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Coordinate-Invariant Lyddane-Sachs-Teller Relationship for Polar Vibrations in Materials with Monoclinic and Triclinic Crystal Systems

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A coordinate-invariant generalization of the Lyddane-Sachs-Teller relation is presented for polar vibrations in materials with monoclinic and triclinic crystal systems. The generalization is derived from an eigendielectric displacement vector summation approach, which is equivalent to the microscopic Born-Huang description of polar lattice vibrations in the harmonic approximation. An expression for a general oscillator strength is also described for materials with monoclinic and triclinic crystal systems. A generalized factorized form of the dielectric response characteristic for monoclinic and triclinic materials is proposed. The generalized Lyddane-Sachs-Teller relation is found valid for monoclinic β-Ga$_2$O$_3$, where accurate experimental data became available recently from a comprehensive generalized ellipsometry investigation [Phys. Rev. B **93**, 125209 (2016)]. Data for triclinic crystal systems can be measured by generalized ellipsometry as well, and are anticipated to become available soon and results can be compared with the generalized relations presented here.

The Lyddane-Sachs-Teller (LST) relation [1] sets two important ratios equal for a material with polar vibrations. The square of the ratio of the frequency of longitudinal optic lattice vibrations (phonons) (ω_{LO}) to the frequency of transverse optical lattice vibration (ω_{TO}) for long wavelengths, independent on the phonons' displacement vectors, equals the ratio of the dielectric permittivity at zero frequency ε_{dc} with the dielectric permittivity at frequencies above the TO and LO vibrations where the material is widely transparent (ε_∞) [2],

$$\frac{\varepsilon_{\text{dc}}}{\varepsilon_\infty} = \left(\frac{\omega_{\text{LO}}}{\omega_{\text{TO}}}\right)^2. \tag{1}$$

The LST relation is a fundamental statement, and can be found in many textbooks on condensed matter physics and semiconductor optics [3–11]. The LST relation has been used extensively, either to predict a missing parameter out of the set of the fundamental four, ε_{dc}, ε_∞, ω_{LO}, ω_{TO}, or to check for consistency among the experimentally and/or computationally obtained phonon mode and dielectric permittivity parameters. The LST relation is playing a crucial role in the understanding of the physics of ferro-electric materials [12]. For example, lattice instabilities in ferroelectric [13] perovskite titanates such as SrTiO$_3$ and (Ba, Sr)TiO$_3$ [14,15] across the phase transition affect static dielectric constants and phonon modes. The LST relation has been expanded previously to include situations where multiple branches of phonon modes occur, and the role of poles and zeros in the complex plane to describe the dielectric response functions was identified [16–18].

A generalization of the LST relation for arbitrary crystal symmetry was derived by Cochran and Cowley (CC-LST) [19], which explicitly includes the phonon displacement vector dependence

$$\frac{\varepsilon_{\text{dc},\alpha\alpha}}{\varepsilon_{\infty,\alpha\alpha}} = \prod_{l=1}^{N}\left(\frac{\omega(\alpha)_{\text{LO},l}}{\omega(\alpha)_{\text{TO},l}}\right)^2, \tag{2}$$

where α denotes a direction along a given Cartesian axis, $\varepsilon_{\text{dc},\alpha\alpha}$, $\varepsilon_{\infty,\alpha\alpha}$ are diagonal tensor components of the static and high-frequency dielectric permittivity (dielectric function tensor, ε), respectively, and $\omega(\alpha)_{\text{TO},l}$ and $\omega(\alpha)_{\text{LO},l}$ are the frequencies of N modes whose displacements, transverse and longitudinal to their corresponding wave vectors, respectively, are parallel to the α direction [19]. Venkataraman, Feldkamp, and Sahni later extended the CC-LST relation to arbitrary directions [3]. The CC-LST relation has been found correct for anisotropic materials whose major axes of polarization align with orthogonal axes [9,18,20]. Such situations include materials with cubic, hexagonal, trigonal, tetragonal, and orthorhombic crystal systems [21]. Contemporary semiconductor materials are cubic (for example, diamond structure silicon, and zinc blende structure group-III phosphides, arsenides, and selenides), or hexagonal (for example, wurtzite structure group-III nitrides). Very recently, the monoclinic phase of metal-oxide β-Ga$_2$O$_3$ (gallia) has emerged as a potential candidate for use in high-power transistors and switches due to a very large electric break down field value of 8 MV cm^{-1} [22]. First devices exhibited excellent characteristics such

as a nearly ideal pinch-off of the drain current, an off-state breakdown voltage over 250 V, a high on-off drain current ratio of around 10^4, and small gate leakage current [23]. Few reports exist on long wavelength characterization of monoclinic $LiAlSi_2O_6$ [24,25], $MgCaSi_2O_6$ [26], $CdWO_4$ [27], CuO [28], $MnWO_4$ [29], and Y_2SiO_5 [30], where the application of the LST relation was not discussed. A generalized ellipsometry analysis [9] of phonon modes and free charge carrier properties in β-Ga_2O_3 was reported very recently, and an alternative approach to the LST relation was suggested for materials with monoclinic symmetry [31]. Virtually no information is available on triclinic materials, which appears as a widely uncharted field of condensed matter physics.

For mononclinic and triclinic systems, the CC-LST relations become problematic, because, in general, for such systems an α direction cannot be found anymore along which the displacement directions of multiple TO and LO modes line up. For example, the displacement vectors of all TO and LO modes within the monoclinic plane of β-Ga_2O_3 each possess a different direction, which was obtained from experiment and verified by density-functional theory calculations [31]. Furthermore, the ratios equaled in Eq. (2) depend on the choice of the α direction, and, hence, the choice of the coordinate system within which an experimentally determined tensor ε is cast. Hence, the CC-LST parameters $\omega(\alpha)_{LO,l}$ do not necessarily coincide with the LO mode frequencies in crystals with monoclinic and triclinic symmetries [32]. The purpose of this present work is to provide a generalization of the LST relation to a coordinate-invariant form, which comprises the parameters of all long wavelength active phonon frequencies regardless of their displacement directions. This form is then applicable to any crystal symmetry, regardless of the choice of the Cartesian coordinate system within which the dielectric response is described. The Letter follows a derivation of a general expression of the dielectric function tensor for materials with polar vibrations in the harmonic approximation. A simple superposition of eigendielectric displacement polarizability functions using Lorentzian oscillators and their displacement vector dependence leads to a coordinate-dependent tensor description, from where a general, coordinate-invariant LST relation is obtained. The oscillators approach is equivalent to the result of the microscopic description of the long wavelength lattice vibrations given by Born and Huang in the harmonic approximation [33], where the interatomic forces are considered constant and the equations of motion are determined by harmonic potentials.

Vibration modes, which can be excited by long wavelength electromagnetic waves (long wavelength active phonon modes) in materials can be represented as intrinsic dielectric polarizations (eigendielectric displacement modes). Each mode produces an electric dipole charge oscillation. The dipole axis can be associated with a

characteristic vector (unit eigen displacement vector $\hat{\mathbf{e}}_l$). The orientations of the N eigenvectors, $\hat{\mathbf{e}}_l$, and the frequency responses of their eigendisplacements determine the optical character of a given, dielectrically polarizable material. For certain or all frequency regions, the optical behavior may be isotropic, uniaxial, or biaxial [34]. Within the frequency domain, and within a Cartesian system with unit axes $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$, the dielectric polarizability $\mathbf{P}$ under the influence of an electric phasor field $\mathbf{E}$ along $\hat{\mathbf{e}}_l = \hat{e}_{x,l}\mathbf{x} + \hat{e}_{y,l}\mathbf{y} + \hat{e}_{z,l}\mathbf{z}$ is then given by a complex-valued response function ϱ_l (Fig. 1) [31]

$$\mathbf{P}_{\hat{e}_l} = \varrho_l(\hat{\mathbf{e}}_l\mathbf{E})\hat{\mathbf{e}}_l. \qquad (3)$$

Function ϱ_l must satisfy causality and energy conservation requirements, i.e., the Kramers-Kronig (KK) integral relations and $\text{Im}\{\varrho\} \geq 0$, $\forall \omega \geq 0$ [35,36]. The energy (frequency) dependent contribution to the long wavelength polarization response of an uncoupled electric dipole charge oscillation is commonly described using a Kramers-Kronig consistent oscillator function [9,37]

$$\varrho_l(\omega) = \frac{A_l}{\omega_{TO,l}^2 - \omega^2}, \qquad (4)$$

where A_l and $\omega_{TO,l}$ denote the amplitude and resonance frequency parameters of a vibration mode with transverse optical (TO) character, and ω is the frequency of the driving electromagnetic field. The effect of mode damping (broadening) is omitted here for convenience, and it can be shown that nonzero broadening does not change the findings here [38]. The eigenvectors are located along certain, fixed spatial directions within a given sample of material. Explicit coupling between different eigendisplacement modes, which may lead to description of chiral properties, are ignored here. The linear polarization response of a material with N eigendisplacement modes is then obtained from summation
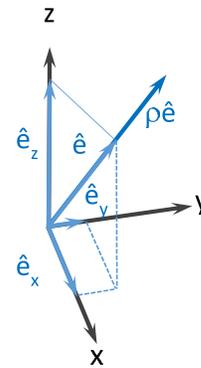

FIG. 1. Unit vector $\hat{\mathbf{e}}$, characteristic for a dielectric eigenpolarizability vibration $\mathbf{P}_{\hat{e}}$, whose frequency response is rendered by a complex-valued response function ϱ.

$$\mathbf{P} = \chi\mathbf{E} = \sum_{l=1}^{N} \mathbf{P}_{\hat{e}_l} = \sum_{l=1}^{N} \frac{A_l(\hat{\mathbf{e}}_l \otimes \hat{\mathbf{e}}_l)}{\omega_{\mathrm{TO},l}^2 - \omega^2} \mathbf{E}, \quad (5)$$

where $\otimes$ is the dyadic product [39]. The index l numerates the contributions of all independent dipole oscillations. It is required here that $\omega_{\mathrm{TO},l} > 0 \forall l$ [40]. The field phasors displacement $\mathbf{D}$, and $\mathbf{E}$ are related by the dielectric function tensor (ε_0 is the vacuum permittivity)

$$\mathbf{D} = \varepsilon_0(\varepsilon_\infty + \chi\mathbf{E}) = \varepsilon_0\varepsilon\mathbf{E}, \quad (6)$$

where a symmetric tensor ε_∞ may account for the high frequency appearance of ε. The high frequency limit here is meant as a frequency region with frequencies sufficiently large against the vibration modes summed over in Eq. (5), and yet small against potential other electronic polarizabilities whose transition energies are at even higher frequencies. The key leading to the LST relation is to inspect the determinant of the dielectric tensor, $\det\{\varepsilon(\omega)\}$, for $\omega \to 0$ and for $\omega \to \infty$. Six real-valued physical material parameters may be required to describe the static (dc) behavior. At high frequencies, similarly six frequency independent elements may be required:

$$\det\{\varepsilon(\omega=0)\} = \varepsilon_{\mathrm{dc},xx}\varepsilon_{\mathrm{dc},yy}\varepsilon_{\mathrm{dc},zz} + 2\varepsilon_{\mathrm{dc},xy}\varepsilon_{\mathrm{dc},yz}\varepsilon_{\mathrm{dc},xz}$$
$$- (\varepsilon_{\mathrm{dc},xx}\varepsilon_{\mathrm{dc},yz}^2 + \varepsilon_{\mathrm{dc},yy}\varepsilon_{\mathrm{dc},xz}^2 + \varepsilon_{\mathrm{dc},zz}\varepsilon_{\mathrm{dc},xy}^2), \quad (7)$$

$$\det\{\varepsilon_\infty\} = \varepsilon_{\infty,xx}\varepsilon_{\infty,yy}\varepsilon_{\infty,zz} + 2\varepsilon_{\infty,xy}\varepsilon_{\infty,yz}\varepsilon_{\infty,xz}$$
$$- (\varepsilon_{\infty,xx}\varepsilon_{\infty,yz}^2 + \varepsilon_{\infty,yy}\varepsilon_{\infty,xz}^2 + \varepsilon_{\infty,zz}\varepsilon_{\infty,xy}^2). \quad (8)$$

According to Eq. (5) each element of ε possesses up to $(N+1)$ terms

$$(\varepsilon)_{ij} = \det\{\varepsilon_\infty\}\hat{e}_{i,\infty}\hat{e}_{j,\infty}$$
$$+ \sum_{l=1}^{N} \varrho_l \hat{e}_{i,l}\hat{e}_{j,l}, i,j \in \{x,y,z\}. \quad (9)$$

Hence, ε is symmetric, and a function of frequency ω. At long wavelength and in the harmonic approximation, all terms in Eq. (9) are independent on the magnitude of the displacement, i.e., the strength and direction of the electric field. The dielectric function tensor in Eq. (6) has six independent complex-valued parameters (spectra), which can be obtained by experiment, for example, using generalized spectroscopic ellipsometry [9,31,42]. Two characteristic sets of N optical modes, transverse optical (TO; $\omega_{\mathrm{TO},l}$), and longitudinal optical (LO; $\omega_{\mathrm{LO},l}$), can be obtained, respectively, from the roots of the determinants of ε^{-1}, and ε,

$$0 = \det\{\varepsilon^{-1}(\omega_{\mathrm{TO},l})\}, \qquad 0 = \det\{\varepsilon(\omega_{\mathrm{LO},l})\}, \quad (10)$$

and a proof for this statement is obtained below. The solutions of Eq. (10), the TO and LO mode of the material rendered by $\varepsilon(\omega)$, are invariant under coordinate rotation, e.g., described by rotation matrix $\mathbf{A}$ [9], since $\det\{\mathbf{A}\varepsilon(\omega)\mathbf{A}^{-1}\} = \det\{\mathbf{A}\}\det\{\varepsilon(\omega)\}\det\{\mathbf{A}^{-1}\} = \det\{\varepsilon(\omega)\}$. The displacement vectors for the TO and LO modes, $\hat{\mathbf{e}}_{\mathrm{TO},l}$ and $\hat{\mathbf{e}}_{\mathrm{LO},l}$, respectively, are obtained from the eigenvector solutions of Eq. (10) [43],

$$0 = \varepsilon^{-1}(\omega_{\mathrm{TO},l})\hat{\mathbf{e}}_{\mathrm{TO},l}, \qquad 0 = \varepsilon(\omega_{\mathrm{LO},l})\hat{\mathbf{e}}_{\mathrm{LO},l}, \quad (11)$$

and it can be shown that $\hat{\mathbf{e}}_{\mathrm{TO},l}$ are identical with $\hat{\mathbf{e}}_l$ in Eq. (3). The LO mode displacement vectors, $\hat{\mathbf{e}}_{\mathrm{LO},l}$, must be obtained numerically, which requires explicit knowledge of all tensor elements of $\varepsilon(\omega)$. The latter can be obtained, for example, from density-functional perturbation theory calculations [44], and from matching model equations using Eqs. (5)–(6) to experimental data [31]. The displacement vectors of all TO and LO modes is thereby determined, and the index l unambiguously identifies mode and vector via Eq. (11). However, vectors $\hat{\mathbf{e}}_{\mathrm{TO},l}$ and $\hat{\mathbf{e}}_{\mathrm{LO},l}$ change upon coordinate rotation, but as an entity, leaving their relative orientation with each other unchanged. Such coordinate rotation is equivalent to rotating a specimen under investigation during experiment, or producing a surface with a different cut from a bulk crystal. It is clear that the internal displacement vectors remain their relative orientation while changing their overall orientation with respect to a chosen Cartesian laboratory coordinate system. For $0 < \omega < \infty$, one can express the determinant of ε through a complex-valued function f, or $f^\dagger$,

$$\det\{\varepsilon(\omega)\} = \det\{\varepsilon(\infty)\} + f(\omega)$$
$$= \det\{\varepsilon(\infty)\}[1 + f^\dagger(\omega)], \quad (12)$$

where $f^\dagger$ is obtained from f by normalization with $\det\{\varepsilon(\infty)\}$. The sum $1 + f^\dagger$ contains up to $6(1+N)^3$ terms. Each term has the following structure:

$$\hat{e}_{i,l}\hat{e}_{j,l}\varrho_{(l)}\hat{e}_{i,m}\hat{e}_{j,m}\varrho_{(m)}\hat{e}_{i,n}\hat{e}_{j,n}\varrho_{(n)}, \quad (13)$$

where the mode indices are $\{l,m,n\} \in \{\text{"}\infty\text{"}, 1, ..., N\}$, and the coordinate indices are $\{i,j\} \in \{x,y,z\}$ [45]. In the calculation of the determinant of ε all terms occur in cyclic permutations of the indices and by alternating plus and minus signatures of all product terms. It is crucial to recognize that in this summation all terms with at least two equal mode indices in l, m, n cancel out. As a result, none of the terms in Eq. (9) occur in the sum $1 + f^\dagger$ with a multiplicity higher than 1. This is consequential when the sum $1 + f^\dagger$ is then factorized into a fraction decomposition with common denominator. The denominator then contains the product over all poles at $(\omega_{\mathrm{TO},(l)}^2 - \omega^2)$ with $l = 1, ..., N$. This result is obtained straightforward by carrying out all multiplications and by summing all terms in

$1 + f^\dagger$ for arbitrary but fixed N. The numerator then presents itself with a polynomial in ω^2 with order equal to N. Hence, the numerator can be factorized according to the Gauß-d'Alembert theorem of algebra by which a polynomial p of degree n possesses n roots in the complex plane [46]. Hence, for the sum $1 + f^\dagger$ one expects N roots in ω^2, which are identical then with the squares of the frequencies $\omega_{\mathrm{LO},(l)}$ in Eq. (10). The determinant of ε can be expressed as follows:

$$\det\{\varepsilon(\omega)\} = \det\{\varepsilon(\infty)\} \prod_{l=1}^{N} \left(\frac{\omega_{\mathrm{LO},l}^2 - \omega^2}{\omega_{\mathrm{TO},l}^2 - \omega^2} \right), \quad (14)$$

and the statements in Eq. (10) can be easily verified. The factorized form in Eq. (14) can be seen as a generalized, coordinate-invariant dielectric function, characteristic for any given material regardless of its crystal system. The particular usefulness of this function originates from its poles and zeros, which reveal all TO and LO frequencies, respectively, of a material under investigation within the spectral range over which the individual components of $\varepsilon(\omega)$ may have been determined, either from computational theory or from experiment. Function $\det\{\varepsilon(\omega)\}$ further factorizes into components for higher symmetries, and which is not further discussed here. Pavinich and Belousov suggested use of the subdeterminant of the dielectric tensor within the **a**-**c** plane for long wavelength phonon mode analysis of monoclinic LiAlSi$_2$O$_6$ [24]. A derivation of the Pavinich and Belousov equation for monoclinic crystal systems is shown by Schubert *et al.* [31] and applied to β-Ga$_2$O$_3$. Setting $\omega = 0$ in Eq. (14), a generalization of the LST relation is then obtained

$$\frac{\det\{\varepsilon(0)\}}{\det\{\varepsilon(\infty)\}} = \prod_{l=1}^{N} \left(\frac{\omega_{\mathrm{LO},l}}{\omega_{\mathrm{TO},l}} \right)^2, \quad (15)$$

where the product expands over all N vibration modes contained within Eq. (5). Note that the displacement vector for every TO and LO mode follows from Eq. (11), and all of which may be different. Equations (14) and (15) are the central results of this Letter. The relations are valid for materials with all crystal systems, and specifically for triclinic. For monoclinic, when without loss of generality the (x, y) plane may be considered as the monoclinic plane, the LST relation is [31]

$$\frac{\varepsilon_{\mathrm{dc},zz}}{\varepsilon_{\infty,zz}} \frac{\varepsilon_{\mathrm{dc},xx}\varepsilon_{\mathrm{dc},yy} - \varepsilon_{\mathrm{dc},xy}^2}{\varepsilon_{\infty,xx}\varepsilon_{\infty,yy} - \varepsilon_{\infty,xy}^2} = \prod_{l=1,k=1}^{N,K} \left(\frac{\omega_{\mathrm{LO},l}\,\omega_{\mathrm{LO},k}}{\omega_{\mathrm{TO},l}\,\omega_{\mathrm{TO},k}} \right)^2, \quad (16)$$

where the products expand over all N modes l and K modes k, respectively, with displacement parallel and perpendicular to the monoclinic plane. Dividing Eq. (16) by the CC-LST relation for $\alpha = z$, the monoclinic LST relation reduces to the form shown in Ref. [[31]], and where it was verified using experimentally determined parameters. For orthorhombic, the generalized LST relation is

$$\frac{\varepsilon_{\mathrm{dc},xx}\,\varepsilon_{\mathrm{dc},yy}\,\varepsilon_{\mathrm{dc},zz}}{\varepsilon_{\infty,xx}\,\varepsilon_{\infty,yy}\,\varepsilon_{\infty,zz}} = \prod_{m=1,l=1,k=1}^{M,N,K} \left(\frac{\omega_{\mathrm{LO},m}\,\omega_{\mathrm{LO},l}\,\omega_{\mathrm{LO},k}}{\omega_{\mathrm{TO},m}\,\omega_{\mathrm{TO},l}\,\omega_{\mathrm{TO},k}} \right)^2, \quad (17)$$

where the products expand over all M modes m, N modes l, and K modes k, respectively, with displacement parallel to axis x, y, and z, respectively. Cyclic division of Eq. (17) by the CC-LST relation, e.g., for $\alpha = x$ and y, recovers Eq. (2), e.g., for $\alpha = z$. Hexagonal, tetragonal and trigonal follow from Eq. (17), where for example z maybe chosen parallel to the c axis, and $M + N$ modes are polarized perpendicular to z, and K modes parallel to z. For cubic, all modes N with displacement parallel to x, y, and z have identical frequencies

$$\left(\frac{\varepsilon_{\mathrm{dc}}}{\varepsilon_\infty} \right)^3 = \prod_{l=1}^{N} \left(\frac{\omega_{\mathrm{LO},l}}{\omega_{\mathrm{TO},l}} \right)^6, \quad (18)$$

and which is the isotropic LST relation in three dimensions. The latter is identical with Eq. (1), after taking the third root, for a material with cubic crystal system and single-mode behavior, e.g., GaAs, where $N = 3$, $A_1 = A_2 = A_3 = A$, $\hat{\mathbf{e}}_1 \| [1, 0, 0]$, $\hat{\mathbf{e}}_2 \| [0, 1, 0]$, $\hat{\mathbf{e}}_3 \| [0, 0, 1]$, $\omega_{\mathrm{TO},1} = \omega_{\mathrm{TO},2} = \omega_{\mathrm{TO},3} = \omega_{\mathrm{TO}}$, $\omega_{\mathrm{LO},1} = \omega_{\mathrm{LO},2} = \omega_{\mathrm{LO},3} = \omega_{\mathrm{LO}}$, and $\omega_{\mathrm{LO}}^2 = \omega_{\mathrm{TO}}^2 + A/\varepsilon_\infty$. Finally, a generalized, coordinate-invariant oscillator strength which combines the polarizability of all long wavelength active vibration modes in a given sample can be derived from Eq. (15) [7,10,35]:

$$F = \sqrt[3]{ \left(\frac{\det\{\varepsilon(0)\}}{\det\{\varepsilon(\infty)\}} - 1 \right) \prod_{l=1}^{N} \omega_{\mathrm{TO},(l)}^2 }, \quad (19)$$

where the product runs over all N polar lattice modes. The appearance of the third root in Eq. (19) reflects the fact that the derivation comprises all modes in all three dimensions. The value of Eq. (19) consists in the possibility to express a generalized, coordinate-invariant oscillator strength in units of the vacuum permittivity ε_0, which can be calculated without explicit knowledge of any LO frequency.

In a recent experiment, the dielectric function tensor components of single crystal monoclinic β-Ga$_2$O$_3$ were measured by generalized ellipsometry in the long wavelength spectral range [31]. All long wavelength active phonon modes predicted by theory were detected as well as their eigenvectors within the monoclinic plane. The tensors of the static and high frequency dielectric constants were determined from experiment and the generalized form of the LST relation was found fulfilled accurately, lending experimental support to the findings reported here. No other experimental data appear to be available for materials with monoclinic or triclinic crystal systems, and future experiments may provide further tests of the LST relations provided here.

A coordinate-invariant generalization of the Lyddane-Sachs-Teller relation is derived for polar vibrations in

materials with monoclinic and triclinic crystal systems. The generalization is derived from an eigendisplacement vector summation approach, which is equivalent to the microscopic Born-Huang description of polar lattice vibrations. The generalized relation is found valid for monoclinic β-Ga$_2$O$_3$, where accurate experimental data became available recently from a comprehensive generalized ellipsometry investigation. Data for materials with triclinic crystal systems can be measured by generalized ellipsometry as well, and are anticipated to become available soon and results can be compared with the generalized relation discussed here.

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