Prediction of new displacive ferroelectrics through systematic pseudosymmetry search. Results for materials with $Pba2$ and $Pmc2_1$ symmetry

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Polar structures with pseudosymmetry related to a hypothetical non-polar configuration are considered as good candidates for ferroelectrics. Recently, a procedure has been developed for a systematic pseudosymmetry search among structures with a given space-group symmetry. The aim of this paper is the extension of the pseudosymmetry procedure to the case of structures with polar symmetry and its application in the search for new ferroelectrics. The results obtained by the generalized pseudosymmetry search among the compounds with symmetries $Pba2$ and $Pmc2_1$ listed in the Inorganic Crystal Structure Database are discussed. The calculations have been performed by the program $PSEUDO$, which forms part of the Bilbao Crystallographic Server (http://www.cryst.ehu.es). In addition, an empirical relation between the atomic displacements necessary to reach the non-polar structure and the transition temperature is proposed and compared with the Abrahams–Kurtz–Jamieson relation.

1. Introduction

If the atomic coordinates of a given structure display an approximate symmetry in addition to the actual space-group symmetry, the structure can be considered as pseudosymmetric with respect to a supergroup containing this additional symmetry. The structural pseudosymmetry may be interpreted as the result of a distortion of a prototype structure of higher symmetry (Igartua *et al.*, 1996). If the distortion is small enough, it is expected that the crystal acquires this more symmetric configuration through a phase transition of Landau type at higher temperatures. The atomic displacements relating the prototype symmetry structure to the original one can be used as a quantitative measure of the pseudosymmetry. Atomic displacements in the range 0.1–0.5 Å are strongly indicative of a possible high-temperature phase transition, while magnitudes smaller than 0.1 Å may arise from wrong or doubtful structure-symmetry assignments. Two important special cases of phase-transition predictions are to be distinguished:

(i) Prediction of displacive ferroelectric materials (Abrahams & Keve, 1971; Abrahams, 1994). Polar structures having atomic displacements smaller than 1 Å with respect to a hypothetical non-polar configuration are considered as materials with a high probability of having a phase transition into this configuration at higher temperatures, *i.e.* as possible ferroelectrics. The application of this condition to the structural data given in the Inorganic Crystal Structure Database (ICSD; Bergerhoff & Brown, 1987) for different polar groups resulted in the prediction of a number of new ferroelectric materials, some of which have already been experimentally verified. A search for ferroelectrics among organic compounds

stored in the Cambridge Structural Database system using the same approach has also been reported by Zikmund *et al.* (1994).

(ii) Prediction of ferroelastic materials (Abrahams & Keve, 1971; Abrahams, 1994; Wadhavan, 1991). The magnitudes of the atomic displacements can reach higher values ($\sim$1.25 Å) in this case. As an additional requirement for ferroelastic behavior, it is necessary to consider the related spontaneous strain (as a measure of the deviation of the lattice from the higher symmetry), which should not be greater than $\sim 10^{-3}$.

The detection of pseudosymmetry in crystalline structures is the aim of several computer programs reported in the literature [*e.g.* see Le Page (1987, 1988), Hundt *et al.* (1999) and references therein]. In general, these programs are not suited for the pseudosymmetry search that we are interested in. The algorithm developed by Hundt *et al.* (1999) is designed for the determination of symmetries and idealized cell parameters of simulated structures. The programs based on the Le Page approach (Le Page, 1987, 1988) are essentially developed for detecting false symmetry assignments (overlooked symmetries) in structural investigations. Since 'brute' force methods are applied in the corresponding procedures, the allowed atomic deviations from the higher-symmetry positions are much smaller than the typical values considered in a pseudosymmetry search.

A rather different pseudosymmetry search method has been proposed by Katkova *et al.* (2000). The estimation of the structural pseudosymmetry is based on an analysis of the pseudosymmetry of the structure factors. The check for pseudosymmetry consists of the calculation of a parameter called the degree of pseudosymmetry, which measures the deviation of the experimental structure's electron density with respect to the one transformed by some additional symmetry operation(s) that belongs to a supergroup of the structure space group.

Recently, we have developed a procedure for a systematic pseudosymmetry search among structures with a given space-group symmetry. It is based on the assumption that the higher approximate symmetry is described by a supergroup of the structure space group. As any group–supergroup chain can be represented by a chain of minimal supergroups, the search for pseudosymmetry is restricted to the minimal supergroups of the structure space group. In the case of non-polar space groups, the number of minimal supergroups is finite and small if the isomorphic ones are limited to those of small index (which is a physically reasonable assumption). The pseudosymmetry check is then reduced to the comparison between the experimental structure and its transformed variants obtained by the action of coset representatives of the decomposition of the minimal supergroup with respect to the structure symmetry group. These controlled search tools enable us to consider pseudosymmetry as a quite loose concept, allowing atomic displacements from the ideal prototype atomic positions of the order of 1 Å. The procedure has been successfully applied to the prediction of possible high-temperature phase transitions for inorganic structures with space groups $P2_12_12_1$ (Igartua *et al.*, 1996) and *Pnma*

(Igartua *et al.*, 1999) listed in the ICSD. Most of the compounds with known (displacive) Landau-type phase transition have been clearly identified as pseudosymmetric with atomic displacements of less than 0.5 Å. About 20 additional structures of $P2_12_12_1$ symmetry have been detected as having distortions of similar magnitude and are considered as good candidates for exhibiting phase transitions at a higher temperature. In the case of *Pnma*, 58 compounds fulfill the pseudosymmetry criterion with deviations in the range 0.15–0.50 Å.

The aim of the present contribution is the generalization of the pseudosymmetry procedure to the case of ferroelectrics (see §3). The main difficulty is due to the infinite number of non-polar supergroups of the polar groups. This implies additional structural considerations for locating the possible origin of the high-symmetry paraelectric supergroup with respect to the low-symmetry polar group. The generalized pseudosymmetry procedure has been used to search for ferroelectrics among compounds with *Pba*2 symmetry (§3.1) and $Pmc2_1$ symmetry (§3.2). The calculations have been performed with the program *PSEUDO* (Kroumova *et al.*, 2001), which forms part of the Bilbao Crystallographic Server (Kroumova *et al.*, 1998).[1] In §4, we discuss the empirical relation between the ferroelectric transition temperature and the atomic displacements of the atoms along the polar axis (Abrahams *et al.*, 1968), and suggest a possible modification allowing approximate but straightforward computer estimations of the transition temperature.

Some of the results of the pseudosymmetry search among compounds with *Pba*2 symmetry have been reported at the Ninth European Meeting on Ferroelectricity (Kroumova *et al.*, 2000).

2. The procedure

The procedure described below is designed for a pseudosymmetry search corresponding to a supergroup (space group) $\mathcal{G}$ of the space group $\mathcal{H}$ of the structure. Any supergroup–group relation $\mathcal{G} > \mathcal{H}$ can be decomposed into a chain of minimal supergroups, and a fundamental step of the pseudosymmetry search procedure is the determination of the minimal supergroups of the space groups. In general, the existing lists of minimal supergroups of space groups (*International Tables for Crystallography*, 1996, Vol. A) cannot be used directly in the search process. They are incomplete in the sense that they only contain types of supergroups and do not distinguish between isomorphic supergroups $\mathcal{G}$ of $\mathcal{H}$ differing by the location and/or orientation of the additional symmetry operations with respect to the setting of $\mathcal{H}$. A full list of these isomorphic minimal supergroups is required as the eventual pseudosymmetry can correspond to any of the supergroups $\mathcal{G}$. This full list can be derived from the data on maximal subgroups of space groups found in the forthcoming volume (A1) of the *International Tables for Crystallography* (to

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[1] The Bilbao Crystallographic Server is a web site with crystallographic programs. The URL is http://www.cryst.ehu.es.

appear) and a knowledge of space-group normalizers (Koch, 1984; Igartua *et al.*, 1996). Each supergroup is described by the representatives g_k in the left cosets decomposition of $\mathcal{G}$ with respect to $\mathcal{H}$: $\mathcal{G} = \mathcal{H} + \sum_{k=2}^{[i]} g_k \mathcal{H}$, where $[i]$ is the index of $\mathcal{H}$ in $\mathcal{G}$.

Once the minimal supergroups are derived, the pseudo-symmetry search is carried out in a straightforward way by checking the compatibility of the initial structure with respect to the additional symmetry elements of the supergroup. It is sufficient to verify this compatibility for all non-trivial coset representatives g_k of the decomposition of $\mathcal{G}$ with respect to $\mathcal{H}$. The check consists of the calculation of the transformed structure $S_k = g_k S_0$ and the comparison of the atomic positions in S_0 and S_k.

Consider an atom l in the unit cell of S_0 with a position $\mathbf{r}_l = (x_l, y_l, z_l)$ and an atom m of the transformed structure with coordinates given by $\mathbf{r}_m^k = (x_m^k, y_m^k, z_m^k) = g_k \mathbf{r}_m$. The structure S_0 is considered as pseudosymmetric for the operation g_k if for each atom l in S_0 it is possible to find a 'pair' atom m in S_k such that the distance between these two atoms $\Delta_{lm}^k = |\mathbf{r}_l - \mathbf{r}_m^k|$ is smaller than some previously given limit Δ_{tol}, which we call the *tolerance limit*.[2] The atoms forming a pair are symmetrically equivalent in the hypothetical high-symmetry structure, which means that the corresponding orbit(s) should follow the Wyckoff position-splitting rules for symmetry change from $\mathcal{H}$ to $\mathcal{G}$ (Wondratschek, 1993). The fact that we are considering distortions of displacive type[3] imposes additional restrictions on the pair-atom candidates: the atoms should correspond to the same chemical element and the corresponding orbits should have the same occupation probability. Atoms that fulfil these criteria are called atoms of the same type.

In general, it is possible to have more than one choice of pair atom m for the atom l. For a given additional symmetry operation g_k, each pairing is characterized by the maximal distance $\Delta_{\text{max}}^k = \max(\Delta_{lm}^k, l = 1, \ldots, N)$ (N is the number of atoms in the unit cell) for the corresponding choice of the pair atoms m. The best pairing corresponds to the minimal value of Δ_{max}^k. The maximal Δ_{max} of the values Δ_{max}^k for $k = 2, \ldots, [i]$ ($[i]$ is the index of $\mathcal{H}$ in $\mathcal{G}$) can be taken as a parameter measuring the deviation of the structure S_0 from the perfect symmetry of the supergroup $\mathcal{G}$.

In the following, we will also use the magnitudes of the atomic displacements d_l that are necessary to obtain the high-symmetry structure from the initial one. They are calculated from the values of the distances Δ_{lm}^k between the paired atoms

corresponding to the best pairing for all of the additional operations g_k. For example, in the case of supergroups of index two (when there is only the representative g_2 of $\mathcal{G}$ with respect to $\mathcal{H}$), the displacements d_l equal half of the distances Δ_{lm}^k ($d_l = \Delta_{lm}^k/2$, $k = 2$). The maximal displacement $d_{\text{max}} = \max(d_l, l = 1, \ldots, N)$ is considered as a measure of the pseudosymmetry of the structure S_0 with respect to the supergroup $\mathcal{G}$.

The main difficulty in applying this pseudosymmetry procedure to the search for ferroelectric materials is due to the infinite number of minimal non-polar supergroups of the polar space groups. In practical terms, this implies that there are no restrictions on the possible location of the additional pseudosymmetry elements (inversion center, mirror plane or binary axis) with respect to the origin chosen for the description of the experimental polar space group (at least along one direction). In more formal terms, this means that the coset representatives of the non-polar supergroup $\mathcal{G}$ with respect to the polar space group $\mathcal{H}$ contain some continuous parameter(s) ε in the translation part, which have to be optimized using some structural criteria.

In the developed program, the pseudosymmetry is checked by applying two alternative methods for choosing the value of ε:

(i) Minimization of the resulting maximal atomic displacement d_{max} necessary to obtain the high-symmetry structure. In other words, the positions of the additional pseudosymmetry elements (which cancel the polarity of the high-symmetry structure) are chosen so that the distortion measured by d_{max} relating the experimental structure and the hypothetical paraelectric one is minimal.

(ii) Requirement that the displacements of the atoms leave the mass center at rest. The basis for this alternative choice of ε is that if the structure is really a result of a ferroelectric phase transition then the distortion should essentially follow the pattern of a frozen optical mode of the high-symmetry structure, and any optical mode keeps the crystal mass center at rest.

Obviously, the procedure described above permits the detection of pseudosymmetry not only with respect to possible paraelectric minimal supergroups but also for any possible supergroup of the structure space group. For example, when the flagged pseudosymmetry of a polar structure corresponds to a polar space group, the search can be continued along the chain of minimal supergroups. In the case of pseudosymmetry with respect to more than one supergroup, it is very likely that the structure displays higher pseudosymmetry corresponding to common supergroups of the flagged pseudosymmetry groups. In general, the pseudosymmetry search can be continued following the chain of minimal supergroups until no more pseudosymmetry is found.

3. Search for ferroelectrics

The procedure for the pseudosymmetry search described above has been applied to the compounds with symmetry $Pba2$ and $Pmc2_1$ listed in the ICSD. The group $Pba2$ has been

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[2] The distances Δ_{lm}^k between the atomic positions in the initial and the transformed structures are calculated using relative components. Their values are transformed into absolute units at the end of the calculation. Therefore, the eventual deviations of the initial unit-cell metric from the requirements of the crystal system of the supergroup are in general neglected during the pseudosymmetry check. In cases when the crystal systems of the flagged supergroup $\mathcal{G}$ and $\mathcal{H}$ differ, an additional check of the pseudosymmetry of the unit cell is carried out.

[3] In general, this pseudosymmetry search method is not designed for predicting order–disorder phase transitions as we are analyzing atomic displacements. However, pseudosymmetry resulting from a full order–disorder mechanism will also be detected if the disordered sites are separated by distances smaller than the tolerance limit.

Table 1
Minimal supergroups $\mathcal{G}$ of index $[i] = 2$ and 3 of the group $\mathcal{H} = Pba2$.

Each supergroup is further specified by the relations between the basis ($\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$) of the group $\mathcal{H}$ and the $\mathcal{G}$ basis ($\mathbf{a'}$, $\mathbf{b'}$, $\mathbf{c'}$) and by an origin shift $\mathbf{p}$ (given in the basis of the group $\mathcal{H}$) of the supergroup $\mathcal{G}$ with respect to the origin of $\mathcal{H}$. ε is a continuous parameter. The coset representatives of $\mathcal{G}$ with respect to $\mathcal{H}$, which are different from the unit element, are listed in the column g_k. The coset representatives are given in the basis of $\mathcal{H}$.

$\mathcal{G}$	$[i]$	$\mathbf{a'}, \mathbf{b'}, \mathbf{c'}$	$\mathbf{p}$	g_k
$Pma2$	2	$\mathbf{a}, \mathbf{b}/2, \mathbf{c}$		$(x+\frac{1}{2}, \bar{y}, z)$
$Pba2$	3	$\mathbf{a}/3, \mathbf{b}, \mathbf{c}$		$(x+\frac{1}{3}, y, z), (x+\frac{2}{3}, y, z)$
$Pba2$	3	$\mathbf{a}, \mathbf{b}/3, \mathbf{c}$		$(x, y+\frac{1}{3}, z), (x, y+\frac{2}{3}, z)$
$Pba2$	3	$\mathbf{a}, \mathbf{b}, \mathbf{c}/3$		$(x, y, z+\frac{1}{3}), (x, y, z+\frac{2}{3})$
$Pma2$	2	$-\mathbf{b}, \mathbf{a}/2, \mathbf{c}$	$\frac{1}{2}\,\frac{1}{2}\,0$	$(\bar{x}-1, y-\frac{1}{2}, z)$
$Aba2$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$		$(x, y+\frac{1}{2}, z+\frac{1}{2})$
$Aba2$	2	$-\mathbf{b}, \mathbf{a}, \mathbf{c}$	$\frac{1}{2}\,\frac{1}{2}\,0$	$(x+\frac{1}{2}, y, z+\frac{1}{2})$
$Cmm2$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$		$(x, \bar{y}, z)$
$Iba2$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$		$(x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2})$
$Pban$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$	$\frac{1}{4}\,\frac{1}{4}\,\frac{\varepsilon}{2}$	$(\bar{x}, y, \bar{z}+\varepsilon)$
$Pcca$	2	$\mathbf{a}, \mathbf{c}, \mathbf{b}$	$0\,\frac{3}{4}\,\frac{\varepsilon}{2}$	$(\bar{x}+\frac{1}{2}, y, \bar{z}+\varepsilon)$
$Pcca$	2	$-\mathbf{b}, \mathbf{c}, \mathbf{a}$	$\frac{3}{4}\,\frac{1}{2}\,\frac{\varepsilon}{2}$	$(x, \bar{y}+\frac{1}{2}, \bar{z}+\varepsilon)$
$Pbam$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$	$0\,0\,\frac{\varepsilon}{2}$	$(\bar{x}+\frac{1}{2}, y+\frac{1}{2}, \bar{z}+\varepsilon)$
$P4bm$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$		$(\bar{y}, x, z)$
$P4bm$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$	$\frac{1}{2}\,0\,0$	$(\bar{y}-\frac{1}{2}, x+\frac{1}{2}, z)$
$P4_2bc$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$		$(\bar{y}, x, z+\frac{1}{2})$
$P4_2bc$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$	$\frac{1}{2}\,0\,0$	$(\bar{y}-\frac{1}{2}, x+\frac{1}{2}, z+\frac{1}{2})$
$P\bar{4}b2$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$	$0\,0\,\frac{\varepsilon}{2}$	$(y, \bar{x}, \bar{z}+\varepsilon)$
$P\bar{4}b2$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$	$\frac{1}{2}\,0\,\frac{\varepsilon}{2}$	$(y-\frac{1}{2}, \bar{x}-\frac{1}{2}, \bar{z}+\varepsilon)$

chosen because compounds with this symmetry have already been studied by Abrahams (1989) and Abrahams *et al.* (1996) using a different method, which allows a comparison of the accuracy and efficiency of both approaches. There are no similar studies for compounds with symmetry $Pmc2_1$.

The search for pseudosymmetry has been performed among all of the minimal supergroups of the structures' space groups with a tolerance limit $\Delta_{tol} = 1.5$ Å, which restricts the maximal atomic displacement d_{max} to be less than 0.75 Å for supergroups of index 2. In general, pseudosymmetries corresponding to displacements of less than 0.1 Å were not considered as relevant for possible high-temperature phase transitions. Usually, such displacements suggest a doubtful symmetry assignment, *i.e.* the detected pseudosymmetry may be an overlooked symmetry in the structure determination (Abrahams, 1988).

The position of the origin in the polar group with respect to that of a non-polar supergroup is determined by optimizing the parameter ε so as to obtain the smallest absolute displacement d_{max}. The position of the origin that will keep the mass center at rest is derived from the optimized origin position by subtracting the mass center displacement. The latter is only along the polar axis z, and it will lead to a change in the values of the atomic displacements only along this axis.

The procedure described in the previous section uses the conventional bases for the supergroup and the subgroup. The structure data given with respect to a non-conventional setting in the database have been transformed to the conventional one before the search for pseudosymmetry.

3.1. Results for compounds with symmetry *Pba*2

There are 26 records in the ICSD for the space group $Pba2$, corresponding to 22 different compounds. For three of them, there are no data for the atomic positions in the database: $NaOH(H_2O)_{3.1}$, $In_4(P_2Se_6)_3$ and $(Bi_2O_3)_3(Nb_2O_5)_{17}$. In addition to the compounds studied by Abrahams (Abrahams, 1989; Abrahams *et al.*, 1996), there is one new record in the ICSD for $Ba_2Na(Nb_5O_{15})$.

One of the compounds studied is the known antiferro-electric $PbZrO_3$. Recent experimental results (Teslic & Egami, 1998) show that the symmetry of the antiferroelectric phase is $Pbam$ rather than $Pba2$, so this compound has been excluded from the study.

The search for pseudosymmetry has therefore been performed for 18 compounds. All minimal supergroups of $Pba2$ of index 2 and 3 (Table 1) have been checked.[4]

The 17 compounds for which some pseudosymmetry has been detected are shown in Table 2. The column $\mathcal{G}$ contains the non-polar supergroup for which the structure is pseudo-symmetric. The two compounds $KAl_2(PO_4)_2F(H_2O)_4$ and $KAl_2(PO_4)_2(OH)(H_2O)_4$ are exceptions, since only polar pseudosymmetry is obtained for them. For $[(Cl_3P)_2N](MoOCl_4)$ there are two records differing in the description of the two Mo-atom sites in the structure: in case (*a*) these atoms are regarded as equivalent and in case (*b*) as non-equivalent. The pseudosymmetry-search results on the absolute values of the maximal displacements along the polar axis for the optimized value of ε, d_{max}^z, and the maximal displacements along the polar axis when the mass center is kept at rest, d_{max}^{MC}, are similar to the maximal displacements along the polar axis, d_{max}^A, reported by Abrahams (Abrahams, 1989; Abrahams *et al.*, 1996). The maximal relative displacements along the polar axis defined as $d_{max}^{rel} = d_{max}^z - d_{min}^z$ (d_{max}^z and d_{min}^z are the values of the maximal and the minimal displacements along the polar axis taken with their corresponding signs) do not depend on the value of ε. The compounds with non-polar pseudosymmetry in Table 2 are ordered by the value of d_{max}^z. Note that in general d_{max}^z is not the quantity minimized in the optimization of ε. As mentioned above, the optimization of ε is related to the minimization of the modulus of the total displacement d_{max}. However, in many cases, the atomic displacements are restricted to the z axis, and both quantities (d_{max}^z and d_{max}) coincide. In these cases, the value of d_{max}^z corresponding to the optimized parameter fulfills the relation $d_{max}^z < d_{max}^{MC}$. In the contrary case, when the distortion involves atomic displacements along the x and y axes and therefore $d_{max}^z \neq d_{max}$, the relation $d_{max}^z < d_{max}^{MC}$ is not ensured.

Strikingly, in most cases, the requirement of unmoved mass center essentially yields equivalent results to the minimization of the maximal atomic displacement. The difference is not

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[4] The supergroups $\mathcal{G}$ are represented by the set of coset representatives (different from the unit element) of $\mathcal{G}$ with respect to $Pba2$ that are generated and used by the program *PSEUDO*. This automatic generation is the reason that in some cases the chosen set of coset representatives is not the simplest and most obvious one.

Table 2
Pseudosymmetric structures found among the compounds with symmetry $Pba2$.

$\mathcal{G}$ is the supergroup for which the pseudosymmetry has been obtained. ε is the value of the continuous parameter related to the origin shift of $\mathcal{H} = Pba2$ with respect to $\mathcal{G}$ (see Table 1) optimized in order to minimize the maximal value of absolute atomic displacement. d_{max}^z is the maximal displacement along the polar axis for the optimized value of ε. d_{max}^{MC} is the maximal atomic displacement along the polar axis when the mass center is kept at rest. d_{max}^A is the maximal displacement along the polar axis reported by Abrahams (1989) and Abrahams et al. (1996). $d_{max}^{rel} = d_{max}^z - d_{min}^z$ is the maximal relative displacement along the polar axis. The displacements are given in Å. The compounds with measured phase transitions are indicated with (*).

Compound	$\mathcal{G}$	ε	d_{max}^z	d_{max}^{MC}	d_{max}^A	d_{max}^{rel}
$Ca_2Ge_7O_{16}$	$P\bar{4}b2$	−0.008	0.018	0.022	0.035	0.034
$[(Cl_3P)_2N](MoOCl_4)$ (a)	$Pbam$	−0.003	0.047	0.058	0.050	0.093
$In_{0.6667}Ga_{0.6667}Fe_{0.6667}O_3$	$Pbam$	−0.351	0.099	0.109	0.140	0.199
(*)$Ba_2Na(Nb_5O_{15})$	$P4/mbm$	0.425	0.113	0.169	–	0.225
$(Ba_{0.6}K_{0.4})BiO_{2.23}$	$Pbam$	−0.047	0.142	–	0.232	0.285
(*)$K_{0.6}FeF_3$	$P4/mbm$	0.080	0.159	0.180	0.318	0.319
(*)$Tb_2(MoO_4)_3$	$P\bar{4}2_1m$	0.003	0.174	0.162	–	0.317
$K_3Sb_5O_{14}$	$Pbam$	0.021	0.174	0.183	0.252	0.349
(*)$Gd_2(MoO_4)_3$	$P\bar{4}2_1m$	0.004	0.215	0.204	–	0.402
(*)$Na_{13}Nb_{35}O_{94}$	$Pbam$	−0.017	0.236	0.262	0.270	0.472
$Ba_{3.75}Pr_{9.5}Ti_{18}O_{54}$	$Pbam$	0.032	0.264	–	0.318	0.529
$Mo_{17}O_{47}$	$Pbam$	0.004	0.332	0.333	0.333	0.665
$[(Cl_3P)_2N](MoOCl_4)$ (b)	$Pbam$	−0.005	0.421	0.427	–	0.843
$Bi_3Nb_{17}O_{47}$	$Pbam$	0.124	0.431	0.448	0.467	0.863
$(C(NH_2)_2(N_2H_4))ZrF_6$	$Pbam$	0.011	0.669	0.684	0.711	1.143
$KAl_2(PO_4)_2F(H_2O)_4$	$P4bm$	–	0.133	0.133	–	0.267
$KAl_2(PO_4)_2(OH)(H_2O)_4$	$P4bm$	–	0.115	0.115	–	0.229

larger than 0.02 Å for all of the compounds except $Ba_2Na(Nb_5O_{15})$.

There are five compounds with experimentally verified high-temperature phase transitions [indicated by (*) in Table 2]. Their maximal displacements are within the range 0.1–0.3 Å. The displacements necessary to obtain the non-polar structure are only along the polar axis for all compounds except $Gd_2(MoO_4)_3$ and $Tb_2(MoO_4)_3$, two well known improper ferroelectrics, which accordingly should have a non-polar primary distortion associated with the order parameter. The pseudosymmetry search among the minimal supergroups of $Pba2$ for these two compounds shows that the only minimal supergroup for which they are pseudosymmetric is $Cmm2$, with maximal displacements along the polar axis of 0.159 Å together with displacements of the same order along the [100] and [010] directions. As this supergroup is polar, the search has been continued among its minimal supergroups, and both structures have been found to be pseudosymmetric for $P\bar{4}2_1m$, which is in fact the experimentally known symmetry of the high-temperature phase. The only chain of minimal supergroups that relates $Pba2$ and $P\bar{4}2_1m$ is that containing $Cmm2$ (Fig. 1a). The basis $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$ of $P\bar{4}2_1m$ is related to that of $Pba2$ by $\mathbf{a}' = (\mathbf{a} + \mathbf{b})/2$, $\mathbf{b}' = (-\mathbf{a} + \mathbf{b})/2$ and $\mathbf{c}' = \mathbf{c}$. The origin shift with respect to the group $Pba2$ basis is $\mathbf{p} = (\frac{1}{4}\ \frac{3}{4}\ \frac{\varepsilon}{2})$.

For $Gd_2(MoO_4)_3$ and $Tb_2(MoO_4)_3$, the cell changes from orthorhombic to tetragonal. Therefore, an additional check of the cell compatibility with the crystal class of the supergroup is performed. The orthorhombic strain $(\varepsilon_1 - \varepsilon_2)/2$ of the cell in this case is $\sim 1.5 \times 10^{-3}$ for $Gd_2(MoO_4)_3$ and $\sim 1.0 \times 10^{-3}$ for $Tb_2(MoO_4)_3$. These examples show that the method also detects improper ferroelectrics where the polar distortion is superposed with much more complex and, in general, more

important distortions associated with the non-polar order parameter.

The compounds $Ba_2Na(Nb_5O_{15})$ and $K_{0.6}FeF_3$ have been found to be pseudosymmetric for three different minimal supergroups of $Pba2$, namely $P\bar{4}b2$, $P4bm$ and $Pbam$, so the search has been continued among the minimal supergroups of the flagged groups. As a result, both structures have been found to be pseudosymmetric for $P4/mbm$ (Fig. 1b). The bases of $P4/mbm$ and $Pba2$ are related by a unit transformation matrix with an origin shift of $\mathbf{p} = (0\ 0\ \frac{\varepsilon}{2})$ for $K_{0.6}FeF_3$ and $\mathbf{p} = (\frac{1}{2}\ 0\ \frac{\varepsilon}{2})$ for $Ba_2Na(Nb_5O_{15})$. In addition to the displacements along the polar axis (Table 2), there are displacements along the x and y axes. However, their values are small compared with those along the polar axis. Here again, the cell parameters have to be checked for compatibility with the tetragonal cell of the supergroup. The orthorhombic cell strain $(\varepsilon_1 - \varepsilon_2)/2$ is $\sim 4.4 \times 10^{-3}$ for $K_{0.6}FeF_3$ and $\sim 2.3 \times 10^{-3}$ for $Ba_2Na(Nb_5O_{15})$, confirming the tetragonal pseudosymmetry. The high-temperature phase transitions of both compounds have been experimentally verified without determining the corresponding symmetry groups. In the case of $K_{0.6}FeF_3$ (Ravez et al., 1989), the space group $P4/mbm$ is given as the most probable space group of the high-temperature phase, while $4/mmm$ is indicated as the point group of the non-polar phase for the case of $Ba_2Na(Nb_5O_{15})$ (Toledano, 1975). Both results agree with our pseudosymmetry analysis.

A high-temperature phase transition has also been observed experimentally for $Na_{13}Nb_{35}O_{94}$ (Abrahams et al.,
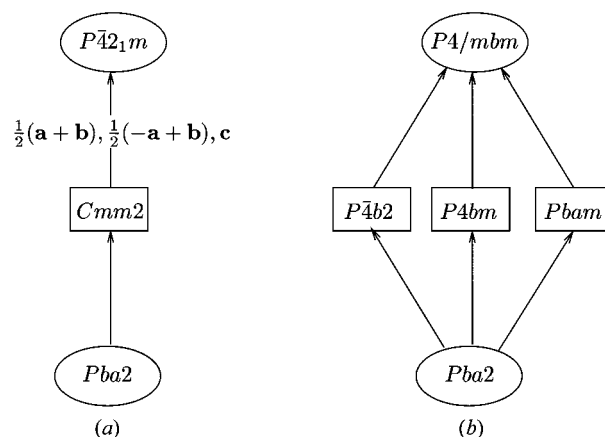
Figure 1
Chains of minimal supergroups that relate (a) $Pba2$ to $P\bar{4}2_1m$ and (b) $Pba2$ to $P4/mbm$. Figure (a) contains the relation between the basis $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ of $Cmm2$ and the basis of the supergroup $P\bar{4}2_1m$. For the remaining cases, the bases of the group and the supergroup coincide.

Table 3
Minimal supergroups $\mathcal{G}$ of index $[i] = 2$ and 3 of $\mathcal{H} = Pmc2_1$, specified as in Table 1.

$\mathcal{G}$	$[i]$	$\mathbf{a}', \mathbf{b}', \mathbf{c}'$	$\mathbf{p}$	g_k
$Abm2$	2	$\mathbf{b}, -\mathbf{a}, \mathbf{c}$	$\frac{1}{4}\,0\,0$	$(\bar{x}+\frac{1}{2}, \bar{y}, z)$
$Amm2$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$	$0\,\frac{1}{4}\,0$	$(\bar{x}, \bar{y}+\frac{1}{2}, z)$
$Pmm2$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}/2$		$(\bar{x}, \bar{y}, z)$
$Pmc2_1$	2	$\mathbf{a}/2, \mathbf{b}, \mathbf{c}$		$(x+\frac{1}{2}, y, z)$
$Pmc2_1$	2	$\mathbf{a}, \mathbf{b}/2, \mathbf{c}$		$(x, y+\frac{1}{2}, z)$
$Pmc2_1$	3	$\mathbf{a}/3, \mathbf{b}, \mathbf{c}$		$(x+\frac{1}{3}, y, z), (x+\frac{2}{3}, y, z)$
$Cmc2_1$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$		$(x+\frac{1}{2}, y+\frac{1}{2}, z)$
$Ima2$	2	$\mathbf{a}, \mathbf{b}, \mathbf{c}$	$\frac{1}{4}\frac{1}{4}0$	$(\bar{x}+\frac{1}{2}, \bar{y}+\frac{1}{2}, z)$
$Pmma$	2	$\mathbf{c}, \mathbf{a}, \mathbf{b}$	$0\,0\,\frac{\varepsilon}{2}$	$(\bar{x}, \bar{y}, \bar{z}+\varepsilon)$
$Pnma$	2	$\mathbf{c}, \mathbf{a}, \mathbf{b}$	$\frac{1}{4}\frac{1}{4}\frac{\varepsilon}{2}$	$(\bar{x}+\frac{1}{2}, y+\frac{1}{2}, \bar{z}+\varepsilon)$
$Pbam$	2	$\mathbf{b}, \mathbf{c}, \mathbf{a}$	$0\,\frac{1}{4}\,\frac{\varepsilon}{2}$	$(x, \bar{y}+\frac{1}{2}, \bar{z}+\varepsilon)$
$Pbcm$	2	$\mathbf{b}, \mathbf{c}, \mathbf{a}$	$\frac{1}{4}0\,\frac{\varepsilon}{2}$	$(x+\frac{1}{2}, \bar{y}, \bar{z}+\varepsilon)$

Table 4
Pseudosymmetric structures among the compounds with symmetry $Pmc2_1$.

$d_{\max}^y$ is the absolute value of the maximal displacement along [010]. For a description of the remaining columns see Table 2.

Compound	$\mathcal{G}$	ε	$d_{\max}^y$	$d_{\max}^z$	$d_{\max}^{MC}$	$d_{\max}^{rel}$
(*)$(NH_2)_2CS$	$Pnma$	0.028	0.348	0.218	0.146	0.290
(*)$CuAgS$	$Cmcm$	0.038	0.394	0.227	0.178	0.301
(*)$CsEuNaNb_5O_{15}$	$Pmmm$	0.449	0.178	0.310	0.314	0.620
$Ca_3Mn_{1.2}Fe_{1.8}O_8$†	$Pmma$	0.478	0.223	0.343	–	0.686
$BaHgS_2$	$Pbam$	0.284	0.423	0.361	0.457	0.675
$Ca_3TiFe_2O_8$†	$Pmma$	0.460	0.347	0.421	–	0.761
Nd_4GeO_8	$Cmcm$	0.963	0.469	0.439	0.509	0.834
$Sr(OH)_2(H_2O)$	$Pmma$	0.119	0.388	0.447	–	0.895
$(Fe_{0.3}Mn_{0.7})Ta(O_2)O_2$†	$Pmma$	0.149	0	0.448	–	0.896
β-$Ba(OH)_2(H_2O)$	$Pmma$	0.088	0.404	0.468	–	0.937
$NaBa_2Nd(SiO_4)_4$	$Pmma$	−0.489	0.280	0.536	0.554	1.073
$Na(AlSi_2O_6)(H_2O)_{1.1}$	$Pmma$	0.467	0.666	0.551	–	0.981
$La_2Fe_{1.76}S_5$	$Pmma$	−0.008	0.099	0.677	–	1.355
$CaPtP$	$Pmc2_1$		0.179	0.398		0.796
$KCu(CO_3)F$	$Amm2$		0.467	0.501		1.002

† Not considered as possible ferroelectrics (see text).

1989) with no data for the non-polar phase symmetry. Our pseudosymmetry study, as well as the result of Abrahams (1989), indicates the group $Pbam$ as a possible symmetry group of the high-temperature phase.

The small values of the displacements of the first three compounds in Table 2 make their symmetry assignment doubtful. In addition, there are three more compounds that probably have to be excluded from the list of possible 'candidates' for ferroelectrics. Recent experimental results show that the room-temperature phases of $K_3Sb_5O_{14}$ (Hong, 1974) and $(Ba_{0.6}K_{0.4})BiO_{2.23}$ (Shiyou *et al.*, 1991) have symmetry $Pbam$ and not $Pba2$. Further, the lower-symmetry phase of $[C(NH_2)_2(N_2H_4)]ZrF_6$ has been recently redetermined to be $P2_1/n$ (Ross *et al.*, 1998).

Disregarding these atypical cases, there are four compounds $\{Ba_{3.75}Pr_{9.5}Ti_{18}O_{54}$, $Mo_{17}O_{47}$, $[(Cl_3P)_2N](MoOCl_4)$ and $Bi_3Nb_{17}\}$ with a non-polar pseudosymmetry that can be considered as 'candidates' to be ferroelectrics. From Table 2, it

can be seen that the atomic displacements for these compounds for the two methods of optimization, as well as those obtained by Abrahams (Abrahams, 1989; Abrahams *et al.*, 1996), are less than 0.5 Å. For $Mo_{17}O_{47}$, the results for the three origin choices are the same. In the remaining cases, the maximal displacement obtained by choosing the origin shift so as to minimize the maximal distortion or to leave the mass center at rest is less than the one given in Abrahams (1989) and Abrahams *et al.* (1996). This is related to the fact that in these references, when choosing the origin shift, only the displacements of some of the atoms in the structure are considered, while the optimization performed here includes all the atoms. In some cases the difference is very important if considered quantitatively in empirical formulas for the transition temperature (Abrahams *et al.*, 1968) (see §4). A further advantage of conducting a systematic pseudosymmetry search is that one can predict the possible symmetry group of the high-temperature (non-polar) phase even when it is not a minimal supergroup of the initial structure group.

3.2. Results for compounds with symmetry $Pmc2_1$

There are 59 records in the ICSD with symmetry given by the space group $Pmc2_1$, which correspond to 45 different compounds, seven of them with more than one record. There are no data for the atomic positions of four of these structures.

Eight of the 41 remaining compounds have also been excluded from the current study: $NaNbO_3$ (Shuvaeva *et al.*, 1993), because its polar structure has been obtained under an electric field; $FeTiD_x$ for $x = 1, 1.1, 2.1$, for which the polar phase exists under pressure (Fischer *et al.*, 1978); WO_2Cl_2 (Abrahams *et al.*, 1993) and Pb_2O_3 (Bouvaist & Weigel, 1970), since their symmetry has been redetermined and shown to be different from $Pmc2_1$; Fe_3O_4 (Iizumi *et al.*, 1982), as the listed $Pmc2_1$ data are in fact an approximate model facilitating the analysis of the complicated monoclinic structure; and $Na_3(AlSiO_4)_3 \cdot (H_2O)$, which has 'wrong coordinates' according to the database.

The remaining 33 compounds were checked for pseudosymmetry for all minimal supergroups of $Pmc2_1$ of index $[i] = 2, 3$ (Table 3; see also footnote **4**). No pseudosymmetry within the tolerance limit of $\Delta_{tol} = 1.5$ Å has been found for 16 of the compounds. Two further cases are excluded from our study: $CuGeO_3$ (Roessli *et al.*, 1994) is a clear example of an 'overlooked symmetry' case with zero displacements necessary to achieve the $Pmma$ supergroup symmetry, and for $Pb_2Sr_2CuFeO_6$ (Rouillon *et al.*, 1995), apart from the data assigning it to $Pmc2_1$, there is an additional file in the ICSD where the structure symmetry of the same phase corresponds to the space group determined as pseudosymmetric.

The results of the pseudosymmetry search for the remaining 15 compounds are shown in Table 4. At the bottom of the table are listed two structures for which only polar pseudosymmetry has been obtained: $KCu(CO_3)F$ (Mercier & Leblanc, 1996), with pseudosymmetry given by the group $Amm2$, and $CaPtP$ (Wenski & Mewis, 1986), for which the isomorphic supergroup $Pmc2_1$ with $\mathbf{b}' = \mathbf{b}/2$ has been flagged

as pseudosymmetric. The compounds with non-polar pseudosymmetry $\mathcal{G}$ in the table are ordered by the values of maximal absolute displacement along the polar axis d_{max}^z. The maximal displacement along the polar axis when the mass center is kept at rest, d_{max}^{MC}, is not calculated for compounds whose atomic sites are not fully occupied or where there are different types of atoms occupying the same orbit. The values under d_{max}^y give the maximal displacement along y.

There are three structures with non-polar pseudosymmetry for which the corresponding ideal non-polar configuration would imply an important change in the cations' coordination. Taking into account that, in general, ferroelectric phase transitions do not provoke such drastic changes, these compounds, namely $Ca_3Mn_{1.2}Fe_{1.8}O_8$, $Ca_3TiFe_2O_8$, and $(Fe_{0.3}Mn_{0.7})Ta(O_2)O_2$, were excluded from further considerations.

3.2.1. Compounds with measured phase transitions. There are three compounds in $Pmc2_1$ with a known higher-temperature phase transition. The entries corresponding to these compounds in Table 4 are indicated by an asterisk (*). Two of them are known to be ferroelectrics.

The pseudosymmetry detected for thiourea $(NH_2)_2CS$ is characterized by the supergroup $\mathcal{G} = Pnma$, and this is in accordance with the experimentally observed ferroelectric phase transition $Pmc2_1 < Pnma$ with an intermediate incommensurate phase (Zuñiga *et al.*, 1989).

$CsEuNaNb_5O_{15}$ is flagged as pseudosymmetric for the minimal supergroups $Pmma$ and $Pmm2$. The displacements corresponding to $Pmma$ are mainly along the polar axis with a maximal value of 0.116 Å for Na, but there are also small displacements along [100] and [010] for Nb, O(1), O(2), O(5), O(6), O(7) and O(8), with maximal values $d_{max}^y = 0.011$ Å and $d_{max}^x = 0.038$ Å corresponding to O(1) and O(2). The check for pseudosymmetry among the common minimal supergroups of $Pmma$ and $Pmm2$ shows that the structure is pseudosymmetric for $Pmmm$. Displacements along the three directions (with $d_{max}^x = 0.228$ Å, $d_{max}^y = 0.178$ Å and $d_{max}^z = 0.310$ Å) are necessary to obtain a structure with symmetry $Pmmm$. The chain of minimal supergroups relating both groups is shown in Fig. 2(*a*). The bases of $Pmc2_1$ and $Pmmm$ are related by $\mathbf{a}' = \mathbf{c}/2$, $\mathbf{b}' = \mathbf{a}$ and $\mathbf{c}' = \mathbf{b}$, where $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$ is the basis of $Pmmm$. There are experimental results confirming a phase transition at $T_c = 565$ K, and the symmetry of the high-temperature phase is given as $Pmcm$ (the non-conventional symbol of $Pmma$ when transformed to the basis of $Pmc2_1$) or $Pmmm$ (Dion *et al.*, 1984), in agreement with our results. The facts that there is no possibility of a continuous (direct) phase transition from $Pmmm$ to $Pmc2_1$ (Stokes & Hatch, 1988) and that the measured phase transition does not appear to be first order suggest a $Pmcm$ symmetry of the non-polar phase. The

existence of the higher $Pmmm$ pseudosymmetry would indicate a second phase transition at higher temperatures related to a change in the structure symmetry from $Pmcm$ to $Pmmm$.

The case of $CuAgS$ is different from the other compounds with symmetry $Pmc2_1$ as the phase with this symmetry exists at low temperatures. There is a second-order phase transition at approximately 250 K, related to a change of symmetry from $Pmc2_1$ to $Cmc2_1$ (Baker *et al.*, 1991). The ICSD contains two different records for the structure, with symmetry $Pmc2_1$ corresponding to temperatures 120 K and 13 K (Baker *et al.*, 1991). Both structures are pseudosymmetric for $Pnma$, $Pmma$ and $Cmc2_1$, with smaller displacements in the structure measured at higher temperature, as expected. A further check among the common minimal supergroups of these groups indicates that both polar structures are pseudosymmetric for $Cmcm$. The chain of minimal supergroups relating $Pmc2_1$ and $Cmcm$ for this structure is presented in Fig. 2(*b*). The transformation matrices (different from the unit one) relating the bases of the groups on each step of the group–supergroup chains are also given in the figure. The basis of the supergroup $Cmcm$ is the same as that of $Pmc2_1$ with an origin shift of $\mathbf{p} = (\frac{1}{2}\frac{1}{2}\frac{\varepsilon}{2})$, where the position of the origin along z is not fixed and has been optimized as explained above. These displacements are in the yz plane with maximal values $d_{max}^y = 0.394$ Å and $d_{max}^z = 0.227$ Å for the structure measured at 120 K (see Table 4) and $d_{max}^y = 0.481$ Å and $d_{max}^z = 0.431$ Å for that at 13 K.

The room-temperature phase of this compound has been reported to have symmetry $Cmc2_1$ (Baker *et al.*, 1991). As the search for pseudosymmetry in the low-temperature phase gave higher pseudosymmetry than $Cmc2_1$, the room-temperature reported structure has also been checked for pseudosymmetry. The search among the minimal supergroups of $Cmc2_1$ shows that the structure is pseudosymmetric for $Cmcm$ with maximal displacements necessary to obtain the non-polar structure $d_{max}^y = 0.033$ Å and $d_{max}^z = 0.013$ Å, with no change in the position of the origin. These values are in the range that normally corresponds to an overlooked symmetry. However, a direct change of symmetry from $Cmcm$ to $Pmc2_1$
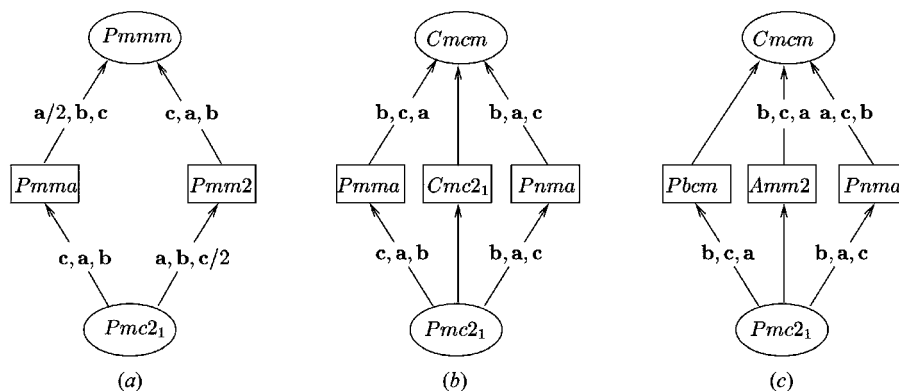
Figure 2
Chains of minimal supergroups relating $Pmc2_1$ to $Pmmm$ (*a*) and $Cmcm$ (*b*) and (*c*). The lattice vectors $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$ of the minimal supergroups are expressed as combinations of the bases $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ of the group for each step of the group–supergroup graph. The trivial relation $(\mathbf{a}' = \mathbf{a}, \mathbf{b}' = \mathbf{b}, \mathbf{c}' = \mathbf{c})$ is not indicated.

cannot be achieved through a Landau-type phase transition (Stokes & Hatch, 1988). This would mean that either the system undergoes a non-Landau first-order phase transition $Cmcm$–$Pmc2_1$, in contrast with the reported second-order phase transition (Baker *et al.*, 1991), or that there is indeed an intermediate $Cmc2_1$ phase and two consecutive phase transitions. Further investigations are necessary in order to determine the exact symmetry of the room-temperature phase and the sequence of phase transitions for this compound.

3.2.2. Possible ferroelectrics. The seven compounds detected as pseudosymmetric with respect to a non-polar supergroup and for which there are no experimental data for a high-temperature phase transition can be considered as good candidates for ferroelectrics. The atomic positions of the compounds for the experimental polar phases and the possible high-temperature non-polar phases obtained from the pseudosymmetry search are given in the supplementary material.[5]

BaHgS₂ (Rad & Hoppe, 1981). A schematic representation of the atomic arrangement in the room-temperature structure of this compound is presented in Fig. 3(*a*). This structure is pseudosymmetric for the supergroup $Pbam$. The displacements necessary to obtain a structure with such symmetry are in the yz plane. Along y, the maximal displacement is $d^y_{max} = 0.423$ Å for S(3). For the position of the origin corresponding to the optimized value of the parameter ε, all the atoms except S(2) and S(3) are displaced in the same direction along the z axis, with maximal displacements 0.361 Å corresponding to S(1) and S(4). The maximal displacement in the opposite direction is 0.314 Å for S(2). The values of the maximal displacement along the polar axis for the different choices of the origin are given in Table 4. A schematic representation of the atomic arrangement in the calculated non-polar structure (in the plane bc) is shown in Fig. 3(*b*).
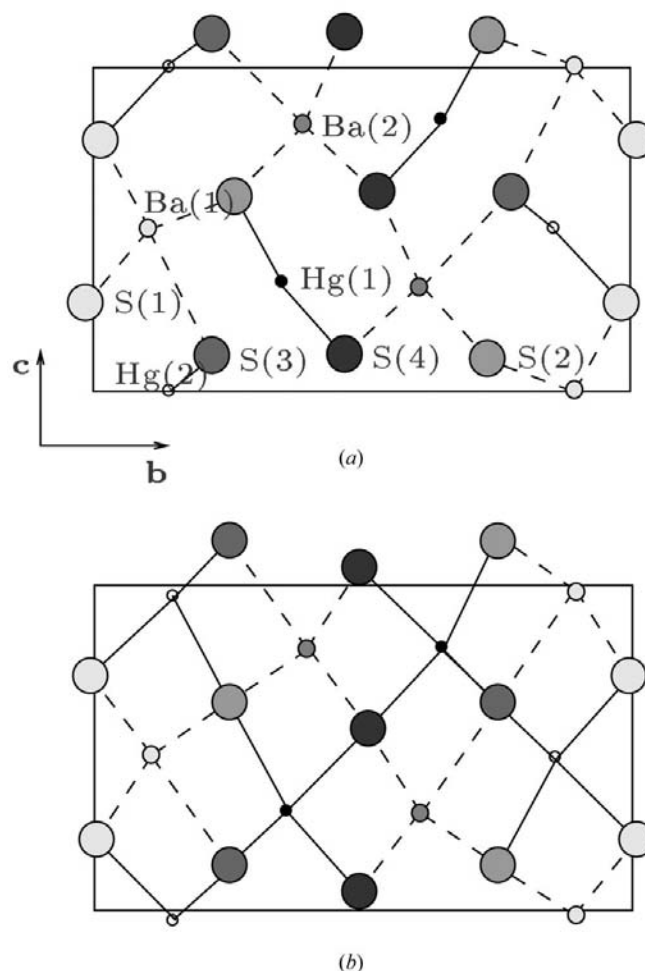
In the calculated structure with symmetry $Pbam$ (see Table 1 of the supplementary material), both types of Hg atoms become symmetry equivalent, and the same holds for the two types of Ba atoms. The displacements of the S atoms do not lead to changes in the environments of the Hg or the Ba atoms.

Nd₄GeO₈ (Merinov *et al.*, 1978). The room-temperature structure of this compound is formed by layers of oxygen polyhedra interleaved with GeO₄ layers. The search for pseudosymmetry among the minimal supergroups of $Pmc2_1$ gave the result that this structure is pseudosymmetric for $Amm2$, $Pbcm$ and $Pnma$. Following the chains of minimal supergroups a pseudosymmetry has been found for $Cmcm$ (see Fig. 2c). The origin in the non-polar structure is shifted by $\mathbf{p} = (\frac{3}{4}\,\frac{3}{4}\,\frac{\varepsilon}{2})$ with respect to the origin chosen in the polar structure.

The displacements necessary to obtain a non-polar structure with symmetry $Cmcm$ are along the three directions with maximal values $d^x_{max} = 0.259$ Å, $d^y_{max} = 0.469$ Å and $d^z_{max} = 0.439$ Å (corresponding to the optimized value of ε).

These displacements lead to changes in the distribution of the atoms into orbits: the 12 independent orbits of O atoms in the polar structure form four different orbits in the calculated structure with symmetry $Cmcm$ (see Table 2 of the supplementary material); the six Nd orbits in the initial structure constitute three independent orbits in the calculated one; and the two Ge orbits merge into one orbit.

Sr(OH)₂(H₂O) and *β-Ba(OH)₂(H₂O)*. These two isostructural compounds are represented by two records in the ICSD, corresponding to measurements with X-rays (Buchmeier & Lutz, 1986) and by neutron diffraction (Kuske *et al.*, 1988). The only difference between the two records is in the positions of the H atoms in the hydroxide ions – while in the results from the X-ray diffraction these ions are considered as 'rigid groups' and only the position of the O atom is given, the neutron diffraction data give the positions of each one of the atoms in these groups. The coordinates of the polar and non-polar structures of both compounds can be found in Tables 3 and 4 of the supplementary material.

Figure 3
Schematic projection in the plane *bc* of the polar structure with symmetry $Pmc2_1$ (*a*) and the calculated non-polar structure with symmetry $Pbam$ (*b*) for BaHgS₂. The non-polar structure is represented with respect to the basis of the subgroup; the transformation is given in Table 3.

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[5] Supplementary data for this paper are available from the IUCr electronic archives (Reference: CK0014). Services for accessing these data are described at the back of the journal.
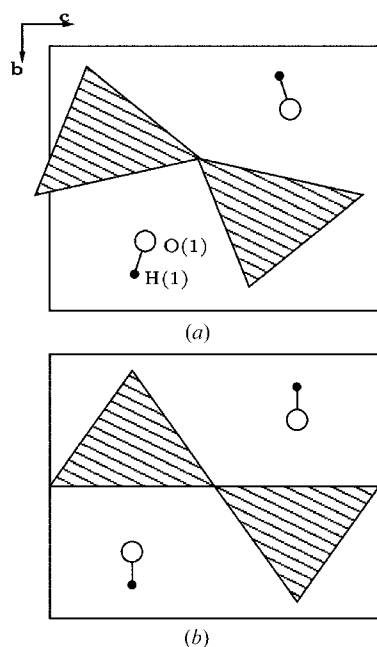
A schematic representation of the polar structure of $Sr(OH)_2(H_2O)$ is given in Fig. 4(a). The search for pseudosymmetry among the minimal supergroups of $Pmc2_1$ with tolerance limit $\Delta_{tol} = 1.5$ Å detects as pseudosymmetric only the structures determined by X-ray diffraction. $Sr(OH)_2(H_2O)$ has a pseudosymmetry given by the supergroup $Pmma$. For β-$Ba(OH)_2(H_2O)$, there are three supergroups for which the structure is pseudosymmetric: $Pmma$, $Pbam$ and $Amm2$. We restrict our further consideration to the supergroup $Pmma$ as the one giving the symmetry of the possible high-temperature phase because for this group the displacements are only along the polar axis and their values are smaller than those corresponding to the other two supergroups.

A schematic representation of the calculated non-polar structure with symmetry $Pmma$ for $Sr(OH)_2(H_2O)$ is given in Fig. 4(b).

No pseudosymmetry has been obtained for the neutron diffraction data because the H(2) and H(3) atoms are not included in the structure resolved from X-ray data and have positions that are not pseudosymmetric for any of the minimal supergroups of $Pmc2_1$ within the tolerance limit used (1.5 Å). Displacements of the order of 0.9 Å (tolerance limit ~1.8 Å) are necessary for these H atoms in order to obtain the supergroup $Pmma$. Taking into account their relatively high thermal displacements {~0.6 Å along [010] for H(2) in β-$Ba(OH)_2(H_2O)$}, we would rather consider both compounds as being ferroelectric.

$NaBa_6Nd(SiO_4)_4$ (Tamazyan & Malinovskii, 1987). The room-temperature structure of this compound can be represented as a small distortion from a structure formed by SiO_4

(a)

(b)

Figure 4
Schematic projection in the plane bc of the polar structure with symmetry $Pmc2_1$ (a) and the calculated non-polar structure with symmetry $Pmma$ (b) for $Sr(OH)_2(H_2O)$: dashed areas represent SrO_6; O(1)—H(1) represent water molecules.

tetrahedra sharing corners with NaO_6 and NbO_6 octahedra. The polar structure is pseudosymmetric for the supergroup $Pmma$. The displacements necessary to obtain the higher-symmetry structure are along the [010] and [001] directions, except for O(3) and O(4), which are displaced along all three axes, although the displacements along [100] are very small (0.008 Å). The atoms of Ba, Na and Si are displaced in the same direction along the polar axis and that of Nd in the opposite one. The maximal displacement along [010] is 0.280 Å for O(11) and O(12). The maximal displacements along [001] for the two different choices for the position of the origin are given in Table 4. The structure obtained from the calculated displacements coincides with the ideal structure for this compound proposed by Tamazyan & Malinovskii (1987).

$Na(AlSi_2O_6)(H_2O)_{1.1}$ (Yakubovich & Tarasov, 1988). A schematic representation of the bc projection for the (Si/Al) tetrahedra and the Na atoms in the polar structure of this compound is given in Fig. 5(a) (for the coordinates, see also Table 5 of the supplementary material). This structure is pseudosymmetric for the supergroup $Pmma$ of $Pmc2_1$. The displacements necessary to obtain the high-symmetry structure are along the z axis for all of the atoms with maximal value $d_{max}^z = 0.551$ Å for to O(5). The atoms O(2), O(4) and H(1) are also displaced along the y axis with maximal displacement $d_{max}^y = 0.666$ Å for H(1). A schematic representation of the calculated non-polar structure is given in Fig. 5(b).

The displacements are related to rotations of the SiO_4 tetrahedra so that in the high-symmetry structure their O(2)—O(2) edges are parallel to the c axis and the Si—O(3) bond is perpendicular to this axis. Also, the atoms are arranged in planes at $x = 0$ and $x = \frac{1}{2}$. Along the c axis, they have coordinates with values $z = 0, \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$, which lead to higher symmetry for all of the atomic orbits. The water molecules in the non-polar structure are aligned in the plane containing the Na and O(3) atoms.

$La_2Fe_{1.76}S_5$ (Besrest & Collin, 1978). The pseudosymmetry found for this compound corresponds to the supergroup $Pmma$. All of the atoms are displaced along the polar axis with maximal displacement for S(18) and S(20) (see Table 6 of the supplementary material). There are also displacements along the [010] direction for the La atoms and some of the S atoms, but these displacements are small compared with that along z. The maximal one is $d_{max}^y = 0.099$ Å for S(14).

In the calculated non-polar structure, the environment of the Fe(7), Fe(5) and Fe(8) atoms is slightly different from the initial one, and the distribution into orbits of the atoms of La and S also changes (some of the independent orbits of the polar structure merge into one orbit in the calculated non-polar structure).

3.3. Comparison between $Pba2$ and $Pmc2_1$ pseudosymmetry results

A comparison of the pseudosymmetry results obtained for $Pba2$ and $Pmc2_1$ shows that there are some differences related mainly to the directions of the atomic displacements necessary

to obtain the high-symmetry (non-polar) structure from the initial (polar) one. While in the case of $Pba2$ these displacements are mostly along the polar direction, for the compounds with symmetry $Pmc2_1$ they are often also along the [010] direction.

This empirical observation is easy to understand taking into account the fact that the pseudosymmetry-search procedure is based on the assumption of a group–supergroup relation between the high-symmetry (pseudosymmetry) and low-symmetry (initial) phases. This requirement imposes restrictions on the directions and the amplitudes of the displacements necessary to achieve the hypothetical high-symmetry structure: all such displacements have to be compatible with the initial structure symmetry. In other words, the pattern and the number of independent allowed displacements for a certain orbit of atoms are determined by the variable para-
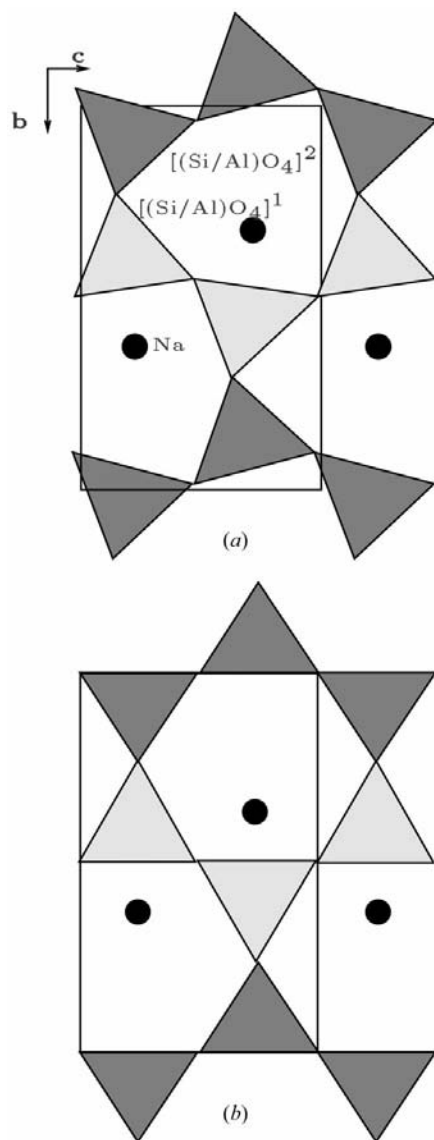
Figure 5
Schematic projection in the plane bc of the (Si/Al) tetrahedra and the Na atoms in the polar structure with symmetry $Pmc2_1$ (a) and the non-polar structure with symmetry $Pmma$ (b) obtained for $Na(AlSi_2O_6)(H_2O)_{1.1}$.

meters in the Wyckoff-position description of the coordinates. Atoms occupying Wyckoff positions without variable parameters remain fixed during the group–supergroup phase transition. Conversely, atoms occupying a general-position orbit can undergo independent displacements in the three directions but their patterns have to be compatible with the constraints of the initial structure symmetry.

There are two special positions of $Pba2$, $2a$ $0, 0, z$ and $2b$ $0, \frac{1}{2}, z$, and atoms that occupy these positions (which is often the case for the homopolar atoms) can experience displacements along the polar z axis only, as the coordinates along the other two directions are fixed by symmetry constraints. It is interesting to note that in the case of the $Pba2$ pseudosymmetric structures this one-dimensional rule is characteristic also for atoms occupying the general position. The magnitudes of the few [100] and [010] displacements determined by the pseudosymmetry search are negligible compared with those along the polar axis. {An exception to this rule are the cases of $Tb_2(MoO_4)_3$ and $Gd_2(MoO_4)_3$, whose displacements along [010] and [001] have similar amplitudes, a case explained by the improper character of the ferroelectricity in these compounds.}

The two variable parameters of the Wyckoff-position description of the two special positions of $Pmc2_1$, $2a$ $0, y, z$ and $2b$ $\frac{1}{2}, y, z$, indicate that displacements along [010] and [001] are compatible with the symmetry constraints. This 'two-dimensional' displacement rule is typical for almost all pseudosymmetric $Pmc2_1$ structures: the displacements necessary to acquire the high-symmetry phase are confined to the yz plane.

4. Estimation of the transition temperature

The general procedure proposed here for the search for ferroelectrics gives as a result the space group $\mathcal{G}$ of a possible high-temperature phase and the displacements of all of the atoms necessary to obtain a structure with symmetry given by this group. Several efforts have been made to relate these displacements to the transition temperature. The first one is the empirical law proposed by Abrahams *et al.* (1968) (the AKJ relation) according to which

$$T_c = C(d^{hp})^2 \, [\text{K}], \qquad (1)$$

where $C \simeq 2.0 \times 10^4$ K Å^{-2} and d^{hp} is the displacement along the polar axis (in Å) associated with the metal atom that forms the shortest and fewest ionic bonds in the structure (the homopolar atom).

However, it should be taken into account that this relation is expected to have some empirical and theoretical basis only in proper ferroelectrics and also that C is only an approximate empirical constant (Samara, 1971).

Attempts have been made to relate the transition temperature T_c and the displacement along the polar axis d_z in the form $T_c \propto d_z^n$, where $n \neq 2$ (Singh & Bopardikar, 1984; Singh *et al.*, 1988).

Table 5
Known ferroelectrics used to obtain the empirical law represented by (1).

T_c is the transition temperature in K, $\mathcal{H}$ and $\mathcal{G}$ are the space groups of the polar and the non-polar phase, $d^{\,hp}$ is the displacement of the homopolar atom along the polar axis as given by Abrahams *et al.* (1968), $d^{\,rel}_{max}$ is the calculated maximal relative displacement along the polar axis necessary to obtain the high-symmetry structure. Displacements are represented in Å.

Compound	T_c (K)	$\mathcal{H}$	$\mathcal{G}$	$d^{\,hp}$(Å)	$d^{\,rel}_{max}$ (Å)
SbSI	296	$Pna2_1$	$Pnam$	0.144(Sb)	0.197
$Pb_{10}Fe_5Nb_5O_{30}$	388	$R3m$	$R\bar{3}m$	0.091(Nb)	0.091†
$BaTiO_3$	399	$P4mm$	$Pm3m$	0.132(Ti)	0.154
$Ba_{1.3}Sr_{3.74}Nb_{10}O_{30}$	408	$P4bm$	$P4/mbm$‡	0.106(Nb)	0.473
$Ba_6Ti_2Nb_8O_{30}$	505	$P4bm$	$P4/mbm$‡	0.174(Ti,Nb)	0.221
$KNbO_3$§	708	$Bmm2$	$Pm3m$	0.160(Nb)	0.200
$PbTiO_3$	763	$P4mm$	$Pm3m$	0.299(Ti)	0.465
$LiTaO_3$	891	$R3c$	$R\bar{3}c$	0.197(Ta)	0.633
$LiNbO_3$	1468	$R3c$	$R\bar{3}c$	0.269(Nb)	0.696
$Ba_{10}Cu_5W_5O_{30}$	1473	$P4mm$	$Pm3m$	0.328(W)	0.638†

† Experimental value for the relative displacement.   ‡ The supergroup $\mathcal{G}$ corresponds to the result from the pseudosymmetry search.   § Improper ferroelectric.

4.1. AKJ relation

The AKJ relation was obtained from the experimental data for ten ferroelectrics (known in 1968), and later it was successfully used for the estimation of the transition temperature for a number of compounds predicted by Abrahams and his group [see *e.g.* Abrahams *et al.* (1996) and the references therein] as possible ferroelectrics.

However, their interpretation of the displacements $d^{\,hp}$ varies significantly with the structure under investigation. For example, the displacements $d^{\,hp}$ were defined as the relative displacement of the homopolar atom with respect to the oxygen framework by Abrahams *et al.* (1968). In treating structures with $Pba2$ symmetry (Abrahams, 1989; Abrahams *et al.*, 1996) the displacements $d^{\,hp}$ are taken either as the largest displacements along the polar axis for the homopolar atom or as the average of the displacements among the homopolar atoms.

Obviously, such a structure-dependent approach for the calculation of $d^{\,hp}$ is difficult to incorporate into a computer program designed for a general systematic search. Moreover, the values of $d^{\,hp}$ are in general ambiguous, as they depend on the location of the pseudosymmetry non-polar elements [ε parameter(s)]. We have therefore reconsidered the structural data originally employed for the derivation of (1) with the aim of establishing a more direct general relationship between T_c and the atomic displacements involved in the ferroelectric phase transitions. After testing the T_c dependences on different types of atomic displacements (relative, maximal, average *etc.*) we obtained an approximate empirical relation between T_c and the maximal relative displacement along the polar axis that can be considered as an alternative to (1).

4.2. Relation between the transition temperature and the relative displacement

Table 5 lists the ten compounds that were used by Abrahams *et al.* (1968) to find the AKJ relation. For each compound, we have listed the displacements of the homopolar atom along the polar axis as given by Abrahams *et al.* (1968),

$d^{\,hp}$, and the calculated maximal relative displacements along the polar axis, $d^{\,rel}_{max}$, necessary to obtain the high-temperature non-polar structure from the initial polar one. For two of the compounds, $Pb_{10}Fe_5Nb_5O_{30}$ and $Ba_{10}Cu_5W_5O_{30}$, no data have been found for the atomic positions in the polar structure, and the maximal relative displacements provided by Platonov *et al.* (1967) are given in Table 5. For the rest of the compounds, the search for pseudosymmetry has been performed on their experimental structures, the same as those considered by Abrahams *et al.* (1968). The supergroups obtained as space groups of the high-temperature phases coincide with the experimental ones for all of the compounds for which the space group of the non-polar phase has been experimentally determined. For $Ba_{1.3}Sr_{3.74}Nb_{10}O_{30}$, the experimental results show that the high-temperature phase (corresponding to temperatures above $T_c = 408$ K) has point group $4/mmm$, but the exact space group is not known. The space group $\mathcal{G} = P4/mbm$ obtained from the pseudosymmetry search is in accordance with this point symmetry, and it is the one given in Table 5 instead of $P\bar{4}b2$ from Abrahams *et al.* (1968). The symmetry $P\bar{4}b2$ for the high-temperature phase of $Ba_6Ti_2Nb_8O_{30}$ was assigned by Jamieson & Abrahams (1968) in analogy with the one assigned to $Ba_{1.3}Sr_{3.74}Nb_{10}O_{30}$, but no experimental data confirm such symmetry. According to our calculations, the structure is pseudosymmetric for $\mathcal{G} = P4/mbm$ and this is the supergroup listed in Table 5.

The AKJ fit (Abrahams *et al.*, 1968) of the data of Table 5 [T_c *versus* $(d^{\,hp})^2$] is reproduced in Fig. 6(*a*). Alternatively, we have checked a relation of the form

$$T_c = \alpha \left(d^{\,rel}_{max}\right)^2 + \beta, \qquad (2)$$

where $d^{\,rel}_{max}$ is the maximal relative displacement along the polar axis and α and β are the parameters whose values are fitted using the experimental values for T_c and the calculated values of $d^{\,rel}_{max}$ given in Table 5. The data for $KNbO_3$ have been excluded from the fit as it is, in fact, an improper ferroelectric.

There are two main differences between the relation given by (2) and the AKJ relation. First, the displacement used in (2) is unambiguous as it does not depend on the choice of the origin in the polar phase with respect to that of the non-polar

one. Second, there is an additional parameter β, which is related to the fact that the atomic displacements correspond to some temperature that, in general, is non-zero. The parameter β can be interpreted as the temperature T_f at which the ferroelectric structure has been measured. The zero limit for the displacement should yield a T_c equal to the experimental temperature T_f and not 0 K.

The relation $T_c(d_{max}^{rel})$ is shown in Fig. 6(b). The fit of the parameters α and β is made using a nonlinear least-squares algorithm. The values of the parameters obtained from this fit are $\alpha = 0.22\,(4) \times 10^4$ K Å^{-2} and $\beta = 300\,(100)$ K. All ferroelectric structure data used in the fit are from room-temperature measurements, so $T_f \simeq 293$ K in agreement with the parameter β that is obtained. As expected, the relation is not fulfilled for KNbO$_3$, and its data are not included in Fig. 6(b). The comparison of plots (a) and (b) shows that the quality of both fits is similar. This suggests the possibility of using this alternative empirical law for an estimation of T_c. The maximal relative displacement d_{max}^{rel} is easy to apply in a systematic search program: it is unambiguous and does not depend on the origin choice.
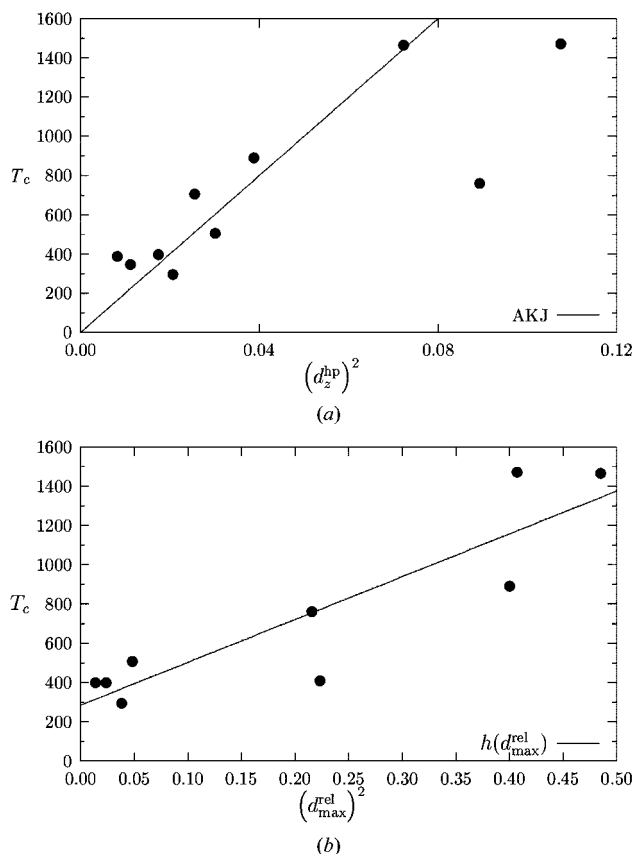
Figure 6
Relation between the transition temperature and the displacements from the high-temperature phase for the compounds used to obtain the AKJ relation (Table 5). (a) Relation between T_c and the displacement of the homopolar atom d_z^{hp} as used by Abrahams *et al.* (1968). (b) Relation between T_c and the maximal relative displacement d_{max}^{rel} obtained from the pseudosymmetry search. $h(d_{max}^{rel}) = \alpha(d_{max}^{rel})^2 + \beta$, where $\alpha = 0.22\,(0.04) \times 10^4$ K Å^{-2} and $\beta = 300\,(100)$ K are the values of the parameters in (2).

Table 6
Estimated transition temperatures for the 'candidates' for proper ferroelectrics among the compounds with symmetry $Pba2$ and $Pmc2_1$.

T_c^{estim} is obtained using (2) with $\alpha = 0.22 \times 10^4$ K Å^{-2}, $\beta = T_f = 293$ K.

Compound	$\mathcal{H}$	$\mathcal{G}$	d_{max}^{rel} (Å)	T_c^{estim} (K)
Ba$_{3.75}$Pr$_{9.5}$Ti$_{18}$O$_{54}$	$Pba2$	$Pbam$	0.529	900 (100)
Mo$_{17}$O$_{47}$	$Pba2$	$Pbam$	0.665	1300 (200)
BaHgS$_2$	$Pmc2_1$	$Pbam$	0.675	1300 (200)
[(Cl$_3$P)$_2$N](MoOCl$_4$)†	$Pba2$	$Pbam$	0.843	1900 (300)
Bi$_3$Nb$_{17}$O$_{47}$	$Pba2$	$Pbam$	0.863	1900 (300)
Sr(OH)$_2$(H$_2$O)	$Pmc2_1$	$Pmma$	0.895	2000 (300)
β-Ba(OH)$_2$(H$_2$O)	$Pmc2_1$	$Pmma$	0.937	2200 (400)
Na(AlSi$_2$O$_6$)(H$_2$O)$_{1.1}$	$Pmc2_1$	$Pmma$	0.981	2400 (400)
NaBa$_6$Nd(SiO$_4$)$_4$	$Pmc2_1$	$Pmma$	1.073	2800 (500)
La$_2$Fe$_{1.76}$S$_5$	$Pmc2_1$	$Pmma$	1.355	4300 (700)

† The Mo sites are considered as non-equivalent.

4.3. Ferroelectrics with polar symmetry $Pba2$ and $Pmc2_1$

Among the compounds with symmetry $Pba2$ and $Pmc2_1$ there are few known ferroelectrics. Two of them are proper ferroelectrics for which the estimated and the experimental transition temperature can be compared. The transition temperature is estimated using (2) with $\alpha = 0.22 \times 10^4$ K Å^{-2} and $\beta = T_f$, where T_f is the temperature corresponding to the ferroelectric phase in K. For (NH$_2$)$_2$CS, the experimental value is $T_c = 202$ K, which is comparable with the estimated value $T^{estim} = 300\,(100)$ K ($T_f = 123$ K). For the other proper ferroelectric, Na$_{13}$Nb$_{35}$O$_{94}$, the agreement between the experimental value $T_c = 340$ K and the estimated one $T^{estim} = 800\,(100)$ K is not so good. The transition temperature of this compound has also been estimated by Abrahams (1989). In this case, the author has used the average of the maximal displacements of the homopolar atoms, $d = 0.13$ Å. This displacement corresponds to $T_c \simeq 340$ K, which is very close to the experimental T_c. (However, if the maximal relative displacement of the homopolar atom is used, $d = 0.243$ Å, the estimated temperature using the AKJ relation would be ~1180K.) If the paraelectric phase for CsEuNaNb$_5$O$_{15}$ has symmetry $Pmma$ then this compound is a proper ferroelectric, and its transition temperature can be estimated from (2). With a maximal relative displacement for this supergroup of 0.231 Å and $T_f = 293$K (the ferroelectric phase is measured at room temperature), the estimated transition temperature is $T_{estim} = 400\,(100)$ K, while the experimental T_c is 565 K.

The estimated values of the transition temperature for the candidates for proper ferroelectrics with symmetries $Pba2$ and $Pmc2_1$ are given in Table 6. The compounds are ordered by the value of the relative displacement starting with the smallest one. The quite high values for the transition temperature corresponding to the compounds at the end of the table suggest that the paraelectric phase will not be reached before melting or decomposition. The possibility of twinning and domain switching may, however, exist.

5. Conclusions

A general procedure for pseudosymmetry detection has been further developed to include the case of polar structures. The

procedure can be used for the search of materials with high-temperature phase transitions and, in particular, of new ferroelectrics. Its application to the structures with symmetry $Pba2$ and $Pmc2_1$ listed in the ICSD has been used as a benchmark of the method. The results obtained for the group $Pba2$ coincide with previous results obtained for structures with this symmetry (Abrahams, 1989; Abrahams *et al.*, 1996). Among the 45 different compounds with symmetry $Pmc2_1$, seven possible new ferroelectrics were detected. In addition, an empirical relation between the transition temperature and the atomic displacements is proposed. This relation can be used as an alternative to the Abrahams–Kurtz–Jamieson relation (Abrahams *et al.*, 1968) in systematic studies related to the prediction of new ferroelectrics.

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