CHAPTER IV
ANOMALIES IN
HIGHER ORDER
ELASTIC CONSTANTS
4.1 Introduction

4.2 The free energy of the crystal

4.3 Variation in the third order elastic constants

4.4 Fourth order elastic constants

References
In the last chapter, we have considered the anomalous changes in the second order elastic constants near a phase transition and had given expressions for $\Delta C_{11}$, $\Delta C_{12}$, $\Delta C_{61}$, $\Delta C_{62}$, $\Delta C_{63}$ and $\Delta C_{66}$ both above and below the transition temperature. The higher order elastic constants, which arise from the nonlinear effects, also show anomalous behaviour near a phase transition. Higher order elastic constants provide an insight into the anharmonic potential energy of the crystal lattice. A few experimental results on the variation of third order elastic constants with temperature have been published in recent past. Third order elastic constants are useful in studying the anharmonic nature of thermal expansion, temperature dependence of second order elastic constants and attenuation of high frequency sound waves in solids. They are also useful in calculating the relative magnitude of the coupling constants. Swarts et al (1972, 1975) studied the complete set of twelve third order elastic constants of Tin and Tin Indium alloys experimentally from the temperature dependence of second order elastic constants and obtained third order elastic constants from the temperature dependence of second order elastic constants. Cain et al (1973) measured six third order
elastic constants for single crystal \( \delta \) phase of Copper Aluminium alloys using ultrasonic pulse superposition technique and calculated high temperature thermodynamic Grünisen parameter in the anisotropic continuum model. Puri and Varma (1977) also obtained third order elastic constants from the pressure derivatives of the second order elastic constants and predicted that the failure of Cauchy's relation is due to many body interactions. Yamshita and Tatsuzaki (1984) found that the absolute values of the third order elastic constants \( C_{111}, C_{112}, \) and \( C_{123} \) increased considerably with decreasing temperature near the transition point and showed that Cauchy's relations for second and third order elastic constants break down below the transition temperature.

No experimental work seems to be available about the variation of fourth order elastic constants near a phase transition. Holder and Granato (1971) give an account of the fourth order elastic constants obtained from the pressure derivatives of second order elastic constants. A theoretical analysis of fourth order elastic constants is given by Garber and Granato (1975). They derived fourth order elastic constants of some materials such as LiBr, RbF, KCl etc from temperature dependence of second order elastic constants by studying nearest and next nearest interactions.
With the three second order elastic constants \( (C_{11}, C_{12}, \text{ and } C_{44}) \), they studied about 11 fourth order elastic constants.

In this chapter we derive expressions for the anomalous changes in the third order and fourth order elastic constants above and below the transition temperature. These expressions could throw light on the temperature dependence of the higher order elastic constants near the transition temperature for crystals like KDP for which the dominant coupling term is of the form \( CQ \gamma^6 \), and could also show how the anharmonic force changes anomalously in this range. A careful study of the anomalous changes in the third order elastic constants could provide a method for evaluating the coupling constants \( B, C, \text{ and } D \) in the free energy.

4.2 The Free Energy Of The Crystal.

Since we are interested in the third and the fourth order elastic constants, we start with an elastic free energy that contains the third and fourth order terms also. The total free energy of the crystal can be written as

\[
F = F_0 + F_Q + F_{el} + F_C
\]

(1)

where \( F \) is the zero point energy from which all changes of
energies are measured.

$F_\phi$ is the Landau free energy; as before it is given by

$$F_\phi = \frac{1}{2} \phi Q^2 + \frac{1}{4} \beta Q^4$$  \hspace{1cm} (2)

with $\phi = \phi\left(T - T_c\right)$  \hspace{1cm} (3)

where $T_c$ is the transition temperature.

As stated in chapter III, the coupling constant $\phi$ is strongly dependent on temperature through the relation (3) while $\beta$ is weakly dependent on temperature.

$F_{el}$ is the elastic free energy of the crystal and comprises of second, third and fourth order elastic deformation energy.

We can write

$$F_{el} = F^{(2)} + F^{(3)} + F^{(4)}$$  \hspace{1cm} (4)

For a tetragonal crystal the expressions for $F^{(2)}$ and $F^{(3)}$ are well known; for sake of completeness, we quote them here.

We have

$$F^{(2)} = \frac{1}{2} \left[ C_{11} \left( \gamma_1^2 + \gamma_2^2 \right) + C_{33} \gamma_3^2 \right]$$

$$+ 2 C_{12} \gamma_1 \gamma_2 + 2 C_{13} \left( \gamma_1 \gamma_3 + \gamma_2 \gamma_3 \right)$$
The expression for the fourth order elastic energy for tetragonal crystals is very long. As we are evaluating the anomalies for the principal fourth order elastic constants, we quote here the general expression. We have

\[
F^{(4)} = \frac{1}{4} \sum_{ijkl} \sum_{k'k''l'} C_{ijkl} \gamma_i \gamma_j \gamma_k \gamma_l
\]  

(7)
For the coupling between the strains and the order parameter, we use the same expression (5) of the chapter III. We have

\[ F_c = B \gamma^2 (\gamma_1 + \gamma_2 + \gamma_3) + C \mathcal{Q} \gamma_6 + D \mathcal{Q}^{\prime}_4 \gamma_5 \tag{8} \]

The transformation properties of this expression have been described in detail in chapter III. The coupling energy is invariant under the group of transformation of the crystal.

The time dependent relaxation of order parameter is described by Landau-Khalatnikov equation and is written as

\[ \mu \frac{\partial \gamma}{\partial t} = - \frac{\partial F}{\partial \gamma} \tag{9} \]

As stated in chapter III, we can expand \((\mathcal{Q})\) as Taylor series around the equilibrium values of \(\mathcal{Q}\) and \(\gamma_i\).

We get

\[ (\frac{\partial F}{\partial \gamma})_0 = \left( \frac{\partial^2 F}{\partial \gamma^2} \right)_0 \gamma^* + \frac{\xi}{\xi_c} \left( \frac{\partial^3 F}{\partial \gamma \partial \gamma_i} \right)_0 \gamma^*_i \]

\[ + \frac{\xi}{\kappa_i} \left( \frac{\partial^3 F}{\partial \gamma \partial \gamma_j} \right)_0 \gamma^*_i \gamma^*_j \]

\[ + \frac{\xi}{\kappa_i \kappa_j} \left( \frac{\partial^3 F}{\partial \gamma_i \partial \gamma_j \partial \gamma_k} \right)_0 \gamma^*_i \gamma^*_j \gamma^*_k \tag{10} \]

Assuming time dependence for \(\mathcal{Q}^*\), of the form
\[ Q(t) = \exp(i\omega t), \text{ we get} \]

\[
(1 + i\omega \tau) \mathcal{Q}^* = \frac{\tau}{\mu} \left[ \frac{\varepsilon}{k} \left( \frac{\partial^2 F}{\partial \alpha \partial \alpha} \right)_{\alpha} \mathcal{Q}^* \\
+ \frac{1}{2} \frac{\varepsilon}{k} \left( \frac{\partial^2 F}{\partial \alpha \partial \alpha^2} \right)_{\alpha} \mathcal{Q}^*^2 \\
+ \frac{\varepsilon}{k} \left( \frac{\partial^2 F}{\partial \alpha \partial \alpha^0 \partial \gamma} \right)_{\alpha} \mathcal{Q}^* \mathcal{Q}^* \right]
\]

(11)

Where \( \mu \) is the viscosity coefficient and \( \tau \) is the relaxation time. This formula shows that \( Q \) is a linear function of \( \mathcal{Q}^* \), \( \mathcal{Q}^*^2 \) and \( \mathcal{Q}^* \mathcal{Q}^* \). They satisfy the relation

\[
\frac{\tau}{\mu} = \left( \frac{\partial^2 F}{\partial \alpha^2} \right)_{\alpha}^{-1} \tag{12}
\]

We get from (11) immediately the following relations:

\[
\left( \frac{\alpha^2}{\alpha \mathcal{Q}^*} \right)_0 = -p \left( \frac{\partial^2 F}{\partial \alpha^2} \right)_{\alpha}^{-1} \left( \frac{\partial^2 F}{\partial \alpha \alpha} \right)_{\alpha} \tag{13}
\]

\[
\left( \frac{\partial^2 \mathcal{Q}^*}{\partial \mathcal{Q}^*^2} \right)_0 = -p \left( \frac{\partial^2 F}{\partial \alpha^2} \right)_{\alpha}^{-1} \left( \frac{\partial^2 F}{\partial \alpha \alpha} \right)_{\alpha} \tag{14}
\]

\[
\left( \frac{\partial^2 \mathcal{Q}^*}{\partial \mathcal{Q}^* \partial \gamma} \right)_0 = -p \left( \frac{\partial^2 F}{\partial \gamma^2} \right)_{\alpha}^{-1} \left( \frac{\partial^2 F}{\partial \alpha \alpha \gamma} \right)_{\alpha} \tag{15}
\]
where \( P = 1/(1 + i \omega) \)

4.3 Variation In The Third Order Elastic Constants

As stated in chapter III, the free energy \( F = F(Q, \gamma^*) \) is a function of the order parameter as well as the strain variables. Further the order parameter itself is a function of strain variables, so that

\[
F = F(Q(\gamma^*_1, \gamma^*_2))
\]  
(16)

and hence

\[
\frac{dF}{d\gamma^*_i} = \left( -\frac{\partial F}{\partial \gamma^*_i} \right)_{\omega=0} + \frac{\partial \omega}{\partial \gamma^*_i} \frac{\partial F}{\partial \omega}
\]  
(17)

Denoting the derivative occurring in the left hand side by \( d/d\gamma^*_i \), we have the operator equation

\[
\frac{d}{d\gamma^*_i} = \frac{\partial}{\partial \gamma^*_i} + \frac{\partial \omega}{\partial \gamma^*_i} \frac{\partial}{\partial \omega}
\]  
(18)
The above operator equation can successively be used to obtain the partial derivatives of \( F \) of any order.

By successive operation of the equation (18) three times, one obtains

\[
\frac{d^3}{d\eta_i^* d\eta_j^* d\eta_k^*} = \frac{\partial^3}{\partial \eta_i^* \partial \eta_j^* \partial \eta_k^*} + \frac{\partial^2 \partial \eta_j^*}{\partial \eta_k^*} + \frac{\partial^3 \partial \eta_i^*}{\partial \eta_j^* \partial \eta_k^*}
\]

\[
+ \frac{\partial^2}{\partial \eta_j^* \partial \eta_k^*} + \frac{\partial^3}{\partial \eta_i^* \partial \eta_j^* \partial \eta_k^*} + \frac{\partial^3}{\partial \eta_j^* \partial \eta_k^* \partial \eta_i^*}
\]

\[
+ \frac{\partial^3}{\partial \eta_i^* \partial \eta_j^* \partial \eta_k^*} + \frac{\partial^3}{\partial \eta_j^* \partial \eta_k^* \partial \eta_i^*} + \frac{\partial^3}{\partial \eta_i^* \partial \eta_j^* \partial \eta_k^*}
\]

\[
and similarly one can verify
\]

\[
(19)
\]
Though this expression appears long, most of the terms will give zero contribution with the expression for \( F_c \) given by (20).

Let us first consider the third order elastic anomalies and write

\[
C_{ijk}^* = C_{ijk} + \Delta C_{ijk}^*, \text{ so that }
\]

\[
\Delta C_{ijk}^* = C_{ijk}^* - C_{ijk} \tag{21}
\]

For infinitesimal strains, the third order elastic constants \( C_{ijk}^* \) is the third derivative of \( F \) with respect to the strain variables \( \xi_i^* , \eta_j^* \) and \( \kappa_k^* \).

\[
C_{ijk}^* = \left( \frac{d^3 F}{d \xi_i^* d \eta_j^* d \kappa_k^*} \right) \tag{22}
\]

From the equation (19) we may write \( C_{ijk}^* \) as below. Since \( Q \sim 10^{-10} \text{ cm} \) and \( \nu \sim 10^{-6} \text{ cm} \), we ignore terms of the order of \( \frac{\partial^3 \Theta}{\partial \xi_i^* \partial \eta_j^* \partial \kappa_k^*} \) and higher orders. Hence
Using the above expression for corrections to the third order elastic constants, we find that,

For \( T > T_c \),

\[ \Delta C_{111}^* = 0 \]

\[ \Delta C_{112}^* = 0 \]

\[ \Delta C_{123}^* = 0 \]
\[ \Delta C_{116}^* = \frac{2 B P^2 C^2}{\xi^2} \]

\[ \Delta C_{456}^* = -\frac{P \Delta C (E^2 - P)}{\xi} \]

(24)

With \( P = 1/(1 + i\omega \tau) \) From (24) we see that nonzero corrections emerge for the elastic constants \( \Delta C_{116}^* \) and \( \Delta C_{456}^* \). These are temperature dependent and diverge as \( 1/(T-T_c)^2 \) and \( 1/(T-T_c) \) respectively.

For \( T < T_c \), we can evaluate the changes in accordance with the formula (23). Here we note that

\[ \left( \frac{\partial^2 F}{\partial \alpha^3} \right)_0 = 6 \beta \omega_0 = 6 \beta \left( -\frac{\omega^2}{\beta} \right)^{1/2} \]

(25)

(Appendix 1 in chapter III)

We find that the expressions are more complicated and are given by:

\[ \Delta C_{111}^* = \frac{24 P^2 B^2 (\xi_0 / \beta^3)}{\xi_0^2} \left[ 1 - \frac{2 P \beta^3 (-\omega^2 / \beta)}{\xi_0^2} \right] \]
\[ \Delta C_{112}^* = \frac{24}{\xi_0} \frac{p^2 B^3}{\xi_0^2} \left( -\frac{c}{\beta} \right) \left[ 1 - 2 \frac{p \beta (-\frac{c}{\beta})}{\xi_0} \right] \]
\[ \Delta C_{123}^* = \frac{24}{\xi_0^2} \frac{p^2 B^3}{\xi_0^2} \left( -\frac{c}{\beta} \right) \left[ 1 - 2 \frac{p \beta (-\frac{c}{\beta})}{\xi_0} \right] \]
\[ \Delta C_{116}^* = \frac{24}{\xi_0^2} \frac{p^2 B^3}{\xi_0^2} \left( -\frac{c}{\beta} \right) \left[ 1 - 2 \frac{p \beta (-\frac{c}{\beta})}{\xi_0} \right] \]
\[ \Delta C_{456}^* = \frac{24}{\xi_0^2} \frac{p^2 B^3}{\xi_0^2} \left( -\frac{c}{\beta} \right) \left[ 1 - 2 \frac{p \beta (-\frac{c}{\beta})}{\xi_0} \right] \]

where

\[ \xi_0 = \alpha - \frac{3 \beta \alpha (T-T_C)}{\beta^2} + \frac{6 \beta \alpha^2 (T-T_C)}{\beta^3} \]

(See equation in appendix 1 of chapter III; distinct behaviour of \( \xi \) is given there.)

These expression show that the corrections for \( \Delta C_{111}^* \), \( \Delta C_{112}^* \), \( \Delta C_{123}^* \) and \( \Delta C_{116}^* \) have a leading term that diverges as \((T-T_0)^{-3}\). Besides they contain another term that diverges as \(1/(T-T_C)^2\). Yamshita and Tatsuzaki have studied approximately the variation of third order elastic constants.
of Aluminium chloride near the transition temperature and have reported that \( C_{111}, C_{112} \) and \( C_{123} \) rapidly increase as the temperature approaches the transition point. Besides they find that the third order anharmonic term \( 1/54 (C_{111} + 6C_{112} + 2C_{123}) \) in the elastic free energy which is related to the volume dilation, reveals rapid variation near \( T_c \). Now from

\[
\Delta (C_{111}^* + 6C_{112}^* + 2C_{123}^*) = \frac{192 \beta^2 B^3}{\xi_0} (-\xi^2 \beta^2) \left[ 1 - \frac{2\beta \rho}{\xi} (-\xi^2 \beta^2) \right]
\]

(28)

Our formula is quantitatively in agreement with the experimental observations, though we are unable to evaluate the coefficients of various divergent terms as well as the coupling constants in our expressions, due to lack of experimental values.

### 4.4 Fourth Order Elastic Constants

Very little work has been done on the evaluation of the anomalies of the fourth order elastic constants. We shall evaluate in this section, the changes in some of the
principal fourth order elastic constants near a phase transition. These are not only of academic interest for understanding anomalies in higher order elastic constants, but can be useful in studies on the propagation of solitons in solids. For example, the equation of motion of elastic wave propagation in \((100)\) direction is given by the nonlinear equation

\[
\left( \frac{\partial^2 u}{\partial t^2} \right)_{\text{pol}} = C_{ij} \left( \frac{\partial^2 u_x}{\partial x^2} \right) + 2 C_{i1j1} \left( \frac{\partial^2 u_x}{\partial x^2} \right) + 3 C_{ij11} \left( \frac{\partial^2 u_x}{\partial x^2} \right)^2 - \frac{3}{2} \left( \frac{\partial^2 u_x}{\partial x^2} \right)^3
\]

The equation involves both the third order and the fourth order elastic constants. Knowledge of variation of these constants near a phase transition will help to understand the anomalies in the propagation of solitons in elastic solids. The expression for \(\Delta C_{ijkl}^*\) is very long and cumbersome. As before, we write

\[
C_{ijkl}^* = C_{ijkl} + \Delta C_{ijkl}
\]

\[
\Delta C_{ijkl}^* = C_{ijkl}^* - C_{ijkl}
\]

Then for small strains,
From (20) we find that

\[ c_{ijkl}^* = \frac{d^4 F}{d q_i^* d q_j^* d q_k^* d q_l^*} \]

\[ c_{ijkl}^* = \left( \frac{d^4 F}{\partial q_i^* \partial q_j^* \partial q_k^* \partial q_l^*} \right) + \left( \frac{d^3 q_i^*}{\partial q_j^*} \right) + \left( \frac{d^3 q_j^*}{\partial q_i^*} \right) \]

\[ \left( \frac{d^4 F}{\partial q_i^* \partial q_j^* \partial q_k^* \partial q_l^*} \right) + \left( \frac{d^3 q_i^*}{\partial q_j^*} \right) + \left( \frac{d^3 q_j^*}{\partial q_i^*} \right) \]

\[ \left( \frac{d^3 q_i^*}{\partial q_j^*} \right) + \left( \frac{d^3 q_j^*}{\partial q_i^*} \right) + \left( \frac{d^3 q_k^*}{\partial q_l^*} \right) + \left( \frac{d^3 q_l^*}{\partial q_k^*} \right) \]

\[ + \left( \frac{d^3 q_i^*}{\partial q_j^*} \right) + \left( \frac{d^3 q_j^*}{\partial q_i^*} \right) + \left( \frac{d^3 q_k^*}{\partial q_l^*} \right) + \left( \frac{d^3 q_l^*}{\partial q_k^*} \right) \]

\[ + \left( \frac{d^4 F}{\partial q_i^* \partial q_j^* \partial q_k^* \partial q_l^*} \right) + \left( \frac{d^3 q_i^*}{\partial q_j^*} \right) + \left( \frac{d^3 q_j^*}{\partial q_i^*} \right) \]

\[ + \left( \frac{d^3 q_k^*}{\partial q_l^*} \right) + \left( \frac{d^3 q_l^*}{\partial q_k^*} \right) + \left( \frac{d^3 q_i^*}{\partial q_j^*} \right) + \left( \frac{d^3 q_j^*}{\partial q_i^*} \right) \]

\[ + \left( \frac{d^3 q_k^*}{\partial q_l^*} \right) + \left( \frac{d^3 q_l^*}{\partial q_k^*} \right) \]

\[ + \left( \frac{d^3 q_i^*}{\partial q_j^*} \right) + \left( \frac{d^3 q_j^*}{\partial q_i^*} \right) \]
It is easy to see that the elastic anomalies for a large number of elastic constants vanish for $T > T_c$.

\[
\begin{align*}
\Delta C_{1111}^* &= \Delta C_{1112}^* = \Delta C_{1123}^* = \Delta C_{1122}^* = \Delta C_{1144}^* = \\
\Delta C_{1255}^* &= \Delta C_{4444}^* = \Delta C_{4455}^* = \Delta C_{1155}^* = \\
\Delta C_{1456}^* &= \Delta C_{1266}^* = \Delta C_{1255}^* = 0
\end{align*}
\]

In the low temperature phase, for $T < T_c$, we find that
It is seen from the above equation that the anomalies in the fourth order elastic constants are strongly dependent on temperature near the phase transition and diverge as $(T-T_0)^{-4}$.

Again we obtain

$$\Delta C_{1144}^* = \Delta C_{1456}^* = \Delta C_{1255}^* = \Delta C_{4455}^* = \Delta C_{4444}^* = 0$$  \hspace{1cm} (33a)$$

$$\Delta C_{1266}^* = \frac{2\mu \rho^2 B^2 C^2 \beta \left(-\frac{\alpha}{\beta}\right)^{1/2}}{(\xi^-)^4}$$  \hspace{1cm} (34)$$

This constant has the same temperature dependence $(T-T_0)^{-4}$ as the constants listed in the equation (33), but it is multiplied by a different factor and besides has a different sign. In the presence of strong singular term $1/(T-T_0)^4$, the fourth order elastic constants are strongly influenced by temperature near the phase transition.
Temperature dependence of ToE Constants (Yumshita & Tatsuzaki, 1984)

Temperature dependence of C_{III} in TMO measured by acoustic harmonic generation with 530 MHz fundamental frequency

Temperature dependence of ΔC_{III} which is due to the order parameter contribution
REFERENCES


