomic coordinates with respect to the operation $(x, y, \bar{z})$. According to Abrahams (1999) such a pseudosymmetry is indicative of a possible phase transition to a paraelectric phase with the symmetry $I4/m$, which is not a supergroup of $I4_1$.

The application of our 'direct' method and the program *KPLOT/RGS* show that indeed the structure is pseudosymmetric with respect to a reflection of the type $(x, y, \bar{z})$. However, the polar structure is not found to be pseudosymmetric with respect to the rest of the elements of $I4/m$, *i.e.* the prediction of a possible paraelectric phase with $I4/m$ symmetry is not confirmed. This 'apparent contradiction' is easy to understand, taking into account the fact that the pseudosymmetry operation of $(x, y, \bar{z})$ is an element of the supergroup $P4_2/m$ of the polar group $I4_1$, with half the c constant (Fig. 1*a*). Therefore, $Sr_3(FeF_6)_2$ is pseudosymmetric with respect to a supergroup containing the mirror plane detected in Abrahams *et al.* (1984). This pseudosymmetry has been confirmed by the program *PSEUDO*: the displacements necessary to obtain the hypothetical structure with symmetry $P4_2/m$ are along the three directions with maximal value ~0.7 Å.

2.2. β-NbO_2

The polar phase of this compound has symmetry given by the space group $I4_1$ and cell constants $a = 9.693$ and $c = 5.985$ Å (Schweizer & Gruehn, 1982). According to Abrahams (1999) an origin shift along z with the value −0.0052 reduces the atomic deviations from a non-polar structure with symmetry given by the space group $I4/m$ to less than 0.19 Å (*cf.* Table 6 of Abrahams, 1999). The direct verification of this result is not possible as the pseudosymmetry operations for which the given displacements have been calculated are not specified. Our direct-method calculations show that the structure β-NbO_2 is not pseudosymmetric with respect to $I4/m$ and that the listed displacements are very similar to those corresponding to a pseudosymmetry inversion center at (0, 0, −0.0052) with respect to the origin of the $I4_1$ structure reported in Schweizer & Gruehn (1982).

The systematic search among the supergroups of $I4_1$ demonstrated that indeed the structure is pseudosymmetric for the supergroup $P4_2/mnm$, with index $[i] = 16$. This supergroup has been obtained following the chains of minimal supergroups given in Fig. 1(*b*). The position of the origin (0, 0, 0.0078) of the non-polar group with respect to the polar one is determined by the optimization *PSEUDO* procedure, so that the maximal atomic displacement necessary to obtain the non-polar supergroup symmetry of $P4_2/mnm$ has the value ~0.2 Å. In fact, the structure is also pseudosymmetric for all intermediate groups forming the $I4_1$–$P4_2/mnm$ graph of minimal supergroups (Fig. 1*b*).

One should note that the values of the displacements given in Table 6 of Abrahams (1999) are practically the same as those obtained for the intermediate supergroup $P4_2/m$, with index $[i] = 4$.

The program *KPLOT/RGS* also determines the structure β-NbO_2 as pseudosymmetric with respect to $P4_2/mnm$. This result is in fact in accordance with the conclusions of Schweizer & Gruehn (1982), who found that β-NbO_2 has a deformed rutile-type structure.

2.3. $TlBO_2$

The compound has polar symmetry given by the space group $P4_1$ with cell constants $a = 7.38$ and $c = 9.35$ Å (Touboul & Amoussou, 1978). According to Abrahams (1999), a shift of the origin along z with 0.0463 leads to an atomic array forming a structure which is pseudosymmetric with respect to $P4/m$, where all displacements are less than 0.7 Å.

However, application of the direct pseudosymmetry search does not show any $P4/m$ pseudosymmetry of $TlBO_2$. Our attempts to find pseudosymmetry operations with the displacements listed in Abrahams (1999) were not completely successful. The best agreement (with the exception of the atoms Tl1 and B1, *cf.* Table 2 of Abrahams, 1999) is

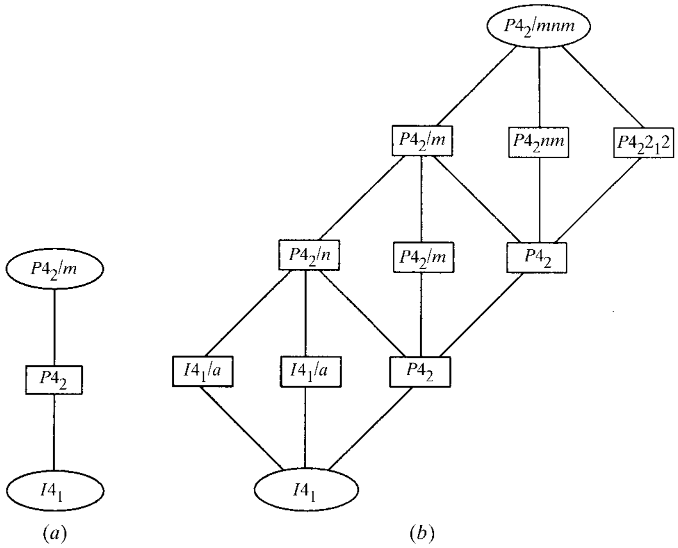

Figure 1
Chains of minimal supergroups that relate: (*a*) $I4_1$ with $P4_2/m$. The basis $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$ of the supergroup $P4_2/m$ is related with the basis $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ of the group $I4_1$, as follows: $\mathbf{a} = \mathbf{a}' - \mathbf{b}'$, $\mathbf{b} = \mathbf{a}' + \mathbf{b}'$, $\mathbf{c} = \mathbf{2c}'$ with an additional origin shift of $(0\ \frac{1}{2}\ 0)$. (*b*) $I4_1$ with $P4_2/mnm$. The basis $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$ of the supergroup $P4_2/mnm$ is related with the basis $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ of the group $I4_1$, as follows: $\mathbf{a} = \mathbf{2a}'$, $\mathbf{b} = \mathbf{2b}'$, $\mathbf{c} = \mathbf{2c}'$ with an additional origin shift of $(-\frac{1}{2}\ 0\ 0)$.

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[1] The program is available on-line at http://www.cryst.ehu.es/cryst/pseudo.html.

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obtained for the pseudosymmetry operation $\bar{x}, y, \bar{z} - 0.5926$, which in fact is an element of supergroup $P4_122$ of $P4_1$ with an origin shift of 0.2963.

The search for pseudosymmetry among the minimal supergroups of $P4_1$ shows that $TlBO_2$ is pseudosymmetric for $P4_122$. The optimization procedure applied in *PSEUDO* determines an origin shift of 0.162 along z so that the displacements necessary to obtain the structure with symmetry $P4_122$ are not larger than 0.34 Å.

2.4. $CrOF_3$

The symmetry of this compound is given by the space group $P4_1$ with cell constants $a = 5.174$ and $c = 8.921$ Å (McHughes *et al.*, 1986). According to Abrahams (1999) the origin shift of 0.018 should lead to a non-polar $P4/m$ symmetry with the exception of two F atoms whose coordinates are not related by a $P4/m$ operation (*cf.* Table 3 of Abrahams, 1999). The conclusion of the author is that 'the ferroelectric to para-electric phase transition predicted in $CrOF_3$ is without a symmetry change'. Our searches in $CrOF_3$ (excluding the two F atoms) for pseudosymmetry inversion centers or mirror planes, and for $P4/m$ pseudosymmetry with the reported displacements were not successful.

The check for pseudosymmetry among the minimal supergroups of $P4_1$ detected that the structure is pseudosymmetric for $P4_122$. According to the results of the *PSEUDO* optimization minimal displacements of ~0.657 Å relating the polar and non-polar supergroup are obtained for an origin shift of (0, 0, 0.0565).

3. Conclusions

The structures of the compounds previously reported as possible ferroelectrics for which there is no group–supergroup relation between the polar and the non-polar symmetry have been studied. We could not confirm any of the results reported by Abrahams (1999) indicating structural pseudosymmetry with respect to crystallographic operations belonging to a space group which is not a supergroup of the initial space group. In fact, for all of them a pseudosymmetry corresponding to a supergroup of the initial space group has been found. This means that these systems are indeed possible ferroelectrics, but fulfilling the expected group–supergroup symmetry relation between the ferroelectric and paraelectric phases. As none of the studied structures can be considered to be close to a non-polar configuration without a group–subgroup relation, there is no special reason to expect a polar–non-polar phase transition without the group–subgroup relation.

No experimental data has been found confirming the phase transitions of the compounds discussed here, except for $Sr_3(FeF_6)_2$. However, in this case there is no experimental information about the symmetry of the detected high-temperature phase. According to the previous analysis this phase could have a supergroup symmetry as high as $P4_2/m$.

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