

## Lyddane-Sachs-Teller Relation and Dielectric Constant in Crystals\*

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The validity of Lyddane-Sachs-Teller (LST) relation in describing the behavior of the dielectric constant in crystals is studied. We derive an expression for the dielectric constant which takes into account explicitly both the LST contribution and the Debye-like contribution of the disorder. It is shown that the Debye-like term is the predominant one or at least of same magnitude of the LST-term whenever a disorder mechanism is present. The phase diagram for the activation energy related to the disorder will indicate the main dielectric properties of the crystal and will inform about the phonon structure.

Estuda-se a validade da relação de Lyddane-Sachs-Teller (LST) na descrição do comportamento da constante dielétrica em cristais. Derivamos uma expressão para a constante dielétrica que leva em conta, explicitamente, tanto a contribuição LST como a contribuição tipo Debye da desordem. Mostra-se que o termo tipo Debye é o predominante ou, pelo menos, da mesma grandeza do termo LST, sempre que esteja presente um mecanismo de desordem. O diagrama de fase para a energia de ativação relacionada a desordem irá indicar as características principais das propriedades dielétricas do cristal, bem como informar sobre a estrutura dos fonons.

Recently, careful experimental work<sup>1,2,3</sup> was performed in  $\text{NaNO}_2$  and  $\text{LiIO}_3$  with the aims: a) to verify the validity of the generalized Lyddane-Sachs-Teller (LST) relation for those high dielectric constant crystals; b) to try to tie the dielectric constant behavior as function of temperature to the frequency behavior of any possible soft mode; c) in the case of  $\text{NaNO}_2$ , to find out to what extent Cochran's soft mode model could explain the paraelectric-ferroelectric phase transition in a crystal of order-disorder type. Naturally, those questions asked above are closely related since if Cochran's soft mode model<sup>4</sup> fails to explain the phase transition, the Lyddane-Sachs-Teller relation<sup>5</sup> also fails in predicting the increase of the dielectric constant at the critical temperature ( $T_c$ ).

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If the crystal is of order-disorder type, we would expect that this crystal can be described at least by considering two sublattices. One would be a sublattice of "normal" oscillators and the other one would be a sublattice of random motion particles which is strongly related to the order-disorder mechanism. Besides, one would expect that the sublattice of random motion particles would show a dielectric relaxation process which would be most likely of Debye relaxation type. Usually in the literature<sup>6,7</sup> both problems are treated separately mainly concerning ferroelectric-paraelectric transition. We would like to emphasize some important characteristics which turn out whenever one treats explicitly the contributions of both processes to the dielectric constant and to phase transition.

Let us first consider the total dipole polarization for the two sublattices. The total dipole polarization  $\mathbf{P}$  is a sum of two parts; one,  $\mathbf{P}'$ , is the dipole polarization due to electrons and atoms (or ions) which includes all polarization by displacement and a part  $\mathbf{P}_d$  due to the brownian motion particles which usually are best described by a self-diffusion process defined by a correlation time  $\tau_c = \tau_0 \exp[\Delta U/kT]$ . Here,  $\Delta U$  is the activation energy for the jumping between two equivalent positions and  $\tau_0$  obeys the Eyring's relationship  $\tau_0 = h/kT$ . The electric displacement  $\mathbf{D}$  is defined as  $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} = \epsilon\mathbf{E}$ . For our case, one has  $\mathbf{D} = 4\pi\mathbf{P}_d + 4\pi\mathbf{P}' + \mathbf{E}$ , since  $\mathbf{P} = \mathbf{P}' + \mathbf{P}_d$ . Dividing our expression for  $\mathbf{D}$  by  $\mathbf{E}$ , one has

$$\begin{aligned} \epsilon = \mathbf{D}/\mathbf{E} &= 4\pi(\mathbf{P}/\mathbf{E}) + 4\pi(\mathbf{P}'/\mathbf{E}') + 1 \\ &= 4\pi\chi_d + 4\pi\chi' + 1 \\ &= \epsilon_d + \epsilon'. \end{aligned} \tag{1}$$

So, our dielectric constant has two terms: one associated to the "normal" oscillator sublattice denoted by  $\epsilon$  and a term associated to the self-diffusion process (or Debye relaxation term) denoted by  $\epsilon_d$ .

Explicit expressions for  $\epsilon_d$  and  $\epsilon$  can be obtained using the normal procedure found in the literature<sup>6,7</sup>. Assuming that  $\epsilon$  is of Debye relaxation type, the orientational part of the polarizability depends on the applied frequency  $\omega$  as for  $\epsilon \sim \exp[i\omega t]$  and the Debye polarizability is given by

$$\alpha(\omega) = \frac{\alpha_0}{1 - i\omega\tau}, \tag{2}$$

where  $\tau$  is the dielectric relaxation time and  $\alpha_0$  is the static orientational polarizability, the susceptibility  $\chi_d$  is equal to  $\alpha_0 N/(1 - i\omega\tau)$  and  $\epsilon_d$  is given by

$$\varepsilon_d = \frac{4\pi \alpha_0 N}{1 - i\omega\tau}, \quad (3)$$

$N$  being the number of particles.

An expression for  $\varepsilon'$  can be deduced by using the well known Clausius-Mosotti relation given by

$$\varepsilon' = \frac{1 + 2\beta}{1 - \beta}, \quad \beta = \frac{4\pi}{3} \sum_j N_j \alpha_j \quad (4)$$

$N_j$  is the number of particles per unit volume (molecules or ions) and  $\alpha$ , the polarizability defined as  $\alpha = \mathbf{P}/\mathbf{E}_{\text{loc}}$  where  $\mathbf{E}_{\text{loc}}$  is the local electric field at the respective particle. Following Ref. 6, we can write the static dielectric constant for  $\varepsilon'(0)$  as

$$\varepsilon'(0) = \frac{1 + 2(\beta_{\text{el}} + \beta_{\text{ion}})}{1 - (\beta_{\text{el}} + \beta_{\text{ion}})}. \quad (5)$$

For high frequency, the ionic polarizability does not contribute to the dielectric constant because the inertia of the ions which means  $\beta_{\text{ion}} = 0$  and  $\varepsilon'(\infty)$  is

$$\varepsilon'(\infty) = \frac{1 + 2\beta_{\text{el}}}{1 - \beta_{\text{el}}} \quad (6)$$

Still following Ref. 6, using the two-oscillator model for electrons and ions and taking  $\mathbf{P}' = \mathbf{P}_{\text{el}} + \mathbf{P}_{\text{ion}}$ , one obtains a relationship between the ratio  $\varepsilon'(0)/\varepsilon'(\infty)$  and the ratio between the frequency  $\omega_L$  of longitudinal optical phonons and the frequency  $\omega_T$  of transversal optical phonon given by

$$\frac{\varepsilon'(0)}{\varepsilon'(\infty)} = \frac{\omega_L^2}{\omega_T^2} \quad (7)$$

which is the LST relation. Eq. (1) can be re-written then as

$$\frac{\varepsilon(0)}{\varepsilon'(\infty)} = \frac{4\pi \alpha_0 N}{\varepsilon'(\infty)} + \frac{\omega_L^2}{\omega_T^2} \quad (8)$$

or, in a more general way,

$$\varepsilon(\omega) = \frac{4\pi \alpha_0 N}{1 - i\omega\tau} + \sum_j \frac{S_j \omega_j^2}{\omega_j^2 - \omega^2 - i\omega\Gamma_j} + \&0,, \quad (9)$$

(where  $S_j$  and  $\omega_j$  are respectively the strengths and the frequencies of the harmonic oscillators describing the ionic motion) if one uses the two oscillator model described by Barker and Loudon<sup>8</sup>. It should be noted that the polarizability due to the Debye relaxation term can not be inclu-

ded in the definition for  $\beta$  given by Eq. (4). This is because the local field which is effective in dipole orientation is likely to be inappreciably different from the externally applied field<sup>7</sup> so the dielectric constant owing to a self-diffusion process does not satisfy the Clausius-Mossotti relation.

Both Eqs. (8) and (9) deduced in a very simple way show many interesting features of the dielectric behavior of solids: 1) the LST relation is only strictly valid for crystals without possibilities of order-disorder or Ising-like degrees of freedom; 2) crystals for which the LST relation is valid should not show dispersion of the dielectric constant at low frequencies; 3) dispersion of the dielectric constant at low frequencies in which the real part of  $\epsilon$  falls smoothly with frequency might be a good indication of an order-disorder mechanism in the solid; 4) the order-disorder mechanism contribution to the dielectric constant falls as  $\omega^{-2}$  so we expect that at high enough frequencies (hopefully below any of the TO phonons) the value of  $\epsilon$  will tend to that given by  $\epsilon'(0)$  of the LST relation; 5) it is obvious from Eqs. (8) and (9) that the variation of  $\epsilon$  with temperature might be due either to the softening of an  $\omega_{\text{TO}}$  phonon or to the change of the relaxation time  $\tau_c$  of the diffusion process or both; 6) phase transition may be due to the behavior of a "soft" phonon (in this case the activation energy  $\Delta U = 0$ ) or to the behavior of the order-disorder mechanism  $\Delta U \neq 0$  (in this case no  $\omega_{\text{TO}} \rightarrow 0$  or both. The activation energy  $\Delta U = 0$  and  $\Delta U \neq 0$  defines the two extreme cases. The Mason's relaxation dielectric expression<sup>8</sup> for the term corresponding to the Debye relaxation term illustrates very well this situation because it is given explicitly in function of  $\Delta U$  and  $\delta$  the distance between two equivalent positions. For  $\Delta U = 0$ ,  $\delta$  is zero and  $\alpha_0$  in Eqs. (8) and (9) vanishes.

Figs. 1, 2 and 3 taken from Refs. 10, 11, and 12 illustrate the behavior of the dielectric constant as a function of  $\omega$  and T for  $\text{NaNO}_2$  and  $\text{LiIO}_3$ . In the case of  $\text{NaNO}_2$ , as has been shown by many authors, the disorder mechanism is fundamentally a hindered rotation of the  $\text{NO}_2$  ion which will make the dipole associated with the ion point in either the positive or negative b axis of the crystal. As a matter of fact, the dielectric constant behavior with  $\omega$  and T is dominated by the first term in Eqs. (8) and (9) but as the frequency increases we expect  $\epsilon$  to tend to the value obtained by the LST relation for  $\text{NaNO}_2$ ; this frequency is higher than that shown in Fig. 1. For  $\text{LiIO}_3$ , we see from Fig. 3 that the limiting LST value of  $\epsilon(\omega)$  is attained at  $\sim 5\text{MHz}$  even though the identification of the relaxation mechanism is still under study.

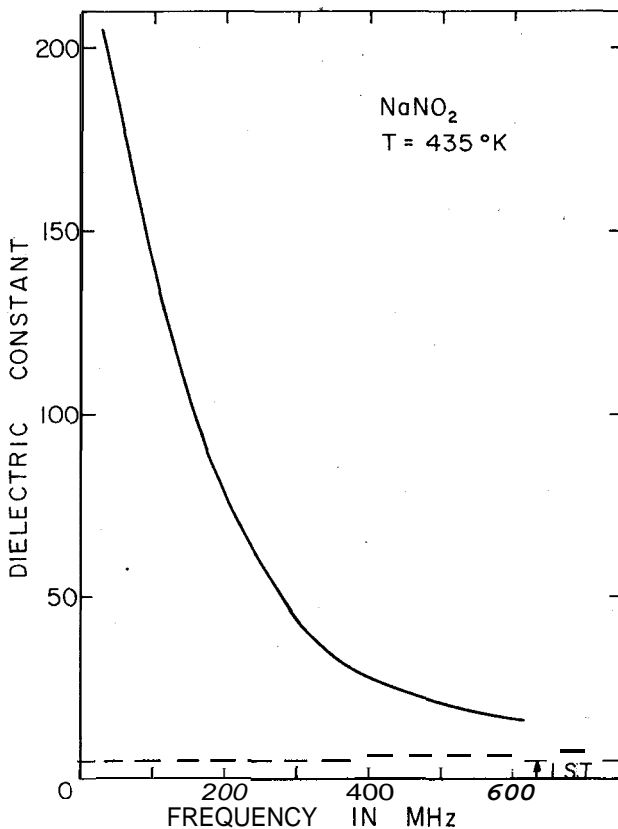


Fig.1 - The real part of the dielectric constant (Ref. 10) of  $\text{NaNO}_2$  as a function of frequency and the limiting value given by LST relation at high frequency.

As a final remark, we can say that the self-diffusion process will also affect the linewidth of the phonons of the crystal. If the diffusion process can be described by the spectral density of the type  $\tau_c / (1 + \omega^2 \tau_c^2)$ , the linewidth of the phonons which is in some way related to the diffusion process will be proportional to this spectral density, which means that for small  $\omega$ , the linewidth might be overdamped. It is interesting to mention that, assuming the existence of a smooth dielectric dispersion as a strong evidence of an order-disorder mechanism involved, we would expect that KDP,  $\text{BaTiO}_3$ , TGS, Rochelle Salt and many other crystals would follow Eq. (8) and (9). It is expected that hydrated ferroelectric crystals as for instance  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  and all the hydrogen bonded crystals will follow also Eqs. (8) and (9).

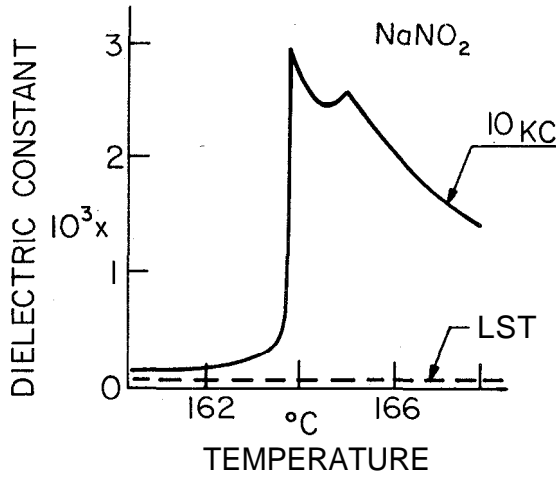


Fig. 2 - Comparison between the static dielectric constant (Ref. 11) of  $\text{NaNO}_2$ , as a function of temperature and the LST value.

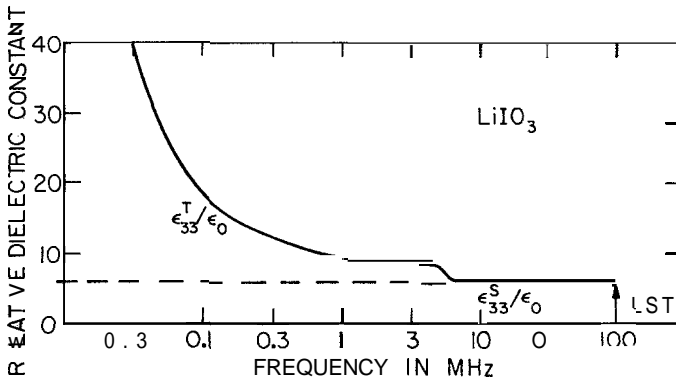


Fig. 3 - The relative dielectric constant (Ref. 12) of  $\text{LiIO}_3$  as a function of frequency compared to the LST value.

So it seems that much effort should be exerted in determining an explicit relationship between phonons and disorder mechanism which lead to a hard core frequency at transition temperature. We strongly believe that the fact  $AU \neq 0$  at transition temperature is very important and it has been practically overlooked in present research on dielectric properties. Besides we think that a proper theory for dielectric properties of order-disorder crystals (including ferro and non-ferroelectric) should contain a Langevin equation describing the brownian motion particles and rate

equations for the population in a double well potential. A suitable combination of generalized Langevin equation<sup>13</sup> and dipole polarization rate equation given by Mason's dielectric relaxation theory would describe most of dielectric properties of order-disorder materials. The effect of anharmonic self-energy terms on the Lyddane-Sachs-Teller relation can be determined in a similar way to the one developed by Maradudin<sup>14</sup> et al. describing nonequilibrium processes in isotopically disorder crystals. It is possible that the formalism recently developed by M. Lax<sup>15</sup> would be very helpful for establishing these sets of equations.

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