

GENERALIZED LYDDANE–SACHS–TELLER RELATION

A.S. Chaves* and S.P.S. Porto

Departments of Electrical Engineering and Physics; University of Southern California,
Los Angeles, California 90007, U.S.A.

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A generalized Lyddane–Sachs–Teller relation is derived. The assumption that the ionic motion is described by a set of independent damped oscillators is relaxed, and the derivation is based simply on causality and energy conservation, plus the assumption that ϵ has a finite number of poles and zeroes. The parameters appearing in the factorization have a somewhat different meaning from that previously accepted, but they are more directly related to the observable quantities in neutron and Raman scattering, and infrared experiments.

INTRODUCTION

THE LYDDANE–SACHS–TELLER relation has played an important role in the investigations of long-wavelength infrared active phonons. It was rigorously derived for the first time in 1941 by the investigators from whom it derived the name,¹ for cubic crystals with only one IR-active mode, and established a connection between the values of the dielectric constant at visible frequencies (ϵ_∞) and at frequency zero (ϵ_0), and the TO and LO frequencies of that mode at the center of the Brillouin zone. It can be expressed as

$$\epsilon_0 = \epsilon_\infty \frac{\omega_L^2}{\omega_T^2} \quad (1)$$

The LST relation was extended by Kurosawa,² and Cochran and Cowley³ to include several polar modes and non-cubic symmetries, and by Barker⁴ to allow damping. A common starting point in those papers was the assumption that the ionic motion of the crystal can be described by independent oscillators. Lax and Nelson⁵ avoided this explicit assumption in their approach to the problem. However, as damping was not allowed, their result cannot encompass the

situations in which the coupling between phonons takes place. It has been recognized for some time that in the presence of damping the vibrational modes of same symmetry can become coupled in first order.⁶ These couplings evidently destroy the validity of the LST relation in the way it was established. The same happens if the crystal has any internal motion non-describable by damped harmonic oscillators, such as, tunneling modes, rotation of molecules, or any other diffusion process.⁷

In this communication we deduce the LST relation basing on less restrictive conditions which allow phonon coupling as well as other essentially anharmonic effects.

THEORY

For crystals with orthorhombic or higher symmetry we can diagonalize the dielectric constant tensor simultaneously for all frequencies, so we will restrict, as usual, to those cases and refer to a particular element of the diagonalized dielectric constant. The electronic contribution can be split out; so we have

$$\epsilon(\Omega) = \epsilon_\infty + 4\pi\chi(\Omega). \quad (2)$$

* Fellow from the National Research Council of Brazil.

$\chi(\Omega)$ is a generalized susceptibility and this imposes serious conditions on its behavior, all derived from causality and energy conservation.⁸ We will make use of some of those conditions, made explicit below.

$$(i) \chi(-\Omega^*) = \chi^*(\Omega).$$

(ii) $\chi(\Omega)$ has no poles in the upper semi-plane of Ω .

(iii) $\chi(\Omega)$ is real on the imaginary axis [results from (i)] but at no other point of the upper semi-plane of Ω .

(iv) On the positive imaginary axis $\chi(\Omega)$ decreases monotonically from a given value at the origin to zero at infinity.

$\epsilon(\Omega)$ must have all the properties above with the evident modification that it goes to ϵ_∞ at high frequencies. From statements (i)–(iv) result the following conditions on the poles and zeros of $\epsilon(\Omega)$:

$$(a) \text{ If } \Omega \equiv \omega_\nu^T - \frac{i}{2} \gamma_\nu^T \text{ is a pole, so is } (-\Omega_\nu^T)^* \equiv -\omega_\nu^T - \frac{i}{2} \gamma_\nu^T.$$

$$(b) \text{ If } \Omega_\nu^L \equiv \omega_\nu^L - \frac{i}{2} \gamma_\nu^L \text{ is a zero, so is } (-\Omega_\nu^L)^* \equiv -\omega_\nu^L - \frac{i}{2} \gamma_\nu^L.$$

(c) γ_ν^T and γ_ν^L are all positive or zero.

We make the additional assumption that $\epsilon(\Omega)$ is rational, i.e.

$$\epsilon = \frac{P_1(\Omega)}{P_2(\Omega)},$$

where $P(\Omega)$ are polynomials. As ϵ goes to ϵ_∞ at high frequencies P_1 and P_2 have both the same degree. So

$$\epsilon(\Omega) = A \frac{\Omega^m + \sum_{i=0}^{m-1} a_i \Omega^i}{\Omega^m + \sum_{j=0}^{m-1} b_j \Omega^j} \quad (3)$$

The boundary condition at high frequency means that $A = \epsilon_\infty$. We can write $\epsilon(\Omega)$ as:

$$\epsilon(\Omega) = \epsilon_\infty \prod_{\nu=1}^m \frac{\Omega_\nu^L - \Omega}{\Omega_\nu^T - \Omega} \quad (4)$$

Now suppose that the system does not have poles at the imaginary axis. This means that $m = 2n$, where n is integer, and we can group the symmetrical pairs of poles and zeroes together to have:

$$\epsilon(\Omega) = \epsilon_\infty \prod_{\nu=1}^n \frac{(\omega_\nu^L - \frac{i}{2} \gamma_\nu^L - \Omega)(-\omega_\nu^L - \frac{i}{2} \gamma_\nu^L - \Omega)}{(\omega_\nu^T - \frac{i}{2} \gamma_\nu^T - \Omega)(-\omega_\nu^T - \frac{i}{2} \gamma_\nu^T - \Omega)} \quad (5)$$

or

$$\epsilon(\Omega) = \epsilon_\infty \prod_{\nu=1}^n \frac{|\Omega_\nu^L|^2 - i\Omega\gamma_\nu^L - \Omega^2}{|\Omega_\nu^T|^2 - i\Omega\gamma_\nu^T - \Omega^2} \quad (6)$$

When allowing the appearance of zeroes and poles at the imaginary axis, two very distinct situations must be considered separately. In the first one two symmetrical poles go to meet each other at that axis, accompanied or not by the same behavior of two zeroes. This occurs, for instance, if we represent one of the modes by a harmonic oscillator that becomes overdamped. The motion of the mode is described by the response function

$$g(\Omega) = \frac{1}{\omega_0^2 - \Omega^2 - i\Omega\gamma},$$

which has poles at

$$\Omega_\pm = -i\gamma/2 \pm (\omega_0^2 - \gamma^2/4)^{1/2} \equiv -i\gamma/2 \pm \omega_T$$

If ω_0 softens down to values equal or smaller than $\gamma/2$, ω_T will become imaginary. The behavior of Ω_\pm is shown in Fig. 1, where γ was taken arbitrarily as constant and ω_0 was made to soften:

Equation (5) will stay correct in such occurrence and equation (6) can include also this case if just written with the modifications

$$|\Omega_\nu^T|^2 \rightarrow (\omega_\nu^T)^2 + (\gamma_\nu^T/2)^2, \text{ and } |\Omega_\nu^L|^2 \rightarrow (\omega_\nu^L)^2 + (\gamma_\nu^L/2)^2.$$

A different approach is to be taken if unpaired pure imaginary poles exist. When there is more than one 'single' pole we cannot draw general conclusions. If we have only one 'single' imaginary pole, this will imply $m = 2n + 1$, and one single imaginary zero must exist also. The LST relation now becomes

$$\epsilon(\Omega) = \epsilon_\infty \frac{i\gamma_d^L + \Omega}{i\gamma_d^T + \Omega} \prod_{\nu=1}^n \frac{(\omega_\nu^L)^2 + (\gamma_\nu^L/2)^2 - i\Omega\gamma_\nu^L - \Omega^2}{(\omega_\nu^T)^2 + (\gamma_\nu^T/2)^2 - i\Omega\gamma_\nu^T - \Omega^2} \quad (7)$$

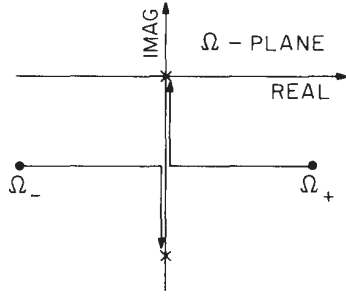


FIG. 1.

This situation is expected to occur in ferroelectrics of the disorder kind and in all solids in which an order–disorder mechanism exists, but in which there is only one parameter to describe the disorder along each crystallographic axis. The relaxation frequency γ_d^L is probably in the microwave region or below, in the case of ferroelectrics, and because the electric dipole moment associated with the internal diffusion is usually large, γ_d^L is much higher than γ_d^T . In the region of very low frequencies the phonon contribution to ϵ can be considered frequency independent unless we have a soft mode, and equation (7) can be rewritten as

$$\epsilon(\Omega) = \epsilon_\infty^1 \frac{\gamma_d^L/\gamma_d^T - i\Omega/\gamma_d^T}{1 - i\Omega/\gamma_d^T} \quad (8)$$

where ϵ_∞^1 takes into account the electronic plus the phonon contributions to ϵ . For $\omega \ll \gamma_d^L$ equation 8 will be:

$$\epsilon(\omega) = \frac{\epsilon(0)}{1 - i\omega/\gamma_d^T} \quad (9)$$

which has the same form as the Debye equation for polarization relaxation in liquids and which has been shown to describe the low frequency response of ϵ for many order–disorder ferroelectrics^{7,9}

In displacive ferroelectrics Ω_\pm shown in the figure goes to zero (as ω_0 goes to zero) and Ω_- goes to $-i\gamma$, or else, both Ω_\pm and Ω_- go to zero without ever becoming imaginary, as in Cochran's theory of soft modes.¹⁰

Going back to equation (7), we remark that to each pole of the dielectric function corresponds a peak in the system's response to transverse external

stimuli and to each zero corresponds a peak in the response to longitudinal ones. The zeros and infinities of ϵ which are used in equation (7) are not necessarily associated with normal modes, in the conventional meaning of decoupled resonances, but they are in fact what has practical interest because they are the peaks that are obtained in experiments with Raman or neutron scattering, after corrected properly for the Bose population factor.

The LST relation, now reinterpreted and put on a more solid basis, can be a strong instrument in the investigation of the dynamics of solids. After observing all the TO and LO resonances group-theoretically predicted for a crystal we must be able to calculate the low frequency dielectric constant $\epsilon_\alpha(0)$ for each crystallographic axis α . Disagreement of these values with the electrically measured values of $\epsilon_\alpha(0)$ indicate that either the crystal does not have the acknowledged symmetry or it has other ionic motions in addition to its phonons, i.e. the crystal is disordered. Let us consider as an example BaTiO₃ in its tetragonal phase. Bringing the frequencies of maximum intensities in their TO and LO Raman spectra, taken for the A_1 phonons, into the LST formula, Pinczuk *et al.*¹¹ obtained the value of 38 ± 6 for $\epsilon_{\parallel}(0)$. This is much less than the value $\epsilon_{\parallel} = 80$ obtained with capacitors at 250 MHz.¹² This is a very strong indication that BaTiO₃ is disordered, what agrees with the recent suggestion of Comes *et al.*¹³ One more remark can be made to show the validity of the LST relation in BaTiO₃. From the polariton dispersion Pinczuk *et al.* obtained $\epsilon_{\parallel}(0) = 37 \pm 5$, in agreement with their 'LST value'. This occurs because the slope of the lowest polariton is related to ϵ at far infrared, where ϵ is not affected by the disorder. A similar fact occurs in the xy -plane. From the analysis of the lowest polariton of E symmetry, Laughman *et al.*¹⁴ obtained $\epsilon_{\perp}(0) = 1500$. The LST relation would give the value 1700 ± 300 ; these values, although in mutual agreement, are below the number 2300 obtained by capacitance measurements,¹² which again would indicate an order–disorder mechanism of BaTiO₃ in the xy -plane. For a further corroboration we should note that the LST relation gives sometimes a smaller value for $\epsilon(0)$ than that obtained by electrical measurements, but, to our knowledge, the opposite has never been reported. It is certain to conclude that the observed discrepancies indicate the existence of other poles in the complex dielectric function, rather than a failure of the LST relation.

As a final remark, we emphasize that the adiabatic approximation used to split apart the electronic contribution to ϵ is not required. We could have included also the electronic modes in the factorization and ϵ_∞ would be equal to 1.

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Une relation de Lyddane–Sachs–Teller générale est calculée. La supposition que le mouvement ionique est décrit par un ensemble d'oscillateurs amortis n'est plus requise; le calcul est simplement basé sur les concepts de causalité et de conservation d'énergie plus le fait que ϵ a un nombre fini de pôles et zéros. Les paramètres qui apparaissent dans la mise en facteur ont un sens un peu différent de celui accepté jusqu'à présent, mais ils sont plus directement liés aux quantités mesurées en diffusion de neutrons et celle de Raman ainsi qu'aux expériences dans l'infra-rouge.