ISAS - INTERNATIONAL SCHOOL
FOR ADVANCED STUDIES

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Thesis submitted for the degree of
"Magister Philosophiæ"

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1 Introduction.

$SrTiO_3$ belongs to the family of oxygen-containing perovskites, the typical representative of which is $BaTiO_3$. The latter being known to be ferroelectric for a long time, $SrTiO_3$ was extensively studied in search for a possible phase transition into a ferroelectric phase. Actually it was found to undergo a structural phase transition at $T_a = 105K$ when its structure changes from simple cubic high temperature phase into tetragonal low temperature phase. The tetragonal phase, however, is not ferroelectric, and is characterized by an antiferrodistortive rotation of the oxygen octahedra with respect to their positions in the cubic lattice. In fact, $SrTiO_3$ under zero stress has never been observed to become ferroelectric, not even at $T = 0$, in spite of the fact that its dielectric constant acquires very high values ($\sim 10^4$) at helium temperatures. For this property it was originally termed as *incipient ferroelectric* and later as *quantum paraelectric*. Recently a new indication for a possible phase transition has been reported in [11] and it is predominantly this phenomenon which motivates the present work. The aim of the introduction is first to summarize the known experimental facts concerning the incipient ferroelectric behaviour of $SrTiO_3$ and then to point to the current level of the theoretical understanding of that. After this we describe in detail the recently discovered anomaly and propose a possible explanation, which will then be further developed in subsequent chapters.

1.1 Incipient ferroelectric behaviour of $SrTiO_3$.

The ferroelectric behaviour, according to the soft-mode theory, is related to a strong temperature dependence of the frequency of a particular zone-center TO phonon mode. We therefore start with several general remarks concerning the phonon spectra of $SrTiO_3$. The structure of its high temperature phase ($T > T_a = 105K$) is *cubic* perovskite which consists of 5 interpenetrating simple cubic lattices and contains 1 formula unit per unit cell. Symmetry analysis [3] shows that in the center of the zone we have (apart from 3 acoustic modes with $\omega \rightarrow 0$) one triply degenerate optical mode Γ_{25} and 3 triply degenerate optical modes Γ_{15}. Each of these latter triplets is for any finite wavevector split into a longitudinal mode and a doubly degenerate transverse mode. The mode of our interest is the lowest lying TO mode corresponding to Γ_{15} (or F_{1u}), which is dipole-active, and would therefore yield ferroelectricity upon softening. In the tetragonal phase below T_a this mode becomes split, because the point symmetry group of the crystal is now D_{4h} instead of O_h, and gives rise to a single A_{2u} mode and a doubly degenerate E_u mode. The former, at least to our knowledge, has never been observed experimentally, but according to the measurements of the c-axis dielectric constant [6] its frequency should be about twice that of the E_u mode. It is therefore the latter which is responsible for incipient ferroelectricity and quantum paraelectric phenomena strictly parallel to the (001) plane. It has been extensively studied by various techniques, particularly Raman and neutron scattering. The temperature dependence of its frequency is shown on the Fig.1.1. We see that both techniques are in very good agreement, and indicate softening above $\sim 35K$, *but not below.*

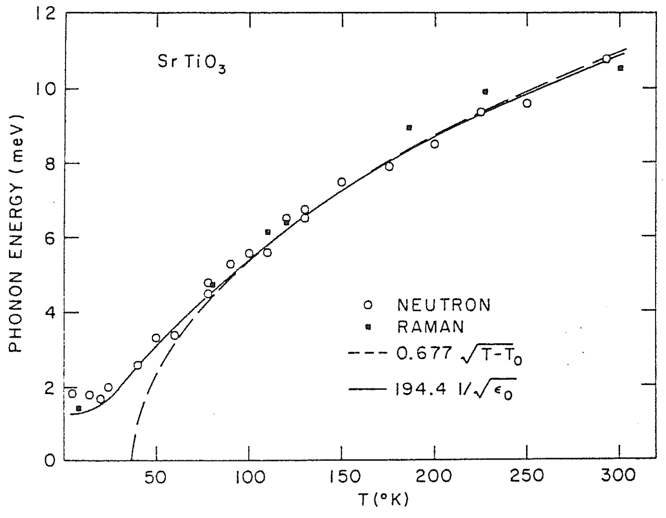

Figure 1.1: Temperature dependence of soft optical mode at $\vec{q} = 0$. Several selected values of the results of Raman scattering experiment by Fleury and Worlock are given by squares. Solid line corresponds to the temperature dependence calculated with Lyddane-Sachs-Teller relation and observed values of ϵ_0. Dashed curve is calculated assuming Curie-Weiss type temperature dependence in ϵ_0. (After [7].)

According to the generalized LST relation the frequencies of the optical branches are related to the static and high frequency dielectric constant ϵ_0 and ϵ_∞, respectively, as follows

$$\frac{\epsilon_0}{\epsilon_\infty} = \frac{\prod_i \omega_{iLO}^2}{\prod_i \omega_{iTO}^2} , \tag{1.1}$$

provided the phonon system is *quasiharmonic* and the mode damping is low. If we assume that the frequencies of all modes except for the soft mode are temperature independent, then (1.1) implies a relation between the temperature dependence of ϵ_0 and that of the soft mode frequency $\omega_1(0)$

$$\omega_1(0) = \frac{A}{\sqrt{\epsilon_0}} , \tag{1.2}$$

$$\text{where} \quad A = \sqrt{\frac{\prod_i \omega_{iLO}^2}{\prod_{i>2} \omega_{iTO}^2} \epsilon_\infty} . \tag{1.3}$$

As we see on the Fig.1.1 this relation is very well satisfied in the whole temperature range under investigation down to the lowest temperatures. The dielectric constant ϵ_0 behaves for temperatures $T > 60K$ according to the Curie-Weiss law with a critical temperature $T_c \sim 37K$. Below 60 K, however, considerable deviations from this behaviour are observed and ϵ_0 instead of diverging at 37 K ceases to increase and gradually stabilizes at a high value $\sim 2 \times 10^4$. The most striking feature is that for $T < 3K$ this high value is *completely temperature independent*, as Müller et al. have shown in [12], measuring down to $30mK$. This kind of behaviour has then been termed as *quantum paraelectric behaviour.* The simplest qualitative explanation of it can be worked out within the frame of a dynamic mean-field single mode theory, as was shown in [12]. We consider it instructive to review their derivation briefly because it clearly illustrates the basic physics of the problem.

We consider a single mode hamiltonian as it is usually employed for structural phase transitions

$$H = \sum_l \frac{p_l^2}{2M} + \sum_l U(q_l) - \frac{1}{2}\sum_{l,l'} v_{ll'} q_l q_{l'} \;, \tag{1.4}$$

$$\text{where} \quad U(q) = \frac{1}{2} m\Omega_0^2 q^2 + \frac{1}{4}\gamma q^4 \tag{1.5}$$

is the potential acting on the Ti ion inside a single cell. The corresponding equation of motion for q_l is

$$m\ddot{q}_l = -m\Omega_0^2 q_l - \gamma q_l^3 + \sum_{l'} v_{ll'} q_{l'} \;. \tag{1.6}$$

Now introduce a mean field approximation replacing $q_{l'} \to <q_l>$. Moreover, linearize the 3^{rd} order term by replacement $q_l^3 \to 3<q_l^2>q_l$, where $< >$ means thermal average. One obtains the following expression for the zone center soft-mode frequency ω

$$m\omega^2 = m\Omega_0^2 + 3\gamma<q_l^2> - \; v(0) = m\Omega^2(T) - v(0) \;, \tag{1.7}$$

where $\Omega(T)$ is the single particle frequency at temperature T and $v(0) = \sum_{l'} v_{ll'}$. Now if the motion were classical, we could calculate the mean square displacement $<q_l^2>$ using the equipartition theorem which yields

$$<q_l^2> = \frac{kT}{m\Omega^2(T)} . \tag{1.8}$$

Substituting this into (1.7) and putting $\omega = 0$ we obtain an expression for the classical critical temperature T_C^{cl}

$$3\gamma \frac{kT_C^{cl}}{m\Omega^2(T_C^{cl})} = v(0) - m\Omega_0^2 . \tag{1.9}$$

We can now express the temperature dependence of the soft-mode frequency near the critical temperature as

$$\omega^2 = \frac{3\gamma k}{m^2\Omega^2(T_C^{cl})}(T - T_C^{cl}) \tag{1.10}$$

and similarly for the static susceptibility, for which we obtain the familiar classical Curie-Weiss law

$$\chi = \frac{m\Omega^2(T_C^{cl})}{3\gamma k(T - T_C^{cl})} . \tag{1.11}$$

For sufficiently low temperatures, however, we cannot use the classical expression for the mean square displacement (1.8) and we must replace it by the quantum-mechanical value

$$<q_l^2> = \frac{\hbar}{2m\Omega} \coth \frac{\hbar\Omega}{2kT} , \tag{1.12}$$

which yields always a larger value than the former. Moreover for $T \to 0$ it tends to a finite value $\hbar/2m\Omega(0)$ whereas the classical displacement tends to zero. Then, if the parameters of the model are such that $m\Omega_0^2 - v(0)$ is negative and small, in the classical picture the phase transition would occur for some finite temperature, whereas quantum-mechanically we can have even at $T = 0$

$$3\gamma <q_l^2> = \frac{3\gamma\hbar}{2m\Omega(0)} > v(0) - m\Omega_0^2 , \tag{1.13}$$

which means that the soft mode frequency remains finite. This summarizes the present understanding of the mechanism by which the phase transition in $SrTiO_3$ is suppressed. We can easily calculate the static susceptibility for this case and obtain

$$\chi = \frac{M}{(T_1/2)\coth(T_1/2T) - T_C^{cl}} , \tag{1.14}$$

where $M = m\Omega^2(T_C^{cl})/3\gamma k$ and $T_1 = \hbar\Omega(T_C^{cl})/k$. The expression is in this last form valid over the temperature interval near T_C^{cl} and was for the first time derived by Barrett in [13], however, in a different context.

The above theory is of course too simple to fit adequately the experimental curves of χ versus T. It accounts, however, for the essential feature of those, namely for the flattening of χ as $T \rightarrow 0$. Its main shortcoming is the single-mode approximation, because the coupling of the soft mode to acoustic modes is not negligible. The adequate microscopic theory taking into account this coupling in a natural way was for the first time worked out by Migoni et al. [14] and its main ingredients are the shell model with an anisotropic and nonlinear intraionic polarizability of the oxygen ions. The results of this theory were in very good agreement with the measured dispersion curves of $SrTiO_3$ and $KTaO_3$. The most detailed present version of the theory of ferroelectricity in oxygen containing compounds is the polarizability model developed by Bilz et al.[15]. Similarly to the simple model described above, *none of these descriptions* implies a phase transition at or near T_C^{cl}, but simply a crossover from classical paraelectric for $T \gg T_C^{cl}$ to quantum paraelectric for $T \ll T_C^{cl}$.

1.2 Neutron inelastic scattering from the soft mode.

To obtain information about the nature of the soft mode it is not enough to determine its frequency alone. The linewidth has to be investigated as well and this was done by both neutron and Raman spectroscopy. The results reveal that the soft phonon is *underdamped* over the whole temperature range down to $T \to 0$ [5],[7]. This together with the fact that the LST relation is well satisfied suggests that $SrTiO_3$ belongs to the class of displacive type ferroelectrics in which the fluctuations of polarization are entirely due to the excitation of optical phonons which can be treated in the *quasiharmonic* approximation. An independent evidence for the validity of this picture could be provided by investigation of integrated intensity in neutron scattering experiment. Since this is a particularly interesting point, we mention it in greater detail.

Provided the phonon system is quasiharmonic the expression for the total integrated intensity due to one phonon scattering reads (for $\vec{Q} = const.$) [8]

$$\frac{d\sigma}{d\Omega} \propto \frac{k_f}{k_i} \frac{n(j\vec{q}) + 1}{\omega(j\vec{q})} |F_{in}(j\vec{Q})|^2 , \tag{1.15}$$

where k_i and k_f are the momenta of the incident and scattered neutrons and $\vec{Q} = \vec{k}_i - \vec{k}_f$ is the momentum transfer. The phonon wavevector $\vec{q}$ is given by $\vec{Q} = \vec{q} + \vec{G}$, where $\vec{G}$ is a reciprocal lattice vector, and the occupation number of the phonon mode $(j\vec{q})$ with frequency $\omega(j\vec{q})$ is $n(j\vec{q})$. The inelastic structure factor $F_{in}(j\vec{Q})$ for the mode $(j\vec{q})$ and momentum transfer $\vec{Q}$ is

$$F_{in}(j\vec{Q}) = \sum_{k}^{unit\ cell} m_k^{-\frac{1}{2}} [\vec{Q}.\vec{w}_k(j\vec{q})] b_k \exp(-W_k) \exp(i\vec{G}.\vec{R}_k) , \tag{1.16}$$

where index k labels the nuclei, and b_k, W_k and m_k are the neutron scattering length, the Debye-Waller factor and the mass, respectively, of the nucleus k. For pure transverse modes we may assume that the Debye–Waller factors for all atoms in the cell are the same and factorize the momentum transfer $\vec{Q}$ out of (1.16) leaving the *reduced* structure factor which depends only on the reciprocal lattice vector $\vec{G}$ and is periodic in the reciprocal space. The volume over which it repeats is, however, larger than the Brillouin zone over which the phonon frequency $\omega(j\vec{q})$ repeats, and therefore for each phonon wavevector $\vec{q}$ there are several points $\vec{Q}$ in the reciprocal space with different reduced structure factors. For example in the (100) plane (we are using the pseudocubic notation) there are 4 such points, namely (000),(100),(010) and (110).

Neutron scattering by Yamada and Shirane [7] revealed an interesting anomaly in the temperature dependence of the integrated intensity, which may yield important information about the nature of the TA–TO mode coupling in $SrTiO_3$. If the phonon system is well described in the quasiharmonic approximation, the main temperature dependence in (1.15) will be that of the phonon occupation number $n(j\vec{q})$ and apart from this as well that of the mode frequencies. Using the measured values of $\omega(j\vec{q})$ one can then predict the behaviour of $\frac{d\sigma}{d\Omega}$ as a function of temperature. The energy spectra of scattered neutrons were measured near various reciprocal lattice points and for different phonon polarizations. The results for the $q = 0$ soft TO mode and TA mode with polarization along [110] were in good agreement with theoretical predictions confirming the validity of the quasiharmonic approximation. However, the integrated intensity of the TA mode observed at point (4,0.1,0) (polarization along [100] and wavevector $q = 0.15\mathring{A}$) drops for temperatures less than 50 K to a value which is itself very small and much smaller then predicted by (1.15). On the other hand the integrated intensity of the soft TO mode observed at the same point is in the same temperature interval about twice as high as predicted by (1.15).

No anomaly of this kind was seen around (300) reciprocal lattice point. Similar effects were observed as well in other similar perovskites like $KTaO_3$ and $PbTiO_3$ and at the time of observation no explanation was known for this behaviour. [1]

A first successful theoretical explanation of these effects was given in [8] and was based on the assumption of quasiharmonic q-dependent coupling between acoustic and optic modes. We shall devote more space to this in the second chapter. For the moment we just mention that with decreasing temperature the frequency of the soft TO mode falls down strongly and as it approaches the TA mode from above the coupling between the modes becomes more and more important. It is operative for $q \neq 0$ only and in the lowest order proportional to q^2 (this is the consequence of the fact that the crystal has a center of symmetry). For $q = 0$ it therefore does not act, which is in agreement with the observation in [7], where no anomaly was seen for the $q = 0$ TO mode, and with the usual temperature dependence of the limiting sound velocity. For finite q it is manifested both on frequencies and eigenvectors of the acoustic modes. The TA frequency shows a depression and a substantial amount of $\vec{q} = 0$ TO mode is admixed out of phase into the TA mode eigenvector. This is the mechanism responsible for the lowering of the inelastic structure factor in the neutron scattering experiment. For case of $KTaO_3$ an attempt was done in [8] to predict quantitatively the temperature dependence of the inelastic structure factors including this TO-TA coupling. The result was fairly satisfactory, particularly in the prediction of a completely different behaviour around different reciprocal lattice points. Of course, the knowledge of polarization vector of the $\vec{q} = 0$ soft TO mode is necessary

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[1] Two years earlier, in [16], another anomalous phenomenon related to TA modes in these materials was found. The frequencies of TA modes for $\vec{q} = (\zeta, 0, 0)a^*$ in $KTaO_3$ show a temperature dependence which is quite strong and of opposite sign (the frequency decreases with decreasing temperature) with respect to most materials. However, ultrasound measurements at very long wavelengths did not confirm this observation and revealed rather a weak temperature dependence of the usual sign.

for such a calculation. This eigenvector was determined in [17] for $KTaO_3$, $SrTiO_3$ and $RbMnF_3$ by refinement of the integrated intensity of inelastic neutron scattering measured at many reciprocal lattice points, however, only at room temperature. The conclusion for $SrTiO_3$ was that the TO mode consists predominantly of the so-called Slater mode in which the Sr atoms are at rest and the Ti ion vibrates against the O_6 octahedron with a small admixture of so-called Last mode in which a rigid TiO_6 group vibrates out of phase with the Sr ions. No substantial distortion of the octahedra is involved in the mode. Because of the antiferrodistortive transition at 105 K, however, the polarization pattern of the soft ferroelectric mode below this temperature is certainly somewhat different (the lattice is now tetragonal) from that in the cubic phase, and to our knowledge it has not been neither measured nor calculated. Its detailed knowledge would be very useful because it would allow us to interpret also the new, very recent neutron scattering data [18]. In this work the dispersion curves of TA modes of $SrTiO_3$ were measured for very low values of q in the vicinity of (111) reciprocal lattice point and an anomalous loss of the inelastic structure factor was observed for the [100] branch around $T = 40K$. In agreement with [7] no anomaly was observed for [110] branch. This suggests, that the TA-TO coupling is anisotropic in the q-space, namely maximal for [100] direction and irrelevant for the [110] direction. We mention this point explicitly now because it will become important in the next chapter.

1.3 The EPR anomaly.

Before describing the anomaly itself we remember some basic considerations related to the EPR measurements and to the way in which these are interpreted. To observe an EPR spectrum, a paramagnetic ion is substituted into a nonmagnetic crystal. Due to the presence of the crystal potential, spin levels which in the free ion are $(2S+1)$ times degenerate, become split, and the amount of splitting is related to the strength and the symmetry of the potential. An external magnetic field is then applied which lifts even the remaining degeneracy and the resulting levels are a function of the field orientation relative to the crystal axes. The frequencies corresponding to the transitions between the levels are usually in the microwave region and therefore can be determined by measuring the microwave absorption. A convenient way of representing the experimental situation is to introduce an effective spin hamiltonian, which for our case of tetragonal symmetry reads [11]

$$\mathcal{H} = g\beta\vec{H}\vec{S} + \frac{a}{6}(S_x^4 + S_y^4 + S_z^4 - C) + D[S_\zeta^2 - \frac{1}{3}S(S+1)] \,, \tag{1.17}$$

where a represents the cubic and D the tetragonal splitting, respectively, and ζ is parallel to the tetragonal axis. Because the spin hamiltonian has the point symmetry of the site on which the host atom is placed, EPR spectroscopy is a useful and very sensitive method for investigation of structural phase transitions.

Using Fe^{3+} EPR Unoki and Sakudo [19] for the first time clarified the nature of the 105 K phase transition in $SrTiO_3$ and concluded that the order parameter is the rotation angle ϕ of the antiferrodistortive rotation of the corner-sharing oxygen-octahedra. Its temperature dependence $\phi(T)$ was then determined by Müller et al. (Fig.1.2) using EPR as well. In order to explain the observed behaviour Pytte and Feder worked out a microscopic mean-field theory which reproduced $\phi(T)$ very well in the temperature interval $38K < T < 105K$. For $T < 38K$, an additional reproducible feature was observed (Fig.1.2) , which looks as if at $T = 38K$ there were an onset of an *additional order parameter*. At the time of the observation, no explanation at all was known for this phenomenon.

Because the antiferrodistortive system has already undergone a phase transition at 105 K, one might think that the additional feature is caused by coupling of its order parameter ϕ to another degree of freedom, which has its proper phase transition at T_q. In other words, $\phi(T)$ would in this temperature interval act as a secondary order parameter. If such assumption were true, then two questions would arise:

1) What might be the primary order parameter ? Is it structural, or of another nature ?

2) Are there possibly other secondary order parameters which exhibit an anomalous behaviour near T_q ?

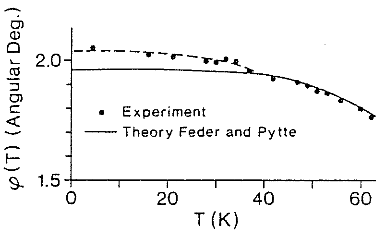

Figure 1.2: Antiferrodistortive rotation-angle measurements in $SrTiO_3$ for $H \parallel [100] - 32^\circ$ in a (001) plane between 4.2 and 50 K at K-band. (After [11].)

Searching for an answer to these questions, a further EPR investigation of $SrTiO_3$ was performed as described in [11]. We shall briefly resume the results of these measurements, referring for details to the original paper. Attention was concentrated on the temperature dependence of the spin hamiltonian parameters themselves and an anomalous behaviour of these was indeed observed both in the tetragonal and in the $< 111 >$ pressure induced trigonal phase. First we describe the effect observed in the tetragonal phase. With the hamiltonian (1.17) and the external magnetic field $\vec{H}$ parallel to the $[11\bar{2}]$ pseudocubic direction, five microwave transitions with $|\Delta M_S| = 1$ are observed. For a tetragonal $\{001\}$ single domain, the distances between the two outer and the two inner spectral lines

Phase	Parameter	
	δa	$\delta\|D\|$
Tetragonal	-1.0	-0.5
Trigonal	-0.9	-0.6

Table 1.1: *Approximate sizes of EPR parameter anomalies in* $10^{-4}cm^{-1} = 1.068 Gauss$ *(*$g = 2.0037$*). Accuracy* $\sim 20\%$*. (After [11].)*

are, in first order of perturbation theory,

$$\Delta H_o^{tet} = \frac{5}{4}a + D \tag{1.18}$$

$$\text{and} \quad \Delta H_i^{tet} = a - 2D \; , \tag{1.19}$$

respectively. On the Fig.1.3 both splittings are plotted as functions of temperature. We see that at $T_q \sim 37K$, ΔH_o^{tet} shows a dip, while ΔH_i^{tet} does not show any anomaly. From the latter fact and from (1.19) we deduce that $\delta a = 2\delta D$ holds for the dip, and from (1.18) it is then possible to calculate the values of δa and δD. These are given in Tab.1.1 and we point to the fact that both a and D are *reduced* at $T = T_q$, while promptly recovering for $T < T_q$.

Investigation under applied $< 111 >$ uniaxial stress revealed a similar effect, perhaps even more pronounced. The EPR spin hamiltonian in this case is also characterized by two splitting parameters, a and D_{trig}, which are both reduced in absolute value (Tab.1.1) at T_q, like in the tetragonal phase (Fig.1.3). Moreover, the pressure dependence of T_q was determined. It is plotted on Fig.1.4, on which the Potts phase boundary between pseudotetragonal and trigonal phase is also shown. We see that as far as the sample remains in the pseudotetragonal phase, the temperature T_q is hardly pressure dependent at all. On the other hand, it is strongly pressure dependent in the trigonal phase, T_q decreasing with increasing pressure. It is important to mention that the anomaly occurs

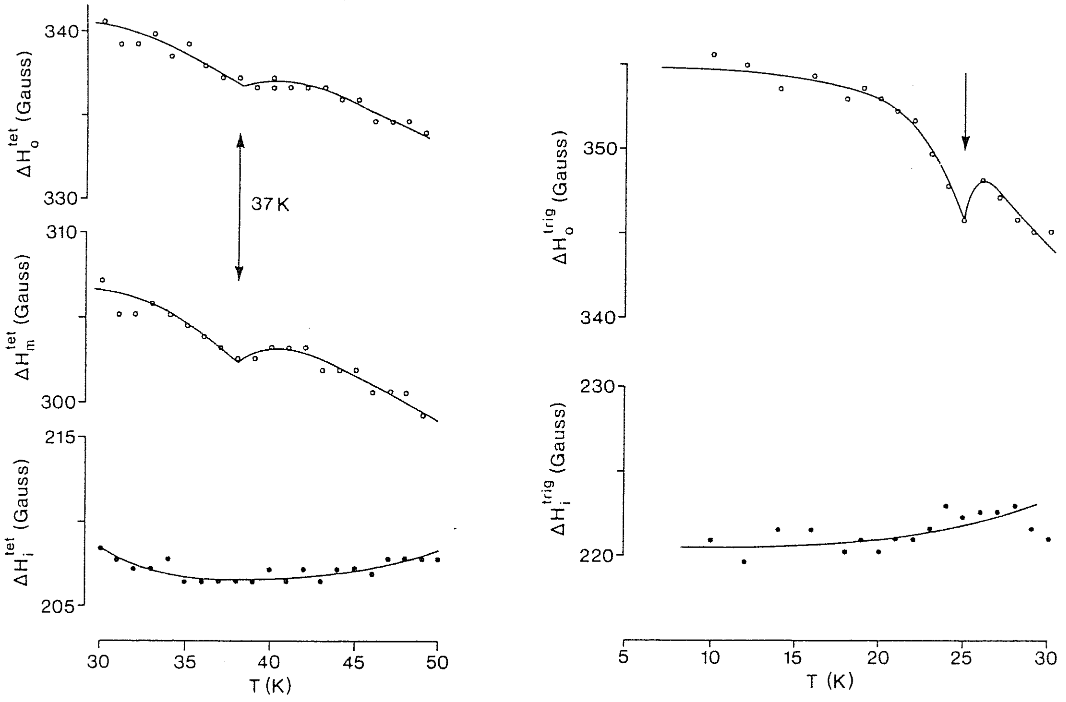

Figure 1.3: Left:Outer and inner Fe^{3+} fine-structure magnetic-field splittings with $\vec{H} \parallel [11\bar{2}]$ measured at a [111] stress of $1.97kg/mm^2$ in the $SrTiO_3$ tetragonal phase between 30 and 50 K due to the {001} domains. The middle splitting H_m^{tet} is due to {100} and {011} domains, which is not further discussed, but clearly shows the anomaly as well. Right: Outer $M = \pm 5/2 \leftrightarrow \pm 3/2$ and inner $M = \pm 3/2 \leftrightarrow \pm 1/2$ fine-structure magnetic resonance field differences with $\vec{H} \parallel [11\bar{2}]$ at a [111] stress of $31.4kg/mm^2$ in the trigonal phase. (After [11].)

at about the same temperature on both sides of the tetragonal-trigonal phase boundary.

In both above mentioned cases, apart from the shift of the outer spectral lines, neither their *number* nor *linewidth* change at T_q. This is a striking feature of the data because it assures that *the spatial symmetry of the lattice does not change at* T_q. A change of the point symmetry of the Ti site would be signaled by an additional splitting of the lines, while an onset of a static incommensurate modulation would be accompanied by a characteristic line broadening due to the loss of translational symmetry in the direction of the modulation. Because it is known that EPR is the most sensitive local method to

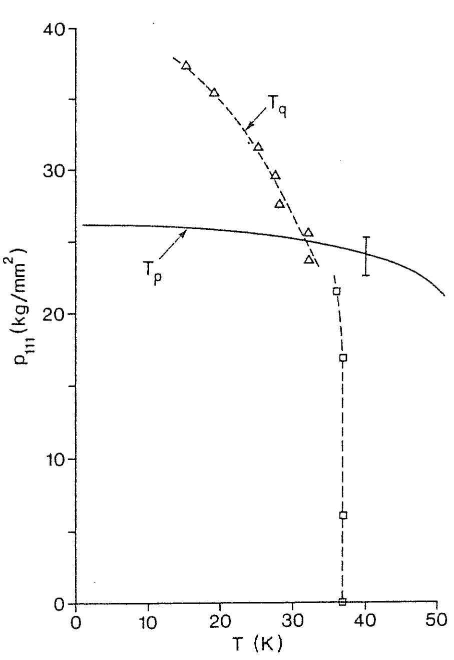

Figure 1.4: Phase diagram of [111] uniaxially p_{111} stressed $SrTiO_3$ as a function of temperature, showing the three-dimensional Potts line between the lower tetragonal and upper trigonal phases, and the dotted line T_q in both phases. (After [11].)

detect structural phase transitions in solids, both possibilities seem to be ruled out. One is thus led to pose a natural question: what does the dip at T_q reflect ? In [11], this point is discussed considering various possibilities. To ensure that the effect in question is really an intrinsic property of the $SrTiO_3$ lattice, a possible local mode dynamics of the Fe^{3+} impurity has to be excluded first. EPR measurements of the Fe^{3+} ion in MgO, in which the oxygen environment of the probe ion is the same (octahedral) as in $SrTiO_3$, did not reveal any analogous phenomenon. Moreover, the sharpness of the dip clearly points to the collective nature of the effect. Because the concentration of Fe^{3+} ions in the sample was very low, it is highly improbable that these would be substantially involved in the effect, which therefore has to be attributed to the *host lattice itself.* As all the splittings

a, D_{tet} and D_{trig} become smaller in absolute value at T_q, the effect mimics a full cubic widening of the lattice.

The shape of the dip suggests that this might indeed be a manifestation of enhanced fluctuations at a phase transition. A suitable candidate for the fluctuating quantity which is sensed by the EPR parameters of the impurity ion could be the *local strain.* This idea is further supported by the observation that the additional feature below 38 K on the $\phi(T)$ curve corresponds to the relative increase of ϕ by about 5%, which is close to about 7% observed by Uwe and Sakudo [6] at the onset of *stress induced ferroelectricity.* On the other hand, T_q is very close to the extrapolated Curie-Weiss temperature of 37 K, where $SrTiO_3$ would become ferroelectric, were it not for quantum effects. We are thus led to an idea of a phase transition in which possibly the lattice strains and the ferroelectric mode are involved at the same time, even if we are not yet able to specify the actual primary order parameter.

Several other arguments can now be presented in favour of such idea. Bednorz and Müller [20] observed, that it is possible to induce an XY-type ferroelectricity in $SrTiO_3$ by doping it with Ca. The onset of ferroelectricity is observed at concentration $x_{Ca} = 0.0018$ and with increasing x_{Ca} the Curie temperature first progressively increased and then saturated at $T_S \sim 35K$. Maglione et al. [25] measured the frequency dependence of the dielectric constant in $SrTiO_3$ at low temperatures and fitted this with a Debye expression. Approaching from below the temperature of $\sim 40K$, the relaxation time goes to zero.

How is it possible to combine all the above facts into a consistent and meaningful picture ? We already mentioned in the last section that with decreasing temperature the coupling between the lattice strains and the ferroelectric mode becomes more and more important. As was first pointed out by Axe [8], such TA–TO coupling can lead to a depression of the TA dispersion curve, and being sufficiently strong, even to a formation of a minimum on this for $k_0 \neq 0$ (Fig.1.5). We shall investigate such situation in detail in the next chapter. If the TA curve were really depressed to zero, then an incommensurate phase would onset, which, as we mentioned above, does not seem to be the case. If the curve, however, does not go to zero, then one is reminded of the rotonic minimum on the curve of elementary excitations of liquid ^4He, in which a phase transition into a *superfluid coherent quantum state* occurs. In analogy to this, we suggest that in our case a phase transition into a *quantum melted incommensurate phase* may occur, and we may expect such state to have some peculiar coherence properties.

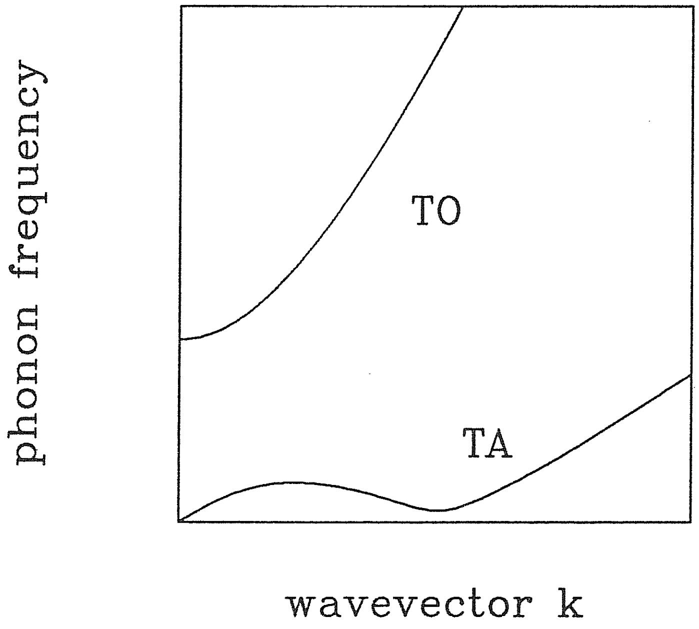

Figure 1.5: Dispersion curves of TA and TO phonons in presence of their mutual coupling. The minimum at k_0 on the TA curve is visible.

The rest of the thesis is devoted to investigation of this idea, which was qualitatively put forward in [11]. First we describe, in the second chapter, the properties of the corresponding *classical* incommensurate phase. In the third chapter we then speculate about the way in which such phase may be affected and destroyed by quantum fluctuations, and we try to figure out some of its properties. In the fourth, final chapter, we discuss the available results and draw some tentative conclusions.

2 Classical mechanics: possibility of a modulated (incommensurate) phase.

In this chapter we consider the onset of an incommensurate phase at T_q as a kind of classical precursor phenomenon of the observed effect. In the present context, the possible relevance of an incommensurate ferroelectric state was suggested to the authors of [11] by H. Thomas. It is known that certain materials exhibiting structural phase transitions, rather than transforming at some temperature T_C directly from the high temperature commensurate phase to the low temperature commensurate phase, undergo instead two successive transitions. With decreasing temperature they first, at a certain temperature T_I, undergo a second order phase transition into the incommensurate (INC) phase, characterized by the onset of a spatially modulated order parameter. The specific feature distinguishing this phase transition from others is that at least one component of the modulation wavevector q is an irrational multiple of the corresponding basic reciprocal lattice vector. The modulated phase is therefore, strictly speaking, not crystalline, because it does not anymore possess a translational symmetry in the direction of modulation. By further decreasing the temperature, the amplitude of the modulation progressively increases and the modulation wavevector q changes slightly, but continuously. This temperature dependence of the modulation wavevector is a characteristic feature of a genuine INC phase. In certain cases the modulation pattern with decreasing temperature exhibits a pronounced structuration into domains. Inside each domain, the structure of the phase is close to commensurate. The domains are separated by domain walls, sometimes called "spatial solitons", "phase solitons", or "discommensurations", in which the modulation abruptly changes its phase. Domains and sharp domain walls, it should be stressed, are quite common, but by no means a universal feature of the INC phase. Sometimes the modulation is totally continuous, without detectable domain walls. Reaching a lower temperature $T_L < T_I$, the INC systems usually undergo another (INC-C) phase transition, which may be of first or of second order. The phase stable for $T < T_L$ is a low symmetry commensurate phase, which is characterized by a spatial modulation with a wavevector q, whose components are simple rational multiples of the basic reciprocal lattice vectors of the high-temperature phase. They also are, unlike in the INC phase, temperature independent. This phase transition is usually called the "lock-in" transition, since it causes all the elementary periods of the system to "lock-in" on certain multiples of the reciprocal lattice vectors. In certain cases, the lock-in transition may be absent - the system then remains in the INC phase down to $T = 0$. We shall not be concerned with lock-in transition anyfurther, and focus on the properties of a hypothetical INC phase in $SrTiO_3$.

Like other transitions, the phase transition to INC phase can be described on the phenomenological level within the frame of extended Landau theory [1]. The necessary extension consists essentially in accounting for the expansion of the free energy density as a function not only of the components of the order parameter, but also of their spatial derivatives. The global free energy therefore becomes a functional of spatially dependent components of the order parameter and the equilibrium configuration for given values of temperature and external parameters is found as a solution of a variational problem.

The continuum Landau theory allows a natural classification of the possible forms of the free-energy functional for an INC transition. A dividing criterion is the presence of the so-called Lifshitz invariant. The incommensurate phases arising from free energy functionals containing the Lifshitz invariant are referred to as type I INC phases and those arising from functionals without this invariant as type II INC phases [2]. The properties of those two kinds of INC phases are markedly different. In type I INC phases the lock-in transition is either continuous, or only slightly discontinous, and approaching the temperature T_L they exhibit the structuration of the modulated phase into the "soliton lattice". On the other hand, the modulation of the type II INC phases remains practically sinusoidal down to the temperature T_L and the lock-in transition is always of the first order. It is the type II INC phase scheme which we are going to consider in what follows, in the context of $SrTiO_3$.

2.1 The free energy of the model.

There have been several constructions of the Landau expansion of the free energy of $SrTiO_3$ related both to the antiferrodistortive phase transition at 105 K [4] and to the incipient ferroelectricity [5]. The most complete of such treatments, that of Uwe and Sakudo [6], expanded the Helmholtz free energy density f as a function of polarization components P_i, octahedron rotation angles Φ_i and homogeneous lattice strains e_{ij}. Their expression for the high temperature $T > 105K$ cubic phase reads

$$f(P_i, \phi_i, e_{ij}) = f_0 \quad + \quad \frac{1}{2}\gamma_0 \sum_i P_i^2 + D^x(\sum_i P_i^2)^2 + \frac{1}{2}D_n^x \sum_{i \neq j} P_i^2 P_j^2$$

$$
\begin{aligned}
&+ \quad \frac{1}{2}\kappa_0 \sum_i \Phi_i^2 + A^x\Big(\sum_i \Phi_i^2\Big)^2 + \frac{1}{2}A_n^x \sum_{i\neq j} \Phi_i^2 \Phi_j^2 \\
+\frac{1}{2}\sum_{ijkl} c_{ijkl} e_{ij} e_{kl} &- \sum_{ijkl}\left(g_{ijkl} e_{ij} P_k P_l + b_{ijkl} e_{ij} \Phi_k \Phi_l + t^x_{ijkl} P_i P_j \Phi_k \Phi_l\right), \qquad (2.1)
\end{aligned}
$$

where the coefficients g_{ijkl} account for the electrostrictive coupling between the components of polarization and lattice strain and the last term corresponds to the 4-th order coupling between the components of the two distinct order parameters. This expression will serve us as a starting point for our considerations.

As we already mentioned in the Introduction, the ferroelectric behaviour of $SrTiO_3$ is XY like. What this means is that once the antiferrodistortive order parameter has set in, $< \phi_3 > \neq 0$ for $T < 105K$, then the possibility to force ferroelectricity along the same direction (i.e. $< P_3 > \neq 0$) is suppressed. In our model we shall therefore restrict ourselves to polarization vectors lying in the (001) plane, i.e. only P_1 and P_2 will be allowed to be non-zero. Because the anomaly we want to explain occurs at temperatures $T_q \leq 37K$, which is quite far from the 105 K antiferrodistortive transition, we do not expect the antiferrodistortive mode to be primarily involved. It has been noted in [11], however, that some involvement could arise, since precisely near $\sim 35K$ the antiferrodistortive and the ferroelectric soft mode frequencies at $\vec{q} = 0$ cross. As a first approximation we shall therefore not include the octahedron rotations Φ_i among the variables on which the free energy depends. We may assume that the free energy has already been minimized with respect to Φ_i and all the remaining parameters have then been properly renormalized. Clearly, further refinements will be needed when considering small changes of $< \phi_3 >$ induced by the INC phase.

We must now choose the directions along which our continuum variables (or fields) will be spatially dependent. Actually, at the moment, nothing is known about the dispersion curves of the phonons in *tetragonal* $SrTiO_3$ for wavevectors off the xy plane. Neutron scattering measurements of Stirling [24] were performed at the lowest temperature of 90 K at which $SrTiO_3$ is still almost cubic. From the phonon dispersion curves [7] of TA and soft TO phonons with wavevectors *in the xy plane* it can be seen that the direction of lowest frequency is along [100]. Soft phonons with such wavevectors are therefore most likely to condense, and this agrees with the anisotropic character of the TA-TO coupling mentioned in section 1.2. It is however clear that we cannot *a priori* exclude the possibility of a modulation also along the tetragonal c-axis. In any case we believe that a possible unstable wavevector should be of the form $\vec{k} = (k_x, 0, k_z)$ rather than $\vec{k} = (k_x, k_x, k_z)$. For the sake of simplicity we shall develop the model for modulation directions restricted to the xy-plane, since all the relevant physics can be demonstrated within this frame. In the end of this chapter we then briefly mention the case of modulation also along the c-axis. All the variables involved are therefore P_1, P_2, e_{11}, e_{22} and e_{12}, and depend on spatial coordinates x_1 and x_2.

Now having left only polarization components and lattice strains in the free energy expansion we obtain a model in which the softening of a phonon branch leading finally to an onset of INC phase results from the mutual interaction of a polar optical and a non-polar acoustical mode. As we already mentioned in the section 1.3, this idea was first expressed in 1970 by Axe et al [8]. They spoke about a "phase with sinusoidally modulated spontaneous displacements", which is just the INC phase. The idea was then subsequently formalized by Aslanyan and Levanyuk [9], [10], who considered it as a mechanism of formation of an INC structure in quartz, a type II case, where the free energy does not contain the Lifshitz invariant, because the order parameter has only one component.

To obtain the model for an INC phase we must now supply the free energy with terms containing the spatial gradients of the fields. First of all, in spite of the fact, that we have two components of polarization, the free energy *cannot contain the Lifshitz invariant*, because that is incompatible with the presence of the center of symmetry. We therefore introduce a coupling between the lattice strains and the components of polarization of the form

$$\sum_{ijkl} h_{ijkl} e_{ij} \frac{\partial P_k}{\partial x_l}, \tag{2.2}$$

which is a generalization of the form adopted in [9]. Apart from the coupling, we must add terms providing the dispersion of bare optical phonons, at least near $\vec{q} = 0$. We therefore introduce a squared gradient term of the form

$$\sum_{ijkl} s_{ijkl} \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l}. \tag{2.3}$$

In order to have an INC phase this term must become, after renormalization due to the coupling, negative for some direction in the (001) plane in the k-space. To stabilize the dispersion we must therefore introduce another term quadratic in $\vec{P}$ and of higher order than 2 in $\vec{k}$. Due to the presence of the center of symmetry this must be of 4-th order in $\vec{k}$ and for simplicity we can take it isotropic like

$$r\,(\nabla^2 \vec{P})^2 . \tag{2.4}$$

The form of the 4-th rank tensors h_{ijkl} and s_{ijkl} is dictated by the point group of the symmetry of the crystal. The point group of the tetragonal phase of $SrTiO_3$ is D_{4h} and it can easily be seen that it admits 3 invariants in the term (2.2) and 4 invariants in the term (2.3). It is important to take all these terms into consideration because they will give rise to the angular dependence of the stiffness in k-space and therefore determine the possible directions of INC modulation. We can now recast the total free energy of the system in the form

$$\begin{aligned}
F &= F_0 + \int f(P_i(\vec{r}), e_{ij}(\vec{r}))\, d^3\vec{r} && (2.5)\\
f &= \frac{1}{2}\alpha(P_1^2+P_2^2) + \frac{1}{4}\beta_1(P_1^4+P_2^4) + \frac{1}{2}\beta_2 P_1^2 P_2^2 + \\
&+ \frac{1}{2}c_{11}(e_{11}^2+e_{22}^2) + c_{12}e_{11}e_{22} + 2c_{66}e_{12}^2 - \\
&- g_{11}(e_{11}P_1^2 + e_{22}P_2^2) - g_{12}(e_{11}P_2^2 + e_{22}P_1^2) - g_{66}e_{12}P_1P_2 + \\
&+ h_1(e_{11}+e_{22})\left(\frac{\partial P_1}{\partial x_1} + \frac{\partial P_2}{\partial x_2}\right) + h_2(e_{11}-e_{22})\left(\frac{\partial P_1}{\partial x_1} - \frac{\partial P_2}{\partial x_2}\right) + \\
&+ h_3 e_{12}\left(\frac{\partial P_1}{\partial x_2} + \frac{\partial P_2}{\partial x_1}\right) + s_1\left[\left(\frac{\partial P_1}{\partial x_1}\right)^2 + \left(\frac{\partial P_2}{\partial x_2}\right)^2\right] + \\
&+ s_2\left[\left(\frac{\partial P_1}{\partial x_2}\right)^2 + \left(\frac{\partial P_2}{\partial x_1}\right)^2\right] + s_4\frac{\partial P_1}{\partial x_1}\frac{\partial P_2}{\partial x_2} + s_5\frac{\partial P_1}{\partial x_2}\frac{\partial P_2}{\partial x_1} + \\
&+ r\,(\nabla^2\vec{P})^2\,, && (2.6)
\end{aligned}$$

where some of the tensor components have been grouped together. As usually we assume all the coefficients to be temperature independent except for α. However, since we are in the region in which the temperature dependence of this coefficient is determined by quantum effects, we shall not try to specify it more explicitly and just state, that for $SrTiO_3$ under zero stress, $\alpha > 0$ for all $T > 0$.

To proceed further it is convenient to deal with the spatial Fourier transforms of the fields. We therefore introduce them with the relations

$$\begin{aligned}
P_i(\vec{r}) &= \sum_{\vec{k}} P_{i\vec{k}} \exp(i\vec{k}.\vec{r}) && (2.7)\\
u_i(\vec{r}) &= \sum_{\vec{k}} u_{i\vec{k}} \exp(i\vec{k}.\vec{r}) && (2.8)\\
e_{ij}(\vec{r}) &= \epsilon_{ij} + \frac{i}{2}\sum_{\vec{k}\neq 0}(k_i u_{j\vec{k}} + k_j u_{i\vec{k}})\exp(i\vec{k}.\vec{r})\,, \quad i,j = 1,2 \quad , && (2.9)
\end{aligned}$$

where we expressed the lattice strains $e_{ij}(\vec{r})$ through the acoustic displacements $\vec{u}(\vec{r})$ and separated the contribution of homogeneous strains ϵ_{ij}. Substituting these relations into (2.6) we obtain

$$\begin{aligned}
F &= F_0 + V \sum_{\vec{k}} f_{\vec{k}} &\quad (2.10)\\
f_{\vec{k}} &= \frac{1}{2}\alpha(|P_{1\vec{k}}|^2 + |P^2_{2\vec{k}}|) + \\
&+ \frac{1}{4}\beta_1 \sum_{\vec{k}'\vec{k}''\vec{k}'''} (P_{1\vec{k}}P_{1\vec{k}'}P_{1\vec{k}''}P_{1\vec{k}'''} + P_{2\vec{k}}P_{2\vec{k}'}P_{2\vec{k}''}P_{2\vec{k}'''})\,\delta(\vec{k}+\vec{k}'+\vec{k}''+\vec{k}''') + \\
&+ \frac{1}{2}\beta_2 \sum_{\vec{k}'\vec{k}''\vec{k}'''} P_{1\vec{k}}P_{1\vec{k}'}P_{2\vec{k}''}P_{2\vec{k}'''}\,\delta(\vec{k}+\vec{k}'+\vec{k}''+\vec{k}''') + \\
&+ \frac{1}{2}c_{11}(\epsilon_{11}^2 + \epsilon_{22}^2) + c_{12}\epsilon_{11}\epsilon_{22} + 2c_{66}\epsilon_{12}^2 + \frac{1}{2}c_{11}(k_1^2|u_{1\vec{k}}|^2 + k_2^2|u_{2\vec{k}}|^2) + \\
&+ c_{12}k_1k_2u_{1\vec{k}}u^*_{2\vec{k}} + \frac{1}{2}c_{66}(k_1^2|u_{2\vec{k}}|^2 + k_2^2|u_{1\vec{k}}|^2 + 2k_1k_2u_{1\vec{k}}u^*_{2\vec{k}}) - \\
&- g_{11}\left(\epsilon_{11}|P_{1\vec{k}}|^2 + \epsilon_{22}|P_{2\vec{k}}|^2\right) - g_{12}\left(\epsilon_{11}|P_{2\vec{k}}|^2 + \epsilon_{22}|P_{1\vec{k}}|^2\right) - g_{66}\epsilon_{12}P_{1\vec{k}}P^*_{2\vec{k}} - \\
&- g_{11}i \sum_{\vec{k}'\vec{k}''} (k_1u_{1\vec{k}}P_{1\vec{k}'}P_{1\vec{k}''} + k_2u_{2\vec{k}}P_{2\vec{k}'}P_{2\vec{k}''})\,\delta(\vec{k}+\vec{k}'+\vec{k}'') - \\
&- g_{12}i \sum_{\vec{k}'\vec{k}''} (k_1u_{1\vec{k}}P_{2\vec{k}'}P_{2\vec{k}''} + k_2u_{2\vec{k}}P_{1\vec{k}'}P_{1\vec{k}''})\,\delta(\vec{k}+\vec{k}'+\vec{k}'') - \\
&- g_{66}\frac{i}{2} \sum_{\vec{k}'\vec{k}''} (k_1u_{2\vec{k}} + k_2u_{1\vec{k}})P_{1\vec{k}'}P_{2\vec{k}''}\,\delta(\vec{k}+\vec{k}'+\vec{k}'') + \\
&+ h_1(k_1u_{1\vec{k}} + k_2u_{2\vec{k}})(k_1P^*_{1\vec{k}} + k_2P^*_{2\vec{k}}) + h_2(k_1u_{1\vec{k}} - k_2u_{2\vec{k}})(k_1P^*_{1\vec{k}} - k_2P^*_{2\vec{k}}) + \\
&+ \frac{h_3}{2}(k_1u_{2\vec{k}} + k_2u_{1\vec{k}})(k_2P^*_{1\vec{k}} + k_1P^*_{2\vec{k}}) + s_1(k_1^2|P_{1\vec{k}}|^2 + k_2^2|P_{2\vec{k}}|^2) + \\
&+ s_2(k_2^2|P_{1\vec{k}}|^2 + k_1^2|P_{2\vec{k}}|^2) + (s_4 + s_5)k_1k_2P_{1\vec{k}}P^*_{2\vec{k}} + rk^4(|P_{1\vec{k}}|^2 + |P^2_{2\vec{k}}|)\,. &\quad (2.11)
\end{aligned}$$

2.2 Loss of stability of the high-temperature phase.

In this section we shall investigate the stability of the homogeneous commensurate phase with respect to the formation of an INC modulated phase. For this purpose we need to consider only the quasiharmonic part of the free energy as a function of $P_{1\vec{k}}, P_{2\vec{k}}, u_{1\vec{k}}, u_{2\vec{k}}$.

This reads

$$\begin{aligned}
f'_{\vec{k}} &= \frac{1}{2}\alpha(|P_{1\vec{k}}|^2 + |P_{2\vec{k}}|^2) + \frac{1}{2}c_{11}(k_1^2|u_{1\vec{k}}|^2 + k_2^2|u_{2\vec{k}}|^2) + \\
&+ c_{12}k_1k_2u_{1\vec{k}}u^*_{2\vec{k}} + \frac{1}{2}c_{66}(k_1^2|u_{2\vec{k}}|^2 + k_2^2|u_{1\vec{k}}|^2 + 2k_1k_2u_{1\vec{k}}u^*_{2\vec{k}}) + \\
&+ \gamma_1(k_1^2u_{1\vec{k}}P^*_{1\vec{k}} + k_2^2u_{2\vec{k}}P^*_{2\vec{k}}) + \gamma_2k_1k_2(u_{1\vec{k}}P^*_{2\vec{k}} + u_{2\vec{k}}P^*_{1\vec{k}}) + \\
&+ \gamma_3\left[k_1k_2(u_{2\vec{k}}P^*_{1\vec{k}} + u_{1\vec{k}}P^*_{2\vec{k}}) + k_1^2u_{2\vec{k}}P^*_{2\vec{k}} + k_2^2u_{1\vec{k}}P^*_{1\vec{k}}\right] + \\
&+ s_1(k_1^2|P_{1\vec{k}}|^2 + k_2^2|P_{2\vec{k}}|^2) + s_2(k_2^2|P_{1\vec{k}}|^2 + k_1^2|P_{2\vec{k}}|^2) + \\
&+ s_3k_1k_2P_{1\vec{k}}P^*_{2\vec{k}} + rk^4(|P_{1\vec{k}}|^2 + |P_{2\vec{k}}|^2) \quad , \qquad (2.12)
\end{aligned}$$

where we denoted $\gamma_1 = h_1 + h_2$, $\gamma_2 = h_1 - h_2$, $\gamma_3 = h_3/2$, $s_3 = s_4 + s_5$.

It is convenient now to pass to longitudinal and transverse coordinates of P_1, P_2, u_1, u_2. We introduce these through relations

$$\begin{aligned}
u_{l\vec{k}} &= u_{1\vec{k}}\cos(\vartheta) + u_{2\vec{k}}\sin(\vartheta) \\
u_{t\vec{k}} &= -u_{1\vec{k}}\sin(\vartheta) + u_{2\vec{k}}\cos(\vartheta) \quad , \qquad (2.13)
\end{aligned}$$

and similarly for $P_{l\vec{k}}$, $P_{t\vec{k}}$. The angle ϑ is the angle between the wavevector $\vec{k}$ and the x-axis. If the system were isotropic in the plane, then these coordinates would be just the eigenvectors of bare acoustical and optical phonons. Substituting to (2.12) we get

$$\begin{aligned}
f'_{\vec{k}} &= (\frac{1}{2}\alpha + rk^4)(|P_{l\vec{k}}|^2 + |P_{t\vec{k}}|^2) + \\
&+ \Big[\frac{1}{2}(c_1 - c_0\cos 4\vartheta)|u_{l\vec{k}}|^2 + \frac{1}{2}(c_2 + c_0\cos 4\vartheta)|u_{t\vec{k}}|^2 + \\
&+ \frac{1}{4}(\gamma + \gamma_0\cos 4\vartheta)u_{l\vec{k}}P^*_{l\vec{k}} + \frac{1}{4}(\gamma' - \gamma_0\cos 4\vartheta)u_{t\vec{k}}P^*_{t\vec{k}} + \\
&+ \frac{1}{4}(s + s_0\cos 4\vartheta)|P_{l\vec{k}}|^2 + \frac{1}{4}(s' - s_0\cos 4\vartheta)|P_{t\vec{k}}|^2 + \\
&+ \sin 4\vartheta\left(c_0u^*_{l\vec{k}}u_{t\vec{k}} - \frac{1}{4}\gamma_0(u_{l\vec{k}}P^*_{t\vec{k}} + u_{t\vec{k}}P^*_{l\vec{k}}) - \frac{1}{2}s_0P_{l\vec{k}}P^*_{t\vec{k}}\right)\Big]\,k^2 \, , \qquad (2.14)
\end{aligned}$$

where we introduced the following new coefficients

$$\begin{array}{lll} c_0 = -\frac{1}{4}(2c_{66} - c_{11} + c_{12}) \ , & s_0 = s_1 - s_2 - \frac{1}{2}s_3 \ , & \gamma_0 = \gamma_1 - \gamma_2 - 2\gamma_3 \ , \\ c_1 = c_{11} - c_0 \ , & s = 3s_1 + s_2 + \frac{1}{2}s_3 \ , & \gamma = 3\gamma_1 + \gamma_2 + 2\gamma_3 \ , \\ c_2 = \frac{1}{2}(c_{11} - c_{12}) - c_0 \ , & s' = s_1 + 3s_2 - \frac{1}{2}s_3 & \gamma' = \gamma_1 - \gamma_2 + 2\gamma_3 \ . \end{array} \tag{2.15}$$

Now for modes with sufficiently low frequency, like the soft optical modes close to the phase transition and acoustical modes with small wavevector, it is the free energy F that plays the role of potential energy in the corresponding dynamical problem. The long wavelength lattice vibrations are represented by the small oscillations of the displacements and polarizations around their equilibrium values. Since the homogeneous lattice strains cannot follow the much faster optical vibrations, the latter go on practically at constant values of ϵ_{ij} corresponding to equilibrium state and for the case of zero stress these are zero. Therefore we do not keep in our quasiharmonic free energy $f'_{\vec{k}}$ terms quadratic in $P_{1\vec{k}}, P_{2\vec{k}}$ which originate from the electrostrictive coupling. Introducing the appropriate "mass densities" m_u and m_P (m_P contains the effective ionic charge per unit volume and does not have the dimension of mass), and adding the kinetic energy term

$$T = \int t(\dot{P}_i(\vec{r}), \dot{u}_i(\vec{r}))\, d^3\vec{r} \tag{2.16}$$

$$t(\vec{r}) = \frac{1}{2}m_u \sum_i \dot{u}_i^2(\vec{r}) + \frac{1}{2}m_P \sum_i \dot{P}_i^2(\vec{r}) \tag{2.17}$$

to (2.12) we obtain the effective quasiharmonic hamiltonian (we set the volume $V = 1$)

$$H_{qh}^{eff} = \frac{1}{2}m_u \sum_{i,\vec{k}} \dot{u}_{i\vec{k}} \dot{u}^*_{i\vec{k}} + \frac{1}{2}m_P \sum_{i,\vec{k}} \dot{P}_{i\vec{k}} \dot{P}^*_{i\vec{k}} + \sum_{\vec{k}} f'_{\vec{k}} \ . \tag{2.18}$$

The equations of motion for the spatial Fourier components of $\vec{P}$ and $\vec{u}$ then yield

$$m_u \omega^2 u_{i\vec{k}} = \frac{\partial f'_{\vec{k}}}{\partial u^*_{i\vec{k}}} \tag{2.19}$$

$$m_P \omega^2 P_{j\vec{k}} = \frac{\partial f'_{\vec{k}}}{\partial P^*_{j\vec{k}}} \quad , \quad i, j = l, t \ , \tag{2.20}$$

which is a 4×4 matrix problem for the eigenfrequencies ω .

To be rigorous at this point we notice that the above formulation of the dynamical problem does not take into account the coupling of the polarization to the macroscopic electric field resulting from the longitudinal part of the optical displacement and therefore does not lead to the splitting between TO and LO phonon frequencies at $q = 0$. Phenomenologically, we could introduce a splitting just replacing by hand the stiffness α in (2.14) by another stiffness α_l corresponding to $P_{l\vec{k}}$. According to [5] at $T \sim 40K$ the lowest LO phonon frequency is an order of magnitude higher than that of the soft TO phonon and therefore α_l would be about two orders of magnitude higher than α. This means that the longitudinal component $P_{l\vec{k}}$ is effectively decoupled from the problem. Therefore we shall use the free energy in the above form and from now on set simply $P_{l\vec{k}} = 0$.

Now the stability of the homogeneous commensurate phase will be lost if the frequency of one of the branches becomes equal to 0 for a wavevector $q \neq 0$. This is most likely to happen for the TA branch which is pushed down due to its interaction with the soft TO branch. Let us therefore investigate in more detail the TA dispersion curve resulting from (2.20), for the moment e.g. for wavevectors along [100] direction, i.e. $\vartheta = 0$. Since for this high symmetry direction the longitudinal component $u_{l\vec{k}}$ is decoupled (2.14), we have only a 2×2 matrix problem to solve:

$$\begin{vmatrix} (c_2 + c_0)k^2 - m_u\omega^2 & \frac{1}{4}(\gamma' - \gamma_0)k^2 \\ \frac{1}{4}(\gamma' - \gamma_0)k^2 & \alpha + \frac{1}{2}(s' - s_0)k^2 + 2rk^4 - m_P\omega^2 \end{vmatrix} = 0 \qquad (2.21)$$

This eigenvalue equation for sufficiently strong coupling (represented in this case by $\gamma' - \gamma_0$) will give rise to dispersion curves for the transverse branches shown in the Fig.1.5. With decreasing temperature (we remember that the only temperature dependent quantity is

$\alpha(T)$ which is proportional to the square of the bare TO phonon frequency $\Omega^2_{TO}(T)$) both the optical and the acoustical branches soften and the loss of stability occurs when the minimum on the TA branch first touches the $\omega = 0$ axis. At this point the following 2 conditions must be simultaneously satisfied

$$\begin{aligned} \omega_{TA}(k_0) &= 0 \\ \left.\frac{d\omega_{TA}(k)}{dk}\right|_{k=k_0} &= 0 \,. \end{aligned} \tag{2.22}$$

In our case they read

$$\alpha(T_I) + \left[\frac{1}{2}(s' - s_0) - \frac{(\gamma' - \gamma_0)^2}{16(c_2 + c_0)}\right] k_0^2 + 2rk_0^4 = 0 \tag{2.23}$$

$$\alpha(T_I) + \left[s' - s_0 - \frac{(\gamma' - \gamma_0)^2}{8(c_2 + c_0)}\right] k_0^2 + 6rk_0^4 = 0 \ . \tag{2.24}$$

Solving them we obtain the temperature T_I and wavevector k_0 of the instability. We shall give the solution later on when we approach the problem slightly more generally. At the moment we just want to point out two facts. First, as we can see from (2.24), the coefficient of the term quadratic in k_0 in this equation must be negative, if the equation is to have a real solution for $\alpha(T) > 0$. This gives a quantitative meaning to the words "sufficiently strong coupling" used above. Second, from the same equation we see that irrespective of the sign of $\gamma' - \gamma_0$ the coupling always tends to destabilize the system.

Now we shall investigate a more general situation not restricting ourselves to wavevectors along any particular direction. Searching for temperature and wavevector at which the frequency of some branch first time goes to zero is according to (2.20) equivalent to solving the set of equations

$$\frac{\partial f'_{\vec{k}}}{\partial u^*_{i\vec{k}}} = 0 \tag{2.25}$$

$$\frac{\partial f'_{\vec{k}}}{\partial P^*_{j\vec{k}}} = 0 \ . \tag{2.26}$$

In other words, it is equivalent to minimizing the free energy with respect to all variables and searching for the point, where this minimum for the first time corresponds to their non-zero values.

Substituting for the elastic constants c_{11}, c_{12}, c_{44} their experimental values for $SrTiO_3$ (taken from [6] and converted to SI units these are $c_{11} = 3.36\times10^{11}$, $c_{12} = 1.07\times10^{11}$, $c_{44} = 1.27 \times 10^{11}\ Jm^{-3}$) we obtain $c_0 = 0.06 \times 10^{11}$, $c_1 = 3.42 \times 10^{11}$, $c_2 = 1.20 \times 10^{11}\ Jm^{-3}$. Because $c_0 \ll c_1, c_2$, we can clearly neglect the term which is off diagonal in acoustic displacements in (2.14) (because the elastic properties in the plane are only very slightly anisotropic) and write

$$\begin{aligned}
\frac{\partial f'_{\vec{k}}}{\partial u^*_{l\vec{k}}} &= k^2 c_1 u_{l\vec{k}} - \frac{1}{4} k^2 \gamma_0 \sin 4\vartheta P_{t\vec{k}} = 0 \\
\frac{\partial f'_{\vec{k}}}{\partial u^*_{t\vec{k}}} &= k^2 c_2 u_{t\vec{k}} + \frac{1}{4} k^2 (\gamma' - \gamma_0 \cos 4\vartheta) P_{t\vec{k}} = 0 \ .
\end{aligned} \tag{2.27}$$

Substituting for $u_{l\vec{k}}, u_{t\vec{k}}$ from these equations to (2.14) we get the free energy $f'_{\vec{k}}$ as a function of $P_{t\vec{k}}$ only

$$\begin{aligned}
f'_{\vec{k}} &= \frac{1}{2}\alpha' |P_{t\vec{k}}|^2 \ , \\
\alpha' &= \alpha + \left(\frac{1}{2}(s' - s_0 \cos 4\vartheta) - \frac{1}{16 c_1}\gamma_0^2 \sin^2 4\vartheta - \frac{1}{16 c_2}(\gamma' - \gamma_0 \cos 4\vartheta)^2 \right) k^2 + r k^4 \ .
\end{aligned} \tag{2.28}$$

The instability occurs when the expression denoted as α' becomes equal to zero. Therefore we search for its minimum as a function of both ϑ and k. We obtain

$$\sin 4\vartheta \left[s_0 - \frac{1}{4c_1}\gamma_0^2 \cos 4\vartheta - \frac{\gamma_0}{4c_2}(\gamma' - \gamma_0 \cos 4\vartheta) \right] = 0 \ . \tag{2.29}$$

We see that we have a symmetry-determined extreme if $\sin 4\vartheta = 0$ or an occasional extreme if the expression in the square brackets is equal to zero. We shall consider only symmetry determined extremes which occur for $\vartheta = 0$ or $\vartheta = \pi/4$ and equivalent directions. The conditions for these extremes to be minima are

$$s_0 - \frac{1}{4c_1}\gamma_0^2 - \frac{\gamma_0(\gamma' - \gamma_0)}{4c_2} > 0 \tag{2.30}$$

when $\vartheta = 0$ and

$$s_0 + \frac{1}{4c_1}\gamma_0^2 - \frac{\gamma_0(\gamma' + \gamma_0)}{4c_2} < 0 \tag{2.31}$$

when $\vartheta = \pi/4$.

Now we investigate the behaviour with respect to k for both above cases. For $\vartheta = 0$ we get

$$f'_{\vec{k}} = \left[\frac{1}{2}\alpha + \left(\frac{1}{4}(s' - s_0) - \frac{1}{32c_2}(\gamma' - \gamma_0)^2\right) k^2 + rk^4\right] |P_{t\vec{k}}|^2 \tag{2.32}$$

for the free energy. In order to have a minimum as a function of k, the coefficient of k^2 in this equation must be negative. This implies

$$(\gamma' - \gamma_0)^2 > 8c_2(s' - s_0) \tag{2.33}$$

as the *necessary* condition for the onset of an INC phase. Provided it is satisfied the minimum of (2.32) occurs for a wavevector k_0 which is determined by

$$k_0 = \sqrt{\frac{1}{2r}\left[\frac{1}{32c_2}(\gamma' - \gamma_0)^2 - \frac{1}{4}(s' - s_0)\right]}. \tag{2.34}$$

An INC phase with the modulation wavevector k_0 sets on at a temperature T_I obeying the condition

$$\alpha(T_I) = \frac{1}{2r}\left[\frac{1}{32c_2}(\gamma' - \gamma_0)^2 - \frac{1}{4}(s' - s_0)\right]^2 \quad . \tag{2.35}$$

For $\vartheta = \pi/4$ the equations (2.33),(2.34) and (2.35) are replaced respectively by

$$(\gamma' + \gamma_0)^2 > 8c_2(s' + s_0) \quad , \tag{2.36}$$

$$k_0 = \sqrt{\frac{1}{2r}\left[\frac{1}{32c_2}(\gamma' + \gamma_0)^2 - \frac{1}{4}(s' + s_0)\right]} \tag{2.37}$$

and

$$\alpha(T_I) = \frac{1}{2r}\left[\frac{1}{32c_2}(\gamma' + \gamma_0)^2 - \frac{1}{4}(s' + s_0)\right]^2 \quad . \tag{2.38}$$

2.3 The INC phase and its properties.

The analysis we have performed so far gives us a picture of a high temperature commensurate phase losing its stability at a certain temperature T_I in favour of an INC phase, which is spatially modulated with the wavevector k_0. Due to the tetragonal symmetry in both above analyzed cases $\vartheta = 0$ and $\vartheta = \pi/4$ we may have either one modulation direction corresponding to freezing of 2 vectors of the star of $\vec{k_0}$ or 2 mutually perpendicular modulation directions in case when all 4 vectors of the star of $\vec{k_0}$ get frozen. In order to determine which of these possibilities is actually realized it is necessary to go beyond the quasiharmonic part of the free energy, by taking into account the higher order terms of (2.11).

Since the free energy (2.6) is a functional of the polarization and displacement fields, the INC pattern corresponding to equilibrium is found as a solution of Euler-Lagrange equations resulting from (2.6). We do not have any particular boundary conditions imposed on the fields and therefore the appropriate solution is the one corresponding to the absolute minimum of the functional. This means that we should find the general solution of Euler-Lagrange equations containing integration constants and then perform an additional minimization with respect to all of these. Such approach would not be an easy one because we would have to solve a system of nonlinear *partial differential* equations. Instead of this we adopt the following procedure. We shall assume that the equilibrium solution is a *periodically* modulated phase with the wavevector q which is for the moment unknown. Then it is convenient to make use of the free energy expressed as a function of the Fourier components of the fields (2.11) because the only non-zero components would be those corresponding to the harmonics of the basic wavevector q. Minimizing with respect to those we obtain a system of nonlinear *algebraic* equations which is numerically easy to solve by iteration procedure. This will be described in detail later and for the moment we just establish the equilibrium conditions.

For this purpose it is useful to return to the original cartesian components of the vectors in terms of which the free energy (2.11) is expressed. The equilibrium condition for $P_{1\vec{k}}$ reads

$$\begin{aligned}
\frac{\partial F}{\partial P^*_{1\vec{k}}} &= (\alpha - 2g_{11}\epsilon_{11} - 2g_{12}\epsilon_{22} + 2s_1k_1^2 + 2s_2k_2^2 + 2rk^4)P_{1\vec{k}} + \\
&+ (-g_{66}\epsilon_{12} + (s_4 + s_5)k_1k_2)P_{2\vec{k}} + \\
&+ ((h_1 + h_2)k_1^2 + \frac{h_3}{2}k_2^2)u_{1\vec{k}} + (h_1 - h_2 + \frac{1}{2}h_3)k_1k_2u_{2\vec{k}} \\
&+ \beta_1 \sum_{\vec{k}'\vec{k}''\vec{k}'''} P_{1\vec{k}'}P_{1\vec{k}''}P_{1\vec{k}'''}\,\delta(\vec{k} - \vec{k}' - \vec{k}'' - \vec{k}''') + \\
&+ \beta_2 \sum_{\vec{k}'\vec{k}''\vec{k}'''} P_{1\vec{k}'}P_{2\vec{k}''}P_{2\vec{k}'''}\,\delta(\vec{k} - \vec{k}' - \vec{k}'' - \vec{k}''') - \\
&- 2g_{11}i\sum_{\vec{k}'\vec{k}''} k_1' u_{1\vec{k}'}P_{1\vec{k}''}\,\delta(\vec{k} - \vec{k}' - \vec{k}'') - \\
&- 2g_{12}i\sum_{\vec{k}'\vec{k}''} k_2' u_{2\vec{k}'}P_{1\vec{k}''}\,\delta(\vec{k} - \vec{k}' - \vec{k}'') - \\
&- \frac{1}{2}g_{66}i\sum_{\vec{k}'\vec{k}''}(k_1' u_{2\vec{k}'} + k_2' u_{1\vec{k}'})P_{2\vec{k}''}\,\delta(\vec{k} - \vec{k}' - \vec{k}'') = 0 \ , \qquad (2.39)
\end{aligned}$$

and differentiating with respect to $P^*_{2\vec{k}}$ we obtain an analogous equation. We see that it is impossible to fulfill this system with the basic harmonic only, because the bilinear terms originating from the electrostrictive coupling and 3^{rd} order terms originating from the quartic terms in the free energy generate respectively the 2^{nd} and the 3^{rd} harmonic.

Equilibrium conditions for the acoustic displacements are

$$\begin{aligned}\frac{\partial F}{\partial u^*_{1\vec{k}}} &= ((h_1+h_2)k_1^2 + \frac{h_3}{2}k_2^2)P_{1\vec{k}} + (h_1 - h_2 + \frac{1}{2}h_3)k_1k_2P_{2\vec{k}} + \\ &+ (c_{11}k_1^2 + c_{66}k_2^2)u_{1\vec{k}} + (c_{12}+c_{66})k_1k_2u_{1\vec{k}} + \\ &- ig_{11}k_1\sum_{\vec{k}'\vec{k}''} P_{1\vec{k}'}P_{1\vec{k}''}\,\delta(\vec{k}-\vec{k}'-\vec{k}'') - ig_{12}k_2\sum_{\vec{k}'\vec{k}''} P_{2\vec{k}'}P_{2\vec{k}''}\,\delta(\vec{k}-\vec{k}'-\vec{k}'') - \\ &- \frac{1}{2}g_{66}ik_2\sum_{\vec{k}'\vec{k}''} P_{1\vec{k}'}P_{2\vec{k}''}\,\delta(\vec{k}-\vec{k}'-\vec{k}'') = 0 \qquad (2.40)\end{aligned}$$

and an analogous equation for the derivative with respect to $u^*_{2\vec{k}}$.

The free energy depends also on the homogeneous strains $\epsilon_{11}, \epsilon_{22}$ and ϵ_{12}. Determining the equilibrium conditions with respect to those and solving for the strain components we obtain

$$\begin{aligned}\epsilon_{11} &= a\sum_{\vec{k}}|P_{1\vec{k}}|^2 + b\sum_{\vec{k}}|P_{2\vec{k}}|^2 \\ \epsilon_{22} &= a\sum_{\vec{k}}|P_{2\vec{k}}|^2 + b\sum_{\vec{k}}|P_{1\vec{k}}|^2 \\ \epsilon_{12} &= c\sum_{\vec{k}}P_{1\vec{k}}P^*_{2\vec{k}}\ , \qquad (2.41)\end{aligned}$$

where we denoted $a = \frac{c_{11}g_{11} - c_{12}g_{12}}{c_{11}^2 - c_{12}^2}\ , \quad b = \frac{c_{11}g_{12} - c_{12}g_{11}}{c_{11}^2 - c_{12}^2}\ , \quad c = \frac{g_{66}}{4c_{66}}\ .$ (2.42)

Before turning to the numerical solution of system (2.39), (2.40),(2.41), we investigate the part of the free energy which is projected out from (2.11) by the single plane wave ansatz, which consists in including in the solution just the basic harmonic with the wavevector q_0 found in the last section.

First we analyze the case when the loss of stability occurs for $\vartheta = 0$, i.e. for direction [100]. If only a single modulation direction $\vec{k} = (q_0, 0)$ is present, the only non-zero Fourier components of the polarization will be the *transverse* components $P_{2,\pm\vec{k}}$ which without loss of generality can be considered as real. We notice that the 3^{rd} order electrostrictive terms in (2.11) give zero contribution, because they consist of products of an odd number of basic harmonics. This implies that the equilibrium values of the acoustic displacements are equal to those found in the last section considering just the quasiharmonic part of the free energy. The value of this for the equilibrium acoustic displacements is therefore given by (2.28). To obtain the total free energy we must add to that the contribution of the terms of 4^{th} order in polarization components and also the elastic and electrostrictive terms containing just the *homogeneous* strains. For those we substitute the equilibrium values(2.41). Writing $P_{2,\pm\vec{k}} = p$ and substituting to (2.41) and (2.11) we recast the total free energy as a function of p (we set the volume $V = 1$)

$$\begin{aligned} F &= F_0 + \alpha' p^2 + \left(\frac{3}{2}\beta_1 + d\right) p^4 \quad , \qquad (2.43) \\ \text{where} \quad d &= 2c_{11}(a^2+b^2) + 4c_{12}ab - 4g_{11}a - 4g_{12}b \ . \end{aligned}$$

The equilibrium value of p is given by

$$p_{eq} = \sqrt{\frac{-\alpha'}{3\beta_1 + 2d}} \qquad (2.44)$$

and the *total equilibrium* free energy is

$$F_{eq} = F_0 - \frac{\alpha'^2}{6\beta_1 + 4d} \ . \qquad (2.45)$$

If we assume that two mutually perpendicular modulation directions $\vec{k}_1 = (q_0, 0)$, $\vec{k}_2 = (0, q_0)$ are present in the system, we can proceed along the same lines in order to calculate the corresponding equilibrium free energy and compare it with (2.45). The non-zero Fourier components of polarization are now the 4 transverse components $P_{1,\pm\vec{k}_2}$, $P_{2,\pm\vec{k}_1}$ which can again be taken to be real. Writing $P_{1,\pm\vec{k}_2} = P_{2,\pm\vec{k}_1} = p$ we obtain

$$\begin{aligned} F &= F_0 + 2\alpha' p^2 + (3\beta_1 + 2\beta_2 + d')p^4 \quad , \qquad (2.46) \\ \text{where} \quad d' &= 4(c_{11}+c_{12})(a+b)^2 - 8(g_{11}+g_{12})(a+b) \ . \end{aligned}$$

The equilibrium polarization and free energy are then, respectively,

$$p_{eq} = \sqrt{\frac{-\alpha'}{3\beta_1 + 2\beta_2 + d'}} \,, \tag{2.47}$$

$$F_{eq} = F_0 - \frac{\alpha'^2}{3\beta_1 + 2\beta_2 + d'} \,. \tag{2.48}$$

Actually we do not know the coefficients of the gradient terms in the free energy expansion (2.6). However, equations (2.45) and (2.48) allow us to decide *within the single plane wave ansatz* which of the two possible modulation patterns yields the lower free energy knowing only 4th order terms coefficients β_1, β_2, elastic constants and electrostrictive couplings. The latter are known from [6] to be (converted to SI units) $g_{11} = 1.33 \times 10^{10}$, $g_{12} = 3.24 \times 10^9$, $g_{44} = 2.43 \times 10^9 JmC^{-2}$. The clamped values of $\alpha(T)$, β_1, β_2 (which are the appropriate ones for our free energy expansion) can be found in [5] and for $T = 40K$ they read (in SI units) $\alpha = 15.5 \times 10^6 JmC^{-2}$, $\beta_1 = \beta_2 = 0.9 \times 10^{10} Jm^5C^{-4}$. According to (2.45) and (2.48) the condition to be satisfied in order that the two simultaneous modulation directions pattern be the one with lower energy is

$$3\beta_1 - 2\beta_2 > 4\frac{(g_{11} - g_{12})^2}{c_{11} - c_{12}} \,. \tag{2.49}$$

For the above values of parameters we obtain 9×10^9 for the left hand side and 1.75×10^9 for the right hand side, which means that the condition is well satisfied. We can therefore conclude that if the loss of stability really occurs along the [100] direction, then the single plane wave ansatz predicts the INC phase to be simultaneously modulated in 2 mutually perpendicular directions. Later we shall see that this conclusion is not changed by numerical analysis.

Proceeding along the same lines we investigate the case when the stability is lost for $\vartheta = \pi/4$, i.e. along [110] and equivalent directions. We just quote the result for this case.

The condition equivalent to (2.49) is

$$10\beta_2 - 6\beta_1 > 2\frac{g_{66}^2}{c_{66}} , \tag{2.50}$$

which for $SrTiO_3$ yields $1.8 \times 10^{10} > 4.65 \times 10^7$ and obviously is well satisfied. The phase with lower free energy is again modulated in two directions.

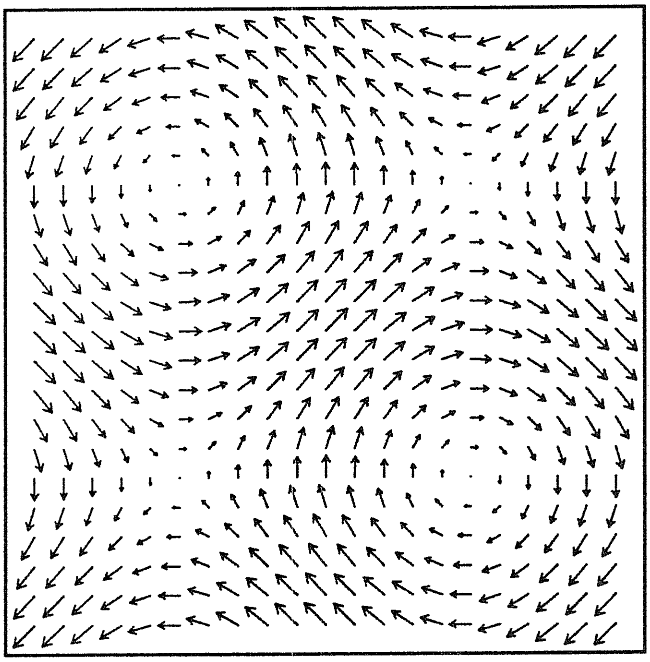

Figure 2.1: The pattern of the polarization in the INC phase with two perpendicular modulation directions.

It is interesting to see this two modulation directions pattern, which we plotted for case $\vartheta = 0$ (Fig.2.1). It is reminiscent of the so-called *flux phases* and consists of regions of positive and negative "vorticity" alternating along the [110] and equivalent directions. Because the vector field is a superposition of frozen *transverse* optical phonons, its divergence is zero which implies zero polarization charge density. The transition into the INC phase is also accompanied by onset of non-zero values of the lattice strains. Because the longitudinal component of the acoustic displacement is decoupled and equal to zero, the pattern of this field is the same as that of polarization, as follows from (2.27), possibly differing in sign (determined by the sign of $\gamma' - \gamma_0$). From the equations (2.41) we see that the *homogeneous* strain has no shear component $\epsilon_{12} = 0$, while the normal components $\epsilon_{11}, \epsilon_{22}$ are non-zero and positive. This means that the crystal expands which was to be expected on the basis of the Le Chatelier principle and the fact that the crystal becomes ferroelectric under applied external stress. On the other hand, due to transversality of the frozen phonons involved, the normal components of the *non-homogeneous* strain (2.9) are zero *within the single plane wave ansatz*, while the shear component is non-zero and is plotted on Fig.2.2. We see that the shear strain oscillates in space and its magnitude reaches maxima in the points of zero vorticity of the polarization field.

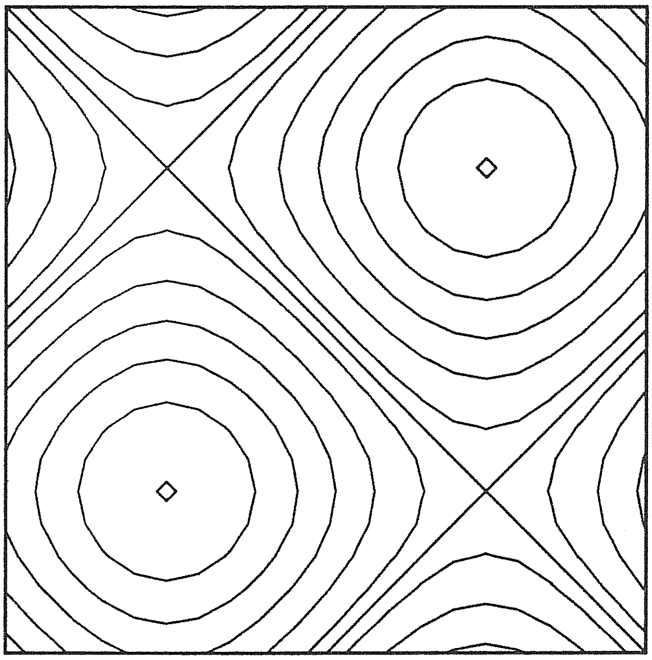

Figure 2.2: The contour plot of the shear strain component e_{12}.

Now we turn to the numerical analysis of the INC phase. We have to fulfill simultaneously the equilibrium conditions (2.39) and (2.40) for all the Fourier components involved and (2.41) for the homogeneous strains. All the wavevectors $\vec{k}, \vec{k}', \vec{k}'', \vec{k}'''$ in the system are of the form

$$\vec{k} = (iq, jq)\,, \qquad i, j \ \text{ integer}\,, \tag{2.51}$$

where q determines the fundamental period of the solution. This is unknown and therefore we must minimize the free energy with respect to it, too. The q-dependent part of the total free energy can be written as

$$\begin{aligned}
\tilde{F}_q &= uq + vq^2 + wq^4\,, && (2.52)\\
u &= -g_{11} i \sum_{\vec{k}\vec{k}'\vec{k}''} (iu_{1\vec{k}} P_{1\vec{k}'} P_{1\vec{k}''} + ju_{2\vec{k}} P_{2\vec{k}'} P_{2\vec{k}''})\, \delta(\vec{k} + \vec{k}' + \vec{k}'') - \\
&- g_{12} i \sum_{\vec{k}\vec{k}'\vec{k}''} (iu_{1\vec{k}} P_{2\vec{k}'} P_{2\vec{k}''} + ju_{2\vec{k}} P_{1\vec{k}'} P_{1\vec{k}''})\, \delta(\vec{k} + \vec{k}' + \vec{k}'') - \\
&- g_{66} \frac{i}{2} \sum_{\vec{k}\vec{k}'\vec{k}''} (iu_{2\vec{k}} + ju_{1\vec{k}}) P_{1\vec{k}'} P_{2\vec{k}''}\, \delta(\vec{k} + \vec{k}' + \vec{k}'')\,, && (2.53)\\
v &= \sum_{\vec{k}} \Big[\frac{1}{2} c_{11} (i^2 |u_{1\vec{k}}|^2 + j^2 |u_{2\vec{k}}|^2) + \\
&+ c_{12} ij u_{1\vec{k}} u^*_{2\vec{k}} + \frac{1}{2} c_{66} (i^2 |u_{2\vec{k}}|^2 + j^2 |u_{1\vec{k}}|^2 + 2ij u_{1\vec{k}} u^*_{2\vec{k}}) - \\
&+ h_1 (iu_{1\vec{k}} + ju_{2\vec{k}})\, (iP^*_{1\vec{k}} + jP^*_{2\vec{k}}) + h_2 (iu_{1\vec{k}} - ju_{2\vec{k}})\, (iP^*_{1\vec{k}} - jP^*_{2\vec{k}}) + \\
&+ \frac{h_3}{2} (iu_{2\vec{k}} + ju_{1\vec{k}})\, (jP^*_{1\vec{k}} + iP^*_{2\vec{k}}) + s_1 (i^2 |P_{1\vec{k}}|^2 + j^2 |P_{2\vec{k}}|^2) + \\
&+ s_2 (j^2 |P_{1\vec{k}}|^2 + i^2 |P_{2\vec{k}}|^2) + (s_4 + s_5) ij P_{1\vec{k}} P^*_{2\vec{k}} \Big]\,, && (2.54)\\
w &= r \sum_{\vec{k}} (i^2 + j^2)^2 (|P_{1\vec{k}}|^2 + |P^2_{2\vec{k}}|)\,, && (2.55)
\end{aligned}$$

and minimizing it with respect to q we have

$$\left. \frac{\partial \tilde{F}(q)}{\partial q} \right|_{q = q_{eq}} = u + 2v q_{eq} + 4w q^3_{eq} = 0\,. \tag{2.56}$$

This is the condition for the equilibrium modulation wavevector q_{eq}, which closes our system.

It is convenient to use the iteration method for the numerical solution of the system. Putting the linear terms in (2.39) and (2.40) to the left side we can for each $\vec{k}$ solve a system of 4 linear equations for $P_{i\vec{k}}, u_{j\vec{k}}$, and express each of these variables as a function of the nonlinear terms. We then iterate until we obtain a self-consistent solution for all the Fourier components and homogeneous strains. After this we solve the equation (2.56) for the new wavevector q and all the procedure is repeated until we reach self-consistency in q. As the starting approximation we can use the results of the single plane wave ansatz.

We performed such numerical analysis on a rescaled free energy, using all the experimentally known parameters, choosing suitable values for the coefficients s_i and r and taking for the coupling coefficient h_3 (we put $h_1, h_2 = 0$) the minimal possible value which leads to the loss of stability at temperature $T \sim 40K$. The amplitudes of the higher harmonics of the self-consistent solution were of the order of magnitude of few percent of that of the basic harmonic and the free energy was reduced by about the same amount with respect to its value calculated within the single plane wave ansatz. This is a direct consequence of the presence of the term proportional to k^4 in the free energy, as Michelson has first shown in [21]. The general conclusion is that in case when the free energy does not contain the Lifshitz invariant and contains rather a term of 4^{th} order in k, the amplitudes of the higher harmonics in the equilibrium solution are small and therefore the INC phase remains practically sinusoidally modulated down to the temperature of the lock-in transition. The single plane wave ansatz is thus a very good description of this kind of INC phases and our conclusion concerning the number of modulation directions in $SrTiO_3$ remains valid.

Now we briefly mention the case when the unstable wavevector is off the xy-plane, and is of the form $\vec{k}_0 = (k_x, 0, k_z)$. The corresponding star then consists of 8 vectors and analogically to what we found in the 2D case, we may assume that all of these would get frozen. The polarization field will then be a superposition of 8 transverse plane waves and will contain 4 arbitrary phases, with respect to which the free energy projected out by the single plane wave ansatz is *invariant.* The components of the polarization are

$$\begin{aligned} P_y &= P[e^{i(k_1x+k_3z+\phi_1)} + e^{i(k_1x-k_3z+\phi_2)} + c.c.] = 4P\cos k_1x'\cos k_3z' \\ P_x &= P[e^{i(k_1y+k_3z+\phi_3)} + e^{i(k_1y-k_3z+\phi_4)} + c.c.] = 4P\cos k_1y'\cos(k_3z' + \phi)\ , \end{aligned} \quad (2.57)$$

where in the last expressions we have eliminated 3 of the 4 arbitrary phases by shift of the origin of the coordinates. It is interesting to mention that there still remains one degree of freedom ϕ, corresponding to a phason-like mode, which however does not represent just a rigid shift of the INC modulation, but rather a change of the structure of this.

For $\phi = 0$ we obtain a structure which in every (001) plane is the "flux phase" described above, with the amplitude modulated along the z-axis by $\cos k_3z$ factor. Moreover, the sign of vorticity now alternates along the z-axis, too, with a period $\lambda_z = 2\pi/k_z$, which in general may be different from the period along the x and y direction. Anticipating now the considerations of the next chapter, we attribute a special importance to the points of maximal vorticity, and notice that the pattern can be considered as a *3D lattice*, similar to that of $NaCl$ (but not necessarily cubic), consisting of such points with alternating vorticity.

For completeness we now analyze the behaviour of the static dielectric susceptibility

χ_{ij} in the 2D model. This is defined as

$$\chi_{ij}^{-1} = \left. \frac{\partial^2 F}{\partial P_{i0} \partial P_{j0}} \right|_{eq} \tag{2.58}$$

and we have obviously $\chi_{ij} = \alpha^{-1} \delta_{ij}$ for $T > T_I$. We are interested in its behaviour in the INC phase near the transition temperature and we shall investigate this within the single plane wave ansatz. For simplicity we do not take into account the electrostrictive terms and analyze the case with 2 modulation directions along [100] and [010]. The free energy of the INC phase is then given by

$$\begin{aligned} F &= F_0 + \frac{1}{2}\alpha(P_{10}^2 + P_{20}^2) + \frac{1}{2}\alpha'(2P_{1,\vec{k}_2}^2 + 2P_{2,\vec{k}_1}^2) + \\ &+ \frac{1}{4}\beta_1 \left[6(P_{1,\vec{k}_2}P_{1,-\vec{k}_2})^2 + 12P_{10}^2 P_{1,\vec{k}_2}P_{1,-\vec{k}_2} + 6(P_{2,\vec{k}_1}P_{2,-\vec{k}_1})^2 + 12P_{20}^2 P_{2,\vec{k}_1}P_{2,-\vec{k}_1}\right] + \\ &+ \frac{1}{2}\beta_2(2P_{10}^2 P_{2,\vec{k}_1}P_{2,-\vec{k}_1} + 2P_{20}^2 P_{1,\vec{k}_2}P_{1,-\vec{k}_2} + 4P_{1,\vec{k}_2}P_{1,-\vec{k}_2}P_{2,\vec{k}_1}P_{2,-\vec{k}_1}) \end{aligned} \tag{2.59}$$

and we clearly see that due to the presence of the 4^{th} order terms the stiffness with respect to the homogeneous polarization components P_{i0} becomes renormalized. After minimizing with respect to $P_{1,\vec{k}_2}P_{1,-\vec{k}_2}$, $P_{2,\vec{k}_1}P_{2,-\vec{k}_1}$ and some algebra we obtain

$$F = F_0 + \left(\frac{1}{2}\alpha - \alpha' \frac{3\beta_1 + \beta_2}{3\beta_1 + 2\beta_2}\right)(P_{10}^2 + P_{20}^2) , \tag{2.60}$$

from which we see that the susceptibility passes continuously through the transition temperature, because $\alpha'(T_I) = 0$. Immediately below T_I it however starts to decrease with decreasing T and therefore it must have a peak at T_I when its slope has a downward jump (Fig.2.3). Instead of a divergence we thus have only a peak on the curve $\chi(T)$, because the INC phase is not ferroelectric.

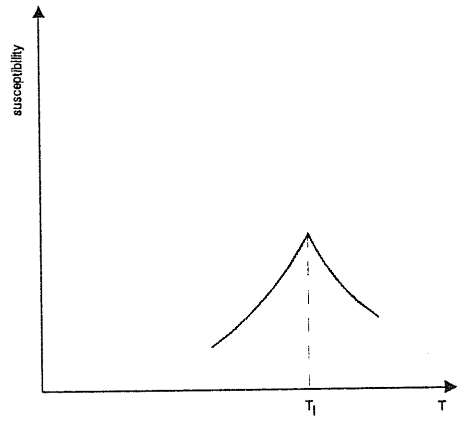

Figure 2.3: The temperature dependence of the static homogeneous susceptibility in our model. At T_I there is a peak, but not a divergence.

3 Quantum mechanics: a new quantum paraelectric state.

The theory we developed in the last chapter is classical and refers to an INC distorted phase, which, based on entirely classical reasoning, $SrTiO_3$ might want to take at low temperatures. On the other hand, in the introduction we discussed features of EPR data (lack of inhomogeneous broadening), which are definitely against such possibility. A simple narrow EPR line might be compatible with dynamically fluctuating domains, but certainly not with a static INC state as in Fig.2.1. How is it possible to justify the dynamical picture, and what properties it might be expected to have ?

. In this chapter we shall try to figure possible answers to these questions. First we propose to describe the state of the system in terms of a wave function, and then we show a simplified model within which such wave function can be treated. Basically, our aim will be to determine the presence of off-diagonal long range order, and we shall do this using the formalism of classical liquids in a way similar to that used in [32].

3.1 Description of the $T = 0$ state in terms of a wave function.

It is known that in case when a Lifshitz invariant present in the free energy gives rise to an INC phase [22], the phase degree of freedom of the (in this case necessarily) doubly degenerate order parameter is governed by the sin-Gordon equation. Adding to the free energy a corresponding kinetic energy term one obtains an effective hamiltonian which can be quantized introducing non-commuting operators for the phase and its conjugate momentum. For a 1D case there are exact results due to Haldane [23] revealing that for whatever small quantum zero fluctuations - i.e. for any finite mass, the ground state is liquid-like, while classically we obtain a static soliton lattice. Such a liquid-like phase can be considered as an incommensurate phase which is already at zero temperature quantum melted by zero fluctuations, and suggests, that something similar may be actually going on in our case.

The effective hamiltonian for our model (2.6) is

$$H^{eff} = \int \left[\frac{1}{2} m_u \sum_i \dot{u}_i^2(\vec{r}) + \frac{1}{2} m_P \sum_i \dot{P}_i^2(\vec{r}) \right] d^3\vec{r} + F \,, \tag{3.1}$$

and represents a classical Φ^4 field. The quantum analogue of this is a quantum Φ^4 field theory. Instead of attempting the field theoretical approach we shall try to treat the problem in a simplified and more intuitive way, building a simple model. First, *restricting ourselves to zero temperature*, we may try to assign to the ground state of our system a variational wave function. We propose this to be of the form

$$\Psi \propto e^{-\gamma F[\vec{P}(\vec{r}),\vec{u}(\vec{r})]} \,, \tag{3.2}$$

where γ plays a role of a variational parameter. The physical meaning of Ψ is the usual one and $\Psi^2[\vec{P}(\vec{r}), \vec{u}(\vec{r})]$ determines the relative probability of different field configurations. Because this function is formally a functional of the fields $\vec{P}(\vec{r}), \vec{u}(\vec{r})$, it is dependent on an infinite number of some generalized coordinates and therefore still practically intractable. If we were now able to identify which field configurations are the most "important" ones, and introduce for these some suitable coordinates, it would be possible to simplify (3.2) to a more familiar form. We shall do so in the next section. Now we only point out, that having a wave function for the system, it is in principle possible to calculate the average value of any measurable quantity, provided we know the corresponding operator. This can always be expressed as a function of the coordinates $\vec{r}_{Lj}$ and momenta $\vec{p}_{Lj}$ of the atoms of the crystal, which in turn can be expressed in terms of the amplitudes of the eigenvectors of the lattice dynamical problem. We remind at this point that the meaning of the variables $\vec{P}(\vec{r}), \vec{u}(\vec{r})$ is that of being the amplitudes of the corresponding TO and TA zone-center mode eigenvectors. Therefore the wave function (3.2) can actually be used to determine the zero-temperature average values of the quantities of experimental interest, and particularly of those measured in EPR experiments, like $< \delta\phi >$, $< a >$ and $< D >$.

3.2 A simplified model for the wave function: the two component quantum plasma.

Now we try to pick the "important" configurations in the wave function (3.2), and for this purpose we make use of the knowledge of the classical solution for the ground state. In the last chapter we found that both in the 2D and the 3D case this corresponds to a periodic lattice of XY-like vortices, with the sign of the vorticity alternating in all relevant spatial directions. Assuming that the "important" configurations of the quantized field are in a sense similar to those appearing in the classical picture, and led by the analogy with the above mentioned 1D sin-Gordon problem, we propose that the objects which retain their identity in the quantum picture are the *vortices.* These would play the role of sin-Gordon solitons in our case, and instead of forming a rigid spatial lattice might be delocalized, giving rise to a liquid-like state preserving the translational symmetry. In such a way, we can treat the vortices as "particles", however, unlike the solitons, which are all identical in nature, there are 2 kinds of vortices, with positive and negative vorticity. Because in the classical picture both kinds alternate periodically, it is tentative to think about the vorticity as being a kind of "charge", due to which the vortices interact with each other in such a way, that the overall charge neutrality is always preserved. To determine the corresponding interaction law, it is, however, necessary to know the effective dimensionality of the problem. As we mentioned in the last chapter, it is not possible to determine this on the basis of available experimental material, and for concreteness in the following we shall assume this to be 3, mainly for aesthetical reasons. The charges in an effectively 3D system should then interact via a Coulomb potential. Because unlike vortices would annihilate each other, if they could approach close, we may think that this is prevented by some short range and strongly repulsive hard-core-like interaction. Since there is no reason to distinguish the vortices of like charge, in the quantum picture they have to be treated as *bosons.* The number of these, or their density, is determined by the modulation wavevector $\vec{k}$, and should therefore be considered as a *conserved* quantity.

Having adopted this picture we can replace the wave function (3.2) of the field by a Jastrow wave function for Bose particles, if we consider the coordinates of these to coincide with the points of maximal vorticity of the field. Such wave function should have a property of describing, depending on the value of the variational parameter γ, both a liquid-like state in the quantum limit and a crystalline state in the classical limit. A general form of wave function, which possesses the above property, is

$$\Psi(\vec{r}_1 \ldots \vec{r}_N, \vec{r}^{\,\prime}_1 \ldots \vec{r}^{\,\prime}_N) =$$

$$\mathcal{A} \prod_{1 \leq i < j \leq N} e^{-\gamma u_{++}(|\vec{r}_i - \vec{r}_j|)} \prod_{1 \leq i < j \leq N} e^{-\gamma u_{++}(|\vec{r}^{\,\prime}_i - \vec{r}^{\,\prime}_j|)} \prod_{1 \leq i, j \leq N} e^{-\gamma u_{+-}(|\vec{r}_i - \vec{r}^{\,\prime}_j|)} ; \qquad (3.3)$$

where $\vec{r}_i$ and $\vec{r}^{\,\prime}_j$ are respectively the coordinates of (+) and (−)-particles, and $\mathcal{A}$ is the normalization constant. This wave function is non-negative and symmetric with respect to the exchange of like particles, and therefore can represent a ground state of a Bose system. Concerning the explicit form of the functions $u_{++}(r)$ and $u_{+-}(r)$, which express the 2-particle correlations, we assume that these have a hard core and a tail, the explicit form of which we shall not try to specify further. Moreover we shall assume that the value of γ is such that (3.3) describes a liquid-like state with unbroken translational symmetry.

3.3 Off-diagonal long range order: single particle and pair condensates in the two component plasma.

Having now such an idealized model wave function, we may ask whether this has some peculiar properties, e.g. a kind of off-diagonal long range order, reflecting a Bose condensation of some objects. In this context, a following argument can be presented, justifying to some extent a search for such properties in our system. A quantum paraelectric material would have become ferroelectric at some finite temperature, were it not for the quantum zero-point fluctuations, which can be considered as "melting" the incipient long range ferroelectric order. This mechanism is very similar to the one, which is operative in liquid ^4He and is responsible for the lack of crystalline long range order in this under normal pressure. In both systems it is possible to induce a genuine diagonal long range order applying an external pressure – ^4He crystalizes, when the pressure is increased, and $SrTiO_3$ becomes ferroelectric under uniaxial stress [6]. We expect therefore, that a quantum paraelectric system at low temperatures might develop a kind of off-diagonal long range order, in the similar way as ^4He does. Actually, the similarity of the phase diagrams of both systems is remarkable, and in the Fig.3.1 we hatched the region of the expected existence of ODLRO in $SrTiO_3$.

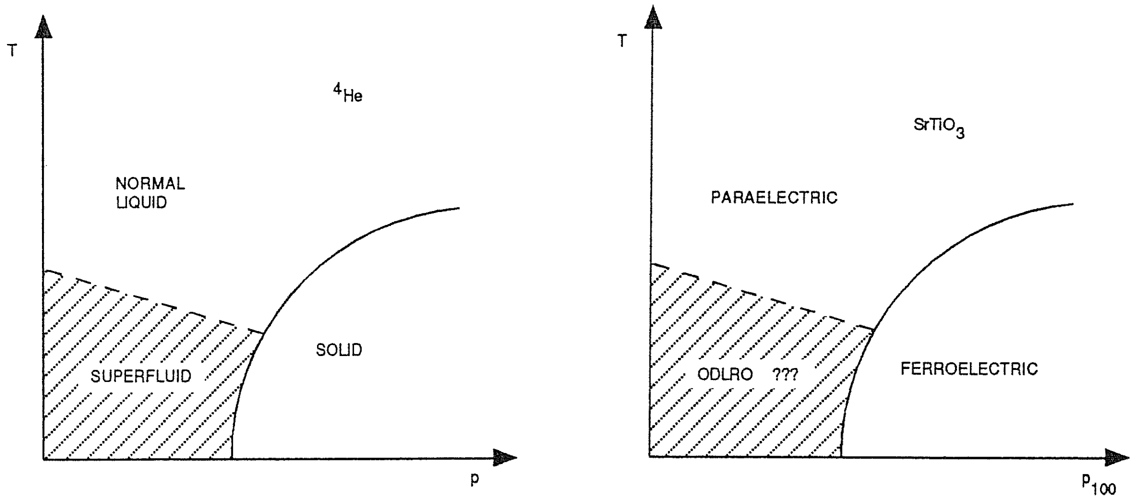

Figure 3.1: The real phase diagram of ^4He and a speculative one of $SrTiO_3$. The region of expected existence of ODLRO in $SrTiO_3$ is hatched.

To our knowledge, the problem of a two component quantum plasma has not been so far considered in the literature. We shall first determine the presence of a single-particle condensate of each kind of particles. This is defined for (+)-particles as

$$n_0^+ = \lim_{|\vec{r}-\bar{\vec{r}}|\to\infty} < G, N_+, N_- | \hat{\Psi}_+^\dagger(\vec{r})\hat{\Psi}_+(\bar{\vec{r}}) | G, N_+, N_- > , \tag{3.4}$$

and analogously for (−)-particles, where $|G, N_+, N_- >$ is the ground state of the system containing N particles of each kind. In [32], Chester and Reatto showed how the density n_0 of Bose condensate can be determined in a *one component* quantum liquid described by the same kind of Jastrow wave function (3.3). They demonstrated that the problem maps to a classical problem of two impurity particles in a liquid, where the impurities are distinct due to the fact, that they do not interact with each other, while interact with the particles of the liquid via 1/2 of the true interparticle potential. Actually, their result is readily applicable to our case, and reads

$$n_0^+ = \frac{n}{\lim_{r\to 0} g_{++imp}(r)} , \tag{3.5}$$

for (+)-particles, and analogously for (−)-particles. In the last expression, $g_{++imp}(r)$ is the radial distribution function for very diluted impurities. The wave function therefore contains two single-particle condensates, consisting of vortices and antivortices, respectively.

We can proceed to search for more complicated correlations now. Since the interaction between the particles of opposite charge is attractive, led by the analogy with superconductivity one may expect a presence of some kind of "Cooper pairs", or "molecules", consisting of a vortex-antivortex pair. For this purpose we shall investigate the average value

$$\phi(|\vec{r}-\vec{r}^{\,\prime}|) = \ < G, N_+, N_- | \hat{\Psi}_+^\dagger(\vec{r}) \hat{\Psi}_-^\dagger(\vec{r}^{\,\prime}) | G, (N-1)_+, (N-1)_- > \ . \tag{3.6}$$

First we notice, that for $|\vec{r}-\vec{r}^{\,\prime}| \to \infty$ this must factorize as

$$< \hat{\Psi}_+^\dagger(\vec{r}) \hat{\Psi}_-^\dagger(\vec{r}^{\,\prime}) > \ \to \ < \hat{\Psi}_+^\dagger(\vec{r}) >< \hat{\Psi}_-^\dagger(\vec{r}^{\,\prime}) > \ = \sqrt{n_0^+}\sqrt{n_0^-} , \tag{3.7}$$

which is an obvious manifestation of the presence of single-particle condensates. Now we explicitly calculate the function $\phi(|\vec{r}-\vec{r}^{\,\prime}|)$, which, as is known, can be considered as a "pair wave function". Substituting (3.3) into (3.6) we obtain

$$\begin{aligned}
&\phi(|\vec{r}-\vec{r}^{\,\prime}|) = N\mathcal{A} \int d^3\vec{r}_1 \dots d^3\vec{r}_{N-1} d^3\vec{r}^{\,\prime}_1 \dots d^3\vec{r}^{\,\prime}_{N-1} \\
&\Psi^*(\vec{r}, \vec{r}_1 \dots \vec{r}_{N-1}; \vec{r}^{\,\prime}, \vec{r}^{\,\prime}_1 \dots \vec{r}^{\,\prime}_{N-1}) \Psi(\vec{r}_1 \dots \vec{r}_{N-1}, \vec{r}^{\,\prime}_1 \dots \vec{r}^{\,\prime}_{N-1}) = \\
&= N\mathcal{A} \int d^3\vec{r}_1 \dots d^3\vec{r}_{N-1} d^3\vec{r}^{\,\prime}_1 \dots d^3\vec{r}^{\,\prime}_{N-1} e^{-\gamma u_{+-}(|\vec{r}-\vec{r}^{\,\prime}|)} \prod_{1\le i\le N-1} e^{-\gamma u_{++}(|\vec{r}-\vec{r}_i|)} \\
&\prod_{1\le i\le N-1} e^{-\gamma u_{+-}(|\vec{r}-\vec{r}^{\,\prime}_i|)} \prod_{1\le i\le N-1} e^{-\gamma u_{+-}(|\vec{r}^{\,\prime}-\vec{r}_i|)} \prod_{1\le i\le N-1} e^{-\gamma u_{++}(|\vec{r}^{\,\prime}-\vec{r}^{\,\prime}_i|)}
\end{aligned}$$

$$\prod_{1\le i<j\le N-1} e^{-2\gamma u_{++}(|\vec{r}_i-\vec{r}_j|)} \prod_{1\le i<j\le N-1} e^{-2\gamma u_{++}(|\vec{r}_i^{\,\prime}-\vec{r}_j^{\,\prime}|)} \prod_{1\le i,j\le N-1} e^{-2\gamma u_{+-}(|\vec{r}_i-\vec{r}_j^{\,\prime}|)} \tag{3.8}$$

and we see that after appropriate normalization this expression becomes a radial distribution function for 2 impurity particles of unlike sign, which interact with the particles of the liquid and with each other via 1/2 of the true interparticle potential. We can therefore write

$$\phi(|\vec{r}-\vec{r}^{\,\prime}|) = C g_{+-imp}(|\vec{r}-\vec{r}^{\,\prime}|) \tag{3.9}$$

where the constant C is yet unknown. To determine this we can use the property (3.7) and the fact, that for $|\vec{r}-\vec{r}^{\,\prime}| \to \infty$ we have $g_{+-imp}(|\vec{r}-\vec{r}^{\,\prime}|) \to 1$. We obtain

$$C = \sqrt{n_0^+ n_0^-} = n_0^+ = \frac{n}{g_{++imp}(0)} , \tag{3.10}$$

where we assumed $n_0^+ = n_0^-$ and used (3.5). The total density n_{0pair}^{tot} of condensed pairs is then given by

$$n_{0pair}^{tot} = \int |\phi(\vec{r})|^2 d^3\vec{r} = \frac{n^2}{g_{++imp}^2(0)} \int d^3\vec{r} g_{+-imp}^2(|\vec{r}|) . \tag{3.11}$$

The last result is conveniently rewritten as

$$n_{0pair}^{tot} = \frac{n^2}{g_{++imp}^2(0)} \int d^3\vec{r} \left[g_{+-imp}^2(|\vec{r}|) - 1\right] + n_0^2 V , \tag{3.12}$$

and as such can be given the following interpretation. The second term is simply the density of *"pairs"*, consisting of particles which are *separately and individually condensed.* Therefore it does not provide any new information about the correlations in the system (we remind that in case of fermions this term is absent). The first term, on the other hand, is always nonnegative, because

$$\int (g-1)^2 \, d^3\vec{r} = \int g^2 \, d^3\vec{r} - 2\int g \, d^3\vec{r} + \int d^3\vec{r} = \int (g^2-1) \, d^3\vec{r} \ge 0 , \tag{3.13}$$

where we made use of the fact that $g(r)$ is normalized. Moreover this term has a property of being zero in case of noninteracting particles ($g_{+-imp}(|\vec{r}|) = 1$), and we can therefore consider it to represent the *real density of condensed pairs* arising due to the attractive interaction. To confirm this point of view, however, it is necessary to show, that this quantity is really of order n (n is the total density of particles), and this can be readily seen in the following way. The integrand $g^2_{+-imp}(|\vec{r}|) - 1$ goes to 0 for $|\vec{r}| \to \infty$ and the main contribution to the integral comes from the region where it is significant. The volume of this region is of the order of $\frac{V}{N} = n^{-1}$, and the integral can be estimated as

$$n_{0pair} \sim n \frac{g^2_{+-imp}(r_0) - 1}{g^2_{++imp}(0)} , \tag{3.14}$$

where r_0 is some radius at which the integrand acquires its average value over the region. We can therefore conclude a presence of a finite fraction of condensed vortex-antivortex pairs in the wave function.

Having analyzed the properties of an idealized wave function, we conclude that the model which represents our system contains three condensates. Two of these are single-particle and one is a pair condensate, being a vague analogy to the condensate of Cooper pairs in a superconductor, or (closer) of excitons in an excitonic insulator. In the next chapter we shall try to discuss which might be the consequences of this fact.

4 Discussion and outlook.

4.1 Summary.

We briefly summarize what has been done in the preceding chapters. First, we have discussed the available evidence for unusual phenomena in $SrTiO_3$ near 38 K. Second, starting from a Landau expansion of the free energy and adding to this the appropriate gradient terms we have analyzed in detail the properties of the classical INC phase which would hypothetically set up in $SrTiO_3$ if the TA mode frequency continued to decrease to zero. Since the coefficients of the gradient terms are quantitatively not known, we had to investigate several alternative possibilities. Nonetheless, some arguments are presented, indicating that the most likely case could be the pattern in which the polarization $\vec{P}$ and the acoustic displacement $\vec{u}$, both lying in the (001) plane, are jointly modulated in two mutually perpendicular [100] directions. This polarization pattern can be visualized as a 3D stacking of planes, each containing a "flux phase" consisting of a regular array of XY-like vortices with alternating positive and negative vorticity. We are not able to decide, whether this pattern is further modulated along the tetragonal z-axis, and if so, with what periodicity. As to the detailed nature of the in-plane modulation, numerical minimization of the free energy shows, in accordance with the general concept expressed in [21], that the system is well described by a simple sinusoidal modulation. It does not like to create higher spatial harmonics of the modulation, and therefore does not show a tendency to a structuration into "solitons", or domain walls.

Third, after this classical analysis, we have qualitatively discussed the impact of quantum mechanics on the INC state, and in particular its destruction (melting) by quantum fluctuations. In order to make progress in this context, we have abandoned the continuous field theory in terms of the true fields $\vec{P}$ and $\vec{u}$ in favour of a further simplified model in terms of two kinds of "particles". The particles are a mimic of the vortices in $\vec{P}$ and $\vec{u}$, and form a regular $NaCl$-type lattice in the classical INC phase. The quantum paraelectric state is within this model, what is left after quantum melting of this lattice – very much like liquid ^4He is what is left after melting the solid He lattice. Incidentally, therefore, the model requires studying the properties of a two-component quantum plasma which does not seem to have been studied before. Fourth, we study ODLRO in this model state represented by a Jastrow variational wave function, and find that both single particle and pair condensates are present in this. The presence of symmetry breaking and of order parameters implies a phase transition, if this state has to be arrived at by cooling. It seems at least possible, that the anomaly at T_q might signal precisely this transition.

This is as far as this project has arrived at this moment. We do not know precisely yet how to relate this model back to true measured, or measurable properties of the quantum paraelectric state under study. However, we give below a tentative discussion of possible lines of development in that direction.

4.2 Future work in connection with existing experimental material.

A relevant theory of the phase transition at T_q must, of course, explain first of all the behaviour of the quantities such as $< \delta\phi >$, δa and δD. As mentioned in the section 3.1., the wave function (3.2) allows, at least in principle, a calculation of these quantities for $T = 0$. This calculation is not done, and is not an easy one. What can we expect it will yield ?

An increase of ϕ, i.e. a positive $< \delta\phi >$ is very likely, as was pointed out already in [11]. We can extract from the stress induced ferroelectric state [6] an approximate $< \delta\phi >$ of +7% at the onset of uniform ferroelectricity. An average increase in $< \delta\phi >$ of the order of a few percent – as observed – is therefore very likely for the modulated state, no matter whether it is crystalline (INC phase), or melted.

The dip observed for the crystal-field parameters a and D at the phase transition itself, is more difficult. This requires a finite temperature theory, and at the moment we do not have one. Qualitatively, we can still expect that large strain fluctuations must accompany the onset of our state. It is not implausible that their effect on a and D could be similar to that of large anharmonic thermal fluctuations, whose effect would be precisely to depress a and D.

An extra interesting piece of information is provided by the measurement of the $< 111 >$ stress dependence of the temperature of the anomaly T_q. This remains entirely to be understood, and particularly the fact, that the stress dependence of T_q in the trigonal phase is much more pronounced with respect to that in the pseudotetragonal phase. We notice, that the anomaly of ΔH_{out} is much sharper in the trigonal phase, which is consistent with the assumption of a *quantum effect*, since in this phase the transition occurs at a *lower temperature*.

Another remarkable phenomenon is the effect of Ca doping investigated in [20]. From the present point of view, the existence of a critical Ca concentration, where a true ferroelectric state sets in for the first time, can be interpreted in terms of a pinning of the phase fluctuating dynamic INC state. The crystal becomes ferroelectric when it contains at least one pinning center per domain. Because the typical domain size is proportional to k_0^{-1}, where k_0 is the INC modulation wavevector, the value $x_{Ca} = 0.0018$ of the critical concentration allows us to estimate $k_0^{-1} \sim 8a$ (a is the lattice constant). This is in good agreement with recent neutron data [18], showing that the TA-TO coupling is strongest at the reduced wavevector $\xi = |\vec{q}|a/2\pi \sim 0.035$, not far from a predicted value of $k_0 a/2\pi \sim 0.02$.

4.3 Some predictions, and speculations.

In this final section we shall try to predict further experiments which might contribute to better understanding of the investigated phenomenon. At a phase transition one usually expects anomalous behaviour of various thermodynamic quantities. Since we are, however, in the temperature region where quantum effects are assumed to be important, the behaviour may be very different from the classical case. It is known that for a classical commensurate-incommensurate phase transition the Landau theory predicts a jump of *specific heat* like for any ordinary second-order transition. On the other hand, from the renormalization group study [33],[34], [35] of the quantum-mechanical displacive limit it is known that there is no anomaly of specific heat at the quantum-ferroelectric phase transition. We therefore expect the anomaly, if present, to be rather weak.

The *homogeneous and static dielectric susceptibility* of $SrTiO_3$, as measured in [12], does not show any anomaly at T_q. For a classical INC phase, as in chapter 2, this should have a peak at the transition. In that case, in fact, a divergence is expected for the non-homogeneous susceptibility $\chi(k_0)$ corresponding to the unstable wavevector k_0. For a transition into our quantum state, we may expect $\chi(k_0)$ to have a peak, or a larger maximum. This maximum would reflect the coupled TO-TA mode softening leading to stabilization of a roton-like dip in $\omega_A(k_0)$, as suggested in [11].

Finally we mention possible more exotic consequences of the existence of a kind of off-diagonal long-range vortex order discussed in the last chapter. The existence of a condensate of atoms in liquid ^4He and of that of Cooper pairs in superconductors and ^3He is known to manifest itself in superfluid transport of the objects, which condense. Superfluidity of vortex pairs will only arise, if their total number is a conserved quantity, a question, which is not yet clear. Secondly, even if present, our type of "superfluidity" would not involve a true mass transport, since atoms do not flow. However, one could still imagine would-be experiments, where the existence of ODLRO should in principle be detectable. Imagine, for example, introducing a space and time-dependent strain in the system. Because of the coupling, which is explicit in (2.6), classical INC state as in Chapter 2 would be in turn modulated: the preferred domain shapes and their density would fall in step with the deformation. For the solid INC phase this amount of distortion of the domain structure would represent a compromise between the external forcing and the intrinsically rigid response of the solid INC structure. In the superfluid phase, the local domain density is non-conserved, which means that it can *exactly* adjust to the local strain – provided the time dependence is slow enough to give rise to velocities which are below the critical velocity. A very recent Brillouin scattering experiment [18] has in a way already tried this, but failed to show any sharp features at T_q. However, the critical velocity is by necessity smaller, probably much smaller than the sound velocity, which means a possible "condensate" could not "follow" the sound wave in this experiment.

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