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Domain Structures due to the Non Group-Subgroup Transition in $(C_3H_7NH_3)_2PbCl_4$

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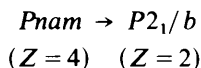
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Abstract

It is shown that the non group-subgroup transition $Pnam \leftrightarrow P2_1/b$ which the compound bis(propylammonium) lead tetrachloride, $(C_3H_7NH_3)_2PbCl_4$, undergoes must lead to domain structures on each side of the transition point. In both of them, the boundary operators are anticipated.

1. Introduction

Very recently (Zangar, Miane, Courseille, Chanh, Couzi & Mlik, 1989), an interesting non group-subgroup transition was observed in bis(propylammonium) lead tetrachloride $(C_3H_7NH_3)_2PbCl_4$. The transition is reversible, occurs at 339 K under 1 atm (10^5 Pa) and follows the sequence



with increasing temperature. Z denotes, as usual, the number of formula units within a cell.

Because of the transition, a domain structure is expected to appear (antiphase domains and twins by merohedry). All possible symmetry operators connecting domains can be derived from the sole knowledge of space groups. To each boundary between domains is associated a coset of operators ('boundary operators'), which thus characterizes the type of

boundary. Any operator belonging to a coset transforms one variant into the variant on the other side of the boundary. Translation (antiphase) boundaries and twin boundaries are commonly observed, especially by electron microscopy or X-ray topography. In addition, group theory predicts in some cases *mixed* (i.e. glide reflections and/or screw rotations) boundaries. The possibility of such a kind of boundary was first predicted in group-subgroup transitions (Guymont, Gratijs, Portier & Fayard, 1976; Guymont, 1978) and indeed is very rarely observed (see, however, Jiang, Zhang, Hei & Kuo, 1985). A boundary is essentially an antiphase one as soon as at least *one* of the operators of the characteristic coset is a pure translation (Guymont, Gratijs, Portier & Fayard, 1976). On the contrary, for a boundary to be essentially mixed (or 'translation-twin'), *all* the operators inside the characteristic coset must be mixed.

The group-theory analysis was afterwards extended to non group-subgroup transitions under rather general conditions (Guymont, 1981) and is applied here to determine the domain structures of $(C_3H_7NH_3)_2PbCl_4$.

2. Symmetry analysis of both structures

The orthorhombic room-temperature structure of $(C_3H_7NH_3)_2PbCl_4$ has been determined recently

(Meresse & Daoud, 1989). We shall take a different setting (already described by Zangar, Miane, Courseille, Chanh, Couzi & Mlik, 1989), more convenient for our analysis.

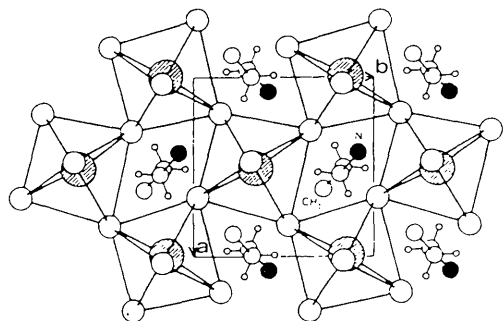


Fig. 1. One layer of orthorhombic $(C_3H_7NH_3)_2PbCl_4$. The directions of axes a and b are indicated.

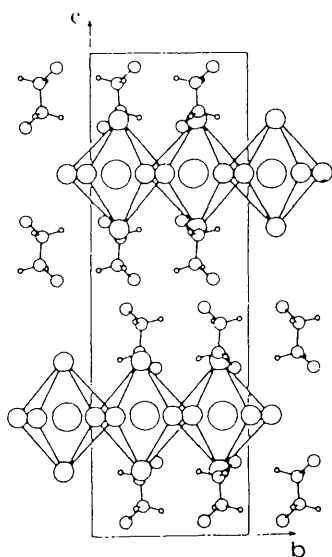


Fig. 2. Projection of orthorhombic $(C_3H_7NH_3)_2PbCl_4$ along a .

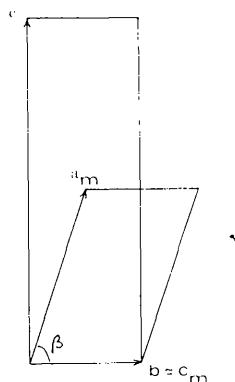


Fig. 3. Relation between the monoclinic and the orthorhombic cells.

The structure consists of layers of corner-sharing $PbCl_6$ octahedra connected by propylammonium groups through hydrogen bonding $N-H \cdots Cl$. The CH_3 extremities are linked to the similar extremities of adjacent layers by van der Waals bonds. We take a and b axes in a plane parallel to one layer of octahedra ($a = 0.781$, $b = 0.795$ nm) with c perpendicular ($c = 2.503$ nm) (Figs. 1 and 2). With this setting, the space group reads $Pnam$.

In these orthorhombic axes $\{a, b, c\}$, the space-group operators are, with the origin at a centre:

$$\begin{aligned} (1|0, 0, 0) & \quad (2_{1[100]}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \\ (2_{1[010]}|\frac{1}{2}, \frac{1}{2}, 0) & \\ (2_{1[001]}|0, 0, \frac{1}{2}) & \\ (\bar{1}|0, 0, 0) & \quad (n_{(100)}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \\ (a_{(010)}|\frac{1}{2}, \frac{1}{2}, 0) & \quad (m_{(001)}|0, 0, \frac{1}{2}). \end{aligned}$$

(This is a slightly redundant combination of Seitz and Hermann-Mauguin notations.)

The monoclinic high-temperature cell $\{a_m, b_m, c_m\}$ is related to the orthorhombic cell as follows (Fig. 3):

$$\begin{aligned} a_m &= 1.35 \text{ nm} \\ b_m &= 0.786 \text{ nm} \cong a \\ c_m &= 0.781 \text{ nm} \cong b \\ \beta &= 71.9^\circ. \end{aligned}$$

In this monoclinic setting ($a_m, b_m = a, c_m = b$), the space-group operators of $P2_1/c$ are, with origin chosen at a centre,

$$\begin{aligned} (1|0, 0, 0) & \quad (2_{1[010]}|0, \frac{1}{2}, \frac{1}{2}) \\ (\bar{1}|0, 0, 0) & \quad (c_{(010)}|0, \frac{1}{2}, \frac{1}{2}). \end{aligned}$$

3. Variant structure due to a non group-subgroup transition

The group-theory analysis of a non group-subgroup transition (Guymont, 1981) shows that the domain structure appearing after a transition is determined by the sole operators *lost* at the transition, that is the operators not included in the group of the structure after the transition. Thus, different structural variants are expected on either side of the transition point, in contrast with the case of a group-subgroup relation where variants appear only on the side of the transition point corresponding to the subgroup.

Let us consider two space groups \mathcal{H} and \mathcal{L} (of orders H and L) not group-subgroup related. The intersection $\mathcal{I} = \mathcal{H} \cap \mathcal{L}$ (of order I) is the maximal common subgroup.

Consider the transition $\mathcal{H} \rightarrow \mathcal{L}$. The operators $\mathcal{H} - \mathcal{L}$ are lost; the operators $\mathcal{I} = \mathcal{H} \cap \mathcal{L}$ remain; and the

operators $\mathcal{L}-\mathcal{I}$ appear. Let us denote by h_k the operators that have disappeared from \mathcal{H} at the transition. The number of variants is given by H/I . The set of operators lost at the transition is distributed among $H/I-1$ cosets.

The set of operators which transform the original variant V_0 into, for example, V_k is $h_k\mathcal{L}$, which includes $h_k\mathcal{I}$.

In general, the invariance group of V_k is $h_k\mathcal{L}h_k^{-1}$, which includes $h_k\mathcal{I}h_k^{-1}$. Therefore, the variants V_0, V_1, V_2, \dots are invariant under the operators of $\mathcal{I}, h_1\mathcal{I}h_1^{-1}, h_2\mathcal{I}h_2^{-1}, \dots$, but also under additional operators since they are invariant under $\mathcal{L}, h_1\mathcal{L}h_1^{-1}, h_2\mathcal{L}h_2^{-1}, \dots$. Only the lost operators are to be taken into account for determining the variant structure which appears, since the gained operators are part of the invariance group of the variant and therefore do not give rise to any other variant. All lost operators h_k can be distributed among the various cosets $h_k\mathcal{I}$ obtained by decomposition of \mathcal{H} into cosets with respect to \mathcal{I} . Let us select one operator h_α in each coset as a *coset representative*, so that every coset can be written $h_\alpha\mathcal{I}$, with α running from 1 to $H/I-1$; α is the index of the coset of operators lost from \mathcal{H} , operators which all transform V_0 into V_α . But, in addition, there are other operators which transform V_0 into V_α : the *complete set* is $h_\alpha\mathcal{L}$.

The method consists in first choosing a cell common to both structures and then in enumerating all operators, described in the common setting. Then the intersection group \mathcal{I} is determined. The index of \mathcal{I} in both groups gives the corresponding numbers of variants. If necessary, the distribution of lost operators among the different cosets with respect to \mathcal{I} most often can be done by simple inspection. Then, we must build the complete characteristic cosets $h_\alpha\mathcal{L}$.

4. Application to $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{PbCl}_4$

Let us choose as common cell the orthorhombic cell $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$. In this setting, $P12_1/c1$ becomes $P2_1/b11$ with a multiple side A -centred cell and therefore must be combined with the translation $(1|0, \frac{1}{2}, \frac{1}{2})$ (group $A2_1/b11$). Its operators are therefore doubled and read now:

$$\begin{aligned} (1|0, 0, 0) & (2_{1[100]}|\frac{1}{2}, \frac{1}{2}, 0) \\ (\bar{1}|0, 0, 0) & (b_{(100)}|\frac{1}{2}, \frac{1}{2}, 0) \\ (1|0, \frac{1}{2}, \frac{1}{2}) & (2_{1[100]}|\frac{1}{2}, 0, \frac{1}{2}) \\ (\bar{1}|0, \frac{1}{2}, \frac{1}{2}) & (c_{(100)}|\frac{1}{2}, 0, \frac{1}{2}). \end{aligned}$$

The intersection group $Pnam \cap A2_1/b$ is only $\{(1|0, 0, 0), (\bar{1}|0, 0, 0)\} \equiv P\bar{1}$. It is rather unexpected that no 2_1 is in common (which would be the case if the orthorhombic group were $Pbmn$ instead of $Pnam$, or if the monoclinic group were $P12_1/a1$ instead of $P2_1/b11$).

4(a) Transition $Pnam \rightarrow P2_1/b$

The index of $P\bar{1}$ in $Pnam$ is 4. There are therefore four variants and three cosets of lost operators, corresponding to three kinds of boundaries with respect to one variant taken as reference. The decomposition into cosets $h_\alpha\mathcal{I}$ is

$$\begin{aligned} Pnam = P\bar{1} + \{ & (2_{1[100]}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), (n_{(100)}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \\ & + \{(2_{1[010]}|\frac{1}{2}, \frac{1}{2}, 0), (a_{(010)}|\frac{1}{2}, \frac{1}{2}, 0)\} \\ & + \{(2_{1[001]}|0, 0, \frac{1}{2}), (m_{(001)}|0, 0, \frac{1}{2})\}. \end{aligned}$$

The characteristic cosets $h_\alpha\mathcal{L}$ are

$$\begin{aligned} (2_{1[100]}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2})A2_1/b & \\ = \{ & (2_{1[100]}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), (n_{(100)}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), (2_{1[100]}|\frac{1}{2}, 0, 0), \\ & (m_{(100)}|\frac{1}{2}, 0, 0), (1|0, 0, \frac{1}{2}), \\ & (\bar{1}|0, 0, \frac{1}{2}), (1|0, \frac{1}{2}, 0), (\bar{1}|0, \frac{1}{2}, 0)\} \\ (2_{1[010]}|\frac{1}{2}, \frac{1}{2}, 0)A2_1/b & \\ = \{ & (2_{1[010]}|\frac{1}{2}, \frac{1}{2}, 0), (a_{(010)}|\frac{1}{2}, \frac{1}{2}, 0), (2_{1[010]}|\frac{1}{2}, 0, \frac{1}{2}), \\ & (m_{(010)}|\frac{1}{2}, 0, \frac{1}{2}), (2_{1[001]}|0, 0, 0), \\ & (m_{(001)}|0, 0, 0), (2_{1[001]}|0, \frac{1}{2}, 0), (b_{1001}|0, \frac{1}{2}, 0)\} \\ (2_{1[001]}|0, 0, \frac{1}{2})A2_1/b & \\ = \{ & (2_{1[001]}|0, 0, \frac{1}{2}), (m_{(001)}|0, 0, \frac{1}{2}), (2_{1[001]}|0, \frac{1}{2}, 0), \\ & (m_{(001)}|0, \frac{1}{2}, 0), (2_{1[010]}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), \\ & (n_{(010)}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), (2_{1[010]}|\frac{1}{2}, 0, 0), (a_{(010)}|\frac{1}{2}, 0, 0)\}. \end{aligned}$$

The first coset describes an antiphase boundary. The two others correspond to two twin boundaries, each of them deriving from the other by an antiphase operation; thus, they are parallel and can both be labelled $m_{(001)}$.

4(b) Transition $P2_1/b \rightarrow Pnam$

The index of $P\bar{1}$ in $A2_1/b11$ is also 4.

Here again we have four variants and three cosets of lost operators:

$$\begin{aligned} A2_1/b11 = P\bar{1} + \{ & (1|0, \frac{1}{2}, \frac{1}{2}), (\bar{1}|0, \frac{1}{2}, \frac{1}{2})\} \\ & + \{(2_{1[100]}|\frac{1}{2}, \frac{1}{2}, 0), (b_{(100)}|\frac{1}{2}, \frac{1}{2}, 0)\} \\ & + \{(2_{1[100]}|\frac{1}{2}, 0, \frac{1}{2}), (c_{(100)}|\frac{1}{2}, 0, \frac{1}{2})\}, \end{aligned}$$

which can be written

$$\begin{aligned} A2_1/b11 = P\bar{1} + (1|0, \frac{1}{2}, \frac{1}{2})\{P\bar{1}\} \\ + (b_{(100)}|\frac{1}{2}, \frac{1}{2}, 0)[P\bar{1} + (1|0, \frac{1}{2}, \frac{1}{2})\{P\bar{1}\}]. \end{aligned}$$

The three variants are each obtained from V_0 by transformation through the following three characteristic cosets:

$(1|0, \frac{1}{2}, \frac{1}{2})Pnam$

$$= \{(1|0, \frac{1}{2}, \frac{1}{2}), (\bar{1}|0, \frac{1}{2}, \frac{1}{2}), (2_{1[100]}|\frac{1}{2}, 0, 0), \\ (m_{(100)}|\frac{1}{2}, 0, 0), (2_{[010]}|\frac{1}{2}, 0, \frac{1}{2}), \\ (n_{(010)}|\frac{1}{2}, 0, \frac{1}{2}), (2_{[001]}|0, \frac{1}{2}, 0), (b_{(001)}|0, \frac{1}{2}, 0)\}$$

$(2_{1[100]}|\frac{1}{2}, \frac{1}{2}, 0)Pnam$

$$= \{(2_{1[100]}|\frac{1}{2}, \frac{1}{2}, 0), (b_{(100)}|\frac{1}{2}, \frac{1}{2}, 0), (1|0, 0, \frac{1}{2}), \\ (\bar{1}|0, 0, \frac{1}{2}), (2_{[001]}|0, 0, 0), \\ (m_{(001)}|0, 0, 0), (2_{1[010]}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}), (n_{(010)}|\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\}$$

$(2_{1[100]}|\frac{1}{2}, 0, \frac{1}{2})Pnam$

$$= \{(2_{1[100]}|\frac{1}{2}, 0, \frac{1}{2}), (c_{(100)}|\frac{1}{2}, 0, \frac{1}{2}), \\ (1|0, \frac{1}{2}, 0), (\bar{1}|0, \frac{1}{2}, 0), (2_{1[001]}|0, \frac{1}{2}, \frac{1}{2}), \\ (b_{(001)}|0, \frac{1}{2}, \frac{1}{2}), (2_{[010]}|\frac{1}{2}, 0, 0), (a_{(010)}|\frac{1}{2}, 0, 0)\}$$

Here we have three antiphase boundaries $(1|0, \frac{1}{2}, \frac{1}{2})$, $(1|0, 0, \frac{1}{2})$ and $(1|0, \frac{1}{2}, 0)$.

The actual shape and extension of the domains are not determined by symmetry alone and are controlled

by local elastic energy (*i.e.* bond energy) minimization. The weak energy of van der Waals bonds strongly suggests that most of the small perturbations in the arrangement of octahedra and molecular groups due to the domain boundaries occurs mainly through them.

It should be noticed that, in addition to these domain structures essentially due to the transition, there may also appear independently twins by pseudomerohedry because of the close values of a and b on the one hand and of b_m and c_m on the other.

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An Estimate of the Number of Structural Parameters Measurable from a Fiber Diffraction Pattern

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Abstract

An estimate of the number of independent structural parameters that can be determined from a fiber diffraction pattern is derived and its application is demonstrated. At resolutions where independent estimates can be made for the intensity of every layer line, this number is set by sampling limits along each layer line [Makowski (1982). *J. Appl. Cryst.* **15**, 546-557]. At resolutions beyond which separation of intensities due to individual layer lines is possible (the deconvolution limit) there may still be usable structural information in the pattern. Even though intensities on individual layer lines cannot be uniquely determined from these data, the data may still represent useful constraints on structural models of the diffracting particles. Here it is shown that beyond the deconvolution limit the total number of structural parameters obtainable increases linearly as a function of resolution.

Introduction

Every diffuse arc of intensity in a fiber diffraction pattern has the potential for acting as a constraint on models of the diffracting object. Quantitative measurement of the intensity of a reflection can be made to some limiting resolution dependent on the distribution of reflections in reciprocal space and the degree of disorientation in the specimen. The limiting resolution is set by the degree of overlap that can be corrected using a numerical deconvolution procedure (Makowski, 1978). Reflections falling beyond this deconvolution limit cannot be accurately measured because their overlap with neighbors due to disorientation cannot be corrected by any numerical procedure. Nevertheless, it is clear that in many cases substantial structural information exists in the diffracted intensity beyond this limit. Fig. 1 is a diffraction pattern from a fiber of the Pap adhesion pili from *E. coli*. With angular deconvolution (Makowski, 1978),