Search for *Pnma* materials with high-temperature structural phase transitions

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Abstract

A systematic search for structures having a high-temperature structural phase transition can be carried out through the identification in the structural databases of those structures that can be considered pseudosymmetric. Pseudosymmetry in a crystal structure indicates the possibility of a similar configuration of higher symmetry. If the distortion relating both structures is small enough, it can be expected that the crystal acquires the more symmetric configuration through a Landau-type phase transition at a higher temperature. Here, we present the results of such a search among inorganic structures with space group *Pnma* retrieved from the Inorganic Crystal Structure Database. Pseudosymmetry has indeed been detected in those compounds with a known (displacive) Landau-type phase transition at higher temperatures. This is measured by a parameter Δ, which measures the maximal atomic displacement relating the pseudosymmetry-transformed structure and the original one. In most of these compounds with a known phase transition, this parameter was smaller than 1.0 Å for at least one minimal supergroup of *Pnma*. The database contains 144 additional structures with pseudosymmetry features under the same quantitative limit. A comparison of the Δ distributions in both sets of compounds suggests a smaller Δ window (with 0.7 Å as maximal value) for selecting the materials having maximal probability of exhibiting a phase transition at higher temperatures. A set of 58 compounds fulfils this criterion.

1. Introduction

In the last decade a method for searching for new ferroelectrics based on structural data has been proposed and applied with great success (Abrahams *et al.*, 1984; Abrahams, 1988, 1989, 1990). Polar structures having atomic 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 at a higher temperature. Using the structural data available in the Inorganic Crystal Structure Database (ICSD: Bergerhoff & Brown, 1987), substances satisfying this condition were found. The method is very efficient; more than 50 new ferroelectric crystals were predicted and the success rate was quite high. Furthermore, an empirical relation makes it possible to estimate the transition temperature from the observed maximum atomic displacement (Abrahams *et al.*, 1968).

This approach can be generalized and applied to any kind of displacive Landau-type structural phase transition for which the low-symmetry phase is the result of some distortion of a high-symmetry structure, both phases being described by group–subgroup-related space groups. In general, in order to find materials with this type of phase transition at higher temperatures one should look for substances having some pseudosymmetry, *i.e.* structures that can be interpreted as slight distortions of higher-symmetry configurations. If the distortion is small enough, it is probable that the system acquires this more symmetric configuration at higher temperatures through a Landau-type structural phase transition (Toledano & Toledano, 1977; Neeham & Cross, 1974).

Pseudosymmetry is considered here as quite a loose concept with atomic deviations from the ideal symmetric position of the order of 1 Å, which differs from the pseudosymmetry concept considered in other contexts, *e.g.* when dealing with structures with overlooked symmetry (Le Page, 1987, 1988). Under these premises, we have developed a general procedure for the detection of pseudosymmetric structures systematically using group–supergroup relations among space groups (Igartua *et al.*, 1996). In fact, the pseudosymmetry search can be limited to the minimal supergroups of the space group associated with the structure under study, because any pseudosymmetry supergroup can be described *via* a chain of minimal supergroups starting at the experimental space group. Hence, as a first step of the process, all possible minimal supergroups of the space group of the structure should be determined. In the case of non-polar space groups, such as the one considered here, the number of possible minimal supergroups is finite and

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small if isomorphic minimal supergroups are limited to those of small order (the only physically relevant ones). In practical terms this implies, for instance, that pseudosymmetric axes and/or planes can only be located at quite specific places with respect to the existing symmetry operations.

Formally, the possible minimal supergroups of a given space group are described by their left coset representatives with respect to the latter. The pseudosymmetry check for each of these supergroups can then be reduced to the comparison between the transformed structure obtained by the action of each of these coset representatives and the original experimental structure (Igartua *et al.*, 1996). Pseudosymmetry is detected when all atomic displacements necessary to make the transformed structure coincident with the original one can be chosen under a given limit. The magnitude of the structural distortion with respect to the higher-symmetry configuration is then measured by the maximum of these atomic displacements, which in the following we shall call Δ. There is no clear argument for deciding the critical value of Δ under which a compound can be considered pseudosymmetric and, as a consequence, as having a probable phase transition at higher temperatures. In polar structures, the prediction of ferroelectric phase transitions has been successful considering Δ parameters as high as 2 Å (Abrahams *et al.*, 1984; Abrahams, 1989, 1990).† However, in our previous study of the non-polar structures of $P2_12_12_1$ symmetry (Igartua *et al.*, 1996), a maximal value of 1.5 Å was still inconclusive and more than 50% of the structures in the database fell under this limit for at least one of the minimal supergroups. For this previous case study, a Δ value of 1 Å seemed already significant, but no clear general criterion could be derived.

In this work, we present the results of a pseudosymmetry search through all inorganic structures of symmetry *Pnma* available in the ICSD. The space group *Pnma* is especially interesting because of the large number of known structures with this symmetry. This should mean that the study of the distribution of Δ values among these compounds has enough statistical significance to draw some general conclusions.

2. Results

First, the full set of minimal supergroups of *Pnma* was derived. In general, the existing lists of minimal supergroups of space groups cannot be used directly in the search process. They are incomplete in the sense that they only contain the types of supergroups but do not distinguish between isomorphic supergroups differing by the location and/or orientation of the additional symmetry operations with respect to the conventional

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† The parameter Δ is comparable to twice the parameter Δz used by Abrahams for the polar groups (see Fig. 3).

Table 1. *Minimal (klassengleiche) supergroups of Pnma of index [2] and [3]*

Each supergroup is specified by the coset representatives of its decomposition with respect to *Pnma*.

Index, supergroups G	Coset representatives of the supergroups with respect to *Pnma* (different from identity)	
[2] *Pcma* (No. 55) (*Pbam*)	$(1, 0\frac{1}{2}0)$	
[2] *Pbma* (No. 57) (*Pbcm*)	$(1, 00\frac{1}{2})$	
[2] *Pnmm* (No. 59) (*Pmmn*)	$(1, \frac{1}{2}00)$	
[2] *Bbmm* (No. 63) (*Cmcm*)	$(1, \frac{1}{2}0\frac{1}{2})$	
[2] *Amma* (No. 63) (*Cmcm*)	$(1, 0\frac{1}{2}\frac{1}{2})$	
[2] *Ccmb* (No. 64) (*Cmca*)	$(1, \frac{1}{2}\frac{1}{2}0)$	
[2] *Imma* (No. 74)	$(1, \frac{1}{2}\frac{1}{2}\frac{1}{2})$	
[3] *Pnma* (No. 62)	$(1, \frac{1}{3}00)$	$(1, \frac{2}{3}00)$
[3] *Pnma* (No. 62)	$(1, 0\frac{1}{3}0)$	$(1, 0\frac{2}{3}0)$
[3] *Pnma* (No. 62)	$(1, 00\frac{1}{3})$	$(1, 00\frac{2}{3})$

origin and setting of the subgroup. A full listing of all these isomorphic minimal supergroups is required as an eventual pseudosymmetry can correspond to any of them. This full list can be derived from the existing data for maximal subgroups of space groups found in the forthcoming Volume H of *International Tables for Crystallography* and knowledge of the space-group normalizers (Koch, 1984; Igartua *et al.*, 1996). For the case of *Pnma* the result is particularly simple. Table 1 lists all its minimal supergroups up to index 3. All of them are *klassengleiche*, the coset representatives of each supergroup being translation operations. These are the supergroups which have been tested as possible pseudosymmetries of the ICSD *Pnma* structures. Minimal supergroups of index higher than 3, not included in Table 1, are only the minimal isomorphic *Pnma* supergroups, which exist for any prime index. However, only those with smaller indices are relevant for our purposes, as they correspond to the simple lattice changes that may happen in a phase transition.

The ICSD contains 3272 files with the space group *Pnma* (No. 62) representing a total of 2222 different compounds. Some files, however, include no data on atomic coordinates, which reduces the set of useful compounds to 2142.

Structures for which some atoms, usually H or N, are not located in the ICSD files have been included in the search. The missing atoms are disregarded in the pseudosymmetry check. We have also included structures containing atom sites with occupation probability different from one, but under the assumption that only atoms with the same occupation probability can be symmetry-related in the supergroup. Therefore, possible phase transitions that change the occupation probability distribution (order–disorder) have not been taken into account.

Many of the *Pnma* structures in the ICSD are stored in non-conventional settings. Hence, a consistent pseu-

Table 2. *Inorganic compounds of symmetry Pnma with known higher-temperature phase transitions characterized by the transition temperature T_c and the symmetry group G_0 of the symmetric phase*

The temperature T at which the *Pnma* structure has been determined is indicated only if it differs from room temperature. The pseudosymmetry minimal supergroup G with the smallest Δ (column 5) for each compound is listed in column 6.

	T_c (K)	T (K)	G_0	Δ	G
$CsBeF_3$	412	—	?–?	1.29	*Amma*
$KCdF_3$	471/485	—	$Cmcm–Pm\bar{3}m$	0.67	*Bbmm*
$KMnF_3$	187	95	$P4/mbm$	0.23	*Imma*
$NaMgF_3$	1033/1173	—	Tetragonal–$Pm\bar{3}m$	0.68	*Imma*
$NaZnF_3$	953	—	?	0.78	*Imma*
NH_4CdF_3	331	—	$Pm\bar{3}m$	0.50	*Pcma*
NH_4BeF_3	536	386	Orthorhombic	1.03	*Amma*
NH_4MnF_3	182	83	$Pm\bar{3}m$	0.24	*Pcma*
$KMgCl_3$	415/485/497/569	4.2	$Cmcm–P4/mbm–Pm\bar{3}m$	0.64	*Pcma*
NH_4MnCl_3	110/258	4.2	$P4bm–Pm\bar{3}m$	0.56	*Pcma*
$TlMnCl_3$	108	4.2	$Pm\bar{3}m$	0.63	*Imma*
$RbCdVl_3$	341/363/388		$Cmcm–P4/mbm–Pm\bar{3}m$	> 2.0	
$CsPbBr_3$	360/420	Wrong coordinates	$P4/mbm–Pm\bar{3}m$	> 2.0	
$CsSnI_3$	425	—	Tetragonal	0.70	*Pcma*
$BaCeO_3$	?	—	$Imma–F\bar{3}cm–Pm\bar{3}m$	0.36	*Imma*
$CaTiO_3$	1533	—	$Pm\bar{3}m$	0.51	*Imma*
$LaFeO_3$	?	—	$Pm\bar{3}m$	0.49	*Imma*
$LaGaO_3$	425/1148(?)	—	$R3c$	0.15	*Imma*
$LaMnO_3$	$\simeq(600/800)$	—	Cubic–$R\bar{3}c$	0.71	*Imma*
$MgSiO_3$	?	—	?	0.52	*Imma*
$NaTaO_3$	853/903	—	$Bmmb–P4/mbm$	0.39	*Imma*
$PrNiO_3$	773		$P\bar{3}c$	0.44	*Imma*
$SmAlO_3$	?	—	$Pm\bar{3}m$	0.40	*Imma*
$SrRuO_3$	?	—	$Pm\bar{3}$	0.40	*Imma*
$SrZrO_3$	973/1103/1443	—	$I4/mcm–Bmmb$–cubic	0.55	*Imma*
$YAlO_3$	?	—	$P6_3/mmm$	0.67	*Imma*
MnAs	399	317	$P6_3/mmc$	0.35	*Amma*
SnS	878	—	$Cmcm$	0.99	*Bbmm*
SnSe	807	—	$Cmcm$	0.92	*Bbmm*
GeSe	930	157	$Fm\bar{3}m$	0.93	*Bbmm*
FeS	600	294/463	$P6_3/mmc$	0.60/0.18	*Amma*
VS	?	—	$P6_3/mmc$	1.40	*Amma*
MnCoGe	480	—	$P6_3/mmc$	1.09	*Amma*
AgTlTe	706	—	?	1.56	*Amma*
$BaCu_4S_3$	913	—	$Cmcm$	1.05	*Amma*
$Pb_2Mg(WO_6)$	312	—	$Fm3m$	0.35	*Pnmm*
$CsReO_4$	?	—	$Pm\bar{3}m$	1.31	*Imma*
$KGaF_4$	465	—	$Pm\bar{3}m$	0.53	*Pbma*
VO_2	?	—	?	1.48	*Bbmm*
K_3OCl	?	—	$Pm\bar{3}m$	0.69	*Pcma*
KPO_3	524/722/923		$P2_1/a–P2_1/a–Pbnm–Bbmm$	0.95	*Amma*

dosymmetry search using the minimal supergroups listed in Table 1 first requires the structures to be transformed into the conventional *Pnma* setting. Accordingly, the results discussed below are given using a conventional setting for the description of the structures, even if the ICSD files use a different one.

2.1. *Compounds with known phase transition(s) at higher temperatures*

We have divided the files under study into two sets: the first set comprises the compounds which are known to have phase transitions at higher temperatures, while the second set is formed by the remaining materials. A significant number of the *Pnma* materials in the ICSD with known phase transitions at higher temperatures (Tomaszewski, 1992) fall into one of the following categories: (i) the symmetry at higher temperatures is not group–subgroup-related to *Pnma*; (ii) the high-symmetry phase is known to be a disordered configuration with respect to the ordered *Pnma* structure; (iii) the compound exhibits polymorphism with respect to the two phases. These substances have been disregarded in our scheme, as they are not expected in general to

exhibit pseudosymmetric features. This leaves 40 compounds where pseudosymmetry is expected, although exceptions are possible since the set includes some materials where the Landau-type and/or the displacive character of the transition could be neither discarded nor confirmed from the scarce bibliographic sources. The results of the pseudosymmetry search for this set of compounds are summarized in Table 2. For compounds having several ICSD files at the same temperature, only the results for a single file are shown. When the same file has been flagged by different supergroups, only the one with the smallest Δ value is included in the table. Most of the compounds (31) have Δ values below 1.0 Å and larger than 0.2 Å. Therefore, like the $P2_12_12_1$ case (Igartua *et al.*, 1996), $\Delta = 1$ Å seems a reasonable choice as a boundary between significant and non-significant pseudosymmetry.

A considerable number of the materials listed in Table 2 have the general formula ABX_3. Most of them are reported to have a cubic phase of $Pm\bar{3}m$ symmetry at higher temperatures (Tomaszewski, 1992), preceded in some cases by other orthorhombic and/or tetragonal phases. In all these cases the three minimal supergroups connecting the $Pnma$ space group with the space group $Pm\bar{3}m$ ($Bbmm$, $Imma$ and $Pcma$) have been detected as pseudosymmetries of the $Pnma$ structure. Table 2, however, only lists the supergroup with the minimal Δ. This means (see Table 1) that these structures exhibit pseudo-centring translations of the type $(\frac{1}{2}, 0, \frac{1}{2})$ (space group $Bbmm$) and $(0, \frac{1}{2}, 0)$ (space group $Pcma$), the third pseudosymmetry ($Imma$) being a trivial consequence of the other two. All these compounds are, in fact, distorted cubic perovskites with a pseudotetragonal orthorhombic cell. The approximate cubic cell is indeed generated by the detected pseudo-translations $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, 0)$, the parameters of the $Pnma$ orthorhombic cell fulfilling approximately the relation $a \simeq c \simeq b/(2)^{1/2}$. The two compounds $CsSnI_3$ and $NaMgF_3$, where deviations from this relation are larger, are also those where the parameter Δ for some of the three groups reaches values larger than 1.0 Å. It should be noted that, in general, the pseudosymmetry check procedure is performed on the atomic positions of the structure, assuming that the unit-cell metric is fully compatible with the postulated pseudosymmetry (Igartua *et al.*, 1996). The approximate compatibility of the lattice unit cell with the detected pseudosymmetry supergroup is subsequently checked to confirm the result. In the case of $Pnma$, all minimal supergroups are also orthorhombic, so they imply no additional restriction on the metric of the lattice. However, for the perovskite family, as the pseudosymmetry originates on the common supergroup $Pm\bar{3}m$, an approximate pseudocubic Bravais lattice is also present.

Among the perovskites the case of $CaTiO_3$ is particularly remarkable. The ICSD contains eleven different files for this material with $Pnma$ symmetry. Apart from those corresponding to structures determined at room temperature, there are four files with structures measured at 673, 1073, 1273 and 1373 K. The files at room temperature give similar Δ values except for an old file with no R factor and Table 2 only lists the results for one of them (Liu & Lieberman, 1993). The other files for higher-temperature structures show that Δ decreases with temperature (see Fig. 1). This temperature variation should approximately describe the behaviour of the transition order parameter if second-order effects are neglected. Similar results can be observed for the files corresponding to different temperatures which are available for $LaTiO_3$ and $NdNiO_3$.

Within the ABX_3 compounds listed in Table 2 there are only two exceptions to the general features discussed above: $RbCdCl_3$ and $CsPbBr_3$. They are not pseudosymmetric for any minimal supergroup up to Δ values as large as 2.0 Å. Both compounds have unit cells with a similar metric, which is clearly different from the pseudocubic one of the other compounds. However, the file for $CsPbBr_3$ contains a warning in the database as having 'obviously wrong coordinates'.

We have exceptionally included in Table 2 the cases of $PrNiO_3$, $LaGaO_3$, $SrRuO_3$ and $LaMnO_3$. These four compounds are also pseudocubic distorted perovskites of the type discussed above, and this is confirmed again by the three minimal supergroups detected as pseudosymmetries. However, the reported high-symmetry phase of each of these three compounds is rhombohedral (Huang *et al.*, 1990; Marti *et al.*, 1994; Bensch *et al.*, 1990; Norby *et al.*, 1995). The symmetry of this rhombohedral phase is not group–subgroup-related to $Pnma$, but can be considered as a subgroup of the cubic space group $Pm\bar{3}m$ of a hypothetical common paraphase (Levanyuk & Sannikov, 1971).

Also in the ABX_3 family, NH_4BeF_3 and $CsBeF_3$ have been flagged as pseudosymmetric for $Amma$. In both cases the space groups of the high-symmetry phases are
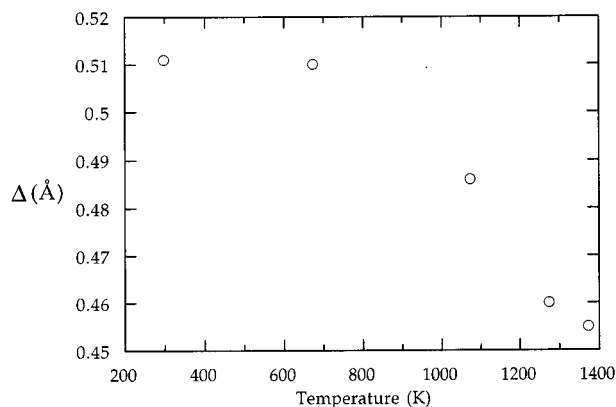

Fig. 1. Pseudosymmetry parameter Δ of $CaTiO_3$ for the minimal supergroup *Imma* as a function of temperature, as obtained from the four ICSD files corresponding to structures determined at 673, 1073, 1273 and 1373 K (Liu & Lieberman, 1993).

not known (Tomaszewski, 1992; Steinfink & Brunton, 1968). The detected pseudosymmetry restricts the possible symmetries for the high-temperature phases. Fig. 2 shows a scheme of the $CsBeF_3$ $Pnma$ structure showing its closeness to an $Amma$ configuration. How this higher-symmetry configuration is determined is demonstrated graphically in Fig. 3. Therein, the transformation of a Wyckoff orbit of atoms through the action of the coset representative $(1, 0\frac{1}{2}\frac{1}{2})$ corresponding to the supergroup $Amma$ is shown. The positions of the non-distorted $Amma$ configuration are easily identified at half the distance Δ separating the closest pairs of atoms between the original and the transformed structure. This is the reason for the factor 2 difference when comparing the Δ values in this work with the distances considered for the case of polar structures in the work of Abrahams, where the atomic displacements refer to the high-symmetry configuration.
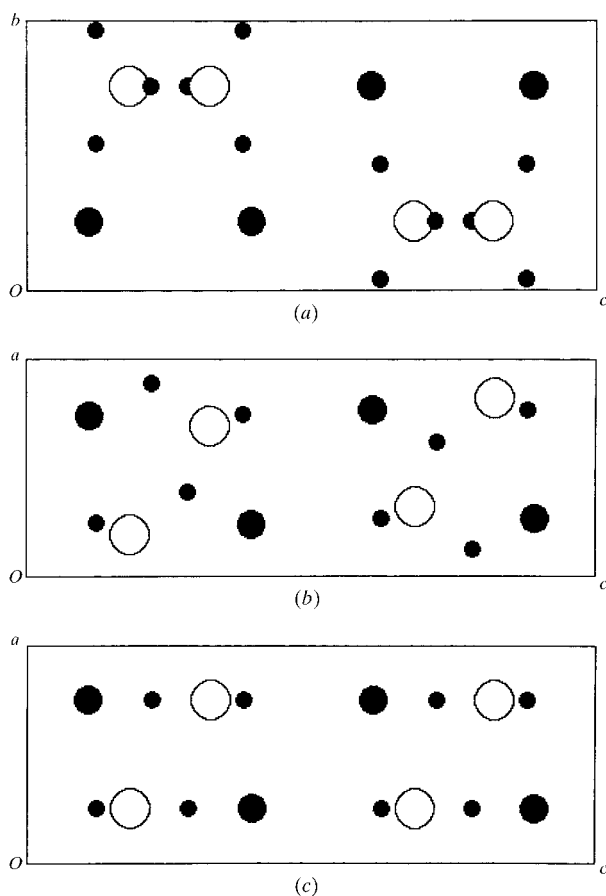
Another family present in Table 2 is formed by the binary compounds with sulfur or selenium: SnS, SnSe, GeSe, VS and FeS. The first three are isomorphous and have been flagged with the same supergroup $Bbmm$, which coincides with the reported symmetry of the high-symmetry phase for the first two of them (Tomaszewski, 1992). VS and FeS also have similar structures and are both reported to have a high-temperature phase of $P6_3/mmc$ symmetry (Tomaszewski, 1992). Both are pseudosymmetric for the space group $Amma$ which is the minimal supergroup in the chain leading to the group $P6_3/mmc$. A similar case is represented by MnAs. For FeS, there are files at two different temperatures, 294 and 463 K, the transition temperature being 600 K. The corresponding Δ values are 0.60 and 0.18 Å, respectively. However, the file at room temperature corresponds to a study under pressure, the $Pnma$ phase of FeS being unstable below 420 K under atmospheric pressure.

The case of MnCoGe ($Mn_{0.997}Co_{0.974}Ge$) is particularly remarkable. The compound is reported to have a hexagonal phase above 340 K and has two $Pnma$ files in the ICSD, one at room temperature and another at 343 K; both have been flagged for the group $Amma$ with $\Delta = 1.09$ and 0.00 Å, respectively. The second file is included in the ICSD as a $Pnma$ file, but in fact it describes the hexagonal $P6_3/mmc$ phase, which was published in the $Pnma$ setting (Jeitschko, 1975) to facilitate comparison with the room-temperature phase (the transition temperature is lowered in the nonstoichiometric substance). The zero value of Δ for $Amma$ confirms the higher symmetry, the space group $Amma$ being the only minimal supergroup in the chain leading to the space group $P6_3/mmc$ with the pseudohexagonal axis along [100].

For the particular case of ferroelectric materials an empirical law for the transition temperature has been proposed (Abrahams et al., 1968). According to this rule, the transition temperature T_c can be estimated from the relation $T_c = Cu_i^2$, where $C = 5 \times 10^3$ K Å^{-2} (see footnote on p. 178) and u_i is the corresponding atomic

Fig. 2. Projections (a) on yz and (b) on xz of the $CsBeF_3$ structure (Steinfink & Brunton, 1968). Small and large filled circles are F and Cs atoms, respectively. Empty circles are Be atoms. The pseudotranslation $(1, 0\frac{1}{2}\frac{1}{2})$ is clearly observable. Deviations from a perfect lattice translation symmetry only take place along the x axis [on the projection yz, the $Pnma$ operation $(m_x, \frac{1}{2}\frac{1}{2}\frac{1}{2})$ ensures for any $Pnma$ structure a perfect symmetry translation $(1, 0\frac{1}{2}\frac{1}{2})$]. (c) xz projection of the ideal $Amma$ configuration.
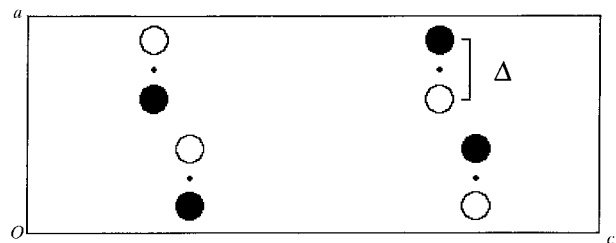

Fig. 3. Graphical representation of the pseudosymmetry parameter Δ for the structure of Fig. 2. Empty circles represent the orbit of F(2) atomic positions of $CsBeF_3$ (Steinfink & Brunton, 1968) projected on the plane xz, while filled circles are the transformed positions obtained by the action of the $Amma$ coset representative $(1, 0\frac{1}{2}\frac{1}{2})$. The mean positions along the Δ-long segments separating each pair of transformed/non-transformed positions correspond to the ideal $Amma$ reference structure.

displacement with respect to the high-symmetry configuration of the so-called 'critical' atom (the metal more strongly bonded and least ionic). This displacement is not necessarily the largest one. This empirical relation seems to be adequate for structures built up from oxygen- and/or halogen-atom octahedra. Note, however, that the authors sometimes relax the rule and, for instance, consider as u_i an average value of all atomic displacements (Abrahams, 1989). As in general the structural distortion varies with temperature, the above relation only has sense if the considered u_i is a *saturated* value, *i.e.* determined at a temperature far enough from T_c. This temperature interval can be quite large. For instance, in the case of $CaTiO_3$, as can be seen in Fig. 1, saturation is only reached after 700 K. In any case, a law of this type could not be detected in the compounds listed in Table 2. For the particular case of the perovskites, for instance, the metal within the halogen/oxygen octahedra often occupies a special position so that its displacement is zero for the action of the flagged minimal supergroups. The listed Δ value ($u_i = \Delta/2$) corresponds in fact to the halogen/oxygen atoms. It is important to note that, although the minimal supergroups checked do not correspond in principle to the symmetry of the high-temperature phase, the atomic displacements associated with the primary distortion (order parameter) should break all intermediate possible symmetries (Aroyo & Perez-Mato, 1998). This fact ensures that the metal atoms cannot have a significant displacement with respect to the configuration corresponding to the high-symmetry phase without also being significant in this first step of minimal pseudosymmetry, which is considered here.

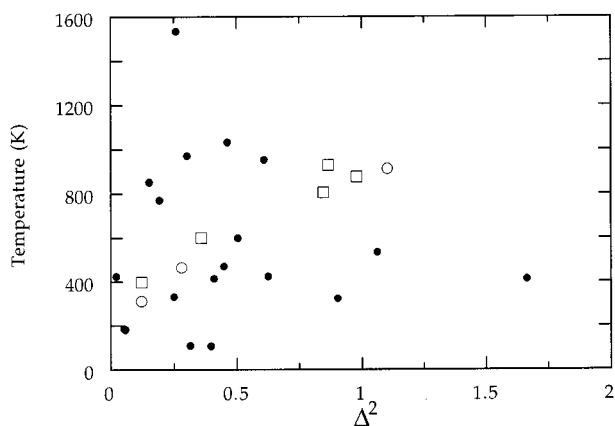As shown in Fig. 4, the pseudosymmetry parameter Δ does not show any clear relation with T_c, not even when

restricted to the perovskites. Only in the family of sulfur and selenium binary compounds does a certain linear correlation between the transition temperature and Δ^2 seem to exist, but the number of cases is not statistically significant.

2.2. *Compounds without reported phase transition(s) at higher temperatures (candidates)*

In order to simplify and clarify the set of compounds under study, we have not included in the subsequent search the numerous files that correspond to nonstoichiometric compounds or solid solutions. This has been done by excluding those ICSD files where the formulae indicate relative compositions with rational numbers. This has necessarily produced the undesired effect of having to leave aside some files which really correspond to pure stoichiometric compounds but have their formula expressed in this form in the file.

Under this constraint, the initial number of candidates to be checked was 1490. From them, 400 were detected as pseudosymmetric with Δ smaller than 1.5 Å and larger than 0.2 Å. The corresponding Δ distribution is shown in Fig. 5(a). Nine compounds were also found with Δ smaller than 0.2 Å (see §2.3 for some erroneous files in this set) but, following the arguments of Abrahams for the case of ferroelectrics (Abrahams *et al.*, 1984; Abrahams, 1988, 1989), they were not considered further. In general, one should expect that values of Δ smaller than 0.2 Å correspond to structures with a wrong symmetry assignment or at least with symmetry under discussion. This was also confirmed in our previous work on $P2_12_12_1$ structures. Note, however, that in the present case the minimal supergroups represent in all cases a smaller Bravais lattice, so that it seems rather improbable that they could be overseen as the real symmetry of the structures.

Like the findings of Igartua *et al.* (1996), the upper limit of 1.5 Å, although significantly smaller than the one considered by Abrahams for ferroelectrics, is still too large to be effective. As shown in Fig. 5, the Δ distributions of the candidates and of the materials of Table 2 (with known phase transitions) are clearly different. While for the compounds with phase transitions the distribution has a clear maximum around 0.6 Å, the distribution for the larger set of candidates shows an essentially monotonic increase with Δ. In this repect it should be noted that for large enough Δ any structure is to be found 'pseudosymmetric' since each transformed atom can be related to itself in the original structure through a displacement under Δ. As in the present case all transformations applied to the structures are non-primitive translations, this type of spurious case should correspond to Δ values equal to the length of the applied translation. Some of the *Pnma* compounds have at least one lattice constant smaller than 3 Å, hence these anomalous situations may appear at values of Δ as

Fig. 4. Transition temperatures of the compounds listed in Table 2 *versus* the square of the corresponding pseudosymmetry parameter Δ. For substances having several transitions, only the lowest transition temperature is represented. Filled circles correspond to perovskites ABX_3, empty squares depict the binary compounds with sulfur, selenium or arsenic, and the remaining three compounds are depicted by empty circles.

small as 0.9 Å (see Table 1). These spurious pseudo-symmetric cases have been systematically detected and discarded before constructing the distributions mentioned above.

From Fig. 5, it seems clear that 1.0 Å could be considered an adequate upper limit for detecting pseudosymmetry as the signature of a phase transition. As discussed above, about 80% of the compounds with phase transitions in Table 2 fall in the interval 0.2–1.0 Å, and this increases to 87% if the interval is extended to 1.1 Å. Among the candidates in the database, 144 lie in the interval 0.2–1.0 Å, including again a numerous set of distorted perovskites (63 compounds). The ratio of compounds under 1.0 Å with respect to the initial set ($\simeq$10%) is similar to that observed in the pseudosymmetry search on $P2_12_12_1$ compounds (Igartua *et al.*, 1996), but in the present case, owing to the large number of initial compounds, the number of chosen compounds

is still too large for practical purposes. The set of candidates can be decreased further and optimized if we take into account the distribution in Fig. 5(*b*). About 80% of the compounds with phase transitions and $\Delta <$ 1.0 Å fall in the interval $0.2 < \Delta < 0.7$ Å, while in the set of candidates only 40% are located in this interval. These particular features are even stronger in the distributions for the smaller but more homogeneous subset formed by the family of ABX_3 compounds (Fig. 6). Nearly 70% of the ABX_3 compounds without a reported phase transition and Δ under 1.0 Å are in the interval 0.7–1.0 Å. In contrast, among the ABX_3 materials for which a higher-temperature phase transition is known, this interval only includes about 17% of the materials. From all these considerations, in order to select an optimal set of candidates with maximal probability of exhibiting a structural instability at higher temperatures, it seems reasonable to reduce the window
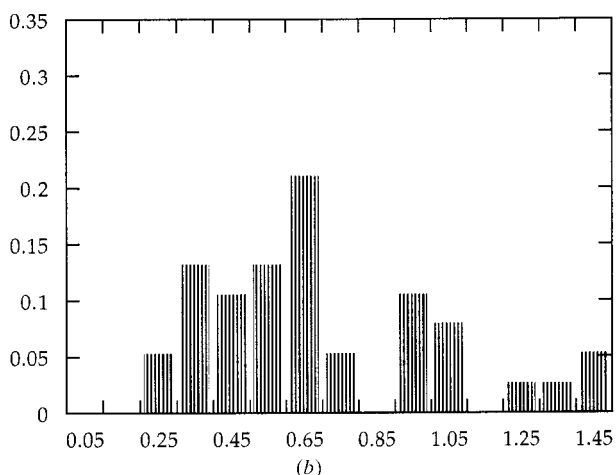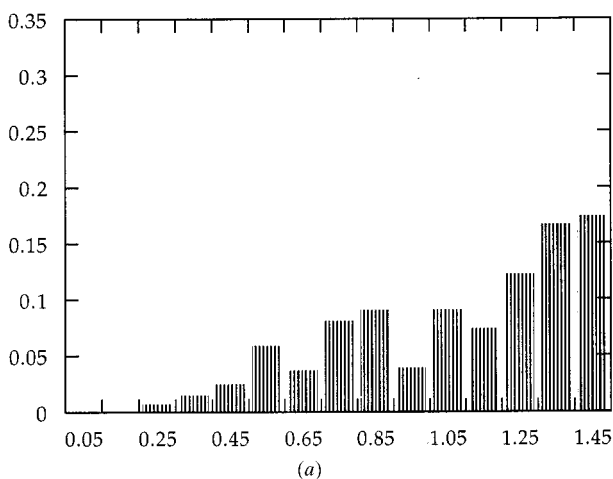

Fig. 5. (*a*) Normalized distribution of *Pnma* ICSD substances (candidates) according to their pseudosymmetry parameter Δ within the interval 0.0–1.5 Å. (*b*) The same for *Pnma* compounds with a known Landau-type phase transition at a higher temperature.
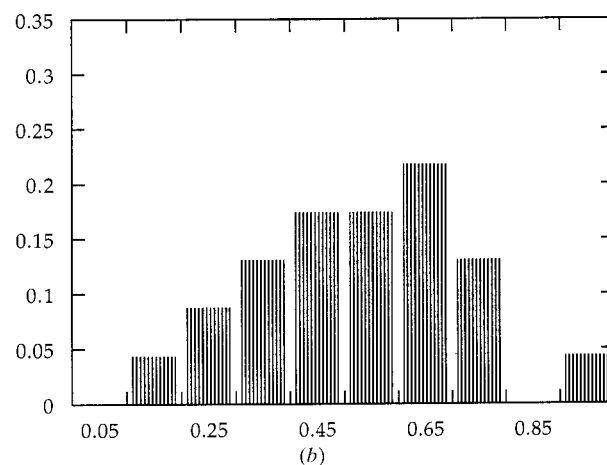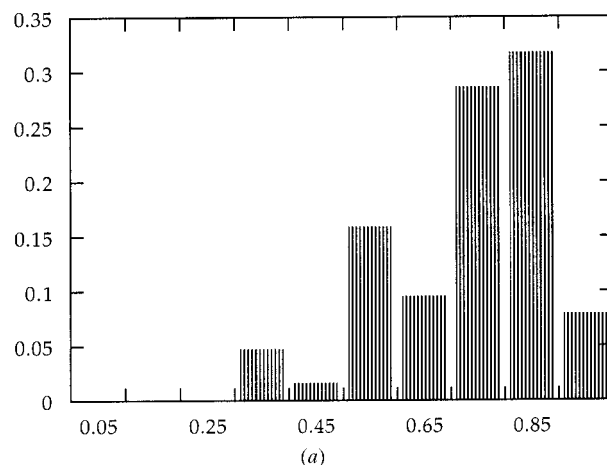

Fig. 6. (*a*) Normalized distribution of ICSD ABX_3 *Pnma* substances (candidates) according to their pseudosymmetry parameter Δ within the interval 0.0–1.0 Å. (*b*) The same for ABX_3 *Pnma* compounds with a known Landau-type phase transition at a higher temperature.

Table 3. *Inorganic compounds with Pnma symmetry having pseudosymmetry group G with Δ between 0.3 and 0.7 Å and no high-temperature phase transition reported yet*

Mean is the mean displacement value (see text). *R* is the *R* factor for each structure as given in the database.

		R	Δ	Mean	G
1	$AlHoO_3$	0.047	0.65	0.139	*Imma*
2	$BaPrO_3$	0.050	0.37	0.251	*Imma*
3	$BaPuO_3$	0.034	0.39	0.217	*Imma*
4	$CaGeO_3$	0.035	0.50	0.277	*Imma*
5	$CaMnO_3$	0.045	0.56	0.315	*Imma*
6	$CeVO_3$	0.067	0.63	0.365	*Imma*
7	$DyCoO_3$	—	0.66	0.485	*Imma*
8	$EuNiO_3$	0.032	0.62	0.405	*Imma*
9	$LaCrO_3$	0.015	0.36	0.203	*Imma*
10	$LaRuO_3$	0.065	0.56	0.309	*Imma*
11	$LaTiO_3$	0.048	0.51	0.300	*Imma*
12	$LaVO_3$	0.047	0.49	0.285	*Imma*
13	$NdCrO_3$	—	0.59	0.370	*Imma*
14	$NdGaO_3$	0.099	0.53	0.335	*Imma*
15	$NdFeO_3$	—	0.62	0.370	*Imma*
16	$NdNiO_3$	0.029	0.53	0.301	*Imma*
17	$PrFeO_3$	0.025	0.66	0.408	*Imma*
18	$PrGaO_3$	0.027	0.58	0.345	*Imma*
19	$SmNiO_3$	0.033	0.59	0.387	*Imma*
20	$SrSnO_3$	0.026	0.58	0.284	*Imma*
21	$KTiF_4$	0.026	0.53	0.182	*Pnma*
22	NH_4FeF_4	0.026	0.64	0.361	*Amma*
23	$CoAs$	0.049	0.58	0.558	*Amma*
24	$CrAs$	0.100	0.64	0.592	*Amma*
25	$FeAs$	0.023	0.61	0.582	*Amma*
26	FeP	—	0.61	0.592	*Amma*
27	$RuSb$	—	0.61	0.609	*Amma*
28	SrV_3O_7	0.029	0.27	0.381	*Pnmm*
29	CaV_3O_7	0.081	0.55	0.190	*Pnmm*
30	CdV_3O_7	0.041	0.56	0.366	*Pnmm*
31	$GdPS$	0.046	0.42	0.243	*Imma*
32	Pt_3Ge_2	0.120	0.49	0.216	*Pbam*
33	Ni_2SnP	0.030	0.38	0.351	*Pnmm*
34	Fe_2BaSe_3	0.089	0.58	0.319	*Bbmm*
35	Eu_2CuS_3	0.057	0.63	0.452	*Amma*
36	K_2SnO_3	0.138	0.69	0.330	*Amma*
37	$BaMnS_2$	—	0.53	0.305	*Amma*
38	$SrZnSb_2$	0.067	0.28	0.236	*Pnmm*
39	MoO_3	—	0.69	0.674	*Bbmm*
40	Co_2TaTe_2	0.036	0.45	0.303	*Pbam*
41	Ca_3AsN	0.046	0.42	0.246	*Pbam*
42	$SrLaFeSnO_6$	0.025	0.47	0.225	*Imma*
43	$SrLaCuRuO_6$	0.041	0.43	0.208	*Imma*
44	$K_2Na_4(FeO_3)_2$	0.045	0.53	0.242	*Bbmm*
45	$K_2Na_4(GaO_3)_2$	0.082	0.54	0.261	*Bbmm*
46	$CsW_8(PO_7)_4O_{12}$	0.022	0.53	0.235	*Amma*
47	La_2NiRuO_6	0.087	0.65	0.317	*Imma*
48	La_2CuTiO_6	0.078	0.61	0.309	*Imma*
49	$CsPdAlF_6$	0.067	0.39	0.191	*Imma*
50	Na_2CuCrF_7	0.035	0.46	0.320	*Imma*
51	$BaLaCuSe_3$	0.050	0.48	0.311	*Amma*
52	$NaBeHSi_3O_8$	0.092	0.52	0.255	*Bbmm*
53	$KHg(CN)_2ClH_2O$	0.062	0.52	0.344	*Amma*
54	$CsCa_2Nb_3O_{10}$	0.028	0.59	0.298	*Amma*
55	$LaWO_4Cl$	0.053	0.48	0.090	*Pnmm*
56	$KMo_2P_3O_{12}$	0.028	0.35	0.187	*Pbam*

Table 3 (*cont.*)

		R	Δ	Mean	G
57	$La_3NbO_5O_2$	0.029	0.26	0.092	*Amma*
58	$CaAl_2Si_2O_7(OH)_2H_2O$	0.023	0.53	0.139	*Amma*

of Δ values to 0.2–0.7 Å. This finally yields a total of 58 candidates, with 20 ABX_3 compounds among them. They are all listed in Table 3. Apart from the numerous set of perovskites listed in Table 3, the number of binary substances isomorphous with FeS is also significant. The value of the Δ parameter is similar in all of them, although the structures of CoAs and FeAs have been determined under pressure, and have only been included in the list for completeness.

It may be argued that the mean value of the atomic displacements (averaged over all atoms in the unit cell) between the transformed structure and the original one could be a better parameter than the maximal atomic displacement for detecting pseudosymmetry. However, taking an average value necessarily diffuses the atomic local structural deviations from the higher symmetry and can be rather misleading (see Table 3). Furthermore, the error of the mean value will depend on the number of atoms in the structure, which means similar values in different structures are not comparable.

2.3. Errors and conspicuous cases in the ICSD

As an offshoot, this study detected some inconsistent *Pnma* files. Seven files (six compounds) yielded Δ = 0 for some supergroup, indicating a perfect higher symmetry in the structure. Apart from the case of MnCoGe, explained above, this also ocurred for files corresponding to the compounds $TlReO_4$, $KAgF_3$, $KHgF_3$, $KPdF_3$ and $NaNiF_3$ (two files). The reason for having the first of these structures classified under *Pnma* is the fact that O atoms are not located in the file. In the case of the perovskite fluorides, we did not find any clear reason. Some of the files are rather old, but no additional files exist which correct them. Only for $NaNiF_3$ are there more recent files with fully consistent *Pnma* structures (see Table 3). A couple of files also had some problems: $LiNa_5(PO_4)_2$ (file 39628) has atomic coordinates that cannot correspond to *Pnma* symmetry; WO_3 (file 836), being the only file that assigns *Pnma* symmetry to this compound, gives some redundant Wyckoff positions in the asymmetric unit.

3. Conclusions

The pseudosymmetry search among the *Pnma* inorganic structures has shown that the deviations from the high-symmetry configurations in non-polar structures should be much smaller than in polar ones in order to consider them significant as a signature for a possible phase

transition at higher temperatures. Taking into account the distribution of the pseudosymmetry parameter Δ, a final list of nearly 60 compounds with strong pseudo-symmetric features has been obtained. In all these compounds the maximal atomic deviation from a configuration of higher symmetry ($\Delta/2$) is of the order of 0.35 Å or less.

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