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Systematic search of materials with high-temperature structural phase transitions: Application to space group $P2_12_12_1$

J. M. Igartua
Fisika Aplikatua II Saila, Zientzia-Fakultatea, Euskal Herriko Unibertsitatea, 644 Postakutxa, Bilbao 48080, Spain

M. I. Aroyo* and J. M. Perez-Mato
Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del Pais Vasco, Apdo. 644. 48080 Bilbao, Spain

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The existence of a pseudosymmetry in a crystal structure is indicative of a slightly distorted structure of higher symmetry. If the distortion is small enough, it can be expected that the crystal acquires this more symmetric configuration at a higher temperature after a phase transition. The aim of the present study is the development of a general procedure for the systematic search of pseudosymmetric structures in the available structural databases. The first step is the determination of all relevant supergroups of the space group associated to the known structure. This problem is reduced to the generation of minimal supergroups of space groups using the existing data on their maximal subgroups and normalizers. The determined pseudosymmetry elements are then applied to the crystal structure and a quantitative comparison of the transformed structure and the original one is performed. Pseudosymmetry is detected when the difference is under a certain threshold. As an example we present the results obtained for inorganic structures with space group $P2_12_12_1$ retrieved from the Inorganic Crystal-Structure Database. A significant number of compounds with known phase transitions at high temperatures have been clearly detected as pseudosymmetric with differences between the transformed and the original structures lower than 1.0 Å. About 20 additional structures were detected with pseudosymmetric features under the same threshold. These compounds are considered as having a high probability of exhibiting a phase transition at higher temperatures. [S0163-1829(96)07242-6]

I. INTRODUCTION

A method for searching new ferroelectrics based on structural data has been proposed in the last decade and applied with great success.[1,2] Polar structures having atomic displacements smaller than 1 Å with respect to a hypothetical nonpolar 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),[3] substances satisfying this condition were sorted out. The method has demonstrated to be very efficient: more than 50 new ferroelectric crystals were predicted and the success rate was very high. Furthermore, an empirical general relation[4] was used to estimate the transition temperature from the observed maximum atomic displacement.

The concepts involved in this search of high-temperature ferroelectric phase transitions are especially simple. In fact, one has only to look for pyroelectric materials where the particular smallness of the atomic displacements producing the spontaneous polarization suggests the possibility of polarization switching, essential for a ferroelectric, and indicates the possible existence of a phase transition at higher temperatures, where these displacements disappear. This basic argument can be expressed in a more general form, and applied to any kind of Landau-type structural phase transition.[5] Basically, in order to find materials with a structural phase transition at higher temperatures, one must look for substances having some pseudosymmetry, i.e., structures that can be interpreted as slight distortions of configurations of higher symmetry. 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.[6]

The detection of pseudosymmetry in a crystalline structure is the aim of several computer programs reported in the literature.[7] These programs were essentially developed for detecting false symmetry assignments in structural investigations and therefore, consider pseudosymmetry in a more restrictive sense than in the present work. Their main aim is to detect atomic deviations from the perfect symmetric position, which indicate that some symmetry has been overlooked in the determination of the structure. This implies atomic deviations somehow smaller than the ones we are interested in. In the search for pseudosymmetry these programs use more or less brute force methods, in the sense that, within a given crystal system, the location of the pseudosymmetry operations with respect to the operations of the real space-group symmetry have in general no aprioristic constraint. The pseudoaxes, planes, etc. are introduced at a location which is systematically varied until eventually a success is achieved. The group internal consistency of the checked operations is not guaranteed *a priori*. In the present work we are thinking of pseudosymmetry as a more loose concept with atomic deviations from the perfect symmetric position of the order of 1 Å or larger, and the search is to be applied not to a single structure, but to all structures of some symmetry in a database. This requires the development of more efficient and controlled search tools. In this respect, we present here a general procedure for the detection of pseudosymmetric structures based on the previous determination of the minimal supergroups of the structure space group. As a

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first application, we report the results obtained for the structures available at the ICSD database with $P2_12_12_1$ symmetry.

II. FERROELECTRIC CASE

The search of potential ferroelectrics is especially simple.[1,2] In a ferroelectric transition, at least an inversion center, a mirror plane, or a binary axis, is lost. Hence, if H is the polar space group of the investigated structure, a minimal supergroup G in the chain connecting H with the symmetry of the paraelectric phase can always be expressed by means of the following coset decomposition:

$$G = H + (g_i|\mathbf{t}_i)H, \tag{1}$$

with the rotational part of the coset representative g_i being $\bar{1}$, m or 2 (i.e., the inversion, a mirror plane or a twofold rotation). The orientation of the mirror plane m or the binary rotation 2 is in general restricted by the structure of the space group H, but the translational parts $\mathbf{t}_i$ of the coset representatives may have any value within some loose limits imposed by the group G. In other words, any location for the lost inversion center, mirror plane or binary axis is possible, with respect to the origin chosen for the description of the group H. This is related to the well-known fact that in a polar structure, the cell origin is chosen arbitrarily at least in one direction, while in a nonpolar group as G, there are always special symmetry points that are chosen as conventional origins. Abrahams and co-workers[1,2] limited their search to pseudosymmetries described by a lost inversion center or a mirror plane. The search was done by relating the atoms in the structure through the chosen lost operation, and calculating the atomic displacements from a perfect symmetry relation. The maximum atomic deviation Δz along the polar axis from the full symmetric position was taken as a quantitative parameter measuring the degree of pseudosymmetry.[8] A crystal was predicted to be ferroelectric, and therefore, expected to transform to a paralectric phase at higher temperatures, if Δz was less than 1 Å and greater than 0.1 Å. An estimation of the transition temperature was obtained from the expression[4]

$$T_c = C(\Delta z)^2 \tag{2}$$

with $C \approx 2.0\times10^4$ K/Å^2. Structures with Δz less than 0.1 Å were considered doubtful, with a high probability of having a wrong symmetry assignment.

One should note that, once detected in the structure a pseudomirror plane or a pseudoinversion center, in general, the corresponding G given by Eq. (1) is not necessarily the space group of the hypothetical paralectric phase. This latter could be a supergroup of G as, for instance, in the case of an antiferrodistortive transition, where the lattice also changes. Abrahams and co-workers[1,2] did not try to identify the actual paraelectric space group, the pseudosymmetry with respect to the minimal supergroup G being enough for postulating the existence of a nonpolar similar structure of higher symmetry.

III. THE SUPERGROUP PROBLEM

In a general case, we are interested in pseudosymmetries associated with a supergroup (space group) G of the space group H of the structure, that should correspond to the symmetry of the nondistorted phase at higher temperatures. Any supergroup-group relation $G>H$ can be decomposed into a chain of intermediate minimal supergroups $G>H_1>H_2>\cdots>H_m>H$.[9] Hence, if pseudosymmetry exists for the physically relevant supergroup G it will also be present for all intermediate minimal supergroups H_i along the chain $G>H$. Therefore the detection of any pseudosymmetry can be reduced to a stepwise search of pseudosymmetry for the minimal supergroups along one chain of minimal supergroups. Hence, a first step of the general pseudosymmetry search is the determination of the minimal supergroups of the structure space group.

There are few papers in the literature treating the supergroups of space groups in some detail.[10,11] In fact, the existing listings of minimal supergroups of space groups are not complete in the sense that they contain only the types of supergroups (Ref. 12 and *International Tables for Crystallography, Vol. A*,[13] in the following referred to as IT A). The entries in IT A under the heading *Minimal nonisomorphic supergroups* provide a list of those space groups G which contain H as a maximal nonisomorphic subgroup. Why such data is not sufficient for our search is clear from the ferroelectric example discussed in the previous section: due to the arbitrariness of the origin choice in a polar structure there are, for instance, infinitely many centrosymmetrical minimal supergroups of a polar group, although there is one single maximal polar subgroup of a particular centrosymmetrical group. As another example, we can consider the group-subgroup chain $P4_12_12>P2_12_12_1$. There is one maximal subgroup $P2_12_12_1$ of the group $P4_12_12$ and the relation between the two groups can be expressed by the coset decomposition of the group with respect to the subgroup:

$$P4_12_12 = P2_12_12_1 + (4_z^+, \tfrac{1}{4}\ \tfrac{3}{4}\ \tfrac{1}{4})P2_12_12_1. \tag{3}$$

However, the search for the minimal supergroups of $P2_12_12_1$, of type $P4_12_12$, shows (see Table I) that there are five additional ones:

$$\begin{aligned}
P4_12_12^{(2)} &= P2_12_12_1 + (4_z^+, \tfrac{3}{4}\ \tfrac{1}{4}\ \tfrac{1}{4})P2_12_12_1,\\
P4_12_12^{(3)} &= P2_12_12_1 + (4_y^+, \tfrac{3}{4}\ \tfrac{1}{4}\ \tfrac{1}{4})P2_12_12_1,\\
P4_12_12^{(4)} &= P2_12_12_1 + (4_y^+, \tfrac{1}{4}\ \tfrac{1}{4}\ \tfrac{3}{4})P2_12_12_1,\\
P4_12_12^{(5)} &= P2_12_12_1 + (4_x^+, \tfrac{1}{4}\ \tfrac{1}{4}\ \tfrac{3}{4})P2_12_12_1,\\
P4_12_12^{(6)} &= P2_12_12_1 + (4_x^+, \tfrac{1}{4}\ \tfrac{3}{4}\ \tfrac{1}{4})P2_12_12_1.
\end{aligned} \tag{4}$$

As space groups, all of them are isomorphic to $P4_12_12$, but as supergroups of $P2_12_12_1$, they can be mathematically distinguished due to the different location and/or orientation of the additional symmetry operations with respect to the conventional origin and setting of $P2_12_12_1$. Due to the isomorphism of the groups of the list given by Eqs. (4) it is clear, that one can transform any of them to the conventional setting and origin of $P4_12_12$, Eq. (3), and choose the transformations so that the conventional description of $P2_12_12_1$ is not changed. From another viewpoint, one can say that Eqs. (4) list all the different expressions that the supergroup given

TABLE I. Minimal translationengleiche supergroups G^i of $P2_12_12_1$. Each supergroup is specified by the coset representatives of its decomposition with respect to $P2_12_12_1$.

Index, Super-groups G	Number of $G^i=G$	Coset representatives of G^i with respect to $P2_12_12_1$ (different from identity)					
		G^1	G^2	G^3	G^4	G^5	G^6
[2] *Pbca* (No. 61)	2	$(\bar{1},000)$	$(\bar{1},\frac{1}{2}\frac{1}{2}\frac{1}{2})$				
[2] *Pnma* (No. 62)	6	$(\bar{1},00\frac{1}{2})$	$(\bar{1},0\frac{1}{2}0)$	$(\bar{1},\frac{1}{2}00)$	$(\bar{1},\frac{1}{2}\frac{1}{2}0)$	$(\bar{1},\frac{1}{2}0\frac{1}{2})$	$(\bar{1},0\frac{1}{2}\frac{1}{2})$
[2] $P4_12_12$ (No. 92)	6	$(4_z^+,\frac{1}{4}\frac{3}{4}\frac{1}{4})$	$(4_z^+,\frac{3}{4}\frac{1}{4}\frac{1}{4})$	$(4_y^+,\frac{3}{4}\frac{1}{4}\frac{1}{4})$	$(4_y^+,\frac{1}{4}\frac{1}{4}\frac{3}{4})$	$(4_x^+,\frac{1}{4}\frac{1}{4}\frac{3}{4})$	$(4_x^+,\frac{1}{4}\frac{3}{4}\frac{1}{4})$
[2] $P4_32_12$ (No. 96)	6	$(4_z^+,\frac{1}{4}\frac{3}{4}\frac{3}{4})$	$(4_z^+,\frac{3}{4}\frac{1}{4}\frac{3}{4})$	$(4_y^+,\frac{3}{4}\frac{3}{4}\frac{1}{4})$	$(4_y^+,\frac{1}{4}\frac{3}{4}\frac{3}{4})$	$(4_x^+,\frac{3}{4}\frac{1}{4}\frac{3}{4})$	$(4_x^+,\frac{3}{4}\frac{3}{4}\frac{1}{4})$
[3] $P2_13$ (No. 198)	4	$(3^+,000)$	$(3^+,\frac{1}{2}\frac{1}{2}0)$	$(3^+,0\frac{1}{2}\frac{1}{2})$	$(3^+,\frac{1}{2}0\frac{1}{2})$		
		$(3^-,000)$	$(3^-,\frac{1}{2}0\frac{1}{2})$	$(3^-,\frac{1}{2}0\frac{1}{2})$	$(3^-,0\frac{1}{2}\frac{1}{2})$		

in Eq. (3) can acquire, depending on the setting and origin choice, when this is conventional for $P2_12_12_1$ but not for its supergroup. In general, one must assume that the investigated structures have been described in the literature without being aware of their eventual pseudosymmetry, it is then expected that the setting and origin used will be in most cases not conventional for the supergroup, and therefore all the possible cases, as listed in Eqs. (4), should be considered and tested.

In practical terms, the existence of the set of supergroups, Eqs. (4), implies that the search of pseudosymmetry described by the space group $P4_12_12$ in a structure of $P2_12_12_1$ symmetry can be reduced to the search of a pseudoquaternary helicoidal axis 4_1 along z passing through either the point (3/4,1/2,0) or (1/4,1/2,0) (with respect to the standard origin used for the $P2_12_12_1$ description), and equivalent searches of analogous operations along the x and y axes.

For the cases relevant to our study, if the space group H is nonpolar the number of minimal supergroups is discrete; finite in the cases of minimal *translationengleiche* and nonisomorphic *klassengleiche* supergroups. Although one can consider minimal isomorphic supergroups of any prime order, only those of small order corresponding to simple lattice changes in the structure are physically relevant and are to be considered. In this sense, once the minimal supergroups have been determined, the search of pseudosymmetry in nonpolar structures can be even simpler than in polar ones. The search is limited to a few supergroups, while in polar structures, a continuous set of possible supergroups exist and a minimization process is required (see Ref. 8).

The determination of all minimal supergroups of a given space group can be done by somehow inverting the data available on the maximal subgroups of space groups. As already mentioned above, this data is only partly published in IT A, but a full listing is the subject of a forthcoming volume of *International Tables for Crystallography, Vol. A1* (Ref. 14) (henceforth referred to as IT A1). Using this full listing, a systematic inversion process to derive the minimal supergroups is possible. In the following, we outline the basic arguments necessary for this.

Consider the group-subgroup chain of space groups $G>H$, where G is a minimal supergroup of H. It is possible to decompose G into cosets with respect to H:

$$G=H+q_2H+q_3H+\cdots+q_nH. \tag{5}$$

The number of the H cosets equals the index of H in G, and q_j, $j=1,\ldots,n$, are the chosen coset representatives, with q_1 being the identity, $q_1=1$.

We are interested in all supergroups G^i of H, which are isomorphic to G, $G^i\cong G$, i.e., belong to the same affine space-group type:

$$G^i=a_i^{-1}Ga_i. \tag{6}$$

Here, a_i is an affine transformation (for details, see Ref. 13). The combination of Eqs. (5) and (6) results in the following coset decomposition of G^i:

$$\begin{aligned} G^i&=a_i^{-1}Ha_i+a_i^{-1}q_2Ha_i+a_i^{-1}q_3Ha_i+\cdots+a_i^{-1}q_nHa_i\\ &=H^i+q_2^iH^i+q_3^iH^i+\cdots+q_n^iH_i. \end{aligned} \tag{7}$$

The notation used in Eq. (7) is obvious: the group H^i belongs to the same affine space group type as H, and $q_k^i=a_i^{-1}q_ka_i$ are the coset representatives of G^i with respect to H^i.

On the other hand, as G^i should be supergroups of H, then they can be also decomposed with respect to H:

$$G^i=H+q_{i,2}H+q_{i,3}H+\cdots+q_{i,n}H. \tag{8}$$

Here again $q_{i,1}$ is chosen as the identity.

The comparison of Eqs. (7) and (8) shows that the supergroups G^i of H can classified into the following two sets:

(i) Supergroups G^i for which the affine transformation a_i belongs to the affine normalizer of H, $a_i\in N(H)$. In this case the image of H under the mapping a_i, coincides with the group H, $H^i=H$, and $q_{i,k}=q_k^i$ $(=a_i^{-1}q_ka_i)$. The procedure for the determination of such G^i is discussed in detail in the literature; see, e.g., Ref. 10, where four different cases are distinguished depending on the group-subgroup relations between the normalizers of H and G. The intersection of the normalizers $N=N(H)\cap N(G)$ plays a key role as the number of supergroups G^i equals the index of N in $N(H)$.

(ii) A more detailed examination of Eqs. (7) and (8) shows that there could exist an affine transformation a_k, not belonging to the normalizer $N(H)$, $a_k\notin N(H)$, such that the

TABLE II. Minimal klassengleiche supergroups G^i of $P2_12_12_1$ of index [2] and [3]. Each supergroup is specified by the coset representatives of its decomposition with respect to $P2_12_12_1$.

Index, Supergroups G	Number of $G^i \simeq G$	Coset representatives of G^i with respect to $P2_12_12_1$ (different from identity)		
		G^1	G^2	G^3
[2] $P2_12_12$ (No. 18)	3	$(1,00\frac{1}{2})$	$(1,0\frac{1}{2}0)$	$(1,\frac{1}{2}00)$
[2] C222_1 (No. 20)	3	$(1,\frac{1}{2}\frac{1}{2}0)$	$(1,\frac{1}{2}0\frac{1}{2})$	$(1,0\frac{1}{2}\frac{1}{2})$
[2] $I2_12_12_1$ (No. 24)	1	$(1,\frac{1}{2}\frac{1}{2}\frac{1}{2})$		
[3] $P2_12_12_1$ (No. 19)	3	$(1,\frac{1}{3}00)$ $(1,\frac{2}{3}00)$	$(1,0\frac{1}{3}0)$ $(1,0\frac{2}{3}0)$	$(1,00\frac{1}{3})$ $(1,00\frac{2}{3})$

supergroup $G^k = a_k^{-1} G a_k$ is still a supergroup of H. In that case $H^k = a_k^{-1} H a_k$ the image of H under the mapping a_k, is only isomorphic to H, $H^k \cong H$. The determination of such supergroups G^k of H does not seem an easy problem as the only restriction on the choice of the corresponding a_k follows from the fact that $a_k \notin N(H)$. However, it is not the case: it is easily seen that the affine transformations leading to the supergroups $G^k \cong G$ can be retrieved from the subgroup data of G. The decomposition of G^k with respect to H, Eq. (8), and the affine equivalence of G^k and G, Eq. (6), leads to the following decomposition of G:

$$\begin{aligned} G = a_k G^k a_k^{-1} &= a_k H a_k^{-1} + a_k q_{k,2} H a_k^{-1} \\ &\quad + a_k q_{k,3} H a_k^{-1} + \cdots + a_k q_{kn} H a_k^{-1} \\ &= H^k + a_k q_{k,2} a_k^{-1} H^k + a_k q_{k,3} a_k^{-1} H^k \\ &\quad + \cdots + a_k q_{k,n} a_k^{-1} H^k. \end{aligned} \tag{9}$$

The group $H^k = a_k H a_k^{-1}$ is a subgroup of G, $H^k < G$. This result indicates the procedure for the determination of the supergroups G^k, with $a_k \notin N(H)$: Each subgroup H^k of G, $H^k \cong H$, determines a_k which gives rise to a supergroup $G^k = a_k^{-1} G a_k$. Obviously, if $a_k \in N(G)$, then $G^k = G$.

Therefore, for a given a group-subgroup chain $G > H$, where H is a maximal subgroup of G, it is possible to obtain all (minimal) supergroups G^i of H, which are isomorphic to G, using the data on maximal subgroups of G and the normalizers of G and H. The above considerations serve as a basis of a systematic procedure for deriving the minimal supergroups of space groups starting from the data on normalizers of space groups (e.g., IT A, Section 15) and the subgroup data of IT A1. For further details on the procedure the reader is referred to a forthcoming paper[15] where also the corresponding software will be presented. The results of the application of the procedure for the case of $P2_12_12_1$ are given in Tables I and II where the complete set of minimal *translationengleiche* and *klassengleiche* supergroups are listed. The different supergroups belonging to the same space group type are specified by sets of coset representatives of their decompositions with respect to $P2_12_12_1$. The minimal *klassengleiche* supergroups are restricted to those of index 2 and 3.

IV. THE SEARCH OF PSEUDOSYMMETRY

Once the possible minimal supergroups have been derived, the second step in the pseudosymmetry search is their checking as eventual pseudosymmetry of the structure. This can be done in a straightforward way.[1,2] If we call S_1 the set of atomic positions corresponding to the observed structure of symmetry H, the application on S_1 of the coset representatives $(g_i|\mathbf{t}_i)$ of one supergroup G of index n, generates $n-1$ additional hypothetical structures:

$$S_i = (g_i|\mathbf{t}_i) S_1 \quad (i = 1, \ldots, n). \tag{10}$$

If the structure S_1 is really the result of a Landau phase transition from a phase with space group G or higher, the structures S_i should only differ from S_1 by a small structural distortion. In fact, in the language of Landau formalism, the atomic configurations S_i would be the physically equivalent configurations associated to the possible domains in the low-symmetry phase. Symbolically, if we call S_0 the hypothetical high-symmetry structure, we can write $S_1 = S_0 + U_1$, where U_1 represents the small structural distortion relating both phases. As S_0 should be invariant by G, we have that

$$S_i - S_1 = g_i U_1 - U_1 \equiv \Delta U_i, \tag{11}$$

which is necessarily small, if U_1 is. We will consider a structure as having pseudosymmetry G, if ΔU_i does not surpass a given threshold for all coset representatives $q_i = (g_i|\mathbf{t}_i)$ in Eq. (5). More explicitly, the algorithm derives all the atomic positions $\mathbf{r}_\mu$ in the unit cell of the experimental structure (S_1) from the atomic positions of the asymmetric unit, $\mathbf{r}_\nu^{\text{asym}}$, given in the database. Then, it calculates the asymmetric unit of S_i, i.e., the transformed atomic positions $(g_i|\mathbf{t}_i)\mathbf{r}_\nu^{\text{asym}}$ (mod. the Bravais lattice). Among the atomic positions of S_1, those which can be related through small displacements to the calculated asymmetric unit of S_{i} are searched and the displacements $\Delta \mathbf{u}_\nu^i$ are calculated:

$$\Delta \mathbf{u}_\nu^i \equiv (g_i|\mathbf{t}_i)\mathbf{r}_\nu^{\text{asym}} - \mathbf{r}_{\nu(i)} \quad (\nu = 1, \ldots, s), \tag{12}$$

where $\mathbf{r}_{\nu(i)}$ represents a particular atomic position in the unit cell of the structure S_1 for an atom of the same species as in $\mathbf{r}_\nu^{\text{asym}}$. If a "pairing" $(\mathbf{r}_\nu^{\text{asym}}, \mathbf{r}_{\nu(i)})$ can be achieved for every coset representative $(g_i|\mathbf{t}_i)$, such that all the displacements $\Delta \mathbf{u}_\nu^i$ are under the chosen threshold, we can assume that $S_i \approx S_1$ for all i, and the structure S_1 can be considered as pseudosymmetric for space group G. In fact, this rather ef-

TABLE III. Inorganic compounds of symmetry $P2_12_12_1$ with known phase transitions characterized by the transition temperature T_c and the symmetry group G_0 of the high-temperature phase. The temperatures T at which the $P2_12_12_1$ structures have been determined are indicated only if they differ from room temperature. The corresponding references are listed in the last column. The pseudosymmetry group G with the smallest Δu (column 1) for each compound is listed in column 4. The number in parenthesis after G follows the labeling scheme in Tables I and II.

	ΔU (Å)	T_c (K)	T (K)	G	G_0	Ref.
$AgErSe_2$	1.93	1073		$Pnma(3)$	$P6_3mc$	39
Ag_2Se	1.24	406		$Pnma(3)$	Cubic	40
As_2O_5	0.41	578		$P4_12_12(1)$	$P4_12_12$	41
As_2PO_5	0.45	873		$P4_12_12(1)$	$P4_12_12$	42
$AsSbO_5$	0.84	1033		$P4_12_12(1)$	$P4_12_12$	42
$BiCu_3S_3$	1.69	391		$Pnma(1)$	$Pnma$	17
CsOD	0.09	230	23	$Pnma(4)$	$Cmcm$	43
	0.17		77	$Pnma(4)$	$Cmcm$	43
GeF_2	0.55	335		$P4_32_12(2)$	Tetra.	45
$K_2Cd_2(SO_4)_3$	0.91	432		$P2_13(1)$	$P2_13$	46
$K_2Mn(SO_4)_3$	0.98	201	183	$P2_13(1)$	$P2_13$	47
$K_4Zn(MoO_4)_2$	0.47	638		$Pnma(1)$	Hex.	48
NH_4BeF_3	0.87	347		$Pnma(1)$	$P\underline{nm}a$	49
$NH_4H_2AsO_4$	1.31	216	157	$I2_12_12_1(3)$	$I\underline{42}d$	50
$NH_4H_2PO_4$	1.47	148	143	$I2_12_12_1(3)$	$I42d$	51
Rb_2S_5	1.60	>300		$Pnma(5)$	?	19
Tl_2S_5	2.04	?		$Pnma(5)$	$Pnca$	20
SiO_2	1.03	453		$Pnma(2)$	?	53
SnF_2	1.21	339		$P4_12_12(2)$	$P\underline{4_1}2_12$	52
Y_2WO_6	1.77	1870		$Pnma(5)$	$P42_1m$	18

ficient restriction of the pseudosymmetry check to the atoms of the asymmetric unit is only rigorously justified if H is a normal subgroup of G. In a more general case, a successful ''pairing'' restricted to the asymmetric unit is a necessary but not sufficient condition for an equally successful pairing of the whole unit cell and a further check for all atoms in the unit cell is to be done.

As a quantitative parameter measuring the deviation from a perfect symmetry relation, we take the maximum displacement Δu, of the set of vectors $|\Delta\mathbf{u}^i_\nu|$. Δu is a generalization of the parameter Δz considered in Refs. 1, 2. For the simplest cases considered there Δu would be approximately $2\Delta z$, if the contribution of the displacements along the other nonpolar directions are neglected.

If G belongs to a different crystal system, the application of Eq. (12) requires further specification. The vectors $(g_i|\mathbf{t}_i)\mathbf{r}^{\text{asym}}_\nu$ and $\Delta\mathbf{u}^i_\nu$ are calculated using relative components. The value of the vector $\Delta\mathbf{u}^i_\nu$ is only transformed into absolute units at the end of the calculation. Therefore, the eventual deviations of the unit-cell metric from the requirements of the crystal system of G are in general neglected. This means, that structures distorted from a higher symmetry only through an arbitrary deformation of the unit cell, would result in null values for $\Delta\mathbf{u}^i_\nu$. We have considered this approach more direct and simpler: the consistency of the lattice metrics with the detected pseudosymmetry can be checked *a posteriori* in each compound. Furthermore, proper ferroelastic materials will be easily detectable even for large values of the spontaneous strain.

It should be noted that those structures having a Landau-type phase transition, where the main ''distortion'' relating both phases is a symmetry-breaking change in the pattern of atomic occupation probabilities, fall out of our framework. In general, this type of pseudosymmetric structures cannot be identified by the simple method explained above.

V. RESULTS FOR $P2_12_12_1$ INORGANIC MATERIALS

The ICSD database contains 442 files with space group $P2_12_12_1$. We have not included in our search those ICSD files for which some atomic positions in the structure are not given, this is the case, for instance, of a set of files with undetermined hydrogen positions. Also, files containing atoms with an occupation probability different from 1 have not been considered, with two exceptions (see below). Under this restriction, the number of files investigated was 407. First of all, the sensitivity of the search to the threshold value for the parameter Δu was tested: 24, 58, and 232 cases were, respectively, detected with Δu smaller than 0.5, 1.0, and 1.5 Å, for at least one minimal supergroup. From these results, it is clear that in order to obtain sensible and manageable results, the threshold must be maintained at values somehow smaller than the analogous one considered in polar structures (2 Å).[1,2]

Another significant result for deciding the threshold to be used is the value of Δu in compounds with a known phase transition at higher temperatures. The dataset contains structural data for 19 such compounds. Most of them are listed, for instance, in the review by Tomaszewski.[16] The results for these structures are summarized in Table III. When several files exist for the same compound, only the one with minimum Δu has been included in the table. The compound

$K_4Zn(MoO_4)_2$ has been included in the list for completeness, because although it has atomic occupation probabilities different from 1, the phase transition does not change them.

All the materials in Table III have Δu smaller than 2.0 Å. However, the compounds in Table III with the Δu larger than 1.5 Å are either irrelevant for our purposes or have a badly characterized transition. For instance, in $AgErSe_2$ the known phase transition ($P2_12_12_1$-$P6_3mc$),[16] has no group-subgroup relation and therefore, is not of Landau type. For $BiCu_3S_3$, the reported phase transition is probably of the reconstructive type, or alternatively order-disorder: Δu is quite large (1.69 Å) for the space group Pnma, but similar values are obtained for other space groups like $C222_1$. In fact, the Pnma group with minimum Δu is detected for a setting that is not the one reported for the high-temperature phase.[16] For this latter the Δu is even larger. Moreover, a detailed look at the observed structure of the compound indicates that the atomic displacements necessary for obtaining the Pnma symmetry in any of the two settings would distort the chemical bonding in an unacceptable way. The reported high-symmetry group could be then only reasonably obtained if some atoms were split into half occupied positions or if the structure acquired a rather different configuration, and this leaves this compound out of our framework. In the case Y_2WO_6, although there is a group-subgroup relation between the space groups reported for the two phases, the material is polymorphic with large ranges of metaestability,[18] so the transition is probably of reconstructive type; it is then not strange that the first minimal supergroup to be flagged (with a high Δu) is not a subgroup of the reported high-temperature space group. A similar situation can be observed in Rb_2S_5 and Tl_2S_5. They seem to be polymorphic[19,20] and the high-temperature phase transitions are badly characterized. In both cases the transition temperatures are unknown, and the high-temperature space group for Rb_2S_5 is undetermined. For Tl_2S_5 the flagged space group is not a subgroup of the reported high-temperature symmetry[16] and similar (large) Δu are obtained for other groups.

If we disregard all these atypical cases, Table III contains 14 compounds with well characterized Landau-type phase transitions, all of them with $\Delta u < 1.5$ Å. From them, 9 compounds have $\Delta u < 1.0$ Å. In contrast to the ferroelectric case [see Eq. (2)], no clear correlation between the values of Δu and the transition temperatures is observed. It is noticeable that all structures have Δu larger than 0.4 Å, except CsOD. This latter case most probably corresponds to a wrong symmetry assignment. Δu is too small according to the criterion proposed by Abrahams[2] and its behavior as temperature is lowered (see the two values at 23 and 77 K) is rather inconsistent; one would expect as the structure is further cooled that Δu increases.

The detected pseudosymmetry coincides in most cases with the space group of the known high-temperature phase. In a few cases, however, this latter is not a minimal supergroup and pseudosymmetry is detected, as should be expected, for one minimal supergroup in the supergroup chain connecting the high- and low-temperature space groups. Thus, for instance, the cases of $NH_4H_2AsO_4$ and $NH_4H_2PO_4$ with the subgroup chain $P2_12_12_1 < I2_12_12_1 < I\bar{4}2d$, or the case of CsOD with the chain $P2_12_12_1 < Pnma < Cmcm$. It should also be noted that the high-temperature phase transition for some of the compounds in Table III, like the langbeinites $K_2Cd_2(SO_4)_3$ and $K_2Mn_2(SO_4)_3$, is known to be first order, although Δu does not surpass in both cases 1 Å. In the case of GeF_2, the symmetry of the reported tetragonal phase above 335 K is not known.[16] From the results in Table III, it can be inferred that the space group for this phase should be $P4_32_12$.

TABLE IV. Exceptional cases of structures with $P2_12_12_1$ symmetry having pseudosymmetry groups G with $\Delta u < 1$ Å. The numbers in parenthesis after G follow the labeling scheme of Tables I and II. The source references for the $P2_12_12_1$ structures and the corresponding structure factor R are also listed. (a) Structures under discussion or with wrong symmetry ($P2_12_12_1$) assignment. (b) ICSD error and structures with $P2_12_12_1$ symmetry under special restrictions.

	Δu (Å)	G	Ref.
	(a)		
$AgNO_3$	0.28	$Pbca(1)$	54
Cs_2HgCl_4	0.58	$Pnma(4)$	55
K_2 [Ru(NO)Cl_5]	0.17	$Pnma(4)$	56
$LiNa_5$ $(PO_4)_2$	0.14	$Pnma(6)$	57
Sn_2F_3Cl	0.03	$P2_13(1)$	58
$Pb_3O_2Cl_2$	0.00	$Pnma(2)$	59

(b)

	Δu (Å)	G	Comment	Ref.
$Ba(NO_2)_2$	0.00	$Pnma(4)$	ICSD error	69
KH_2PO_4	0.87	$C222_1(1)$	Hypothetical	22
TeO_2	0.40	$P4_12_12(2)$	Under pressure (15.8 Kbar)	21

Comparing Table III with the results for the whole dataset of $P2_12_12_1$ symmetry, about 20% of the structures flagged by the program as pseudosymmetric with $\Delta u < 1.0$ Å correspond to compounds which actually are known to have a phase transition at higher temperatures. As we will see below, a significant set of the other flagged structures correspond to false or doubtful symmetry assignments, wrong files, pressure-induced structures, etc. If these are left out from the statistics, the ratio of compounds with known phase transition among those with $\Delta u < 1.0$ Å reaches about 25%. Considering these results, we have chosen 1 Å as a convenient threshold for detecting materials with a high probability of exhibiting a phase transition at higher temperatures. The number of compounds under these conditions, apart from those already listed in Table III, amounts to 34, see Tables IV and V. From them, six cases (see Table IV) could be explained as due to a symmetry assignment which is probably wrong or under discussion. For these six compounds, the database contains structure determinations of the same phase in the space group detected as pseudosymmetry. In all cases Δu is rather small (<0.3 Å), except for Cs_2HgCl_4,[55] where Δu is surprisingly large (0.58 Å) for being a case with controversial symmetry assignment. Apart from a database error, Table IV also lists two structures where the pseudosymmetry is explained because of various reasons not related with a thermal phase transition: in the case of TeO_2 the $P2_12_12_1$ structure is only obtained under pressure, being the system stable with $P4_12_12$ symmetry (the pseudosymmetry detected) at normal pressure and room

TABLE V. Inorganic compounds of $P2_12_12_1$ symmetry having pseudosymmetry groups G with $\Delta u<1$ Å and no high-temperature phase transition reported yet. The numbers in parenthesis after G follow the labeling scheme of Tables I and II. The source references for the $P2_12_12_1$ symmetry and the corresponding structure factor R are also listed.

	Δu (Å)	R	G	Ref.
TeF_4	0.97	0.084	$Pnma(6)$	60
$BaGeO_3$	0.69	0.11	$Pnma(3)$	32
$BaSiO_3$	0.70	0.019	$Pnma(3)$	31
$BaBiSe_3$	0.35	0.073	$Pnma(5)$	27
$BaSbTe_3$	0.55	0.035	$Pnma(5)$	27
$Cs_2O(B_2O_3)_3$	0.91	0.110	$I2_12_12_1$	61
CdF(OH)	0.15	0.031	$P2_12_12$	44
$KTb(CrO_4)_2$	0.8	0.073	$Pnma(1)$	62
K_3AgO_2	0.84	0.076	$P4_12_12(1)$	35
$K_2SO_4SbF_3$	0.95	0.035	$Pnma(4)$	63
PW_3O_{11}	0.55	0.033	$Pnma(3)$	29
PW_4O_{14}	0.61	0.043	$Pnma(3)$	29
$P_4W_8O_{32}$	0.47	0.058	$Pnma(3)$	30
$SrT(VO_4)$	0.79	0.053	$Pnma(4)$	33
$Sr_3Al_2O_5Cl_2$	0.29	0.088	$P2_13(1)$	36
	0.37	0.088	$I2_12_12_1$	36
$RbNb(SiO_3)O_2$	0.44	0.041	$Pnma(3)$	28
$Cs_2(TiO)(P_2O_7)$	0.81	0.026	$Pnma(3)$	64
$CaAl(OH)SiO_4$	0.79	0.043	$Pnma(5)$	65
$CaNi(OH)AsO_4$	0.99	0.068	$Pnma(5)$	66
$Cs_2CS_3H_2O$	0.91	0.097	$Pnma(3)$	67
$TiO(SO_4)(H_2O)$	0.75	0.019	$Pnma(1)$	68
$K\ [VO(SO_4)_2]$	0.60	0.100	$Pnma(3)$	23
$Na(OH)(H_2O)_4$	0.91	0.027	$Pnma(5)$	24
$Rb_7Cs_{11}O_3$	0.37	0.073	$Pnma(5)$	25
$(NO)(IF_8)(NOF)_2$	0.69	0.038	$Pnma(3)$	26

temperature.[21] The $P2_12_12_1$ structure of KH_2PO_4 included in the database is not an experimental one, but a ''gedanken'' structure imagined through some kind of idealization of the known structure.[22]

The rest of the 25 structures having $\Delta u<1.0$ Å for a minimal supergroup are listed in Table V. As the confidence level of the results strongly depend on the correctness of the structural data used, the R factors of these latter are included in Table V. The last four compounds in the table, $K[VO(SO_4)_2]$, $Na(OH)(H_2O)_4$, $Rb_7Cs_{11}O_3$, and $NO(IF_8)(NOF)_2$ correspond to structures obtained at low temperatures, the materials being unstable at room temperature.[23–26] In one of the four cases, $[K(VO(SO_4)_2]$, the authors are aware of the pseudosymmetry and even mention the possibility of a phase transition above the measurement temperature (140 K). Both $BaBiSe_3$ and $BaSbTe_3$ are very close to a Pnma configuration and are very good candidates for exhibiting a phase transition. The authors reporting the structures seem not to be aware of the pseudosymmetry.[27] $RbNbSiO_5$ is also a case with a very small deviation from the Pnma symmetry. The reference reporting the structure does not mention this fact, and they report no phase transition in a thermal measurement up to the melting point (>1200 °C).[28] However, there are references of high-temperature phase transitions in isomorphous compounds of the family, like $RbNbGeO_5$ and $RbTaGeO_5$.[28] Therefore, considering these two facts, a reinvestigation of the phase stability of this compound at high temperatures is advisable. The three tungsten oxides, PW_3O_{11}, PW_4O_{14}, and $P_4W_8O_{32}$, belong to the family of the tungsten bronzes, well-known because of their phase transitions,[29] but in these three particular compounds no transition has been yet reported,[30] and the symmetry change suggested in the table does not correspond to the typical phase transition in this family. $BaSiO_3$ and $BaGeO_3$ are also close to a Pnma configuration. These compounds are known to be polymorphic with crystallization in other forms, but up to now a phase of Pnma symmetry has not been reported.[31,32] The structure of $SrTl(VO_4)$ has been related[33] with that of β-K_2SO_4, a representative of a numerous family of compounds exhibiting structural instabilities with Pnma as the prototype space group.[34] The authors of the structure analysis were aware of this pseudosymmetry, despite being Δu in this case nearly 0.8 Å. Table V includes also the case of CdF(OH) which has occupation probabilities different from 1 (Ref. 44) because the pseudosymmetry does not imply any change on them. The extreme small value of Δu in this compound would suggest, according to Ref. 2, a wrong symmetry assignment. However, in this case this would mean a wrong lattice identification with the measurement of nonexisting superstructure reflections, which seems rather improbable.

There are two single cases, K_3AgO_2 (Ref. 35) and $Sr_3Al_2O_5Cl_2$,[36] where the detected pseudosymmetry corresponds to a higher crystal system. In both cases, the reported lattice parameters are consistent with the flagged supergroup. In fact, pseudosymmetry in these cases is easy to infer from the special metrics of the lattice. Indeed, in contrast with the Pnma pseudosymmetric compounds, the two structural reports mention the pseudosymmetry of the compounds in generic terms (the crystal system). K_3AgO_2 is a clear candidate for a ferrodistortive $P4_12_12$-$P2_12_12_1$ transition with a one-dimensional order parameter,[37] while $Sr_3Al_2O_5Cl_2$ is very close to a cubic configuration. In this latter, pseudosymmetry with very small Δu has been detected for the cubic supergroup $P2_13$, but also for the *klassengleiche* supergroup $I2_12_12_1$. This means that the structure can be described as a small distortion of a structure with space group $I2_13$ (at least), being this group the common minimal supergroup of both $P2_13$ and $I2_12_12_1$. The suggested phase transition $I2_13$-$P2_12_12_1$ is allowed within the Landau framework: a physically irreducible representation at the point H of the Brillouin zone can be assigned to this symmetry change.[37]

VI. CONCLUSIONS

A systematic search of structures having a high probability of exhibiting a high-temperature structural phase transition can be done through the identification in the structural databases of those structures that can be considered pseudosymmetric within some quantitative threshold. Essentially, the pseudosymmetry search can be limited to the minimal supergroups of the structure space group. The method proposed generalizes the one used by Abrahams and co-workers[1,2] for predicting new ferroelectrics. A necessary step of this generalized method is the determination of all relevant minimal supergroups of the space group under study. In contrast to the ferroelectric case, for nonpolar space groups the number of relevant minimal supergroups is finite, but their determination is in general nontrivial, and constitutes the fundamental problem to be solved. A procedure for this determination is presented above, and has been applied to the space group $P2_12_12_1$. It should be noted that the general solution of the ''supergroup problem'' can also be useful in the analysis of non-Landau first-order phase transitions within the so-called ''paraphase'' approach, where the two experimental structures are assumed to be distortions from an hypothetical phase.[38]

Once the set of minimal supergroups are known, the detection of pseudosymmetry is reduced to a rather simple check of the presence in the structure (up to some approximation) of the symmetry operations corresponding to the coset representatives of each supergroup. The deviation from exact symmetry is measured through the maximum atomic displacement, Δu, that has to be considered when comparing the experimental structure with the ones obtained by the action of the coset representatives of the supergroup. The application of the method to the $P2_12_12_1$ structures in the inorganic crystal structure database[3] has demonstrated its feasibility. All 14 compounds with a well characterized and reproducible Landau phase transition at high temperatures were detected with a pseudosymmetry parameter Δu under 1.5 Å, but also under this threshold were found 232 structures. Hence, the parameter Δu does not seem to discriminate in this case so strongly as in ferroelectric structures, where Δu was allowed to attain up to 2 Å in successfully predicted new ferroelectrics.[2] However, from 34 materials with $\Delta u < 1.0$ Å, nine of them are known to exhibit a high-temperature phase transition. The remaining compounds are proposed as materials where in general the existence of a similar transition is worth being checked.

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[*] On leave of absence from the University of Sofia, Faculty of Physics, BG-1126 Sofia, Bulgaria.

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