On the Dynamics of KDP Type Ferroelectrics. I

—Formulation and Acoustic Anomaly—

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KDP type ferroelectrics are investigated on the basis of extended Kobayashi's model in which the proton pseudo-spin system is coupled with the acoustic phonon as well as with the optic phonon in original Kobayashi's model. A perturbational treatment is developed with the aid of the Matsubara Green's functions and a cumulant expansion. Some properties of the phase transition are shown to be inherent in the present model independent of approximations: The renormalized velocity \( V \) of the acoustic mode vanishes at the second order transition point \( T_s \) while the frequency \( \omega_0(0) \) of the soft ferroelectric mode remains finite at \( T_s \). By assuming the Curie law for the electrical susceptibility \( \chi(T) = \chi(\infty) + C_\chi / |T-T_s| \), the results \( (V/V)^c = |T-T_s|/(|T-T_s| + \Delta T_s) \) and \( \omega_0(0) \propto (|T-T_s| + \Delta T_s)^{-1/4} \) are shown to be obtained. Here \( \Delta T_s \) is a constant for \( T>T_s \) and \( \Delta T_s \) is zero for \( T<T_s \). It is shown that the effect of the relaxation of the soft ferroelectric mode leads to the ultrasonic attenuation \( \alpha(\omega) \propto \omega^2 |T-T_s|^{-1/4} (|T-T_s| + \Delta T_s)^{-1/4} \). These features essentially agree with the simple phenomenological theory and consistent with experiments on KDP and DKDP. Calculations in RPA are performed and results are carefully examined.

§ 1. Introduction

Ferroelectric transitions of KDP (KH2PO4) type ferroelectrics are generally ascribed to orderings of the protons (or deuterons) which occupy the double minimum potential on the hydrogen bonds, as first suggested by Slater in 1941. Since Slater's work many theoretical efforts have been devoted to understand the properties of KDP type ferroelectrics from the microscopic point of view. Most of these works are based on the tunneling hamiltonian proposed by de Gennes and extensively studied by Tokunaga and Matsubara, and on its extended form including the proton lattice interaction as was first suggested by Blinc and Ribaric and developed by Kobayashi.

It is well known that the structural phase transition is usually connected with the presence of a soft mode. As for KDP type ferroelectrics the soft mode, which is responsible for the divergence of the dielectric constant at the transition point \( T_c \), is theoretically derived from the tunneling hamiltonian by Brout et al. and Tokunaga. According to Kobayashi's theory this soft mode is a mixed tunneling proton-optical phonon mode. The first experimental obser-
vation of the soft mode in KDP was made in Raman scattering by Kaminow and Damen who found it to be heavily overdamped. Recent Raman measurements on KDP by Shigenari and Takagi have shown that there exists a sharp peak far below $T_c$ which becomes broad and whose frequency decreases as the temperature is approached to $T_c$ from below. Since this mode disappears on deuteration Blinc and Žekš attributed it to the underdamped soft mode which is overdamped above $T_c$ by the use of semiphenomenological equations of motion for the pseudo-spins similar to Bloch equations in the theory of the nuclear magnetic resonance. On the other hand the dynamical susceptibility of DKDP shows the relaxation type and exhibits the critical-slowing down at $T_c$. This suggests that the tunneling between the double minimum of the potential is negligibly small in DKDP. Its behavior, however, considerably deviates from a simple monodispersive relaxation in the Debye theory. Hill and Ichiki pointed out that their data on DKDP could be explained as a polydispersive relaxation, which was further discussed by Yoshimitsu and Matsubara. The damping constant of the soft mode has been calculated on the tunneling hamiltonian by Stinchcombe by means of the perturbational method and also by Moore and Williams using the technique of Blume and Hubbard. However, the first order calculation of the former corresponds to the case of small damping, which is not satisfied for KDP type ferroelectrics, while the latter's method is valid in the high-temperature limit and is therefore obscure regarding the validity near the transition temperature. In other theories the damping constant is introduced phenomenologically.

Since KDP type ferroelectrics are piezoelectrics, the coupling between the soft ferroelectric mode and the transverse acoustic phonon (TA phonon) drives the velocity of the TA phonon to zero. This induces the ferroelectric transition at $T_c$ before the soft ferroelectric mode with wave vector zero vanishes at $T_0(=T_c)$. The divergence of the dielectric constant takes place where the velocity of the acoustic mode vanishes at $T_c$. Experiments on Brillouin scattering for KDP by Brody and Cummins and on ultrasonic measurements for DKDP by Litov and Uehling have clearly shown such an acoustic anomaly at the transition point $T_c$. Dvořák treated this problem theoretically on the basis of extended Kobayashi's model in which the proton pseudo-spin system was coupled with the TA phonon in addition to with the TO phonon in original Kobayashi's model. His treatment, however, is restricted only to region $T>T_c$ and within RPA, i.e., linearized equation of motion for Green's functions. Consequently, the modes for $T<T_c$ and their damping constants were not investigated there. Furthermore, Elliott, Smith and Young found excellent agreement with experiment for a calculation of the elastic constant from extended Kobayashi's model within the random phase approximation. Recently, however, Elliott and Young regarded the agreement as being spurious since the model did not predict the behaviour of other properties such as the polarization close to $T_c$, and proposed the improved model which included four-spin interactions. They showed that
this improved model could lead to a slightly first order transition by adjusting the magnitude of the negative coupling constant of the four-spin interaction and gave a good agreement with the experimental values for the spontaneous polarization.

In view of the microscopic theory the dynamical aspects mentioned above seem yet to be open discussion. In this and a subsequent paper we shall investigate dynamical properties of KDP type ferroelectrics based on extended Kobayashi's model, i.e., the pseudo-spins-phonons coupled model. In this paper we formulate the problem in terms of Matsubara Green’s function and discuss mainly the acoustic anomaly.

§ 2. Model and formulation

2.1 Model Hamiltonian and Mean Field Theory

As mentioned in the Introduction we adopt extended Kobayashi’s model described by the following Hamiltonian:

\[ H = H_p + H_L + H_{p-L}, \]

\[ H_p = -2Q \sum \phi - \frac{1}{2} \sum_{i,j} J_{ij} Z_i Z_j, \]

\[ H_L = \frac{1}{2} \sum_{q, \lambda=0,1} \left\{ Q_q^\lambda P_{-q}^\lambda + \omega_q^\lambda \right\}, \]

\[ H_{p-L} = -\frac{1}{\sqrt{N}} \sum_{q, \lambda=0,1} F_q^\lambda Q_{-q}^\lambda Z_{-q}, \] (2.1)

where \( Q \) and \( J_{ij} \) are the tunneling frequency and the interaction between the proton bonds, respectively. The superscript \( \lambda \) expresses the kind of the phonon, i.e., the TO phonon or the TA phonon, according as \( \lambda = 0 \) or \( \lambda = 1 \). It should be noted that both \( F_q^\lambda \) and \( \omega_q^\lambda \) are linearly dependent on \( |q| \) for small \( |q| \) while both \( Q_q^0 \) and \( Q_q^0 \) can be approximated as non-vanishing constants.

In this paper we neglect the term \( Q_q^0 Q_{-q}^0 \) present in the KDP type ferroelectrics, since it does not give important effects. When this term is added to the present model, we can first diagonalize the quadratic terms \( (Q_q^\lambda Q_{-q}^\lambda) \) of the phonon variables and hence again obtain the new acoustic mode and the new optic mode. Using these new coordinates of the phonon variables, we can rewrite the Hamiltonian into the same form as Eq. (2.1). On the contrary, this term \( (\rho_{00} P_0 x_0) \) is essentially important in the simple phenomenological theory of the proton and the shear strain \( x_0 \) are treated and effects of the proton are not taken into account.

We assume, for simplicity, one proton bond in the unit cell. The Fourier transformations are then defined as follows:

\[ Z_j = \frac{1}{N} \sum_q Z_{q} e^{-i q \cdot r_j}, \]
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\[ J_{ij} = \frac{1}{N} \sum_q J_q e^{-i q \cdot (r_i - r_j)} \]

\[ Q_j^\lambda = \frac{1}{\sqrt{NM}} \sum_{q_i} Q_q e^{-i q \cdot r_i} \]  

(2.2)

Let us introduce mean values \( \langle Z \rangle \) and \( \langle Q_q^\lambda \rangle \),

\[ Z_i = \langle Z \rangle + \bar{Z}_i, \]

\[ Q_q^\lambda = \langle Q_q^\lambda \rangle \delta_{q,q_0} + \bar{Q}_q^\lambda \]  

(2.3)

where \( \bar{Z}_i \) and \( \bar{Q}_q^\lambda \) are the fluctuations around the mean values. In terms of the second quantized form \( Q_q^\lambda = (1/\sqrt{2\omega_q}) (b_q^\lambda + b_{-q}^{\dagger}^\lambda) \), \( b_q^\lambda \) or \( b_{-q}^{\dagger}^\lambda \) is the annihilation or creation operator of the transverse phonon, respectively. With the use of Eq. (2.3), the model hamiltonian (2.1) reduces to

\[ \mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \]
\[ \mathcal{H}_0 = \mathcal{H}_p + \mathcal{H}_L \]

\[ \mathcal{H}_p = -2 \Omega \sum_i X_i - J_0 \langle Z \rangle \sum_i Z_i + \frac{N}{2} J_0 \langle Z \rangle^2 \]

\[ - \frac{1}{\sqrt{N}} \sum_i F_0^\lambda \langle Q_i^\lambda \rangle \sum_i Z_i - \sqrt{N} \langle Z \rangle \sum_i F_0^\lambda \bar{Q}_i^\lambda \]

\[ + \frac{1}{2} \sum_i (\omega_0^\lambda)^2 \langle Q_i^\lambda \rangle^2 + \sum_i (\omega_0^\lambda)^2 \langle Q_i^\lambda \rangle \bar{Q}_i^\lambda \]  

(2.4)

\[ \mathcal{H}_L = \frac{1}{2} \sum \{ F_q^\lambda \bar{P}_{-q}^{\dagger} + (\omega_q^\lambda)^2 \bar{Q}_q^\lambda \bar{Q}_{-q}^{\dagger} \} \]

\[ \mathcal{H}' = - \frac{1}{2} \sum_i J_{ij} \bar{Z}_i \bar{Z}_j - \frac{1}{\sqrt{N}} \sum_{q_1} F_q^\lambda \bar{Q}_q^\lambda \bar{Z}_{-q} \]  

Noticing that both \( F_q^\lambda \) and \( \omega_q^\lambda \) for small values of \( q \), the mean value \( \langle Q_0^\lambda \rangle \) should be evaluated in the limit \( q \rightarrow 0 \) as

\[ F_0^\lambda \langle Q_0^\lambda \rangle = \lim_{q \rightarrow 0} F_q^\lambda \langle Q_0^\lambda \rangle = \sqrt{N} \langle Z \rangle \lim_{q \rightarrow 0} \frac{|F_q^\lambda|^2}{(\omega_q^\lambda)^2} \]  

(2.5)

Thus

\[ \mathcal{H}_p = - \sum_i (2 \Omega X_i + J_0 \langle Z \rangle Z_i) + \frac{N}{2} J_0 \langle Z \rangle^2 \]  

(2.6)

where \( J_0 \) is the coupling coefficient of the pseudo-spins renormalized by phonons.\(^{a)}\)

\(^{a)}\) Strictly speaking, the limit in Eq. (2.7) depends on the direction in which we make \( q \) tend to zero. Therefore the limit should be taken in the direction in which \( J_0 \) takes the maximum value.
$\mathcal{J}_0 = J_0 + \lim_{q \to 0} \sum_{\omega_n} \frac{|F_q|^2}{(\omega_n^2)^2}$.

(2.7)

It is seen in this equation that the acoustic mode gives a constant mean field $-F_q^a\langle Q_q^a \rangle$ to the pseudo-spin system although the coupling constant $F_0^a$ equals to zero. Equation (2.6) tells us that all effects of the phonons only appear in the renormalized coupling coefficient $\mathcal{J}_0$ within the mean field approximation.

Rotating the principal axis in the pseudo-spin space so as to coincide with the mean direction of the spin, one has

\[ X_i = S_i^x \sin \theta + S_i^z \cos \theta, \quad Z_i = S_i^x \cos \theta - S_i^z \sin \theta, \]

\[ \sin \theta = 2\Omega/W, \quad \cos \theta = \mathcal{J}_0 \langle Z \rangle/W, \quad W = \sqrt{(2\Omega)^2 + (\mathcal{J}_0 \langle Z \rangle)^2}. \]

(2.8)

Then Eq. (2.6) turns out to be

\[ \mathcal{H}_R = -W \sum_i S_i^x + \frac{N}{2} \mathcal{J}_0 \langle Z \rangle^2. \]

(2.9)

It should be noted that a mean value $\langle Z \rangle$ introduced above as a parameter should be determined self-consistently, that is, the transition temperature determined from $\langle Z \rangle = 0$ should coincide with that from the divergence of the susceptibility. The molecular field approximation is known, in this sense, to be consistent with the RPA approximation. However, how to determine $\langle Z \rangle$ in higher order calculation beyond RPA is a difficult problem, which has not yet been clarified even in other systems. Then we shall be obliged to confine ourselves to $T > T_c$ for higher order calculations beyond RPA in the subsequent paper. In the molecular field approximation $\langle Z \rangle$ is determined by the self-consistent equation

\[ W/\mathcal{J}_0 = \frac{1}{2} \tanh(W/2T_c), \]

(2.10)

which leads to the equation for the transition temperature $T_c$:

\[ 1 = (\mathcal{J}_0/4\Omega) \tanh(\Omega/T_c). \]

(2.11)

It follows from this equation that there is no phase transition in the molecular field approximation if $\Omega > \Omega_c = \mathcal{J}_0/4$.

2.2 Green's function and perturbational treatment

In this subsection we develop the perturbational theory taking a mean field Hamiltonian as the unperturbed part. The small parameter $s$ in the present perturbational expansion is the inverse of third power of the force range, i.e., $s = v/R_c^3$, where $v$ and $R_c$ stand for the volume of the unit cell and the force range, respectively.

Perturbational calculation is made on Matsubara Green's functions:

\[ D_1(q, \tau) = \langle T_\tau \{ \hat{Q}_q^+ (\tau) \hat{Q}_q^+ (\beta) \} \rangle_\beta / \langle T_\beta \{ \mathcal{F} (\beta) \} \rangle_\beta, \]

(2.12)

here
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Fig. 1. (a) A graph of the spin cumulant; $\Gamma_m(i\omega_n, i\omega_{n1}, \ldots, i\omega_{nm})$. (b) Some typical graphs: Dashed lines and wavy lines represent $J_q$ and $D'_q(q, i\omega_n)$, respectively.

\[ \langle \cdots \rangle_c = \frac{\text{Tr} \{ e^{-\beta S_c} \ldots \} }{\text{Tr} e^{-\beta S_c} } , \]

\[ A(\tau) = e^{H_c} A e^{-H_c} , \]

\[ S(\beta) = \exp \{ - \int_0^\beta \mathcal{H}'(\tau) d\tau \} , \]

and $T_r$ is the time ordered operator. In the above expression the script $i$ denotes the phonons or the pseudo-spins according as $i = \lambda (= o, a)$ or $i = \Lambda$, that is, we define for brevity, $\hat{Q}_q = \hat{Z}_q$. Perturbational expansion is performed with the use of the Wick theorem for phonon-operators while a cumulant expansion is utilized for spin parts as is usually used in the Heisenberg system and also in the pseudo-spin system studied by Stinchcombe. The cumulant average $\langle \cdots \rangle_c$ of the spin operators are given by the relation
Fig. 2. (a) The graph of $D_i(q, i\omega_n)$. (b) Graphs of $H(q, i\omega_n)$: The shaded parts denote renormalized cumulants. (c) Some graphs of the renormalized cumulants. (d) The graph of $D_r(q, i\omega_n)$.

\[ \langle T_r \left\{ \exp \int_0^\beta \xi(\tau)Z_i(\tau) d\tau \right\} \rangle = \exp \left[ \langle T_r \left\{ \exp \int_0^\beta \xi(\tau)Z_i(\tau) d\tau \right\} \rangle - 1 \right]. \]

The Fourier transformation of Green's function $D_i(q, \tau)$ given by Eq. (2.12) is defined in the form

\[ D_i(q, i\omega_n) = \int_0^\beta D_i(q, \tau) e^{i\omega_n \tau} d\tau \quad (2.14) \]

with $\omega_n = 2\pi n T$. Then the perturbational expansions are carried out with the use of the 0-th order phonon Green's function $D_0(q, i\omega_n)$ and cumulants:

\[ D_0(q, i\omega_n) = 1/\{ (\omega_n^2) + \omega_n^2 \}, \quad (2.15) \]

\[ \Gamma_n(i\omega_n, i\omega_n, \ldots, i\omega_n) = \int_0^\beta d\tau_1 \ldots d\tau_n e^{i\omega_1 \tau_1 + \ldots + i\omega_n \tau_n} \langle T_r \{ Z_i(\tau_1) \ldots Z_i(\tau_n) \} \rangle e. \quad (2.16) \]

Some typical graphs are shown in Fig. 1. It is easily seen in this figure that in the calculation of spin Green's function $D_s(q, i\omega_n)$ all effects of phonons only appear as the renormalized interaction $J_q(i\omega_n)$:

\[ J_q(i\omega_n) = J_q + \sum \frac{|F_q^2|^2}{\{ (\omega_n^2) + \omega_n^2 \}}. \quad (2.17) \]
Phonon Green's function $D_\delta(q, i\omega_n)$ can be obtained from spin Green's function through the exact relation

$$D_\delta(q, i\omega_n) = D_\delta^0(q, i\omega_n) + \frac{|F_\delta|^2}{N} D_\delta^0(q, i\omega_n) D_s(q, i\omega_n) D^s_s(q, i\omega_n).$$  \hspace{1cm} (2.18)

Thus we shall concentrate upon spin Green's function $D_s(q, i\omega_n)$ for the spin system with the effective interaction $\tilde{J}_q(i\omega_n)$. The complete form of spin Green's function $D_s(q, i\omega_n)$ is given by

$$D_s(q, i\omega_n) = \frac{\Pi(q, i\omega_n)}{1 - \left(\frac{\tilde{J}_q(i\omega_n)}{N}\right) \Pi(q, i\omega_n)}. \hspace{1cm} (2.19)$$

Here $\Pi(q, i\omega_n)$ is the irreducible part of $D_s(q, i\omega_n)$ which cannot be separated into two parts by cutting a single $\tilde{J}_q(i\omega_n)$ line, as shown in Fig. 2.

§ 3. General properties of the phase transition in the present model and the random phase approximation

3.1 General properties of the phase transition and acoustic anomaly

Let us investigate properties of the phase transition in the present model based on the general form of Green's function $D_s(q, i\omega_n)$ given by Eq. (2.19).

With the use of the Kubo formula and the relation (2.18), the static susceptibility is derived from Green's function $D_s(q, i\omega_n)$ for the TO phonon as follows:

$$\chi(T) = \langle e^* \rangle \lim_{q \to 0} D_s(q, 0),$$

$$= \langle e^* \rangle \left\{ \frac{1}{(\omega_p^0)^2} + \frac{1}{(\omega^0)^2} \frac{|F_\delta|^2}{N} D_s(T) \right\}, \hspace{1cm} (3.1)$$

where $e^*$ is an effective charge and $D_s(T) = \lim_{q \to 0} D_s(q, 0)$. Since the susceptibility should diverge at the transition point $T_c$, one can set

$$D_s(T_c)^{-1} \approx a_{\pm} |T - T_c| \hspace{1cm} (3.2)$$

near $T_c$, $a_+ (a_-)$ being a temperature independent constant for $T > T_c (T < T_c)$.

In the above representation of temperature dependence of $D_s(T)$ we have chosen the critical exponent $\gamma$ being unity, for simplicity. Except for the very vicinity of $T_c$ it is plausible to set $\gamma = 1$. We have, then, the susceptibility near $T_c$ as

$$\chi(T) = \chi(\infty) + \frac{C_\pm}{|T - T_c|}, \hspace{1cm} (3.3)$$

here the Curie constants $C_+$ and $C_-$ are given by

*) In this paper we assume the transition being of second order. In the case of a slightly first order transition $T_c$ should be regarded as a limiting point of stability.
Let us investigate the poles of $D_s(q, z)$ on the unphysical plane, i.e.,

$$D_s(q, z)^{-1} = \Pi(q, z)^{-1} - \tilde{J}_q(z)/N = 0.$$  \hfill (3.5)

Setting $z = \tilde{V}q$ and making $q$ tend to zero in this equation, one has the renormalized velocity $\tilde{V}$ of the acoustic mode:

$$\left(\frac{\tilde{V}}{V}\right)^2 = \frac{ND_s(T)^{-1}}{ND_s(T)^{-1} + (f^s/V)^2},$$ \hfill (3.6)

where $V$ stands for the bare velocity of the TA phonon and $f^s = \lim_{q \to 0} (F^s q)/q$. Inserting Eq. (3.2) into Eq. (3.6), one gets

$$\left(\frac{\tilde{V}}{V}\right)^2 = \frac{|T - T_c|}{|T - T_c| + \Delta T_\pm},$$ \hfill (3.7)

where

$$\Delta T_\pm = (f^s/V)^2 / Na_\pm.$$ \hfill (3.8)

In the simple phenomenological theory widely used in analysis of experiments the similar expression for $(\tilde{V}/V)^2 = (C_{ts}/C_{es})$ can be obtained, where $C_{ts}$ and $C_{es}$ are the elastic constant with the fixed polarization and the one with the fixed electric field, respectively, i.e.,

$$\left(\frac{\tilde{V}}{V}\right)^2 = C_{ts}^2 / C_{es}^2 = \frac{\chi_{xx}^{-1}}{\chi_{xx}^{-1} + C_{tt} / C_{xx} - a_{xx}^{-1}},$$

where $a_{xx}, b_{xx}, \chi_x$ and $\chi_z$ are the piezoelectric stress constant, the piezoelectric strain constant, the susceptibility with the fixed stress and the susceptibility with the fixed strain, respectively. This equation corresponds to Eq. (3.6). Comparing the above expression with Eq. (3.6) one finds that the susceptibility $\chi_x$ in the phenomenological expression corresponds to the spin susceptibility $D_s(T)$ in Eq. (3.6). This difference results from neglecting effects of the protons in the phenomenological treatment. As the temperature departs from $T_c$, the difference becomes important as is easily seen from Eq. (3.1).

Comparing Eq. (3.8) with Eq. (3.4), we have

$$\Delta T_+ / \Delta T_- = C_+ / C_- = (a_- / a_+).$$ \hfill (3.9)

Next setting $q = 0$ first in Eq. (3.5), we obtain two solutions with $q = 0$ which are not affected by the coupling between the TA phonon and the pseudo-spins, since $F^s = 0$:

$$ND_s(T)^{-1} + (f^s/V)^2 = N\{\Pi(0, 0)^{-1} - \Pi(0, z)^{-1}\} + |F^s|^2 z^2 / [(\omega_0)^2 (\omega_0)^2 - z^2].$$ \hfill (3.10)

Assuming $\omega_0 \gg |z|$ near $T_c$, for the soft mode pole as it should be so, one can
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neglect the second term of the right-hand side of Eq. (3·10). Then using Eqs. (3·2) and (3·8) one has

\[ Na_ \pm \{ | T - T_c | + \Delta T_ \pm \} = N \{ II(0, 0)^{-1} - II(0, z)^{-1} \}. \] (3·11)

This relation tells us that the magnitude \(| z |\) for the soft mode pole does not vanish at \(T_c\).

It follows from the above discussion that the velocity of the acoustic mode vanishes at \(T_c\) where the susceptibility \(\chi\) diverges while the frequency of the ferroelectric mode remains finite. It should be noted that the obtained acoustic mode is a mixed mode which consists of the original three modes. Accordingly, this acoustic mode is optically active although its strength is proportional to \(| F_q |^2 \cdot | f_a |^2\) and is very weak.

3.2 Results in the random phase approximation

In this subsection we calculate Green's functions within the random phase approximation. The irreducible part \(\Pi(q, i\omega_n)\) in RPA is given by the lowest cumulant which equals spin Green's function in the mean field approximation itself, i.e.,

\[ \Pi^s(q, i\omega_n) = D^s(q, i\omega_n) \]

\[ = \frac{\sin^2 \theta W \langle S^r \rangle N}{W^2 + \omega_n^2} - \frac{\cos^2 \theta}{4T} \{ 1 - \left( \frac{2W}{J_0} \right)^2 \} N \delta_{n,0}. \] (3·12)

Inserting Eq. (3·12) into Eq. (2·18) we have \(D(q, i\omega_n)\) in RPA.

It should be noted that \(\delta_{n,0}\) appearing in Eq. (3·12) turns out to be

\[ \Gamma_z / (\Gamma_z + |\omega_n|) = u(i\omega_n), \] (3·13)

when relaxation processes in higher order are taken into account. Here \(\Gamma_z\) is the inverse of longitudinal relaxation time of the pseudo-spin. Accordingly, this term gives the relaxation pole to Green's functions below \(T_c\), which is observable in optical experiments, as discussed by Blinc13 by the use of a semiphenomenological approach similar to the Bloch equation in the problem of nuclear magnetic resonance. In RPA one has \(\lim_{\omega_n \to 0} u(i\omega_n) = \delta_{n,0}\) since relaxation processes are perfectly neglected there. In the analytic continuation from \(i\omega_n\) to \(\omega + i\delta\) one must first replace \(\delta_{n,0}\) by \(u(i\omega_n)\) and finally make \(\Gamma_z\) tend to zero if necessary. In this way one obtains the equation for the frequencies of the three modes:

\[ \omega^s - W \{ W - \sin^2 \theta \langle S^r \rangle J_q(\omega) \} = 0. \] (3·14)

We can solve this equation exactly in the two limiting cases of \(q \to 0\) in the same way as described in the preceding subsection. First setting \(q = 0\) in Eq. (3·14), one obtains the following two solutions:

\[ \omega^s = \frac{1}{2} \left[ W (W - \sin^2 \theta \langle S^r \rangle J_0) + (\omega_0)^2 \right. \]

\[ \pm \sqrt{ \left\{ W (W - \sin^2 \theta \langle S^r \rangle J_0) - (\omega_0)^2 \right\}^2 + 4 W \sin^2 \theta \langle S^r \rangle |F_o|^2 \}. \] (3·15)
These solutions are the same as that obtained by Kobayashi. The approximate expressions of Eq. \(3 \cdot 15\) are

\[
\tilde{\omega}_1(0)^2 \simeq (\omega_s)^2 + W \sin^2 \theta \langle S'^* \rangle |F_s^*/\omega_s|^4 + o \left( |F_s^*/\omega_s|^4 \right),
\]

\[
\tilde{\omega}_2(0)^2 \simeq W \left( W - \sin^2 \theta \langle S'^* \rangle J_0 \right) - W \sin^2 \theta \langle S'^* \rangle |F_s^*/\omega_s|^4 + o \left( |F_s^*/\omega_s|^4 \right).
\]

(3.16)

Next, we substitute \( \omega = \tilde{\omega}_s(q) = \tilde{V}_q \) into Eq. \(3 \cdot 14\) and take the limit \( q \to 0 \) after the substitution. Then we get the exact expression in RPA for the renormalized velocity \( \tilde{V} \) of the acoustic mode as follows:

\[
(\tilde{V}/V)^q = \omega_s(0)^2 \left/ \left( \omega_s(0)^2 + W \sin^2 \theta \langle S'^* \rangle (f^*/V)^q \right) \right.,
\]

where we have defined \( \omega_s(q)^2 \) by

\[
\omega_s(q)^2 = W \left( W - \sin^2 \theta \langle S'^* \rangle \tilde{J}_q(0) \right).
\]

(3.17)

Then \( \tilde{\omega}_s(0)^2 \) in Eq. \(3 \cdot 16\) is rewritten with the use of Eqs. \(3 \cdot 18\) and \(3 \cdot 16\):

\[
\tilde{\omega}_s(0)^2 \simeq \omega_s(0)^2 + W \sin^2 \theta \langle S'^* \rangle (f^*/V)^q.
\]

(3.19)

Since \( \omega_s(0) \) vanishes at \( T = T_c \), one can write \( \omega_s^2 \simeq b \pm |T - T_c| \) in the neighborhood of \( T_c \). Then we have again the same expression for \( (\tilde{V}/V)^q \) near \( T_c \) as in Eq. \(3 \cdot 7\) and

\[
\tilde{\omega}_s(0)^2 \simeq b \pm (|T - T_c| + \Delta T_s).
\]

(3.20)

The parameters in Eqs. \(3 \cdot 7\) and \(3 \cdot 20\) are

\[
b_+ = Q \tilde{J}_c \left\{ 1 - \left( 4Q / \tilde{J}_c \right)^2 \right\} / T_c \simeq \tilde{J}_c (1 - \rho^2) (\tanh^{-1} \rho)^q,
\]

\[
b_- = 2b_+ / \left\{ 1 - (1 - \rho^2) (\tanh^{-1} \rho) / \rho \right\},
\]

\[
\Delta T_s = Qp / b_+.
\]

(3.21)

with \( p = 4Q / \tilde{J}_c \). In the derivation of Eq. \(3 \cdot 21\) we have used Eqs. \(2 \cdot 8\), \(2 \cdot 10\) and \(2 \cdot 11\).

It should be emphasized that the inclusion of the effect of the longitudinal relaxation leads to the serious effect on the frequency of the acoustic mode below \( T_c \) if \( \tilde{V}_q \ll \Gamma \). Our results Eqs. \(3 \cdot 17\), \(3 \cdot 18\) and \(3 \cdot 21\) correspond to the case of \( \tilde{V}_q \ll \Gamma \). Contrary, when \( \tilde{V}_q \ll \Gamma \), one gets

\[
(\tilde{V}/V)^q = \omega_s'(0)^2 / \tilde{\omega}_s'(0)^2,
\]

\[
\omega_s'(0)^2 = \omega_s'(0)^2 + W \left( f^*/V \right)^q \left[ \sin^2 \theta \langle S'^* \rangle + \frac{W \cos^2 \theta}{4T} \left\{ 1 - \left( \frac{2W}{\tilde{J}_0} \right)^2 \right\} \right],
\]

\[
\omega_s'(0)^2 = W \left( W - \sin^2 \theta \langle S'^* \rangle \tilde{J}_0 \right) - \frac{W^*}{4T} \cos^2 \theta \left\{ 1 - \left( \frac{2W}{\tilde{J}_0} \right)^2 \right\} \tilde{J}_0
\]

\[
= \tilde{J}_0 \langle Z \rangle \left[ 1 - \frac{\tilde{J}_0}{4T} \left\{ 1 - \left( \frac{2W}{\tilde{J}_0} \right)^2 \right\} \right].
\]

(3.22)
in the ferroelectric region. Near $T_c$ these equations can be rewritten in the same form as in Eqs. (3·7) and (3·20). In this case, however, the parameters $\Delta T_+$ and $\Delta T_-$ satisfy the relation $\Delta T_+ / \Delta T_- = 2$, where $\Delta T_+$ is given by Eq. (3·21).

It should be emphasized that in KDP type ferroelectrics the experimental condition satisfies $\tilde{V}_q \ll T_\ast$, since the magnitude of $\Gamma_\ast$ seems to be of the order of the damping constant of the soft mode; $\Gamma_\ast$, which expresses the dynamical behaviour of the longitudinal component of the pseudo-spin $S^\ast(q)$ necessarily results from the dynamics of the system (noncommutability between $S^\ast(q)$ and the total hamiltonian) as well as the relaxation of the soft mode.\(^*\) This is different from the stand point of Blinc and \v{Z}ekš\(^{5b}\) who attributed $\Gamma_\ast$ to the interaction between the pseudo-spin system and the thermal bath (the lattice system) as in the theory of the nuclear magnetic resonance.

Now let us derive the expression for phonon Green's function $D_\lambda(q, i\omega_n)$. Using the relation Eq. (2·18), after some algebras we have

$$D_\lambda(q, i\omega_n) = \frac{\langle \omega_q \rangle^4 + \omega_n^4}{\langle \omega_q \rangle^4 + \omega_n^4} W \left[ \frac{W - \sin^2 \theta \langle S^\ast \rangle \{ J_q + |F_q^\ast|^2 \} / \left( \omega_q^4 + \omega_n^4 \right) }{\langle \omega_q \rangle^4 + \omega_n^4} \right] (1 - \delta_{n,0}) \left[ \frac{1}{\langle \omega_q \rangle^4 + \omega_n^4} W \langle S^\ast \rangle \sin \theta \{ W / 4T \} \cos \theta \{ 1 - (2W / J_\ast)^3 \} \right] \delta_{n,0}. \tag{3·23}$$

The isothermal electric susceptibility is obtained as

$$\chi_T = (e^*)^2 D_\lambda(0, 0) = \frac{1}{\langle \omega_q \rangle^4 + \omega_n^4} W \langle S^\ast \rangle \sin \theta \{ W / 4T \} \cos \theta \{ 1 - (2W / J_\ast)^3 \} \right] \delta_{n,0}. \tag{3·24}$$

Near $T_c$, we have

$$\chi_T = (e^*)^2 \left[ \frac{1}{\langle \omega_q \rangle^4 + \omega_n^4} \frac{C_\pm}{|T - T_c|} \right] \tag{3·25}$$

with

$$C_\pm = 2C_- = \left| \frac{F_\ast^0}{\omega_0^2} \frac{4Q^2}{b_+ J_\ast} \right|, \tag{3·26}$$

where $b_+$ is defined in Eq. (3·21). It should be noted that the static adiabatic susceptibility $\chi_\ast$ is different from the isothermal one $\chi_T$ within RPA below $T_c$, i.e.,

\(^*\) The relation $S^\ast = S^\ast S^\ast - 1/2$ tells us that the relaxation of the soft ferroelectric mode also leads to the relaxation of the longitudinal component $S^\ast(S^\ast S^\ast)$ corresponds to the ferroelectric optical phonon variable in the phonon model while $S^\ast$ corresponds to the phonon density) and hence the longitudinal damping is of the same order of the damping of the ferroelectric mode.
\[ x_s = \lim_{\omega \to 0} \left( e^{*} \right)^{D_{0}} (0, \omega + i\delta) \]
\[ = \left( e^{*} \right)^{\frac{1}{(\omega_0)^2} + \left( \frac{F_{0}^{*}}{\omega_0} \right)^2 \frac{W(S^*) \sin^2 \theta}{\omega_{s}(0)^2} }, \]

where \( \omega_s(q) \) has been defined by Eq. (3.18). This difference results from the perfect absence of relaxation process in RPA (i.e., \( \Gamma_s = 0 \)). If the relaxation processes are properly taken into account, as will be shown in a subsequent paper in preparation, this defect is remedied and as a result \( x_s \) coincides with \( x_T \), as it should be so.

§ 4. Comparison with experiments

In this section, we compare the results obtained in the previous section with experiments.

1) The renormalized velocity \( \bar{V} \) of the acoustic mode:

At first let us compare the temperature dependence of \( \bar{V} \) given by Eq. (3.7) with the experimental results on the shear elastic constant \( C_{66} \) for KDP by Brody and Cummins.\(^{19}\) When we choose \( \Delta T_{+} = 3.7 \text{ K} \) and \( \Delta T_{-} = 0.36 \text{ K} \), the obtained curves for \( (\bar{V}/V)^2 \) is in fairly good agreement with the experiments as shown in Fig. 3. The discrepancy between the curves thus obtained and the experimental data, however, becomes large in the very vicinity of \( T_s \), i.e., \( |T - T_s| < 0.5 \text{ K} \). The reason for this tendency is not clear.

2) The relation \( \Delta T_{+}/\Delta T_{-} = C_{+}/C_{-} \) and the values of \( C_{+} \) and \( C_{-} \):

We have obtained the ratio \( \Delta T_{+}/\Delta T_{-} = C_{+}/C_{-} \approx 10 \) from fitting the \( (\bar{V}/V)^2 \) curve to experiments mentioned above. Experimental values of those \( C_{+} \) and \( C_{-} \) on KDP are as follows: \( C_{+} = 250 \text{ K} \) (dielectric measurements by Baumgartner\(^{25}\)) = 255 K (sound velocity measurements by Garland and Novotony\(^{26}\)), \( C_{-} = 17.5 \text{ K} \) (Kaminow and Hardings\(^{27}\)) = 30 K (Brody-Cummins\(^{19}\)). These data give the ratio \( C_{+}/C_{-} \approx 8 \sim 15 \) which seems to be consistent with our choice of the value.

As for DKDP we set \( \Delta T_{+} \approx 4.2 \text{ K} \)
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Fig. 3. The graphs of \((\tilde{V}/V)^4\). (a) KDP, (b) DKDP. Solid lines are theoretical curves with \(\Delta T_+=3.7\,\text{K}\) and \(\Delta T_- = 0.36\,\text{K}\) for KDP and with \(\Delta T_+=4.2\,\text{K}\) and \(\Delta T_- = 0.30\,\text{K}\) for DKDP. Experimental values are due to Brody and Cummins (KDP)\(^{19}\) and Litov and Uehling (DKDP).\(^{10}\)

and \(\Delta T_- \approx 0.30\,\text{K}\) in order to fit the curve \((\tilde{V}/V)^4\) to the experiments on \(C_{66}^P\) by Litov-Uehling.\(^{20}\) Then \(\Delta T_+/\Delta T_- = C_+/C_- = 14\) which is a little larger than the experimental results: \(C_+ \approx 265\,\text{K}, C_- \approx 22\,\text{K}\) \((C_+/C_- \approx 12)\) by Litov-Uehling.\(^{20}\) The discrepancy might come from neglect of the effect of electric field in our analysis.

3) The soft ferroelectric mode:

Kaminow and Damen\(^9\) showed in analysis of their Raman data on KDP that the temperature \(T_0\) extrapolated from above \(T_c\), at which the frequency of the soft ferroelectric mode vanishes, is lower than \(T_c\) by about 5 K, i.e., \(\Delta T_+ \approx 5\,\text{K}\). This seems to be in reasonable agreement with the adjusted value \(\Delta T_+ \approx 3.7\,\text{K}\).

Following Kaminow and Damen, assuming

\[ N\{II^{-1}(0,0) - II^{-1}(0, z)\} \approx \theta_\pm (z^2 - 2i\Gamma_\pm z) \]  

for small \(|z|\) and inserting Eq. (4·1) into Eq. (3·11), we get

\[ z^2 - 2i\Gamma_\pm z - \tilde{\omega}_\pm(0)^2 = 0, \]  

where

\[ \tilde{\omega}_\pm(0) = b_{\pm}^\prime \left(|T - T_c| + \Delta T_\pm\right)^{1/2} \]  

with constants \(b_{\pm}^\prime\) and \(b_-^\prime\). This result agrees with Eq. (3·20) in RPA except for the damping \(\Gamma_\pm\).

In addition to the shift \(\Delta T_\pm\) due to the piezoelectric coupling as discussed above, there may exist the apparent shift \(\Delta T_\pm \text{res}\) which results from coupling between the soft ferroelectric mode and a resonance mode, as was pointed out...
by Coombs and Cowley.\textsuperscript{28} Taking account of this coupling we have

\[ N(\Pi^{-1}(0,0) - \Pi^{-1}(0,z)) = z^2 - 2i\Gamma z - \frac{\delta^2 z}{1 + i\delta} \]

\[ \approx \theta \begin{cases} z^2 - 2i\Gamma z & \text{for } z\tau \ll 1 \\ z^2 - 2i\Gamma z - \delta^2 & \text{for } z\tau \gg 1 \end{cases} \]

with \( \Gamma = \Gamma + \delta\tau/2 \), instead of Eq. (4.1).

Inserting this equation into Eq. (3.11), we have the total shift \( \Delta T_{\pm}^{\text{tot}} \) for \( z\tau \gg 1 \):

\[ \Delta T_{\pm}^{\text{tot}} = \Delta T_{\pm} + \Delta T_{\pm}^{\text{res}}, \]

where

\[ \Delta T_{\pm}^{\text{res}} = \theta \delta^2/(Na_{\pm}). \]

Coombs and Cowley ascribed the observed shift \( \Delta T_{\pm}^{\text{tot}} \) to the apparent shift \( \Delta T_{\pm}^{\text{res}} \) neglecting \( \Delta T_{\pm} \) for KDP type ferroelectrics.\textsuperscript{29} However, recent experiments by Lagokas and Cummins\textsuperscript{29} on KDP in Brillouin scattering show that \( \Delta T_{\pm} \approx 0.025 \text{K} \) is negligibly small compared with \( \Delta T_{\pm} \approx 4.3 \text{K} \). Contrary to the case of KDP, large shifts \( \Delta T_{\pm}^{\text{tot}} \) suggest that \( \Delta T_{\pm}^{\text{res}} \) would be large and play an important role in such materials as CsDA and KDA.\textsuperscript{4}

4) The ultrasonic attenuation coefficient \( \alpha(\omega) \):

Now we study the ultrasonic attenuation coefficient taking account of the damping \( \Gamma \) of the soft ferroelectric mode semiphenomenologically, as has been done in Eqs. (4.1), (4.2) and (4.3).

Inserting \( \omega = \delta_s(q) = \bar{V}q + iq^2 \) into Eq. (3.5), we easily obtain

\[ \tau = \frac{(V^2 - \bar{V}^2)\Gamma}{(\delta_s'(0))} = \frac{\theta \Gamma_s(f_s)}{(D_s(T) + (f_s/V)^2)^2} \]

with the aid of Eq. (4.1). This leads to the attenuation \( \alpha(\omega) \):

\[ \alpha(\omega) = \frac{\omega^2(V^2 - \bar{V}^2)\Gamma_s}{\bar{V}^2(\delta_s'(0))^2}. \]

(4.5)

The similar expression can be obtained from the usual phenomenological theory.\textsuperscript{24} Using Eqs. (3.7) and (4.3), we have

\[ \alpha(\omega) = g\omega^2|T - T_c|^{-3/2}(|T - T_c| + \Delta T_{\pm}^{\text{res}})^{-1/2} \]

(4.6)

with \( g = \theta \Gamma_s(f_s/V)^2/(Na_{\pm}). \)

We have analyzed the ultrasonic measurements on DKDP by Litov and Uehling.\textsuperscript{29} Choosing the values \( T_c = 205.6 \text{K} \), \( \Delta T_{\pm} = 4.2 \text{K} \) and \( g = 1.11 \times 10^{-12} \text{dB sec}^2 \text{K}^{-1} \text{cm}^{-1} \), we obtain the curve of \( \alpha(\omega) \) fitted well with experiments in a certain region near \( T_c \) as shown in Fig. 4 (the above values of \( T_c \) and \( \Delta T_{\pm} \) are determined so as to fit the experiments of the elastic constants \( C_{66}^{\pm} \) as

\[ \text{See the Note added in proof.} \]
has been discussed first in this section.)

However, it is clear in the figure that the discrepancy between \( \alpha(\omega) \) and experimental values become large in the region close to \( T_c \), i.e., \(|T-T_c|<1 \text{K}\) and \(|T-T_c|>10 \text{K}\). There are at least two reasons for this discrepancy; (1) the experiment was performed under the electric field of 1.5 KV/cm which reduces the acoustic anomaly in the region close to \( T_c \), the effects of which are ignored in our analysis. (2) the experimental curve plotted on the logarithmic graph reveals the temperature dependence of acoustic attenuation coefficient being \( \alpha(\omega) \propto |T-T_c|^{-\beta/2} \) in the vicinity of \( T_c \) while \( \alpha(\omega) \propto |T-T_c|^{-\beta/2} \) in the region apart from \( T_c \), which suggests that

\[
\alpha(\omega) \propto \omega^\beta |T-T_c|^{-\beta/2} |T-T_c|+\Delta T_\pm|^{-1}. \tag{4·7}
\]

The difference in Fig. 4 for \(|T-T_c|>10 \text{K}\) results from our taking \( g_z \) as constants. This suggests that the damping constant \( \Gamma_z \) in Eq. (4·1) should vary on temperature as \( \Gamma_z \propto |T-T_c|+\Delta T_\pm|^{-1/2} \).

5) Remarks on RPA:

If we use the results in RPA to analyze the experiments of the shear elastic constant \( C_{66}^s \), we get the fairly good agreement with the experiments as follows. It is found from Eqs. (3·18) and (2·8) that the frequency \( \omega(0) \) of the soft mode tends to \( 2\Omega \) in the high temperature limit. Then the experiments by Kaminow and Damen gives \( 2\Omega = 99 \text{ cm}^{-1} \). Using this value and \( T_c = 122 \text{ K} \), we get \( J_0 = 377 \text{ cm}^{-1} \) from Eq. (2·11). Inserting these values into Eq. (3·21), we obtain \( \Delta T_+ \approx 3.7 \text{ K} \) and \( \Delta T_- \approx 0.36 \text{ K} \) which gives \( \Delta T_+/\Delta T_- = 10.3 \). This good agreement was already pointed out by Elliott et al. However, this fairly good agreement seems to be spurious, as was discussed by Elliott and Young, since the experimental condition satisfies \( V_q \ll T_\pm \) and hence for \( T<T_c \) the inclusion of the longitudinal relaxation leads to the large effects as discussed in § 3.2.

§ 5. Summary and discussion

We have investigated KDP type ferroelectrics based on extended Kobayashi’s
model described by the Hamiltonian Eq. (2.1). The perturbational expansion has been developed by the use of Matsubara Green's functions with the aid of the cumulant expansion.

Some general characters of the phase transition are derived independent of approximations, and these are shown to agree with the phenomenological theory essentially. In the present model, however, it is different from the phenomenological one that the spin susceptibility $D_s(T)$ plays the essential role which corresponds to the susceptibility in the usual phenomenological theory. This difference results from neglecting effects of the protons in the phenomenological treatment.

It is generally shown that the velocity $\bar{V}$ of the acoustic mode vanishes at the second-order transition point $T_c$ while the frequency $\tilde{\omega}_2(0)$ of the soft ferroelectric mode remains finite at $T_c$. Assuming the Curie law for the spin susceptibility $D_s(T)$, we have

$$\left(\frac{\bar{V}}{V}\right)^2 = \frac{|T - T_c|}{|T - T_c| + \Delta T_{\pm}},$$

$$\tilde{\omega}_2(0) = b_\pm (|T - T_c| + \Delta T_{\pm})^{1/2}. \tag{4.3}$$

Further, taking account of the damping of the soft ferroelectric mode, we have derived the ultrasonic attenuation $\alpha(\omega)$ in agreement with the phenomenological theory:

$$\alpha(\omega) \propto \Gamma_s \omega^3 |T - T_c|^{-4/3} (|T - T_c| + \Delta T_{\pm})^{-1/3}. \tag{4.6}$$

which is consistent with the experiments on DKDP near $T_c$. However, in order to explain the experimental results in the temperature region apart from $T_c$, the damping constant $\Gamma_s$ cannot be regarded as a constant but it seems to be proportional to $(|T - T_c| + \Delta T_{\pm})^{-1/3}$: This problem remains for the future study.

Now let us briefly discuss the case $Q = 0$ which corresponds to the order-disorder type in the perfect absence of tunnelling. In this case all the effects of the phonons on the pseudo-spins are included in the effective static coupling $\bar{J}_Q(0)$ given by Eq. (2.17) with $\omega_0 = 0$ while the phonons are dynamically independent of the presence of the pseudo-spins since the pseudo-spins $Z_q$ is a constant of motion if $Q = 0$. Therefore, our whole analysis, based on the dynamical relations between the pseudo-spins and the phonons, breaks down. In this case, however, the dynamical behaviour of the pseudo-spins can be thought to result from the interaction between the pseudo-spin system and the thermal bath. Recently, Yamada, Takatera and Huber have investigated the pseudo-spin-phonon coupled model in the absence of the tunnelling based on Onsager's equation of motion. It can be easily seen that when the interaction between the spin system and the TA phonon is taken into account in their theory, a simple analysis of the poles of obtained correlation functions yields the same results concerning
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the acoustic anomaly as the present ones, that is, Eq. (3.7) for the renormalized velocity $\vec{V}$ of the acoustic mode and the form of the ultrasonic attenuation $\alpha(\omega)$ expressed by Eq. (4.6) can be again obtained. The reason for this is that their treatment formally corresponds to taking

$$N\{\Pi(0,0)^{-1}-\Pi(0,z)^{-1}\}=i\Gamma z$$

in Green's function $D_s(q,z)$, which agrees with our assumption Eq. (4.1) for small $|z|$ and hence is within the present content. Accordingly, as for the properties of the acoustic anomaly, the present results are universal even in this case.

Although the random phase approximation can be shown to be of first order of $s$ when $\Omega/J_0=O(1)$, where $s$ is proportional to the inverse of the third power of the force range, the large damping such as in DKDP suggests that $\Omega/J_0<1$. In this case simple perturbational calculations are no more adequate. Moreover, the absence of the relaxation processes in RPA leads to the appearance of the term with Kronecker's delta function $\delta_{z,0}$ in Green's functions, as found in Eq. (3.12) below $T_c$. This defect in RPA is shared with the perturbational treatment of the Heisenberg model by the use of the cumulant expansion. When higher-order effects are taken into account, this term would turn out to be Lorenzian type giving the relaxation pole to Green's functions in the ferroelectric region. These problems will be investigated in the subsequent paper.

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References

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S. Takada, I. Ohnari, H. Kurosawa and Y. Ohmura

23) R. J. Elliott and A. P. Young, to be published.

Note added in proof:
Very recently Lagakos and Cummins (a preprint) have shown that \( \Delta T_{\text{res}} \) is about 0.9 K and is much smaller than \( \Delta T_{\text{res}} \approx 19 \) K.