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Polarization Rotation in the Incommensurate Phase of $Sn_2P_2(Se_xS_{1-x})_6$

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The crystalline family $Sn_2P_2(Se_x\ S_{1-x})_6$ presents particularly interesting features due to its low symmetry. The direction of polarization is thus not symmetry fixed, neither in the ferroelectric, nor in the incommensurate phase. We analyze the situation close to the inc transition, close to, and at the lock-in transition: we use a Landau-Ginzburg functional the minimization of which allows to get results on the polarization rotation as a function of temperature.

Keywords Incommensurate; ferroelectric; Lifshitz point; phase transition

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Introduction

The crystalline family concerned by this study, which undergoes phase transitions, is particularly interesting both for applied and fundamental aspects, in relation with ferroelectricity. The compounds can form solid solutions, and in the composition-temperature phase diagram a Lifshitz point and a tricritical point are encountered [1, 2]. Hence, $Sn_2P_2Se_6$ presents

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an intermediate incommensurate (*Inc*) phase, $Sn_2P_2S_6$ undergoes directly the transition to the ferroelectric phase, and in the solid solution $Sn_2P_2(Se_xS_{1-x})_6$ the modulation wave vector vanishes and the intermediate *Inc* phase disappears for a composition near $x = 0.28$, which defines the Lifshitz point [3, 4]. The phase transitions in this family of compounds have a displacive character evidenced by light [5] and neutron scattering [6] studies, and the coupling between phonon branches at $q \neq 0$ plays an important role in the appearance of the *Inc* phase which is of type II (no Lifshitz invariant) between phases with symmetry $2/m$ and m.

The actual transition sequences in these compounds are thus as follows:

– For $x < 0.28$:

$$\text{Ferro}\,(m) \overset{T_c}{\leftrightarrow} \text{Para}\,(2/m)$$

With $T_c = 338$ K for pure $Sn_2P_2S_6$.

– For $x > 0.28$:

$$\text{Ferro}\,(m) \overset{T_L}{\leftrightarrow} Inc \overset{T_i}{\leftrightarrow} \text{Para}\,(2/m)$$

For $Sn_2P_2Se_6$ the incommensurate and lock-in transition temperatures are respectively equal to: $T_i = 221$ K and $T_L = 193$ K.

The prominent feature of the low temperature ferroelectric phase that follows from its low monoclinic symmetry is that the direction of polarization Π is not symmetry-fixed. So, in spite of the fact that the phase transition is associated with the condensation of a single dimensional Irreducible Representation, two components P_x and P_z along the x and z axes defining the mirror plane are necessary to describe the ferroelectric phase. Both components transform according to the same Irreducible Representation and their value depends on temperature, which leads to the slight rotation of the polarization vector $\Pi(T)$ in the ferroelectric phase when temperature is lowered [7]. In the incommensurate phase the modulation vector θ is directed near the 2-fold symmetry axis y and the polarization vector $\Pi(y)$ remains to be directed in the plane x-z.

The aim of the present communication is to show that the direction of the (modulated) polarization in the incommensurate phase can substantially differ from that in the ferroelectric phase and a jump of polarization direction is expected at the discontinuous lock-in transition, a situation which needs new experiments to be confirmed.

Thermodynamic Potential and its Minimization

Consider first the polarization rotation in ferroelectric phase, that follows from Ref. [7]. Since both components of polarization P_x and P_z are transformed according to the same Irreducible Representation, the Landau functional that accounts for the coupling between these components is written as:

$$F_c = \frac{1}{2}\alpha_{11}P_x^2 + \frac{1}{2}\alpha_{22}P_z^2 + \alpha_{12}P_xP_z + \frac{1}{4}\beta_1P_x^4 + \frac{1}{4}\beta_2P_z^4 + \frac{1}{2}\beta_{12}P_x^2P_z^2 + \beta'_{12}P_xP_z^3 + \beta''_{12}P_x^3P_z \tag{1}$$

where phenomenological coefficients α_{11}, α_{22}, etc., are functions of temperature, pressure, and Se concentration x. Functional F_c becomes unstable towards the formation of the ferroelectric phase at the temperature at which the matrix of quadratic form of coefficients in the expansion of F_c

$$A = \begin{pmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{12} & \alpha_{22} \end{pmatrix} \tag{2}$$

firstly becomes negatively defined, i.e. at the critical temperature $T_c(x)$ at which one of the eigenvalues:

$$\lambda_{12}(T, x) = \frac{1}{2}S \pm \sqrt{S^2 - 4D} \tag{3}$$

(where $S = SpA = \alpha_{11} + \alpha_{22}$ and $D = \det A = \alpha_{11}\alpha_{22} - \alpha_{12}^2$) changes sign. The critical temperature $T_c(x)$ is therefore provided by the condition:

$$D(T_c, x) = 0 \tag{4}$$

The polarization just below the transition is given by the eigenvector of quadratic form (1) that corresponds to the eigenvalue λ_1 taken at T_c (i.e. when $\lambda_1 = 0$). Taking into account the condition (4) we find the relative weight of components P_x, P_z and the angle θ between Π and x:

$$\tan\theta_c = \frac{P_z}{P_x} = \sqrt{\frac{\alpha_{11}(T_c)}{\alpha_{22}(T_c)}} \tag{5}$$

It is convenient to work in the local coordinate frame X, Z in which the matrix (2) is diagonal. The orientation of local frame with respect to the initial coordinate axes depends on the Se concentration x. In the frame X, Z the polarization Π just below T_c is directed along X ($\theta = 0$) and slightly rotates away when temperature decreases following the dependence $\theta(T) \sim (T - T_c)^{3/2}$ because of the nonlinear admixing of the component P_Z [7].

Consider now the formation of type-II incommensurate phase at $x > 0.28$ when the Landau functional becomes unstable toward the formation of the space-modulated harmonic wave of polarization:

$$\begin{aligned} P_x(y) &= P_{qx}(T)\cos[qy + \phi_x(T)] \\ P_z(y) &= P_{qz}(T)\cos[qy + \phi_z(T)] \end{aligned} \tag{6}$$

This occurs at the transition temperature T_i that is larger than the critical temperature T_c defined by Eq. (5) (the transition temperature to the uniform ferroelectric phase). This "finite-q" instability is provided by the negatively defined 2nd order gradient terms and is stabilized by 4th order gradient terms in the gradient energy.

$$\begin{aligned} F_{\text{grad}} = {} & \frac{1}{2}K_1(\partial_y P_x)^2 + \frac{1}{2}K_2(\partial_y P_z)^2 + \frac{1}{2}K_{12}(\partial_y P_x . \partial_y P_z) \\ & + \frac{1}{2}D_1\left(\partial_y^2 P_x\right)^2 + \frac{1}{2}D_2\left(\partial_y^2 P_z\right)^2 + \frac{1}{2}D_{12}\left(\partial_y^2 P_x \cdot \partial_y^2 P_z\right) \\ & + \frac{1}{2}D'_{12}\left(\partial_y P_x \cdot \partial_y^3 P_z\right) + \frac{1}{2}D''_{12}\left(\partial_y^3 P_x \cdot \partial_y P_z\right) \end{aligned} \tag{7}$$

To find the transition temperature $T_i(x)$ and polarization components $P_{qx}(T_i)$, $P_{qz}(T_i)$ just below T_i we substitute the harmonic wave approximation (6) into the Landau functional defined by (1) and (7):

$$F = F_C + F_{\text{grad}} \tag{8}$$

and we perform the averaging over the oscillating functions. The resulting functional has the form of functional (1) but with a dependence on q coefficients.

The transition temperature $T(q)$ to the modulated phase with wavevector θ is given by Eq. (4), but with the q-dependent determinant $D_q(T, x)$. In fact the transition occurs to the phase with maximal transition temperature $T_i = \max_q T(q)$ having the modulation vector θ_i.

The polarization direction below T_i is given by the q-dependent analog of Eq. (5):

$$\tan\theta_i = \frac{P_{q_i z}}{P_{q_i x}} = \sqrt{\frac{\alpha_{11}(q_i, T_i)}{\alpha_{22}(q_i, T_i)}} \tag{9}$$

With an accuracy up to nonlinear corrections $\sim(T_i - T_c)^{2/3}$, the difference $\Delta\theta = \theta_i - \theta_c$ provides the jump of the polarization rotation angle at the lock-in transition at T_C.

Consider the most simple example of functional that gives the incommensurate phase and the jump of polarization rotation:

$$\begin{aligned} F = {} & \frac{1}{2}a(T - T_C)P_x^2 + \frac{1}{2}K_1\left(\partial_y P_x\right)^2 + \frac{1}{2}D_1\left(\partial_y^2 P_x\right)^2 + \frac{1}{2}bP_z^2 \\ & + \frac{1}{2}K_{12}(\partial_y P_x . \partial_y P_z) + \cdots \end{aligned} \tag{10}$$

(only quadratic terms are present). The incommensurate phase appears when $K_1 < 0$. The q-dependent coefficients in matrix A (2) are given by:

$$\begin{aligned} \alpha_{11}(q) &= a(T - T_C) + K_1 q^2 + D_1 q^4 \\ \alpha_{22}(q) &= b \\ \alpha_{12}(q) &= K_{12} q^2 \end{aligned} \tag{11}$$

We use the local reference to have no coupling between polarization components P_x, P_z at $q = 0$ (i.e. $\alpha_{12}(0) = 0$). Therefore the transition to the ferroelectric phase occurs at $T = T_C$ and $\theta_c = 0$. The transition temperature to the modulated state is found from equation $D_q(T, x) = 0$:

$$T(q) = T_C - \frac{1}{a}\left(K_1 q^2 + \left(D_1 - K_{12}^2/b\right)q^4\right) \tag{12}$$

Maximizing this expression over q, we find:

$$T_i = T_C + \frac{1}{4a}\frac{K_1^2}{\left(D_1 - K_{12}^2/b\right)}, \quad q_i^2 = -\frac{K_1}{2\left(D_1 - K_{12}^2/b\right)} \tag{13}$$

and the jump of polarization rotation $\Delta\theta = \theta_i$ where:

$$\tan\theta_i = \frac{K_{12}}{b} q_i^2 = -\frac{K_1 K_{12}}{2\left(bD_1 - K_{12}^2\right)} \tag{14}$$

it vanishes at the Lifshitz point where $K_1 = 0$.

Conclusion

In spite of its apparent simple features, the sequence of phase transitions in this crystalline family reveals subtle properties due to the low symmetry of the systems. Accurate experiments are needed to check the theoretical results. The crystallographic study performed in Ref. [7] revealed that the direction of polarization in the ferroelectric phase is indeed not along a crystallographic axis. To check the results presented here would require the accurate determination of structure of the *Inc* phase, a difficult task since incommensurate satellites are close to Bragg reflections and therefore it is difficult to collect their intensity. Nevertheless simpler experiments, as optical ones, may be interesting since for instance an abrupt rotation of the optical indicatrix should occur at T_L as a consequence of the described effects.

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