THE ANTIFERROELECTRIC PHASE TRANSITION IN THE CH₃NH₃PbCl₃ STUDIED BY MEANS OF PSEUDO-SPIN MODELS

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Abstract

The crystal of CH₃NH₃PbCl₃ (MAPbCl₃) exhibits two order disorder phase transitions. A previous structural study shows two phase transitions according to the phase sequence:

Phase I (Pm 3m) ←→ Phase II (P4/mmm) ←→ Phase III (P222₁).

Three pseudo-spin models are used to describe the mechanism of the phase transitions and predict the antiferroelectric phase (phase III). Pseudo-spin coordinates associated to the orientational disorder of the methylammonium (MA) groups, acting as order-parameters (O.P.’S) are considered.

Keywords : CH₃NH₃PbCl₃ (MAPbCl₃); Order disorder phase transitions; Pseudo-spin coordinates; Antiferroelectric phase.

1. Introduction

There are many examples of solids which display some orientational disorder in the high temperatures phases of their crystalline state [1−4]. Such a situation occurs when the molecules reside on sites with higher symmetry than their own symmetry. The Frenkel picture [5] for orientational disorder, when justified by experimental disorder, provides us with the definition of pseudo-spin co-ordinates linked to the different orientations of the molecule. The "freezing" of one or several co-ordinates depending on the dimension of the pseudo-spin produces phase transitions to orientationally ordered phases, and so, the pseudo-spin variables act as order parameter (O.P.’S) for such transitions [3−4]. The crystal of MAPbCl₃, belongs to this class of materials; it has been the subject of experimental studies by means of DSC, X ray diffraction and Raman scattering [6−8]. In the room temperature phase (phase I), MAPbCl₃ crystallises in the cubic perovskites structure [6].

The exact nature of the orientational disorder of the MA groups in the cubic phase (phase I) is not firmly established. Three models have been considered, from DSC (differential scanning calorimetry) and Raman scattering, which predict the orientational disorder of the MA groups as a function of temperature. The pseudo-spin variables acting as order parameters (O.P.’S) are considered.

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calorimetry) consideration, to analyse the implications of order-disorder mechanisms on the symmetry properties of the system [11]. Figure 2 shows the schematic orientational disorder representation of MA group for the three proposed models.

Figure 1: Raman spectra of polycrystalline sample of CH$_3$NH$_3$PbCl$_3$ in the low wave number range (10-250 cm$^{-1}$) at different temperatures.

In this paper, we will attempt to describe the order-disorder phases transitions observed in MAPbCl$_3$ on the basis of six, twelve and eight dimensional pseudo-spin such as defined in figure 2. We show that both models A and B can explain order-disorder phase transitions and then, predict the antiferroelectric phase (phase III).

2. Pseudo-spin description

It can be stated that order-disorder processes are concerned in the transition mechanisms of MAPbCl$_3$. However, it is also clear that disordering processes alone cannot account for all aspects of the observed phase transitions. Nevertheless, it is very important as first step to analyse the implications of order-disorder mechanism on the symmetry properties of the system. In this section, we tentatively analyse the transitions mechanisms based on different order-disorder models.

2.1. Model A

The MA group has six equivalent orientations along the cube edges and occupies sites with instantaneous C$_h$ symmetry. The $n_i$ designate the occupation probabilities of the groups in each orientations where ($i = 1,2,3,4,5,6$) refers to possible six orientations of the groups. In the disordered phase (phase I) we have:

$$\sum_{i=1}^{6} n_i = 1 \quad \text{with} \quad n_i = 1/6 \quad (i = 1 \text{ to } 6). \quad (1)$$
For the $O_h$ site symmetry, the six $n_i$ variables generate a six dimensional reducible representation, which can be decomposed as follows:

$$\Gamma_R (Pm 3\overline{m}; A) = R_1 + R_5 + R_9$$

$$R_1 = \Gamma_1^+ / A_{1g} ; R_5 = \Gamma_3^+ / E_g ; R_9 = \Gamma_4^- / F_{1u}.$$  

The transition:

$I (Pm 3\overline{m} (Z=1)) \rightarrow II (P4/mmm (Z=1))$ implies an instability to the lattice occurring at the centre of the Brillouin zone (point $\Gamma(000)$). According to a previous work in group theory, investigations on subgroup of $Pm 3\overline{m} [12]$ at the zone centre, the irreducible representation $E_g(r)$ is responsible for the $Pm 3\overline{m} \rightarrow P4/mmm$ transition. So the O.P.S is two-dimensional and belongs to the $E_g$ doubling degenerated representation of the cubic point group $O_h$. Taking account of equation (1), the symmetry breaking co-ordinates are easily obtained by means of the projection operator’s technique, thus giving:

$$\{\sigma_1(E_g, \Gamma)\} = 2n_1 + 4n_2 - 2n_3 - 2n_4 ;$$

$$\{\sigma_2(E_g, \Gamma)\} = 6n_1 - 6n_2 + 6n_3 - 6n_4 .$$

Such pseudo-spins co-ordinates are expected to explain the order-disorder processes at the $I \rightarrow II$ phase transition when acting as primary O.P.'S. Figure 3 shows a schematic representation of the ground state of phase $II$ obtained in the first transition from the resolution with:

$$\{\sigma_1(E_u, Z)\} = 0 ;$$

$$\{\sigma_2(E_u, Z)\} = 0 .$$

leading respectively to $n_0.1=n_1.3 = 1$ and $n_0.3=n_1.1 = 0$.

It is clear from this study that the freezing of appropriate pseudo-spin co-ordinates leads to the same space group when these co-ordinates act as primary order parameter in the frame work of Landau theory [10]. To summarise, a six dimensional pseudo-spin model is able to describe the order-disorder mechanisms at the $I \rightarrow II$ and $II \rightarrow III$ transitions and can predict the antiferroelectric phase (phase III).

2.2. Model B

In the B model, the MA group has twelve equivalent orientations of the $C-N$ axis along the middle of edge (figure 2) and occupies sites with instantaneous $C_s$ symmetry. In the $O_h$ site symmetry, the twelve $n_i$ variables generate a twelve dimensional reducible representation which decomposes as:

$$\Gamma_R (Pm 3\overline{m}; B) = R_1 + R_5 + R_8 + R_9 + R_{10}$$

$$R_1 = \Gamma_1^+ / A_{1g} ; R_5 = \Gamma_3^+ / E_g ; R_8 = \Gamma_5^+ / F_{2g} ;$$

$$R_9 = \Gamma_4^- / F_{1u} ; R_{10} = \Gamma_5^- / F_{2u}.$$  

We notice that the irreducible representation $E_g (\Gamma)$ responsible for the $I \rightarrow II$ phase transition appear on the decomposition of $\Gamma_R (Pm 3\overline{m}; B)$. For the $II \rightarrow III$ transition, the reducible representation spanned by the pseudo-spins at $Z(0,0,1/2)$ point is determined as:

$$\Gamma_R (P4/mmm; B) = R_1 + R_4 + R_{10}$$

$$R_1 = \Gamma_1^+ / A_{1g} ; R_4 = \Gamma_4^+ / B_{2g} ; R_{10} = \Gamma_5^- / E_u .$$
Since the O.P.'S correspond to the $E_u/\tilde{Z}_5^-$ symmetry is responsible of the Pmma$\rightarrow$P2221 transition, we can predict that a twelve dimensional pseudo-spin model is able to describe the order-disorder mechanisms at the phase sequence.

2.3. Model C

The MA group has eight equivalent orientations along the three axes and occupies sites with instantaneous $C_S$ symmetry. In $O_h$ site symmetry, the eight \( n_i \) variables generate eight dimensional reducible representation which decomposes as:

$$ \Gamma_R (Pm \bar{3}m ; C) = R_1 + R_3 + R_8 + R_9. $$

\( R_1 = \Gamma_1^+ / A_{1g}; \ R_3 = \Gamma_2^- / A_{2u}; \ R_8 = \Gamma_5^+ / F_{2g}; \ R_9 = \Gamma_4^- / F_{1u}. \)

It should be noticed that the irreducible representation $E_g (\Gamma)$ responsible for the I$\rightarrow$II phase transition does not appear for the decomposition. So, this model are not able to explain the I$\rightarrow$II phase transition and cannot predict the antiferroelectric phase (phase III).

3. Conclusion

The attempt to describe the order-disorder phase transition in MAPbCl\(_3\) on the basis of a multidimensional pseudo-spins models shows that both models A and B are able to describe the
order-disorder mechanisms for the I → II and II → III transitions and predict antiferroelectric phase. The first transition involves mainly the rotational and orientational motions of the organic cation, but for the second transition it is important to make a coupling of pseudo-spins with particular phonon modes. At present, we can distinguish the three disordered models concerning the orientation of the MA group in the cubic phases of MAPbX$_3$ (X: halogen) crystals for the pseudo-spins considerations.

References