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Anomalies in second order elastic constants and gyrotropic constants of triglycine sulphate near phase transition

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Abstract. The anomalies in second order elastic constants and gyrotropic constants have been considered for the phase transition of triglycine sulphate. Expressions have been derived for the equilibrium values of order parameter and strain variables in both phases. Using Landau–Khalatnikov equation the fluctuation in order parameter is expressed in terms of fluctuations in strain variables. Substitution of these in free energy gives anomalies arising from Landau and coupling energies in second order elastic constants. The real part of the anomalies decreases steeply across the transition temperature and thereafter flatly tend to ferroelectric values. The anomalies in the components of the gyrotropic tensor have been derived and their temperature variation discussed.

Keywords. Elastic anomalies; gyrotropic constants; phase transition; triglycine sulphate

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1. Introduction

Triglycine sulphate (TGS), isomorphous triglycine selenate (TGSe) and triglycine fluoberyllate are useful ferroelectrics. They follow the Curie–Weiss law. In TGS the spontaneous polarization decreases slowly with temperature and shows no discontinuity at the Curie temperature $T_c = 322\,\mathrm{K}$ indicating a second order phase transition. The ratio of slopes of inverse of dielectric constant versus temperature lines [1] taken just below and above the Curie point turns out to be about 2 to 3. Hoshino *et al* [2] measured the specific heat versus temperature for TGS. The pyroelectric coefficient [3] tends to infinity as the temperature tends to Curie point. The elastic constants [4] affected by phase transition are C_{11}, C_{22}, C_{33}, C_{66}, C_{12}, C_{13} and C_{23}. Westwanski and Fugiel [5] proposed a form of scaling function which gives a more accurate description of the critical properties of TGS and TGSe. Banan *et al* [6] discussed the application of modified TGS single crystal (with caesium impurity) for infrared detector applications. General laws of formation of domain structure in pure and impure crystals of TGS is presented by Dontsova *et al* [7].

The crystal class of TGS changes from $2/m(C_{2h})$ to $2(C_2)$ at the transition temperature. The order parameter (Q) is the electric polarization which is zero in high temperature phase and is directed along Y-axis in low temperature phase. There is an inversion symmetry in high temperature phase and the crystal cannot exhibit any gyrotropic effects in the paraelectric phase. Gyrotopic effects could appear in the ferroelectric (low temperature) phase where this symmetry element is destroyed. When spatial dispersion is present in the system the elastic constant matrix [8] acquires the structure

$$C_{ij}(\Omega k) = C_{ij}(\Omega) + i d_{ijl}(\Omega) k_1,$$

where k denotes the wave vector and Ω is the circular frequency of the acoustic wave. The gyrotropic constants d_{ijl} are components of a fifth rank tensor and satisfy the antisymmetry relations with respect to interchange of indices i and j. The number of gyrotropic constants for different classes of crystals has been worked out by Kumaraswamy and Krishnamurty [8].

In this paper we report the anomalies of TGS, near the phase transition in second-order elastic (SOE) constants and gyrotropic constants within the framework of the Landau theory. It is only valid for the equilibrium properties and does not apply to non-equilibrium conditions. The Landau theory has been first applied to the case of barium titanate by Devonshire [9]. While the equilibrium values of strains and order parameter in low temperature phase can be obtained from the stability conditions, the fluctuation in the order parameter has been derived by an appeal to the Landau–Khalatnikov equation. In §2 we derive equilibrium values in both the paraelectric and ferroelectric phases and obtain an expression for the fluctuation in order parameter about the equilibrium value. In § 3 we derive expressions for the SOE anomalies and discuss their temperature variation. In § 4, gyrotropic anomalies are derived and their variation with temperature is discussed.

2. Equilibrium values and fluctuations in order parameter

The free energy of the crystal is the sum of (i) elastic energy F_{ela} (ii) the Landau energy F_Q (iii) the coupling energy F_C between the order parameter and strains (iv) the gyrotropic energy F_{gc} involving order parameter, strains and the spatial derivatives of order parameter and strains

$$F = F_{\text{ela}} + F_Q + F_C + F_{\text{gc}} = F_0 + F_{\text{gc}}. \tag{1}$$

Since the gyrotropic energy term F_{gc} is much smaller than F_C we neglect it in calculating elastic anomalies and use F_{gc} only for phenomena relating to gyrotropic effects. The elastic energy for the monoclinic class is given by

$$F_{\text{ela}} = \frac{1}{2}\sum_{ii} C_{ii}\eta_i^2 + C_{12}\eta_1\eta_2 + C_{13}\eta_1\eta_3 + C_{16}\eta_1\eta_6 + C_{23}\eta_2\eta_3 + C_{26}\eta_2\eta_6 + C_{36}\eta_3\eta_6 + C_{56}\eta_5\eta_6, \tag{2}$$

where $\eta_i (i = 1 \text{ to } 6)$ are the components of the strain tensor and C_{ij} are the elastic constants. In the Landau theory F_Q is a power series in the order parameter square that develops near a phase transition and is given by

$$F_Q = \frac{1}{2}\alpha Q^2 + \frac{1}{4}\beta Q^4, \tag{3}$$

where $\alpha = \alpha'(T - T_c)$ and α' and β are constants. The coupling energy F_C that couples the order parameter with strains is of the form

$$F_C = Q^2(A_1\eta_1 + A_2\eta_2 + A_3\eta_3 + A_5\eta_5), \tag{4}$$

where A_1, A_2, A_3 and A_5 are constants. It can be verified that the strains η_1, η_2, η_3, η_4 and η_5 are invariant under the operations of all the elements of the group C_{2h}. Since $Q \to -Q$ in this phase, these strain coefficients couple with $Q^2 \cdot F_{gc}$ is of the form

$$F_{gc} = a_{4x}\left(Q\frac{\partial\eta_4}{\partial x} - \eta_4\frac{\partial Q}{\partial x}\right) + a_{6x}\left(Q\frac{\partial\eta_6}{\partial x} - \eta_6\frac{\partial Q}{\partial x}\right) + a_{4z}\left(Q\frac{\partial\eta_4}{\partial z} - \eta_4\frac{\partial Q}{\partial z}\right) + a_{6z}\left(Q\frac{\partial\eta_6}{\partial z} - \eta_6\frac{\partial Q}{\partial z}\right) \tag{5}$$

where a_{4x}, a_{6x}, a_{4z} and a_{6z} are constants. It can again be verified that each of the term given in (5) is invariant under the symmetry group of the crystal in paraelectrical phase. The terms $\eta_i(\partial Q/\partial x)$ in (5) ensures that the antisymmetric relation in gyrotropic constants is satisfied.

To get the equilibrium values of the order parameter and the strains in the two phases, we neglect F_{gc} in comparison with other terms in F as it is of smaller order of magnitude. Using the stability conditions given by

$$\frac{\partial F}{\partial Q} = 0 \quad \text{and} \quad \frac{\partial F}{\partial \eta_i} = 0 \; (i = 1 \text{ to } 6), \tag{6}$$

it can be shown that the equilibrium values of the order parameter and strains in high temperature paraelectric phase ($T > T_c$) are given by

$$Q_0 = \eta_{i0} = 0 \quad \text{for} \quad (i = 1 \text{ to } 6). \tag{7}$$

For the low temperature ferroelectric phase ($T < T_c$) the equilibrium values are

$$Q_0^2 = \frac{\alpha}{(2X - \beta)}. \tag{8a}$$

$$\eta_{i0} = \frac{\Delta_i}{\Delta}(-Q_0^2) \quad \text{for} \quad (i = 1 \text{ to } 3 \text{ and } 6). \tag{8b}$$

$$\eta_{40} = A_5 C_{45}(C_{45}^2 - C_{44}C_{55})^{-1}(-Q_0^2). \tag{8c}$$

$$\eta_{50} = A_5 C_{44}(C_{44}C_{55}C_{45}^2)^{-1}(-Q_0^2). \tag{8d}$$

where

$$X = \frac{A_1\Delta_1 + A_2\Delta_2 + A_3\Delta_3}{\Delta} + \frac{A_5^2 C_{44}}{C_{44}C_{55} - C_{45}^2},$$

and Δ is the value of the determinant

$$\Delta = \begin{vmatrix} C_{11} & C_{12} & C_{13} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{36} \\ C_{16} & C_{26} & C_{36} & C_{66} \end{vmatrix}$$

Δ_1, Δ_2, Δ_3 and Δ_6 are obtained by replacing 1st, 2nd, 3rd and 4th columns of Δ by the column $(A_1 A_2 A_3 0)$ respectively.

The Landau–Khalatnikov equation expresses the fact that the regression (dQ/dt) of the order parameter fluctuation towards equilibrium is proportional to the thermodynamic restoring force $(\partial F/\partial Q)$.

$$\dot{Q} = \frac{-1}{\mu}\frac{\partial F}{\partial Q} \tag{9}$$

where μ is the viscosity coefficient. Let us write $Q = Q_0 + Q^*$ and $\eta_i = \eta_{i0} + \eta_i^*$ where Q^* and η_i^* ($i = 1$ to 6) represent the fluctuations in the values of Q and η_i respectively. By expanding $(\partial F/\partial Q)$ about the equilibrium values of Q and strain variables and ignoring higher order terms we have

$$\frac{\partial F}{\partial Q} = \left(\frac{\partial F}{\partial Q}\right)_0 + \left(\frac{\partial^2 F}{\partial Q^2}\right)_0 Q^* + \sum_i \left(\frac{\partial^2 F}{\partial Q \partial \eta_i}\right)_0 \eta_i^* \tag{10}$$

By setting $Q^* = \exp(i\Omega t)$ and substituting (10) in (9) we get the fluctuation in order parameter as

$$Q^* = -(2X - \beta)^{1/2}(\alpha\beta)^{-1/2}(1 + i\Omega\tau)^{-1} \sum A_i \eta_i^* \tag{11}$$

i takes values from 1 to 3 and 5. The relaxation time $\tau = \mu(\partial F^2/\partial Q^2)_0^{-1}$. Equation (11) shows that Q^* is a linear function of the strain variables to a first order of approximation.

3. Second order elastic anomalies

Substituting $Q = Q_0 + Q^*$ and $\eta_i = \eta_{i0} + \eta_i^*$ in the expression for F_0 and considering only terms quadratic in strain variables we get

$$F_2 = \frac{1}{2}\sum C_{ij}^* \eta_i^* \eta_j^* = \frac{1}{2}\sum C_{ij} \eta_i^* \eta_j^* + \Delta F_2,$$

where

$$\Delta F_2 = \sum \frac{1}{2} \Delta C_{ij}^* \eta_i^* \eta_j^*,$$

$$= \sum A_i A_j \eta_i^* \eta_j^* [\beta^{-1}(1 + i\Omega\tau)^{-2} - 2\beta^{-1}(1 + i\Omega\tau)^{-1}]. \tag{12}$$

i and j take values 1 to 3 and 5.

The existence of anomalies in the SOE constants shows that the velocity of elastic waves undergo a change during phase transition, and further the waves are attenuated as ΔC_{ij}^* are complex. The real part of ΔC_{ij}^* is given by

$$\mathrm{Re}(\Delta C_{ij}^*) = \frac{-2}{\beta}(1 + 3\Omega^2\tau^2)(1 + \Omega^2\tau^2)^{-2} A_i A_j. \tag{13}$$

i and j takes values 1, 2, 3 and 5.

The temperature variation of τ is given by Lemanov as [10]

$$\tau = \frac{\tau_0}{T - T_c}, \tag{14}$$

with $\tau_0 = 10^{-11}$ sK. For numerical calculations we shall choose the experimental value of $\Omega = 10^9 \mathrm{s}^{-1}$. At the transition temperature $T = T_c$ $\Omega\tau \to \infty$ so that $R(\Delta C^*_{ij}) = 0$. Next $\Omega\tau$ reaches the value of unity when $T_c - T = \Omega\tau_0 = 10^{-2}$. For this value as well as for $\tau = 0$ we find that

$$\mathrm{Re}(\Delta C^*_{ij}) = -2\beta^{-1} A_i A_j. \tag{15}$$

Again the stationary values of the anomalies are reached when $\Omega\tau = 1/\sqrt{3}$ and for this value

$$\mathrm{Re}(\Delta C^*_{ij}) = \frac{-9}{4\beta} A_i A_j. \tag{16}$$

With the above numerical values, we notice that the SOE constants have uniform value in the paraelectric state, fall steeply within a range of order 10^{-2}K to the value $(-9/4\beta)A_iA_j$ and reach asymptotic value of $(-2/\beta)A_iA_j$ within a range of 10^{-1}K.

4. Gyrotropic anomalies

The high temperature (paraelectric) phase has inversion symmetry, hence all d_{ijl} are zero in this phase. In the low temperature (ferroelectric) phase inversion symmetry is absent and gyrotropic constants arise from the coupling of order parameter with the spatial derivatives of strain and order parameter. We can express F_{gc} in the form

$$F_{gc} = \sum_{ijl} d_{ijl} \eta_i^* \frac{\partial \eta_i^*}{\partial x_i}. \tag{17}$$

The gyrotopic anomalies are then given by

$$\Delta d^*_{ijl} = d_{ijl} = \frac{\partial^2 F_{gc}}{\partial \eta_i^* (\partial \eta_j^* / \partial x_l)}. \tag{18}$$

Substituting the value of Q^* in the expression for F_{gc} we can identify all the gyrotropic anomalies. The anomalies are:

$$d_{i41} = dA_i a_{4x}, \tag{19a}$$

$$d_{i61} = dA_i a_{6x}, \tag{19b}$$

$$d_{i43} = dA_i a_{4z}, \tag{19c}$$

$$d_{i63} = dA_i a_{6z}. \tag{19d}$$

where d is given by

$$d = -(2X - \beta)^{-1/2} (\alpha\beta^2)^{-1/2} (1 + i\Omega\tau)^{-1}. \tag{20}$$

In eqs (19a) to (19d) $i = 1$ to 3 and 5 so that the anomalies are present in 16 gyrotropic constants. The gyrotropic anomalies are complex, temperature dependent and characterized by $d_{ijl} = -d_{jil}$. We can see from (19) and (20) that the gyrotropic anomalies are proportional to $[(T - T_c)^{1/2}(1 + i\Omega\tau)]^{-1}$. The real part of the anomalies are proportional to $(T - T_c)^{3/2}[(T - T_c)^2 + \Omega^2\tau_0^2]^{-1}$. At $T = T_c$ the anomalies vanish. When $\Omega\tau_0 = T - T_c = 10^{-2}$ the anomalies are proportional to 10. In general the variation of the anomalies follow the variation of the term $(T - T_c)^{9/2}[(T - T_c)^2 + \Omega^2\tau_0^2]^{-1}$. The anomalies reach stationary value when $T - T_c = \sqrt{3}\,\Omega\tau_0$. For $(T_c - T) \gg \Omega\tau_0$ the anomalies are proportional to $(T_c - T)$.

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