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Dielectric Properties of Order-Disorder Type Crystals

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Abstract - The soft mode dynamical model has been used to study the dielectric properties of orderdisorder-type crystals. Using the model Hamiltonian proposed by Blinc [Advances in Phys, 29 (1972) 701] and has been modified by Bist et al [GJSFR, 10, 18(2010)], the expressions for the dielectric constant and tangent loss have been derived and discussed for order-disorder, KH2PO4 type-crystals with the help of double time temperature dependent Green's function techniques and Dyson's equation treatment. Using appropriate parameters given by Ganguli et al [Phys Rev. B21, 2937 (1980)] the transverse dielectric constant and observed dielectric constant have been calculated and compared with experimental results of Raman Intensity[Ferroelectrics 52, 91 (1983)], Busch [Helv. Phys. Acta. 11, 265 (1938)], Kaminow et al [Phys. Rev. 138A, 1539 (1963)], and Deguchi et al [J. Phys. Soc. Jpn. 49, 1887 (1980)]. The observed dielectric constant explains the Curie-Weiss behaviour of dielectric constant along the c-axis of KH2PO4 crystal in the paraelectric phase. Also the temperature dependence of tangent loss in paraelectric phase for KH2PO4 at 9.2 GHz for field along the a-axis, and the c-axis have been calculated and compared with experimental results of Kaminow et al [Phys. Rev. 138A, 1539 (1963)]. It is observed that these results are in good agreement with each other and with the results obtained by other methods. At higher temperature the loss deviates from the Curie-Weiss type behaviour and increases linearly with temperature. This behaviour suggests that at higher temperatures the phonon anharmonicity contributes significantly in the observed loss.

Keywords : Green's function; Dyson's equation; phonon anharmonicity; transverse and observed dielectric constant; and tangent loss.

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Notes

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Abstract - The soft mode dynamical model has been used to study the dielectric properties of order-disorder-type crystals. Using the model Hamiltonian proposed by Blinc [*Advances in Phys, 29* (1972) *701*] and has been modified by Bist et al [GJSFR,10,18(2010)], the expressions for the dielectric constant and tangent loss have been derived and discussed for order-disorder, KH₂PO₄ type-crystals with the help of double time temperature dependent Green's function techniques and Dyson's equation treatment. Using appropriate parameters given by Ganguli et al [*Phys Rev.* B21, 2937 (1980)] the transverse dielectric constant and observed dielectric constant have been calculated and compared with experimental results of Raman Intensity[*Ferroelectrics* 52, 91 (1983)], Busch [*Helv. Phys. Acta.* 11, 265 (1938)], Kaminow et al [*Phys. Rev.* 138A, 1539 (1963)], and Deguchi et al [*J. Phys. Soc. Jpn.* 49, 1887 (1980)]. The observed dielectric constant explains the Curie-Weiss behaviour of dielectric constant along the c-axis of KH₂PO₄ at 9.2 GHz for field along the a-axis, and the c-axis have been calculated and compared with experimental results of Kaminow et al [*Phys. Rev.* 138A, 1539 (1963)]. It is observed that these results are in good agreement with each other and with the results obtained by other methods. At higher temperature the loss deviates from the Curie-Weiss type behaviour and increases linearly with temperature. This behaviour suggests that at higher temperatures the phonon anharmonicity contributes significantly in the observed loss.

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I. INTRODUCTION

The phase transition from ferro to non-ferroelectric (paraelectric - hereafter referred to as PE) phase or vice versa, at the transition temperature, is associated with the change in crystal structure as well as anomaly in certain physical properties. In view of the nature of phase transition occurring at transition temperature, the ferroelectrics are classified in two types (i) order-disorder type, and (ii) displacive type. In order-disorder type, as $\rm KH_2PO_4$, the transition is associated with the tunneling of proton through a barrier between two positions of minimum potential energy in the double well potential in the hydrogen bond at the transition temperature. In the other types of transitions, which are called displacive type, the transition are associated with the displacement of a whole sublattice of ions of one type relative to other sublattice, e.g., in BaTiO₃ and most of the double oxide ferroelectrics.

The tunneling proton model has been long believed to be an established model of the phase transition in $\rm KH_2PO_4$ and other hydrogen-bonded crystals. Experimental results of dielectric dispersion ¹, Brillouin spectroscopy² and low frequency Raman spectroscopy³ have shown, however, that the dynamical spectra of polarization fluctuations in pure and mixed crystals $\rm KDP_{l-x}DKDP(KD_2PO_4)_x$ can be well analyzed in terms of the Debye type

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susceptibility⁴, which is characterized by a relaxation time. On the other hand, the origin of spontaneous polarization in KDP was established to be shift of P and O ions relative to K ions, so that the site symmetry of a PO₄ tetrahedron was determined to be C₂ below the transition temperature Tc. Consequently, the Debye susceptibility suggests that the order-disorder of PO₄ dipoles with C₂ site symmetry may be the transition mechanism of KDP. Raman spectroscopic studies confirm that the ferroelectric phase transition in KH₂PO₄, KD₂PO₄ and their mixed crystals is due to the "order-disorder dynamics" of PO₄ dipoles⁵.

The frequency and temperature dependence of dielectric constant near the Curie points of several ferroelectric crystals have investigated by Kaminow⁶. The theoretical studies of temperature dependence of microwave loss in Rochelle salt crystal have been discussed⁷ by considering PLCM model Hamiltonian with phonon anharmonocity up to fourth order and using double time thermal Green's function. Levitsky *et al*⁸, on the basis of the model of relaxational dynamics, have shown that the two particle cluster theory treating the ferroelectric phase transition as a result of an instability in a deuteron (proton) subsystem gives a fair quantitative description of the relaxation soft mode dynamics of quasi-one-dimensional hydrogen bonded crystals.

The dielectric loss is associated with the slow establishment of polarization accompanied by absorption currents. In the high fields, the dielectric loss in these ferroelectrics is due to hysteresis. Microwave loss in the KDP has studied by Kaminow⁶ and Upadhyaya⁹. The temperature dependence of microwave tangent loss in KDP is empirically represented by $(T - T_C)\tan \delta = \alpha + \beta T + \gamma T^2$, this dependence can be explained in terms of slowing down of a relaxational mode. Recently ^{10,11} have experimentally studied the temperature dependence of dielectric constant and loss of KDP measured at 23 kHz before and after the proton irradiation. Formulae were developed to explain ferroelectric transitions in order-disorder ^{7,9,12,13} type crystals.

In our previous studies (hereafter referred to as I^{12} , II^{13}), we have designed the four protons Hamiltonian considers the third-and fourth-order phonon anharmonic interaction terms. Applying the double time thermal Green's function techniques and Dyson's equation the higher order correlations have been evaluated using the renormalized Hamiltonian. The collective mode frequencies and corresponding widths and shifts have been evaluated for PE phase for KDP-type ferroelectric in I. The relaxation processes and ultrasonic attenuation in KDP –type ferroelectric have been studied in II.

In the present study, we use the same Hamiltonian as in I and II, we have evaluated expressions for dielectric constant and tangent loss. Using model parameters given by Ganguli *et al*¹⁴ the transverse dielectric constant and observed dielectric constants have been calculated for $\rm KH_2PO_4$. Their temperature dependence for $\rm KH_2PO_4$ have been calculated and compared with experimental results of others^{6,15-17} in PE phase. The observed dielectric constant explains the Curie-Weiss behaviour of dielectric constant along the c-axis of $\rm KH_2PO_4$ crystal in the PE phase. The temperature dependence of tangent loss of $\rm KH_2PO_4$ at 9.2 GHz for field along the a-axis ($\tan \delta_a$) along the c-axis ($\tan \delta_c$) have been calculated and compared with experimental results of Kaminow *et al*⁶ in PE phase.

II. DIELECTRIC SUSCEPTIBILITY AND TANGENT LOSS

Using double-time thermal Green's function (see Appendix A) technique and Dyson's equation, the general expressions for collective phonon mode frequencies $(\tilde{\tilde{\omega}}_{\pm}^2)$ and corresponding widths $\Delta(q, \omega)$ and shifts $\Gamma(q, \omega)$ for KDP-type ferroelectric (represented by

equations (25), (24) and (28) respectively in I}. We start with acoustic phonon Green's function equation (5) in II) write its equation of motion, Fourier Transform and write it in the Dyson's equation form using model Hamiltonian {equation (3) in I}. In this process we find $\Delta(q, \omega)$ and $\Gamma(q, \omega)$ to be the real and imaginary parts respectively of the response function for soft phonon mode. The response function consists of higher order Green's function, which are solved my renormalized Hamiltonian {equation (27) in I}. Thus dielectric susceptibility, dielectric constant, and dielectric loss (see Appendix B) have been calculated for KDP-type ferroelectrics as.

Notes

a) Dielectric Susceptibility

Following Kuo¹⁸ and Zubarev¹⁹, the dielectric susceptibility is given by

$$\chi(\omega) = \frac{-2N\mu^2 \tilde{\omega}}{[\omega^2 - \tilde{\omega}^2 + 2j\omega \Gamma_P(\omega)]},\tag{1}$$

The range of frequencies used in ultrasound²⁰, Brillouin² and susceptibility²⁰ measurement experiments are such that $\omega \ll \tilde{\tilde{\omega}}$. Thus equation (1) can be written as

$$\chi(\omega) = \frac{2N\mu^2 \tilde{\omega}}{\tilde{\omega}^2 [1 - j\omega\tau_P]},\tag{2}$$

Where the polarization relaxation time (τ_P) is given by equation (9) in II. This approximation of equation (1) is equivalent to a Debye relaxation susceptibility. Furthermore, if $\omega \tau_P \ll 1$, which is true for KDP-system²⁰, equation (2) can be written as

$$\chi(\omega) = \frac{2N\mu^2 \tilde{\omega}}{\tilde{\omega}^2} (1 + j\omega\tau_P), \tag{3}$$

Using equation (B.5) in appendix B, the expression for dielectric constant, from equation (1), can be written as

$$\varepsilon(\omega) - 1 = \frac{-8\pi N\mu^2 \tilde{\omega}[\{(\omega^2 - \tilde{\omega}^2) - 2j\omega\Gamma_P(\omega)\}]}{[(\omega^2 - \tilde{\omega}^2)^2 + 4\omega^2\Gamma_P^2(\omega)]},$$
(4)

The imaginary part of which can be written as

$$\varepsilon''(\omega) = -\frac{8\pi N\mu^2 \tilde{\omega}^2 \omega \Gamma_P(\omega)}{(\omega^2 - \tilde{\omega}^2)^2 + 4\omega^2 \Gamma_P^2(\omega)},\tag{5}$$

and the real part as

$$\varepsilon'(\omega) - 1 = -\frac{8\pi N\mu^2 \widetilde{\omega} (\omega^2 - \widetilde{\omega}^2)}{(\omega^2 - \widetilde{\omega}^2)^2 + 4\omega^2 \Gamma_P^2(\omega)},\tag{6}$$

for the experimental range of frequencies, $\omega \ll \tilde{\tilde{\omega}}$ and $(\omega \tau_p \ll 1 \text{ for KDP})$, equation (6) reduced to $(\varepsilon' \gg 1)$

$$\varepsilon'(\omega) = \frac{8\pi N\mu^2 \tilde{\omega}}{\tilde{\omega}^2 + \omega^2 \tau_P^2} = \frac{8\pi N\mu^2 \tilde{\omega}}{\tilde{\omega}^2}$$
(7)

Notes

where $\tilde{\tilde{\omega}}_{\pm}^2$ and $\tilde{\omega}$ (represented by equation (6) and (7) respectively in II). The $\tilde{\tilde{\omega}}_{\pm}$ mode and $\tilde{\tilde{\omega}}_{-}$ mode are described in II.

b) Tangent Loss

The dielectric tangent loss $(\tan \delta)$ for the dissipation of power in a dielectric sample is given by equation (17) in II. For experimental values of the applied field frequency ω , one has $\omega \tau_p \ll 1$ for KDP system, can be approximated (given by equation (18) in II).

III. NUMERICAL CALCULATIONS

By using Blinc-de Gennes model parameter values for KH_2PO_4 crystal as given by Ganguli *et al*¹⁴(see table 1), we have calculated transverse dielectric constant[$\varepsilon_a(0)$], observed dielectric constant [$\varepsilon_c(0)$] in PE phase for KH_2PO_4 , and tangent loss (tan δ) of KH_2PO_4 at 9.2 GHz for fields along the a-axis (tan δ_a), and c-axis (tan δ_c) are calculated using respective equations (see table 2).

Table 1 : Blinc de Genns model parameters for KDP as given by Ganguli $et al^{14}$

Ω	$J\left(\mathrm{cm}^{-1} ight)$	$J'(cm^{-1})$	$T_C(\mathbf{K})$	V/kT_C
82	334	440	123	0.299

Temperature (K)	$\varepsilon_a(0)$	$\varepsilon_{c}(0)$	$\tan \delta_a$	$\tan \delta_c$
125	63	35714	0.00297	0.068
130	62	6144	0.0048	0.033
135	61	2286	0.00393	0.0279
140	60	874	0.0039	0.0253
145	59	486	0.00393	0.0247
150	58	359	0.00297	0.0241

Table 2 : Calculated values for KDP crystal in PE phase.

IV. Temperature Dependence of $\varepsilon_a(0)$, And $\varepsilon_c(0)$ For KH₂PO₄

The results for transverse dielectric constant { $\varepsilon_a(0)$ } obtained from integrated intensity of Raman spectroscopy²⁰ and those measured by Busch¹⁶ and Kaminow *et al*⁶, together with the theoretical result of Havlin, Litov and Uehling²¹. Their temperature dependence is shown in figure 1. This indicates that the low frequency $\tilde{\omega}_+$ {E(x, y) mode} is closely related to the macroscopic dielectric constant ε_a . This also suggests that the E-mode Raman spectrum originates neither from the second order Raman scattering nor from the density of states due to the local disorder above T_c but from one of the collective modes at the centre of the Brillouin zone. It should be mentioned here that the low frequency E - mode continuous appears also in a deuterated KDP (DKDP), although the intensity is about one-third of that of KDP²², which indicates the possibility that the spectrum is due to the hydrogen collective motion. Using equation (6) given in I, for $\tilde{\omega}_+$ mode, it can be seen that the E-mode collective hydrogen motion has a characteristics damping factor which slowly increases as the temperature approaches T_c , while that of $\tilde{\omega}_{-}$ { B₂(z)} soft mode the damping factor slowly decreases down to a finite value, which agrees with the observations of Kaminow *et al*⁶. The present results agree with the behaviour of the observed E-mode Raman spectrum in the following aspects:

- (i) $\tilde{\omega}_+$ does not change appreciably as $T \to T_C$ in PE phase,
- (ii) $\Gamma_{\mathbf{p}}(\omega_{+})$ is weakly dependent on temperature,
- (iii) Because of the factor $(\omega^2 \tilde{\omega}^2)$ in the numerator of equation (6), the susceptibility derived changes the corresponding spectrum from a simple overdamped form to a more flat one, like the E-mode Raman spectrum of $\text{KH}_2\text{PO}_4^{23}$.



Fig.1 : Temperature dependence of Transverse dielectric constant $\varepsilon_a(0)$ for KH₂PO₄, obtained from Raman intensity ¹⁵ (shown by 0 o 0), Busch ¹⁶(shown by $\Delta \Delta \Delta$), Kaminow *et al* ⁶(shown by***) and solid line represents the present theoretical results.

The observed dielectric constant { (ε_c) } of KH₂PO₄along c-axis are shown in figure 2. The $\tilde{\tilde{\omega}}_{-}$ {B₂(z)} mode may be assigned for the observed temperature dependence of ε_c . As from equation (23b) in I, $\tilde{\tilde{\omega}}_{-}^2 \propto (T - T_C)$, the real part of the dielectric constant associated with this mode, from equation (7), can be expressed as given by equation (15) in II, which explains the Curie-Weiss behaviour of dielectric constant along the c-axis of KH₂PO₄crystal in the PE phase observed by Deguchi *et al*¹⁷, Busch¹⁶ and Kaminow et al⁶ shown in figure 2. For temperature $T \rightarrow T_c$, ε'_c tends to maximum value, which is consistent with the theory of Hill and Ichiki²⁴ for TGS and KDP crystals. While Mason monodisperse theory gives $\varepsilon'_c \rightarrow 0$ as $T \rightarrow T_c$. The origin of this difference in the temperature dependence of ε'_c is easily traced back in monodisperse theory, the critical slowing down of the relaxation time has a dominant effect over the Curie-Weiss law of static dielectric constant, while the Hill-Ichiki²⁴ theory of distribution function of

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relaxation time makes contribution to finite $\tau \neq 0$ to ε'_c more dominant. There are actually, however, many cases in which ε'_c takes a minimum of finite value at $T = T_c$ being neither zero as in Mason's theory nor maximum as in Hill and Ichiki theory.

Fig.2: Temperature dependence of observed dielectric constant $\varepsilon_c(0)$ for KH₂PO₄, obtained by Busch ¹⁶(shown by o o o), Δ Deguchi *et al* ¹⁷(shown by $\Delta \Delta \Delta$), Kaminow *et al* ⁶(shown by***) and solid line represents the present theoretical results.

V. Temperature Dependence of Tangent Loss of KH₂PO₄.

From equations (18) and (9) in II. The $\tilde{\tilde{\omega}}_+$ mode gives the contribution for weakly temperature dependent transverse relaxational behaviour of the observed transverse tangent loss $(\tan \delta_a)$ and $\tilde{\tilde{\omega}}_-$ mode contributes to the longitudinal relaxational behaviour of the observed longitudinal tangent loss $(\tan \delta_c)$ of KH₂PO₄ are shown in figure 3. Under the assumption that the proton moves in a double well potential the dielectric property of KDP - type ferroelectrics in the transition region may be due to the relaxation processes or due to tunneling mode. An interpretation of equation (19) given in II, for experimental data, is remarkable for temperature region $T > T_c$ and suggests that the relaxation mode is possible in PbHPO₄.

The tangent loss is associated with damping parameter Γ , given by equation (17) in II and equation (28) in I. Damping can be understood as the creation of a virtual polarization mode excited by the transverse electromagnetic radiation and its subsequent decay into the real phonons by scattering from crystal defects, higher order phonon anharmonicities, etc. At higher temperature the loss deviates from the Curie-Weiss type behaviour and increases linearly with temperature. This behaviour suggests that at higher temperatures the phonon anharmonicity contributes significantly in the observed loss.

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Fig.3: Temperature dependence of tangent loss of KH_2PO_4 at 9.2 GHz solid line for fields along the a-axis $(\tan \delta_a)^6$, along the c-axis, $(\tan \delta_c)^6$, (o) represent the present theoretical results.

VI. CONCLUSION

Present study reveal that four cluster Hamiltonian alongwith third and fourthorder anharmonities for the KDP-type ferroelectrics, explains well the temperature dependence of transverse dielectric constant, observed dielectric constant and tangent loss. The present results reduce to the results of others ^{25,26} if the width and shift are neglected. Many workers^{27,28} used four proton cluster model but could not explain most of the features of KDP-system except the difference between the Curie and Curie-Weiss temperature. Vaks and Zinenko²⁹ and Havlin and Sompolinsky³⁰ performed extensive calculations for the static thermodynamics behaviour in the four-particle cluster approximation and found satisfactory agreement with the experimental data, but they could not explain the observed relaxational behaviour of dielectric properties and ultrasonic attenuation explicitly. Ganguli et al¹⁴ modified Ramakrishnan and Tanaka³¹ theory by considering anharmonic interaction. Their treatment explains many features of order-disorder ferroelectrics. However, due to insufficient treatment of anharmonic interactions, they could not obtain quantitatively good results and could not describe some interesting properties, like dielectric, ultrasonic attenuation, etc. Our Theoretical results fairly agree with the experimental results of others^{10,11}.

The method of double time temperature dependent Green's function and Dyson's equation formalism have been found convenient and systematic to give the static and dynamical properties on a single framework of KDP-type system. The dielectric properties and ultrasonic attenuation strongly depend on the relaxational mode behaviour of stochastic motion of $H_2PO_4^-$ group in KDP-type ferroelectrics.

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Appendix A: Green's Function

Green's functions of statistical mechanics are the appropriate generalization of the concept of correlation functions. As in quantum field theory three different types of Green's functions can be defined in terms of the average value of the T-product of operators, namely, causal retarded and advanced Green's functions. Here we shall use only the retarded double-time Green's functions.

A.1. The double-time thermal Green's function

For any pair of operators, the retarded Green's function is defined as

$$G(t,t') = \langle \langle A(t); B(t') \rangle \rangle = -i\theta(t-t') \langle [A(t), B(t')] \rangle$$
(A.1)

Where A(t) and B(t') are Heisenberg operators, i.e.,

$$A(t) = e^{\frac{iHt}{\hbar}} A e^{-\frac{iHt}{\hbar}}$$
(A.2)

H being Hamiltonian of the system. The square bracket denotes the commutator or anticommutator of the operators

$$|A,B| = AB - \eta BA; \qquad \eta = \pm 1 \tag{A.3}$$

 η is +1, if A and B are Bose operators, and -1 if they are Fermi operators. Since in the present work we shall be dealing with phonons, these operators are always Bose operators and the square brackets will be commutator. The angular bracket $\langle \dots \rangle$ denotes an ensemble average described by the Hamiltonian, namely for any operator 0 it is given by

$$\left\langle 0\right\rangle = \frac{Tr\left(e^{-\beta H}\,0\right)}{Tr(e^{-\beta H}\,)}\tag{A.4}$$

Where Tr stands for the trace of the expression and $\beta = (K_{\beta}T)^{-1}$, κ_{β} being the Boltzmann constant and T the absolute temperature. $\theta(t)$ is the Heaviside step function having the property

$$\theta(t) = 1 \quad \text{for } t > 0$$

= 0 for $t < 0$ (A.5)

The retarded Green's functions give much detailed dynamical information, because they are expectation values of the ensemble and contain all the statistical mechanical information. For example, the one-particle Green's function has a direct physical interpretation as a particle propagator. It describes the motion of one particle added to the many-particle system.

A.2. Equation for Green's function

The equation of motion for any operator A(t) in Heisenberg representation is

$$i\hbar \frac{d}{dt}A(t) = [A(t), H)] = AH - HA$$
(A.6)

The right hand side of this equation can be evaluated using the explicit form of the Hamiltonian and the commutation relation for the operators. The equation of motion for the Green's function defined by (A.1), can be obtained by differentiating it with respect to time t

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$$i\hbar \frac{d}{dt}G(t,t') = \hbar \frac{d}{dt}\theta(t-t') < [A(t), B(t')] >$$

$$+ << [A(t), H)]; B(t') >>$$
(A.7)

In Heisenberg representation G(t,t') depends upon the difference of the arguments tand t'. The step function $\theta(t)$ can be expressed in terms of the δ -function of t as

$$\theta(t) = \lim_{\varepsilon \to 0} \int_{-\infty}^{\infty} \delta(t') e^{\varepsilon t'} dt'$$
(A.8)

With the help of equation (A.8), the equation of motion for the Green's function G becomes

$$i\hbar \frac{d}{dt}G(t-t') = \hbar\delta(t-t') < [A(t), B(t')] >$$

$$+ << [A(t), H)]; B(t') >>$$
(A.9)

The second term in the right hand side of the above equation, in general, involves Green's Functions of higher order than the original Green's function $\langle A(t); B(t') \rangle \rangle$, except for the trivial case of noninteracting systems when exact solution can be obtained. In general the exact solution is very difficult. One is immediately forced to write equation of motion of the kind (A.9) for the Green's function appearing on the right hand side which in turn leads to a hierarchy of coupled equations for Green's functions. One sees that at every time the order of the Green's function increases. In order to get some physical result one must cut off the endless chain at certain stage by decoupling the higher order Green's functions into simpler double-time Green's functions using some suitable decoupling schemes. The type of decoupling of hierarchy of coupled equations generally depends upon the nature of the problem.

A.3. Time Correlations

Notes

The experimental study of various dynamical properties is usually carried out by measuring the response of the phonon system to different applied external disturbances. Different types of experiments (e.g., ultrasonic attenuation, inelastic neutron scattering and optical measurements) may be described in a unified way by a single phonon correlation function. In general, physical quantities of interest in many problems are time correlation functions or related to them. We define the correlation function as the thermal expectation value of the product of two Heisenberg operators A(t) and B(t) at difference times, namely

$$F_{BA}(t,t') = \langle B(t')A(t)$$
 (A.10a)

$$F_{AB}(t,t') = \langle A(t), B(t') \rangle$$
 (A.10b)

On the attainment of the thermal equilibrium, these correlation functions depend only on the difference of their time arguments as do the Green's functions. Equal time t=t'correlation functions are called the auto-correlation functions and they give the average value of the product of the operators,

$$F_{BA}(0) = < B(t)A(t) > = < B(0)A(0) >$$
 (A.11a)

$$F_{AB}(0) = \langle A(t)B(t) \rangle = \langle A(0)B(0) \rangle$$
 (A.11b)

The time correlation functions also satisfy the same equation of motion as the Green's function in Eq. (A.9) except the omission of discontinuous factor $\delta(t-t')$, i.e.,

$$i\hbar \frac{d}{dt} F_{AB}(t-t') = \langle [A(t), H] \rangle B(t') \rangle$$
 (A.12a)

$$i\hbar \frac{d}{dt} F_{BA}(t-t') = \langle B(t')[A(t), H] \rangle$$
 (A.12b)

The values of the correlation functions can be evaluated directly by integration of Eq. (A.12) using the boundary conditions. However, it is more convenient to evaluate them indirectly by first calculating the Green's function from (A.9). This method is considerably simpler, sine it makes it easier to satisfy the boundary conditions using the spectral theorems.

A.4. Spectral Representations

In order to evaluate the correlation functions (A.10) with the help of the Green's functions, it is convenient to introduce the spectral representations for them. These spectral representations supplement the necessary boundary conditions. We will now obtain the spectral representations for the time correlation functions F_{AB} and F_{BA} .

Let $|n\rangle$ and E_n be the eigenstates and eigenvalues of the Hamiltonian H, i.e.,

$$H\left|n\right\rangle = E_{n}\left|n\right\rangle \tag{A.13}$$

Using the definition of thermal average, the time correlation function F_{BA} can be written

$$F_{BA}(t-t') = z^{-1} \sum_{n} \langle n | B(t') A(t) | n \rangle e^{-\beta E_n}$$
(A.14)

Where z is the partition function given by $z = Tr(e^{-\beta H})$. By virtue of the completeness of the eigenstates, the expression Eq. (A.14) can be written as

$$F_{BA}(t-t') = z^{-1} \sum_{n,m} e^{\frac{-i(E_n - E_m)(t-t')}{\hbar}} \times \left\langle n \middle| B \middle| m \right\rangle \left\langle m \middle| A \middle| n \right\rangle e^{-\beta E_n}$$
(A.15)

Similarly

$$F_{AB}(t-t') = z^{-1} \sum_{n,m} e^{\frac{-i(E_n - E_m)(t'-t)}{\hbar}} \times \langle n | A | m \rangle \langle m | B | n \rangle e^{-\beta E_n}$$
(A.16)

Interchanging the summation indices n and m in (A.16) and doing slight manipulation, we can write (A.15) and (A.16) in the form

$$F_{BA}(t-t') = \int_{-\infty}^{\infty} J(\omega) e^{-i\omega(t-t')} d\omega$$
 (A.17a)

$$F_{AB}(t-t') = \int_{-\infty}^{\infty} e^{\beta \hbar \omega} J(\omega) e^{-i\omega(t-t')} d\omega$$
 (17b)

 $J(\omega)$ is called the spectral density of the function $F_{BA}(t-t')$ and is given by

$$J(\omega) = z^{-1} \sum_{n,m} e^{-\beta E_n} \langle n | B | m \rangle \langle m | A | n \rangle \times \delta(\omega - \frac{E_n - E_m}{\hbar})$$
(A.18)

Equation (A.17) are the required spectral representations for the time correlation functions.

Notes

A.5. Spectral representation for Green's functions

The spectral representation for the retarded Green's Function Eq. (A.1) can easily be obtained by means of the spectral representations, (A.17a) and (A.17b), for the time correlation functions. Let $G(\omega)$ be the Fourier transform of the Green's function G(t-t')then

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(t - t') e^{i\omega(t - t')} d(t - t')$$
(A.19)

$$G(t-t') = \int_{-\infty}^{\infty} G(\omega) e^{-i\omega(t-t')} d\omega$$
(A.20)

Substituting Eq. (A.1) into Eq. (A.19) we get

$$G(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d(t-t') e^{i\omega(t-t')} \theta(t-t') \times \left[\langle A(t)B(t') \rangle -\eta \langle B(t')A(t) \right]$$
(A.21)

Using the spectral representations (A.17a) and (A.17b) for the time correlation function, we obtain

$$G(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} (e^{\beta \hbar \omega'} - \eta) J(\omega') d\omega' \int_{-\infty}^{\infty} dt \theta(t) e^{i(\omega - \omega')t}$$
(A.22)

Time integration in (A.22) can be carried out by using the integral representations for $\delta(t)$ and $\theta(t)$, namely

$$\delta(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ixt} dx$$
 (A.23)

and

$$\theta(t) = \frac{i}{2\pi} \int_{-\infty}^{\infty} \frac{e^{-ixt}}{x + i\varepsilon} dx$$
(A.24)

The result is

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' J(\omega') \frac{(e^{\beta h \omega'} - \eta)}{\omega - \omega' + i\varepsilon}$$
(A.25)

So far we have considered ω to be a real quantity. Assuming ω to be complex, we have

$$G(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \, (e^{\beta \hbar \omega} - \eta) J(\omega') \frac{1}{(\omega - \omega')} \tag{A.26}$$

Where ω is having a small imaginary part, is understood. This shows that the function $G(\omega)$ can be considered to be analytic in the upper half of the complex ω - plane with a singularity on the real axis. In the similar manner, expression for the advanced Green's function is obtained except that the small positive quantity ($\varepsilon \rightarrow +0$) is changed by negative sign in the expression (A.25). We can say that the Fourier transform of the advanced Green's function is analytic in the lower half plane.

The spectral density function $J(\omega)$ can be immediately calculated if the function $G(\omega)$ is known. For this we have

$$G(\omega + i\varepsilon) - G(\omega - i\varepsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' J(\omega') (e^{\beta \hbar \omega'} - \eta)$$

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$$\times \left[\frac{1}{\omega - \omega' + i\varepsilon} - \frac{1}{\omega - \omega' + i\varepsilon} \right]$$
(A.27)

Using the relation

$$\delta(x) = \frac{1}{2\pi i} \left(\frac{1}{x - i\varepsilon} - \frac{1}{x + i\varepsilon} \right) \tag{A.28}$$

We arrive at

$$G(\omega + i\varepsilon) - G(\omega - i\varepsilon) = -i(e^{\beta \hbar \omega} - \eta)J(\omega)$$
(A.29)

es

or

$$\lim_{\varepsilon \to 0} J(\omega) = -\frac{2}{(e^{\beta h \omega} - \eta)} \operatorname{Im} G(\omega + i\varepsilon)$$

Where $\varepsilon \to 0$ is implied and Im stands for the imaginary part.

This relation is very important. Once the retarded Green's function is known, the spectral density function can be obtained the help of (A.29) and taking the requisite Fourier transforms (A.17), one can get the correlation functions at all times and at all temperatures. This enables us to calculate the physical properties of a crystal in terms of one set of functions.

Appendix B: Dielectric Constant and Tangent Loss

General formulation

The response of a dielectric field is conveniently described by the dielectric susceptibility. Following Kuo²⁸ and Zubarev²⁹, the general expression for complex dielectric susceptibility tensor $\chi_{mn}(\omega)$ can be expressed as

 $\chi_{mn}(\omega) = \lim_{\varepsilon \to 0} -2\pi G_{mn}(\omega + j\varepsilon), \qquad (B.1)$

Where $G_{mn}(\omega)$ the Fourier transform of the retarded double-time thermal Green's function between the mth and nth components of the crystal dipole moment operators $\vec{M}(t)$ in the Heisenberg representation and is defined as

$$G_{mn}^{(t-t')} = \langle M_{m}(t); M_{n}(t') |_{\dot{L}\dot{L}} = -j\theta(t-t') \langle [M_{m}(t); M_{n}(t')] \rangle$$
(B.2)

Where $\theta(t-t')$ is the Heaviside step function and the angular brackets $\langle -- \rangle$ denote the thermal ensemble average. The crystal dipole moment $\overline{M}(t)$ depends on the ionic co-ordinates, like potential energy, i.e., on the lattice configurations and can be expanded in a Taylor's series in terms of ionic displacements. Because of the periodic boundary conditions, i.e., symmetry considerations, imposed on the ionic motions, only the low lying relaxational modes have non-zero polarization associated with them. Thus only the expansion coefficients which correspond to lowest frequency mode, i.e., $\overline{M}(q, j)$ –where q = 0 for ferroelectrics, and j relates the modes of spectrum) contribute to the dielectric susceptibility, significantly.

Thus we can write the dielectric susceptibility as

$$\chi_{mn}(\omega) = \lim_{\varepsilon \to 0} -2\pi N\mu^2 G_{mn}(\omega + j\varepsilon), \qquad (B.3)$$

Where N is the number of unit cells in the sample and μ is the effective dipole moment per unit cell, and

$$G_{mn}(\omega + j\varepsilon) = \langle A_q(t); A_q(t') \rangle \rangle$$

= $G'(\omega) - jG''(\omega)$ (B.4)

Where $G'(\omega)$ and $G''(\omega)$ are real and imaginary parts of the Green's function. The dielectric constant can be evaluated using the relation

$$\varepsilon(\omega) = 1 + 4\pi\chi = \varepsilon'(\omega) - j\varepsilon''(\omega) \tag{B.5}$$

Where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are real and imaginary parts of the dielectric constant. The real part of the dielectric constant can be expressed as

$$\varepsilon'(\omega) - 1 = -8\pi N \mu^2 G'(\omega), \qquad (B.6)$$

and the imaginary part

$$\varepsilon''(\omega) = -8\pi N \mu^2 G''(\omega), \qquad (B.7)$$

The dielectric loss $(\tan \delta)$, for the dissipation of power in the dielectric crystal is defined as the ratio of imaginary and real parts of the dielectric constant, i.e.,

$$\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = \frac{G''(\omega)}{G'(\omega)}$$
(B.8)

Notes

The dielectric susceptibility, equation (B.3); dielectric constant equation (B.6); and dielectric loss equation (B.8); can thus be calculated by using the Green's function and the model Hamiltonian.

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