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Lyddane-Sachs-Teller relationship in linear magnetoelectrics

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In a linear magnetoelectric the lattice is coupled to electric and magnetic fields: both affect the longitudinal-transverse splitting of zone-center optical phonons on equal footing. A response matrix relates the macroscopic fields (D, B) to (E, H) at infrared frequencies. It is shown that the response matrices at frequencies 0 and ∞ fulfill a generalized Lyddane-Sachs-Teller relationship. The rhs member of such relationship is expressed in terms of weighted averages over the longitudinal and transverse excitations of the medium, and assumes a simple form for an harmonic crystal.

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The original Lyddane-Sachs-Teller (LST) relationship [1] applies to the simple case of a cubic binary crystal in the harmonic regime. It relates four macroscopically measurable constants as

$$\frac{\varepsilon(0)}{\varepsilon(\infty)} = \frac{\omega_L^2}{\omega_T^2}. \quad (1)$$

Here $\varepsilon(0)$ is the static dielectric constant, which includes the lattice contribution, $\varepsilon(\infty)$ is the so called “static high frequency” (a.k.a “clamped-ion”) dielectric constant, which accounts for the electronic response only, and ω_L (ω_T) is the zone-center longitudinal (transverse) optical frequency [2]. It is remarkable that all *microscopic* parameters (force constants, masses, Born effective charges, cell volume) disappear from Eq. (1).

Magnetoelectrics (MEs) are insulators where electric fields control magnetization, and conversely magnetic fields control polarization; they attracted considerable theoretical and technological interest in recent times [3–11]. The simplest and most studied single-crystal linear ME is antiferromagnetic Cr_2O_3 [3, 5–7]. In any linear ME the role of the dielectric function $\varepsilon(\omega)$ is played by the 2×2 response matrix—called $\mathcal{R}(\omega)$ here—which yields the macroscopic fields (D, B) in terms of (E, H) at frequency ω :

$$\begin{pmatrix} D \\ B \end{pmatrix} = \mathcal{R}(\omega) \begin{pmatrix} E \\ H \end{pmatrix} \equiv \begin{pmatrix} \varepsilon(\omega) & \alpha(\omega) \\ \alpha(\omega) & \mu(\omega) \end{pmatrix} \begin{pmatrix} E \\ H \end{pmatrix}, \quad (2)$$

where ε , μ , and α are permittivity, magnetic permeability, and ME coupling, respectively. In this Letter we are going to show that a generalized LST relationship holds in the form

$$\frac{\text{tr} \{ \mathcal{R}^{-1}(\infty) \mathcal{R}(0) \} - 2}{2 - \text{tr} \{ \mathcal{R}^{-1}(0) \mathcal{R}(\infty) \}} = \frac{\omega_L^2}{\omega_T^2}. \quad (3)$$

In the simple case of a magnetically inert material (i.e. $\mu \equiv \text{constant}$, $\alpha \equiv 0$) the lhs of Eq. (3) equals indeed $\varepsilon(0)/\varepsilon(\infty)$. While in ordinary dielectrics the LO-TO splitting is due to the coupling of the ionic displacements to macroscopic electric fields, in linear MEs it is due to

the coupling of both (electric and magnetic) fields on the same footing: this is perspicuous in the lhs of Eq. (3).

The simple form of Eqs. (1) and (3) requires a crystalline system with only a single IR-active mode at the zone center. The additional requirement of cubic symmetry can be relaxed; it is nonetheless convenient to consider only crystals whose symmetry is orthorhombic or higher; then all crystalline tensors can be simultaneously diagonalized (as e.g. in Cr_2O_3). This allows us to adopt simple scalar-like notations, as in Eqs. (1) and (3) with the proviso that we deal separately with each principal direction.

Over the years the LST relationship has been extended in several ways, to cover cases where more than one IR-active mode per direction exists [12, 13], the crystal is in a low-symmetry class [14, 15], or even the material is noncrystalline and/or anharmonic [16–19]. The general case can be written as

$$\frac{\varepsilon(0)}{\varepsilon(\infty)} = \frac{\langle \omega^2 \rangle_L}{\langle \omega^2 \rangle_T}. \quad (4)$$

The quantities in the rhs are weighted averages, obtained from moments of the appropriate spectral functions. The derivation is based on general principles of statistical mechanics and does not require an Hamiltonian, even less an harmonic one [16, 18]; in the special case of a single IR-active harmonic mode per direction Eq. (4) is equivalent to Eq. (1). In this Letter we generalize the viewpoint of Ref. [18] to the ME case, showing that

$$\frac{\text{tr} \{ \mathcal{R}^{-1}(\infty) \mathcal{R}(0) \} - 2}{2 - \text{tr} \{ \mathcal{R}^{-1}(0) \mathcal{R}(\infty) \}} = \frac{\langle \omega^2 \rangle_L}{\langle \omega^2 \rangle_T}, \quad (5)$$

where the rhs is defined below, Eqs. (10) and (11).

The presentation proceeds as follows. We start at a very general level without any *microscopic* assumption about the ME medium, and using only very general principles in order to arrive at Eq. (5). We will then apply the general results to a crystalline system in the harmonic regime, and finally we will show that Eq. (5) reduces to Eq. (3) in the single-mode case.

We write explicitly the linear response matrix of the ME medium as the sum of its real and imaginary part: $\mathcal{R}(\omega) = \mathcal{R}'(\omega) + i\mathcal{R}''(\omega)$, and analogously for its inverse; both $\mathcal{R}(\omega)$ and $\mathcal{R}^{-1}(\omega)$ obey the Kramers-Kronig relationships in the form

$$\mathcal{R}'(\omega) - \mathcal{R}'(\infty) = \frac{2}{\pi} \int_0^\infty d\omega' \frac{\omega' \mathcal{R}''(\omega')}{\omega'^2 - \omega^2}, \quad (6)$$

$$\mathcal{R}^{-1}'(\omega) - \mathcal{R}^{-1}'(\infty) = \frac{2}{\pi} \int_0^\infty d\omega' \frac{\omega' \mathcal{R}^{-1}''(\omega')}{\omega'^2 - \omega^2}. \quad (7)$$

From these, it follows immediately that the numerator and denominator in the lhs of Eqs. (3) and (5) are

$$\text{tr}\{\mathcal{R}^{-1}(\infty)\mathcal{R}(0)\} - 2 = \frac{2}{\pi} \int_0^\infty \frac{d\omega}{\omega} \text{tr}\{\mathcal{R}^{-1}(\infty)\mathcal{R}''(\omega)\}, \quad (8)$$

$$2 - \text{tr}\{\mathcal{R}^{-1}(0)\mathcal{R}(\infty)\} = -\frac{2}{\pi} \int_0^\infty \frac{d\omega}{\omega} \text{tr}\{\mathcal{R}^{-1}''(\omega)\mathcal{R}(\infty)\}. \quad (9)$$

The integrands in the rhs of Eqs. (8) and (9) are interpreted here as the transverse and longitudinal spectral weights, respectively, by means of which we *define* the second moments

$$\langle \omega^2 \rangle_T = \frac{\int_0^\infty \frac{d\omega}{\omega} \omega^2 \text{tr}\{\mathcal{R}^{-1}(\infty)\mathcal{R}''(\omega)\}}{\int_0^\infty \frac{d\omega}{\omega} \text{tr}\{\mathcal{R}^{-1}(\infty)\mathcal{R}''(\omega)\}} \quad (10)$$

$$\langle \omega^2 \rangle_L = \frac{\int_0^\infty \frac{d\omega}{\omega} \omega^2 \text{tr}\{\mathcal{R}^{-1}''(\omega)\mathcal{R}(\infty)\}}{\int_0^\infty \frac{d\omega}{\omega} \text{tr}\{\mathcal{R}^{-1}''(\omega)\mathcal{R}(\infty)\}}. \quad (11)$$

The reason for the semantics (*transverse* and *longitudinal*) may appear obscure at this point; it will become clear when specializing Eqs. (10) and (11) to an harmonic crystal—see also Eq. (26) below.

In order to arrive at our main result, Eq. (5), we exploit the “superconvergence” theorem [20]. For large ω (i.e. for ω much larger than all the resonances of the medium) $\mathcal{R}''(\omega)$ vanishes; Eqs. (6) and (7) yield, to leading order in $1/\omega^2$,

$$\mathcal{R}(\infty)^{-1}\mathcal{R}(\omega) \simeq \mathcal{I} - \frac{2}{\pi\omega^2} \int_0^\infty d\omega' \omega' \mathcal{R}(\infty)^{-1}\mathcal{R}''(\omega'), \quad (12)$$

$$\mathcal{R}(\omega)^{-1}\mathcal{R}(\infty) \simeq \mathcal{I} - \frac{2}{\pi\omega^2} \int_0^\infty d\omega' \omega' \mathcal{R}^{-1}''(\omega')\mathcal{R}(\infty), \quad (13)$$

where \mathcal{I} is the 2×2 identity. Inversion of Eq. (12) to the same order gives the alternative expression

$$\mathcal{R}(\omega)^{-1}\mathcal{R}(\infty) \simeq \mathcal{I} + \frac{2}{\pi\omega^2} \int_0^\infty d\omega' \omega' \mathcal{R}(\infty)^{-1}\mathcal{R}''(\omega'). \quad (14)$$

Next we take the trace of Eqs. (13) and (14); permuting

the matrices in the product we get the identity

$$\int_0^\infty d\omega \omega \text{tr}\{\mathcal{R}(\infty)^{-1}\mathcal{R}''(\omega)\} = - \int_0^\infty d\omega \omega \text{tr}\{\mathcal{R}(\omega)^{-1}''\mathcal{R}(\infty)\}. \quad (15)$$

In order to arrive at Eq. (5) it is enough to put together Eqs. (8), (9), (10), (11), and (15).

We stress that at the root of the superconvergence identity, Eq. (15), is the assumption that $\omega = \infty$ actually means ω much higher than all the frequencies of ionic motions, yet lower than the frequencies of electronic excitations [2]. Therefore the clamped-ion response $\mathcal{R}(\infty)$ is a real matrix.

Next we address an harmonic crystal. A zone-center optical mode is lattice-periodical; it is then expedient to consider the energy per cell of a (macroscopically homogeneous) solid with a frozen-in phonon distortion. This energy is well defined only when a prescription for taking the thermodynamic limit is given. We cut a sample in the shape of a slab parallel to the principal axes; we remind our assumption that all crystal tensors are diagonal on them. If the slab is free-standing in vacuo, all fields vanish outside ($E=D=H=B=0$), while the value of the fields inside depend on the polarization of the mode. Simple electrostatics and magnetostatics imply that if the phonon polarization is parallel to the slab (“transverse”), both E and H vanish, while if it is perpendicular (“longitudinal”) D and B vanish [22]. The order of the limits (first a slab, then its thickness going to infinity) is essential, and the two energies (longitudinal and transverse) are indeed different in the thermodynamic limit. Similar reasonings apply if the lattice-periodical mode is regarded as the $\mathbf{k} \rightarrow 0$ limit of a finite- \mathbf{k} optical phonon [2].

If the crystal has N IR-active modes in each principal direction, we denote with ω_n the zone-center TO frequencies (i.e those with $E=0$ and $H=0$); equivalently, ω_n^2 are the eigenvalues of *the analytical part* of the dynamical matrix at $\mathbf{k} = 0$. The free energy per cell in function of the normal coordinates u_n , E , and H (taken as independent variables) is expanded to second order as [3, 5]

$$\begin{aligned} F(E, H, \{u_n\}) &= F_0 + \frac{1}{2} \sum_n \omega_n^2 u_n^2 \\ &- \frac{\Omega}{8\pi} [\varepsilon(\infty)E^2 + 2\alpha(\infty)EH + \mu(\infty)H^2] \\ &- \sum_n (u_n Z_n^* E + u_n \zeta_n^* H), \end{aligned} \quad (16)$$

where we adopt atomic Gaussian units [21], and Ω is the cell volume. Z_n^* are the mode-effective charges and ζ_n^* their magnetic analogues; notice that in ordinary units the normal-mode coordinates would include a factor with

the dimensions of $(\text{mass})^{1/2}$, while Z_n^* and ζ_n^* would include a factor with the dimensions of $(\text{mass})^{-1/2}$.

The derivatives of F provide the equations of motion in the form

$$\begin{aligned} D &= -\frac{4\pi}{\Omega} \frac{\partial F}{\partial E} = \varepsilon(\infty)E + \alpha(\infty)H + \frac{4\pi}{\Omega} \sum_n Z_n^* u_n \\ B &= -\frac{4\pi}{\Omega} \frac{\partial F}{\partial H} = \alpha(\infty)E + \mu(\infty)H + \frac{4\pi}{\Omega} \sum_n \zeta_n^* u_n \\ f_n &= -\frac{\partial F}{\partial u_n} = -\omega_n^2 u_n + Z_n^* E + \zeta_n^* H. \end{aligned} \quad (17)$$

We then consider forced oscillations at frequency ω , i.e. $f_n = -\omega^2 u_n$. Elimination of the u_n 's from Eq. (17) provides the linear ME response, including the lattice contribution; we cast it in compact form as

$$\mathcal{R}'(\omega) = \mathcal{R}(\infty) + \frac{4\pi}{\Omega} \sum_n \frac{\mathcal{Z}_n \mathcal{Z}_n^\dagger}{\omega_n^2 - \omega^2} \quad (18)$$

$$\mathcal{R}''(\omega) = \frac{4\pi^2}{\Omega} \sum_n \mathcal{Z}_n \mathcal{Z}_n^\dagger \delta(\omega_n^2 - \omega^2), \quad (19)$$

where the ME lattice coupling vectors are

$$\mathcal{Z}_n = \begin{pmatrix} Z_n^* \\ \zeta_n^* \end{pmatrix}, \quad \mathcal{Z}_n^\dagger = (Z_n^* \ \zeta_n^*). \quad (20)$$

Eq. (18) is the elegant result obtained in 2008 by J. Īñiguez [5]; the TO frequencies ω_n are clearly the N poles of $\mathcal{R}(\omega)$.

Actual computations performed for the paradigmatic material Cr_2O_3 and based on Eq. (18) show that the magnetoelectric coupling $\alpha(0)$ is significantly enhanced by the lattice contribution [5]. Clearly, a large coupling is the key property to be exploited in device applications [3].

It is now expedient to express Eq. (17) in terms of D and B .

$$\begin{pmatrix} E \\ H \end{pmatrix} = \mathcal{R}^{-1}(\infty) \left[\begin{pmatrix} D \\ B \end{pmatrix} - \frac{4\pi}{\Omega} \sum_n \mathcal{Z}_n u_n \right] \quad (21)$$

$$\begin{aligned} -\omega^2 u_n &= -\omega_n^2 u_n - \frac{4\pi}{\Omega} \mathcal{Z}_n^\dagger \mathcal{R}^{-1}(\infty) \sum_{n'} \mathcal{Z}_{n'} u_{n'} \\ &+ \mathcal{Z}_n^\dagger \mathcal{R}^{-1}(\infty) \begin{pmatrix} D \\ B \end{pmatrix}. \end{aligned} \quad (22)$$

As explained above, in the LO modes $D=0$ and $B=0$ by definition [22]. The first line of Eq. (22) clearly shows that the LO eigenmodes are in general different from the TO ones; an explicit $N \times N$ diagonalization is needed in order to find the LO frequencies. We indicate with $\tilde{\omega}_n$ these frequencies, and we also transform the lattice coupling vectors to the LO eigenmodes as $\mathcal{R}^{-1}(\infty) \mathcal{Z}_n \rightarrow \tilde{\mathcal{Z}}_n$, in order to write Eq. (22) as

$$-\omega^2 u_n = -\tilde{\omega}_n^2 u_n + \tilde{\mathcal{Z}}_n^\dagger \begin{pmatrix} D \\ B \end{pmatrix}. \quad (23)$$

Elimination of the u_n 's from Eqs. (21) and (23) provides $\mathcal{R}^{-1}(\omega)$ in the form

$$\mathcal{R}'^{-1}(\omega) = \mathcal{R}^{-1}(\infty) - \frac{4\pi}{\Omega} \sum_n \frac{\tilde{\mathcal{Z}}_n \tilde{\mathcal{Z}}_n^\dagger}{\tilde{\omega}_n^2 - \omega^2} \quad (24)$$

$$\mathcal{R}''^{-1}(\omega) = -\frac{4\pi^2}{\Omega} \sum_n \tilde{\mathcal{Z}}_n \tilde{\mathcal{Z}}_n^\dagger \delta(\tilde{\omega}_n^2 - \omega^2). \quad (25)$$

Using the above results, we arrive at a very transparent expression for the rhs member of Eq. (5):

$$\frac{\langle \omega^2 \rangle_L}{\langle \omega^2 \rangle_T} = \frac{\sum_n \frac{1}{\omega_n^2} \mathcal{Z}_n^\dagger \mathcal{R}^{-1}(\infty) \mathcal{Z}_n}{\sum_n \frac{1}{\tilde{\omega}_n^2} \tilde{\mathcal{Z}}_n^\dagger \mathcal{R}(\infty) \tilde{\mathcal{Z}}_n}, \quad (26)$$

i.e. $\langle \omega^2 \rangle_T$ is the weighted harmonic mean of the ω_n^2 's, with weights $\mathcal{Z}_n^\dagger \mathcal{R}^{-1}(\infty) \mathcal{Z}_n$, and $\langle \omega^2 \rangle_L$ is the weighted harmonic mean of the $\tilde{\omega}_n^2$'s, with weights $\tilde{\mathcal{Z}}_n^\dagger \mathcal{R}(\infty) \tilde{\mathcal{Z}}_n$. The two sets of weights are in general different, except when the transverse and longitudinal eigenmodes happen to be the same. However, ‘‘superconvergence’’, Eq. (15), implies the same normalization in any case:

$$\sum_n \mathcal{Z}_n^\dagger \mathcal{R}^{-1}(\infty) \mathcal{Z}_n = \sum_n \tilde{\mathcal{Z}}_n^\dagger \mathcal{R}(\infty) \tilde{\mathcal{Z}}_n. \quad (27)$$

In the special case where a single IR-active mode exists $\langle \omega^2 \rangle_T = \omega_T^2$ and $\langle \omega^2 \rangle_L = \omega_L^2$: this concludes the proof of Eq. (3).

A well known bound requires the matrix \mathcal{R} to be positive definite [3]. Since this is based on stability arguments, it only concerns $\mathcal{R}(0)$ and $\mathcal{R}(\infty)$: the former is a genuine static property of the real system, while the latter can be regarded as a static property in the infinite nuclear mass limit. At any other frequency the matrix $\mathcal{R}(\omega)$ accounts for the forced oscillations of the system, which is clearly out of equilibrium. Therefore $\mathcal{R}(\omega)$ is not required, in general, to be positive definite; because of the same reason, $\varepsilon(\omega)$ is not a positive real function in ordinary dielectrics [2].

All of the above results reduce to previously known ones for a magnetically inert material, where the 2×2 matrix $\mathcal{R}(\omega)$ has the unique nontrivial entry $\varepsilon(\omega)$. It is worth examining Eq. (26) for $\zeta_n^* = 0$:

$$\frac{\langle \omega^2 \rangle_L}{\langle \omega^2 \rangle_T} = \frac{1}{\varepsilon^2(\infty)} \frac{\sum_n \frac{1}{\omega_n^2} (Z_n^*)^2}{\sum_n \frac{1}{\tilde{\omega}_n^2} (\tilde{Z}_n^*)^2}. \quad (28)$$

The weights in the harmonic means $(Z_n^*)^2$ and $(\tilde{Z}_n^*)^2$ are the (squared) transverse and longitudinal effective charges, respectively. If (and only if) the transverse and longitudinal eigenmodes are the same, then $\tilde{Z}_n^* = Z_n^*/\varepsilon(\infty)$. Actually, this is the well known relationship between the transverse (a.k.a. Born) and longitudinal (a.k.a. Callen) effective charges.

For an ordinary dielectric the N poles of $\varepsilon(\omega)$ are the TO frequencies ω_n , while the N poles of $1/\varepsilon(\omega)$ are the

LO ones $\tilde{\omega}_n$: see Eqs. (18) and (24). Since the response is a single-component function, the poles of $1/\varepsilon(\omega)$ coincide with the zeros of $\varepsilon(\omega)$. Simple considerations about zeros and poles of $\varepsilon(\omega)$ eventually lead to the simple expression

$$\frac{\langle \omega^2 \rangle_L}{\langle \omega^2 \rangle_T} = \prod_{n=1}^N \frac{\tilde{\omega}_n}{\omega_n}, \quad (29)$$

first found in 1961 by Kurosawa [12, 19]. This result *does not* generalize to the ME case, for the good reason that the response is a 2×2 matrix: the present formulation is based on *traces* throughout, and the inverse of the trace bears no simple relationship to the trace of the inverse, at variance with the purely electrical case.

This Letter addresses the linear relationship between the pairs (E, H) and (D, B) throughout, starting with Eq. (2) onwards. Other pairings are possible. In particular the choice (E, B) and (D, H) looks like a more natural one for at least two reasons: (i) the microscopic forces are determined by the (E, B) pair [22], and (ii) a relativistic formulation can be elegantly cast in terms of two four-dimensional field tensors whose entries are (E, B) and (D, H) , respectively [6, 7]. Nonetheless, the same choice in the present context would not be a convenient one. In fact, as explained above (see also Ref. [22]), in a transverse mode $E = 0$ and $B \neq 0$, and in a longitudinal one $D = 0$ and $H \neq 0$.

Throughout this Letter we have stressed the formal equivalence of electric and magnetic fields in their coupling to the lattice in MEs. However, the orders of magnitude of electric and magnetic phenomena in condensed matter are not the same. ME effects are notoriously small [3], and the corrections to the LST relationship in most cases are expected to be small as well. In oxides the dielectric constants—either $\varepsilon(\infty)$ or $\varepsilon(0)$ —are typically in the range 2 to 10, while $|\mu - 1|$ is of the order 10^{-4} [23]; in the most studied linear ME, i.e. Cr_2O_3 , even α is of the order 10^{-4} [5, 6]. An accurate evaluation of the lhs of Eqs. (3) and (5) in “conventional” ME materials would require a measurement of all the entries of the response matrices \mathcal{R} to the same absolute error, which could be problematic. More perspicuous effects are expected in nonconventional materials [3], such as those where the ME effect can be tuned [24].

In conclusion, this Letter shows that the ratio $\varepsilon(0)/\varepsilon(\infty)$ entering the LST relationship must be replaced, for a linear ME, by the lhs of Eqs. (3) and (5), whose ingredients are the full ME responses at frequency 0 and ∞ , i.e. static and clamped-ion. In the most general case the rhs member of our generalized LST relationship is the ratio between spectral moments of the longitudinal and transverse excitations of the medium. It assumes a simple form for a crystalline ME in the harmonic

approximation, and finally is identical to the original LST one when only one mode is IR active. The relationship shows that the LO-TO splitting in a ME originates from the coupling of ionic displacements to both electric and magnetic macroscopic fields.

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