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Improper and proper ferroelectric phase transitions in $TlInS_2$ layered crystal with incommensurate structure

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Abstract

The dielectric constant of $TlInS_2$ crystal was measured in the temperature range including incommensurate (IC1 and IC2) and commensurate (C1 and C2) phase transitions under external bias electric field. It has been revealed that maxima in the temperature dependence of dielectric constant of $TlInS_2$ at the C1 and C2 phase transition points shift to higher temperatures. The anomaly at IC2 transition point shifts to lower temperatures on applying the external electric fields. A new complete theoretical model including the presence of two order parameters and two polar sublattices in $TlInS_2$ has been suggested.

1. Introduction

The ternary compound $TlInS_2$ belongs to the group of chalcogenide semiconductor crystals with layered structure. At room temperature this crystal has a space symmetry group of $C2/c$ [1]. It has been established that, on cooling, $TlInS_2$ exhibits a sequence of structural phase transitions, including transitions to an incommensurate (IC) and commensurate (C) phases. According to structural investigations, the transition to the IC phase takes place at $T_{i1} \sim 216$ K and is associated with condensation of a soft mode at a point in the Brillouin zone characterized by $\boldsymbol{q}_i(\delta, \delta, 0.25)$, where δ is the incommensuration parameter ($\delta = 0.012$) [2]. On subsequent cooling, $TlInS_2$ exhibits IC–C phase transition at the temperature of $T_{c1} \sim 204$ K with condensation of the soft mode at $\boldsymbol{q}_c = (0, 0, 0.25)$ [2] which accompanied by the quadrupling of the unit cell volume along the direction perpendicular to the layers. However, the presence of the ferroelectric soft mode with Curie temperature at about $T_{c2} \sim 200$ K and with the Curie constant $\sim 10^3$ was discovered as a result of submillimetre spectra and dielectric constant measurements [3, 4]. The spontaneous polarization vector of the ferroelectric phase lies in the plane of the layers.

The detailed investigations of dielectric susceptibility and spontaneous polarization in a wide temperature range [5–7] revealed a set of anomalies in the temperature dependence of dielectric constant in $TlInS_2$ at about 216, 206, 204, 201 K and in the range of 190–195 K. Two theoretical approaches have been established for explanation of these anomalies [6, 8]. According to [6], a weak disturbance (such as structural defects, impurities) can lead to splitting of IC–C phase transition in $TlInS_2$ into two closely spaced IC–C phase transitions

at $T_{c1} \sim 204$ K and $T_{c2} \sim 201$ K. In the frame of this model the anomaly at $T_{i2} \sim 206$ K is treated as a result of an abrupt change of incommensuration parameter or appearance of a new incommensurate structure. Anomalous behaviour of $\varepsilon(T)$ in the range of 190–195 K was treated as a result of coexistence of polar regions of above mentioned commensurate phases originating at $T_{c1} \sim 204$ K and $T_{c2} \sim 201$ K. The second approach [8] postulates the existence of an IC–IC phase transition in $TlInS_2$ at 204 K. According to this model, the above-mentioned experimental results can be explained as follows: at $T_i \sim 216$ K a phase transition to the IC phase occurs. This IC phase exists in the temperature interval of 204–216 K (IC1). At $T_{ii} \sim 204$ K the crystal exhibits IC–IC phase transition to the phase IC2 which occurs within 201–204 K and finally the C phase transition takes place at $T_c \sim 201$ K.

Thus, one can see that in spite of detailed experimental and theoretical investigations of low-temperature phase transitions in $TlInS_2$, the theoretical models are incomplete for description of a whole sequence of phase transformations in this compound.

In the present work the dielectric constant measurements as a function of temperature in $TlInS_2$ single crystals under bias electric field near the phase transitions are investigated. A new complete theoretical model for the thermodynamical description of the sequence of phase transitions in $TlInS_2$ is offered as a result of present and previously reported investigations.

2. Experimental details

The crystals were grown in evacuated quartz tubes by using the modified Bridgman method. The samples, which were in rectangular form, were oriented along the polar axis which lies in the cleavage plane (the morphology of crystals permits cleavage to plane parallel plates with mirror-like surfaces). The plates were gently polished, cleaned and covered with silver paste. The dimensions of the electrodes were 5×2 mm^2 with an inter-electrode distance of 1 mm.

Measurements of the real part of the dielectric susceptibility ε' were performed using the capacitance bridge method at frequencies of 50 kHz with instrument sensitivity of 0.1 pF and with accuracy of 1%. A low-temperature cryostat system used in measurements allowed us to scan the temperature with the rate of about 0.1 K min^{-1}. The temperature was measured by a copper–constantan thermocouple placed close to the sample. The accuracy of the temperature measurements was not less than 0.02 K. The static electric fields of intensity E between 0 and 12 kV cm^{-1} were applied along the polar axis.

3. Experimental results

The temperature dependences of the real part of the dielectric susceptibility of $TlInS_2$ under bias electric fields with different intensities are demonstrated in figure 1. The figure shows that increasing the electric field intensity leads to decreasing values of ε in the temperature range of successive phase transitions. To analyse the $\varepsilon'(T)$ curves, it is convenient to consider the behaviour of the phase transition peaks under the bias field separately:

- as seen from the figure, changes in $\varepsilon'(T)$ behaviour near the incommensurate phase transition at $T_{i1} \sim 216$ K are similar to those which have been obtained by applying uniaxial mechanical stress on $TlInS_2$ in the direction perpendicular to the layers [9]. The applied field changes the $\varepsilon'(T)$ profile, but does not affect the phase transition point at $T_{i1} \sim 216$ K;
- the phase transition point at $T_{i2} = 206$ K is shifted to lower temperatures by applying the fields with low intensity (up to 4 kV cm^{-1}). The rate of this shift $\mathrm{d}T_{i2}/\mathrm{d}E$ was

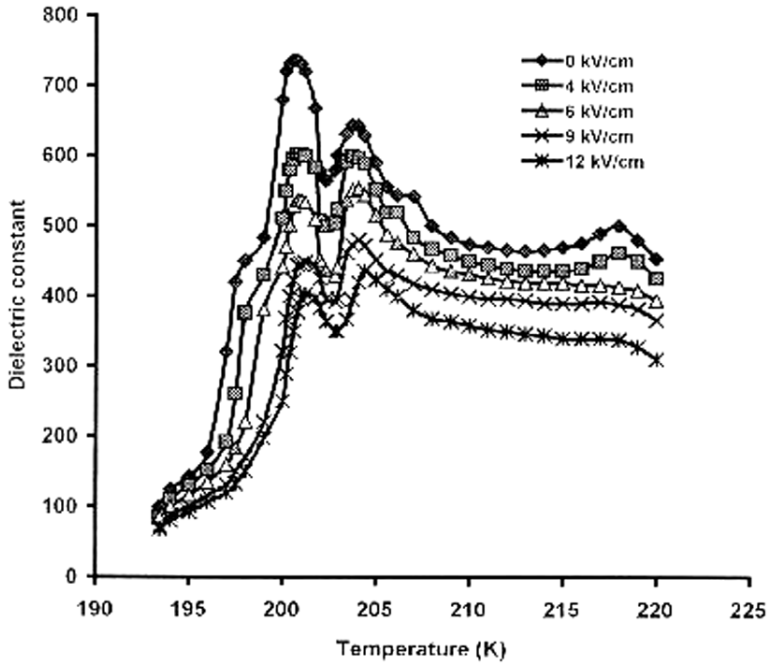

Figure 1. The temperature dependences of dielectric susceptibility of $TlInS_2$ near the phase transitions measured at frequency 50 kHz on applying to the sample external bias electric fields with different intensities.

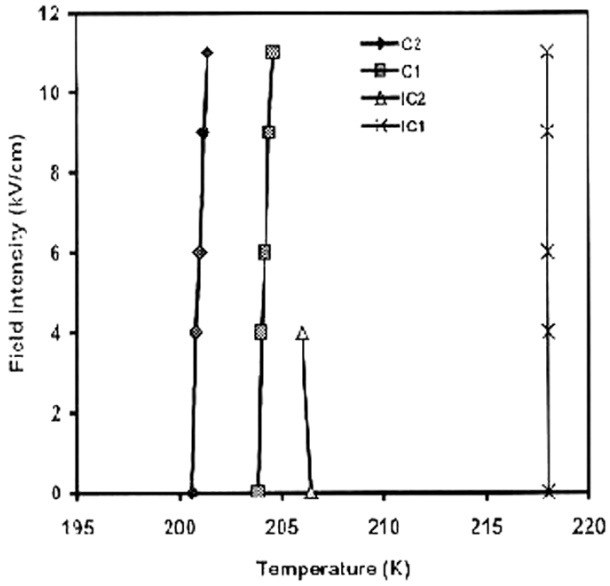

Figure 2. The electric field intensity dependences of the phase transition temperatures in $TlInS_2$ in the (E, T) phase diagram.

about -0.125 K cm kV^{-1}. On applying the fields with higher intensity, the peak of $\varepsilon'(T)$ slightly decreased;

- the IC–C phase transition point at $T_{c1} \sim 204$ K shifted from 203.8 K at $E = 0$ to a higher temperature of 204.4 K at $E = 12$ kV cm^{-1}. The rate of the shift $\mathrm{d}T_{c1}/\mathrm{d}E$ was about 0.05 K cm kV^{-1};
- the IC–C phase transition point at $T_{c2} = 201$ K shifted from 200.6 K at $E = 0$ to 201.4 K at $E = 12$ kV cm^{-1}. The rate was about 0.066 K cm kV^{-1}.

All of these shifts are shown using the (E, T) diagram in figure 2.

4. Discussion of the results

According to structural investigations, the IC–C phase transition in $TlInS_2$ crystal takes place with a quadrupling of the unit cell volume giving rise to an improper ferroelectricity in this compound. Thus, irreducible representations of the space group of symmetry $C2/c$ corresponding to the wavevector $\boldsymbol{q}(0, 0, 0.25)$ determine transformation properties of the order parameter. For $TlInS_2$, the Landau free energy density can be written in terms of the complex order parameter $Q(x)$, representing the one-dimensional modulation of the commensurate structure along the spatial coordinate x, and polarization $P(x)$ [10]:

$$f(x) = \frac{\alpha}{2}QQ^* + \frac{\beta}{2}(QQ^*)^2 + \mathrm{i}\frac{\delta}{2}\left(Q\frac{\mathrm{d}Q^*}{\mathrm{d}x} - Q^*\frac{\mathrm{d}Q}{\mathrm{d}x}\right) + \frac{k}{2}\frac{\mathrm{d}Q}{\mathrm{d}x}\frac{\mathrm{d}Q^*}{\mathrm{d}x} + \frac{\gamma}{2}(Q^8 + Q^{*8}) + \mathrm{i}\xi P(Q^4 + Q^{*4}) + \frac{\eta}{2}QQ^*P^2 + \frac{1}{2\chi_0}P^2 - PE \tag{1}$$

where $\alpha = \alpha_0(T - T_0)$. The polarization P lies in the plane of the layers (YZ), which is perpendicular to the X direction and plays the role of a secondary order parameter. By the minimization of the average free energy density $f(x)$ with respect to the polarization, we can eliminate P from the expression. Then after substitution of the two-component order parameter Q, Q^* by its polar representation $Q = \rho\exp(\mathrm{i}\varphi)$ and application of the constant amplitude approximation [11], the free energy density expansion (1) transforms to

$$f(x) = \frac{\alpha}{2}\rho^2 + \frac{\beta}{4}\rho^4 - \delta\rho^2\left(\frac{\mathrm{d}\varphi}{\mathrm{d}x}\right) + \frac{k}{2}\rho^2\left(\frac{\mathrm{d}\varphi}{\mathrm{d}x}\right)^2 + \gamma\rho^8\cos 8\varphi - \frac{\chi'}{2}(2\xi\rho^4\sin 4\varphi - E)^2$$

where

$$\chi' = \frac{1}{(\chi_0^{-1} + \eta\rho^2)}.$$

In the presence of an electric field ($E \neq 0$), the minimization of the free energy $F = \int f(x)\,\mathrm{d}x$ with respect to the phase $\varphi(x)$ leads to the double sine–Gordon differential equation:

$$k\rho^2\frac{\mathrm{d}^2\varphi}{\mathrm{d}x^2} + 16\gamma'\rho^8\sin 4\varphi\cos 4\varphi - 8\xi\chi'\rho^4E\cos 4\varphi = 0 \tag{2}$$

where $\gamma' = \gamma + \chi\xi^2$. The first integral of the differential equation (2) for the phase $\varphi(x)$ can be written in the form:

$$\frac{k}{2}\left(\frac{\mathrm{d}\varphi}{\mathrm{d}x}\right)^2 = z - 2\gamma'\rho^6\sin^2 4\varphi + 2\xi\chi'\rho^2E\sin 4\varphi$$

where z is a constant of integration.

The solutions $\varphi(x)$ are given by

$$x = \frac{1}{4}\left(\frac{k}{2}\right)^{1/2} \int_0^{4\varphi} \frac{\mathrm{d}u}{[z - g(u)]^{1/2}} \tag{3}$$

where

$$g(u) = \Delta \sin^2 u - \lambda \sin u$$
$$\Delta = 2\gamma'\rho^6 \qquad \lambda = 2\xi\chi'\rho^2 E. \tag{4}$$

The modulation period of $\varphi(x)$ can be separated into regions of positive and negative polarizations, x_+ and x_- respectively. The intersoliton distance,

$$x_0 = \frac{1}{2}(x_+ + x_-) = \frac{1}{8}\left(\frac{k}{2}\right)^{1/2} \int_0^{2\pi} \frac{\mathrm{d}u}{[z - g(u)]^{1/2}}. \tag{5}$$

The minimization of the free energy F with respect to the z parameter leads to

$$\int_0^{2\pi} [z - g(u)^{1/2}]\,\mathrm{d}u = \pi\delta\left(\frac{2}{k}\right)^{1/2}. \tag{6}$$

The IC–C transition temperature $T = T_c$ is determined by the divergence of the modulation period $2x_0 = x_+ + x_-$. In the case of $E \neq 0$ the intersoliton distances are not equal, so that at $T \to T_c$ one of them diverges. The limiting situation at $T = T_c$ is given by the boundary conditions: $\varphi(-\infty) = -\pi/4$; $\varphi(+\infty) = \pi/4$. Thus, from (4) and (5) we obtain the condition for the IC–C transition ($x_0 \to \infty$):

$$z = \Delta + |\lambda|. \tag{7}$$

From (6) and (7) we can obtain in the weak-field regime:

$$T_c(E) - T_c(0) = \frac{\xi\chi'\beta}{6\gamma'\alpha_0}\left[1 + \ln\frac{8\gamma'\rho^4}{\xi\chi'|E|}\right]|E|. \tag{8}$$

Apart from a logarithmic correction, equation (8) suggests a linear dependence of T_c on E. This theoretical result is consistent with the $T_{c1}(E)$ shift obtained in our dielectric constant measurements. If we consider the phase transition at $T_{c1} = 204$ K as an improper ferroelectric phase transition with quadrupling of the unit cell, we can confirm the agreement of the above-mentioned theoretical result with the $T_{c1}(E)$ shift obtained experimentally.

The results of dielectrical [4] and Raman scattering [12] investigations have revealed that the IC–C ferroelectric phase transition in $TlInS_2$ at 201 K is accompanied by condensation of soft ferroelectric mode at the centre of the Brillouin zone and can be referred to a proper ferroelectric phase transition. In this case the spontaneous polarization is a primary order parameter and the phase transition can be described in terms of the thermodynamic potential where no Lifshitz invariant appears [13]. Then we can express the free energy density as

$$f(x) = \frac{a}{2}P^2 + \frac{b}{4}P^4 + \frac{c}{2}\left(\frac{\mathrm{d}P}{\mathrm{d}x}\right)^2 + \frac{d}{2}\left(\frac{\mathrm{d}^2P}{\mathrm{d}x^2}\right)^2 + \frac{f}{2}P^2\left(\frac{\mathrm{d}P}{\mathrm{d}x}\right) - EP$$

where P is a transition parameter (the polarization), a is assumed to be temperature dependent as $a = a_0(T - T_0)$. The thermodynamical analysis of this expansion under the small-field approximation ($E^2/a^2 \ll a/b$) leads to the following expressions for the electrical field dependence of the incommensurate phase transition temperature T_i and the commensurate ferroelectric phase transition temperature T_c in the lowest order of E [14]:

$$T_i(E) - T_i(0) = -3\frac{b}{a_0}[\varepsilon_0\chi(T_i)E]^2$$
$$T_{ci}(E) - T_c(0) = \frac{11}{P_s(T_c)}\frac{E}{a_0}$$

where $\chi(T)$ and $P_s(T)$ are temperature dependent dielectric permittivity and spontaneous polarization functions respectively. The observed shifts of the incommensurate (at $T_{i2} = 206$ K) and commensurate ferroelectric (at $T_{c2} = 201$ K) phase transition temperatures under external electric field in $TlInS_2$ are in qualitative agreement with the above-mentioned theoretical approach which considers the IC–C phase transformation as a proper ferroelectric one.

Thus, taking into account the experimental results and theoretical considerations, we can confirm the presence of two order parameters in $TlInS_2$, which correspond to two lattice instabilities in this crystal. The first of them is a two-component order parameter, which causes an improper ferroelectric phase transition accompanied by multiplication of the unit cell volume. The incommensurate structure preceding this transition is described by the presence of a Lifshitz invariant in the free energy Landau expansion. The second order parameter is one component, which is a spontaneous polarization of the ferroelectric phase appearing at 201 K. The incommensurate structure preceding the proper ferroelectric phase transition is a type II incommensurate phase [15] with no Lifshitz invariant in the Landau free energy expansion. So, we can make an assumption about formation of two sublattice polarizations (P_i and P_p) appearing as a result of improper and proper ferroelectric phase transitions in $TlInS_2$ at the temperatures T_{c1} and T_{c2} respectively. Taking into account all of these remarks, we can suggest a new model for the free energy Landau expansion of $TlInS_2$,

$$f(x) = \frac{\alpha}{2} QQ^* + \frac{\beta}{4}(QQ^*)^2 + \mathrm{i}\frac{\delta}{2}\left(Q\frac{\mathrm{d}Q^*}{\mathrm{d}x} - Q^*\frac{\mathrm{d}Q}{\mathrm{d}x}\right) + \frac{k}{2}\frac{\mathrm{d}Q}{\mathrm{d}x}\frac{\mathrm{d}Q^*}{\mathrm{d}x} + \frac{\gamma}{2}(Q^8 + Q^{*8})$$
$$+\mathrm{i}\xi P_i(Q^4 + Q^{*4}) + \frac{\eta}{2} QQ^* P_i^2 + \frac{1}{2\chi_0} P_i^2 + \frac{a}{2} P_p^2 + \frac{b}{4} P_p^4 + \frac{c}{2}\left(\frac{\mathrm{d}P_p}{\mathrm{d}x}\right)^2$$
$$+\frac{d}{2}\left(\frac{\mathrm{d}^2 P_p}{\mathrm{d}x^2}\right) + \frac{f}{2} P_p^2\left(\frac{\mathrm{d}P_p}{\mathrm{d}x}\right)^2 - P_i E - P_p E.$$

The presence of two different lattice instabilities can be described by the temperature dependences of two constants in the free energy expansion,

$$\alpha = \alpha_0(T - T_1)$$
$$a = a_0(T - T_2).$$

The total spontaneous polarization in $TlInS_2$ is the sum of the sublattice polarizations:

$$P_s = P_i + P_p.$$

The dielectric response is also the sum of sublattice responses:

$$\chi = \frac{\mathrm{d}P_s}{\mathrm{d}E} = \frac{\mathrm{d}P_i}{\mathrm{d}E} + \frac{\mathrm{d}P_p}{\mathrm{d}E} = \chi_i + \chi_p.$$

The offered model is in qualitative agreement with the results of the dielectric constant measurements in the temperature interval of 10–80 K, presented in [7] and [16]. As discussed in [7], the weak ferroelectric phase transition obtained at $T_w \sim 79$ K can only be described using a two-non-equivalent-sublattice model offered in [17].

5. Conclusion

In this paper the influence of the external bias electric field on the successive structural phase transitions in $TlInS_2$ is studied. The measurements of the temperature dependences of the real part of the dielectric susceptibility have been performed. The observed shifts of the phase transition points give information about the nature of these transitions. The

coexistence of improper and proper ferroelectricity in the same crystal structure has been proposed according to experimental results. The free energy Landau expansion describing the phase transformations in $TlInS_2$ have been reinvestigated. A new theoretical model including two order parameters and two sublattice polarizations has been suggested.

References

[1] Henkel W, Hochheimer H D, Carlone C, Werner A, Ves S and v Schnering H G 1982 *Phys. Rev.* B **26** 3211
[2] Vakhrushev S B, Zhdanova V V, Kvyatkovsky B E, Okuneva V N, Allakhverdiev K R, Aliev R A and Sardarly R M 1984 *JETP Lett.* **39** 292
[3] Volkov A A, Goncharov Yu G, Kozlov G V, Allakhverdiev K R and Sardarly R M 1983 *Phys. Solid State* **25** 2061
[4] Aliev R A, Allakhverdiev K R, Baranov A I, Ivanov N R and Sardarly R M 1984 *Phys. Solid State* **26** 775
[5] Salaev F M, Allakhverdiev K R and Mikailov F A 1992 *Ferroelectrics* **131** 163
[6] Suleimanov R A, Seidov M Yu, Salaev F M and Mikailov F A 1993 *Phys. Solid State* **35** 177
[7] Allakhverdiev K R, Turetken N, Salaev F M and Mikailov F A 1995 *Solid State Commun.* **96** 827
[8] Gadjiev B R, Seidov M Yu and Abdurakhmanov V R 1996 *Phys. Solid State* **38** 3
[9] Suleimanov R A, Seidov M Yu, Salaev F M and Mamedov T S 1992 *Phys. Solid State* **34** 975
[10] Gashimzade F M, Gadjiev B R, Allakhverdiev K R, Sardarly R M, Shteinshraiber V Ya 1985 *Phys. Solid State* **27** 2287
[11] Prelovsek P 1983 *J. Phys. C: Solid State Phys.* **16** 3257
[12] Allakhverdiev K R, Babaev S S, Tagiev M M and Shirinov M M 1989 *Phys. Status Solidi* b **151** 7
[13] Ishibashi Y and Shiba H 1978 *J. Phys. Soc. Japan* **45** 409
[14] Kim K-T and Kim J-J 1988 *J. Phys. Soc. Japan* **57** 2213
[15] Bruce A D, Cowley R A and Murray A F 1978 *J. Phys. C: Solid State Phys.* **11** 3591
[16] Allakhverdiev K R, Salaev F M, Mikailov F A and Mamedov T S 1992 *JETP Lett.* **56** 149
[17] Dvorak V and Ishibashi Y 1976 *J. Phys. Soc. Japan* **41** 548