Magnitudes of Nonlinear Susceptibility Coefficients for First Order Transitions in Bulk Ferroelectrics

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Previous calculations[1,2,3] on second- and third-order nonlinear optical effects in bulk ferroelectrics have only been for second-order phase transitions. It would be interesting to extend these calculations to first-order phase transitions since in the ferroelectric (FE) phase most FE materials undergo this type of transition. Here expressions and graphs for two non vanishing tensor elements are given and illustrated for the third-order effects of third harmonic generation and intensity dependent refractive index; in each case first-order transitions are considered and parameter values are estimated from experimental data[4]

Key words: far infrared, ferroelectric materials, nonlinear optics

1. INTRODUCTION

Landau-Devonshire theory is commonly used to give a thermodynamic description of ferroelectrics in a static electric field. With the use of Landau-Khalatnikov (LK) dynamical equations, this theory has been extended by Ishibashi and Orihara[5] to show how expressions describing the dynamic dielectric response can be calculated. This extension has been applied to the calculation of the coefficients through the resonant region in the far infrared (FIR).

2. OUTLINE OF THE GENERAL THEORY

The starting point is the Landau-Devonshire expression for the free energy F, written as an expansion in terms of the polarization P:

$$F = \frac{1}{2}\frac{A}{\varepsilon_0}P^2 + \frac{1}{4}\frac{B}{\varepsilon_0^2}P^4 + \frac{1}{6}\frac{C}{\varepsilon_0^3}P^6 - \mathbf{E}\cdot\mathbf{P} \qquad (1)$$

in which

$$P^2 = P_x^2 + P_y^2 + P_z^2,$$

$$A = A_0(T - T_0),$$

A_0 is a positive constant and $\mathbf{E}\cdot\mathbf{P}$ accounts for coupling of the FIR radiation to the $\mathbf{E}$ field. For a second order transition B is positive, the P^6 term can be omitted by setting $C = 0$, and $T_0 = T_c$, the Curie temperature, which is the transition temperature between the ferroelectric and paraelectric phases in the second-order case; for a first order transition B is negative and C is positive, and T_0 is not given by the Curie temperature, but instead is[6]

$$T_0 = T_c - \frac{3B^2}{16A_0 C} \qquad (2)$$

which is below T_c and called the Curie-Weiss temperature. Note that for second-order transitions there is either a stable ferroelectric state or a stable paraelectric state and T_c marks the transition between the two; whereas a first-order transition is more complicated: below T_0 and T_c either a stable ferroelectric phase (stable meaning that the phase corresponds to an absolute minimum in the free energy) or a meta-stable paraelectric phase (a meta-stable phase corresponds to a local minimum in the free energy which is above the absolute minimum) can exist; between T_c and a temperature[6]

$$T_1 = T_0 + B^2 /(4A_0 C) \qquad (3)$$

a meta-stable ferroelectric phase or a stable paraelectric phase can exist; above T_1, in the absence of an applied electric field, only a stable paraelectric phase exists. Above T_1 an applied electric field can induce a ferroelectric phase up to a certain temperature; this is discussed in Ref.[6]. What is common between the first- and second-order transitions is that a stable ferroelectric phase can only exist below T_c and a stable paraelectric phase can only exist above this temperature.

The frequency dependence is deduced from the LK equations of motion

$$m\ddot{P}_i + \gamma\dot{P}_i = -\frac{\partial F}{\partial P} \qquad (4)$$

where m and γ are inertial and damping parameters respectively. Eq.(4) is nonlinear in $\mathbf{P}$ but linear in $\mathbf{E}$. To obtain the susceptibility tensors this equation is inverted to give

$$P_i = \chi_{ij}^{(1)}E_j + \chi_{ijk}^{(2)}E_jE_k + \chi_{ijkl}^{(3)}E_jE_kE_l \qquad (5)$$

and the summation convention applies. Expressions for these tensors and a detailed discussion of their derivation have been given for the case of an isotropic paraelectric phase by Osman et al.[7]

3. THIRD HARMONICS AND REFRACTIVE INDEX

Here, by setting $B<0$ and $C>0$, we discuss expressions applying to first-order phase transitions for two $\chi_{zzzz}^{(3)}$ processes viz. third harmonic generation (THG) and intensity dependent refractive index (IDRI). We choose a tensor element (also called a NLO, or nonlinear susceptibility coefficient) for each process denoted χ_{zzzz}^{THG} and χ_{zzzz}^{IDRI}. The expressions for which are[7]

$$\chi_{zzzz}^{THG}(\omega) = \frac{1}{2}s(3\omega)s^3(\omega)[g_z^2 s(0)+p] \qquad (6)$$

and

$$\chi_{zzzz}^{IDRI}(\omega) = \frac{1}{2}s^3(\omega)s^*(\omega)[g_x^2 s(0)+p] \qquad (7)$$

where

$$g_x = -2P_0(B+2CP_0^2/\varepsilon_0), \quad g_z = -2P_0(3B+10CP_0^2/\varepsilon_0)$$

and

$$p = -2(\varepsilon_0 B+10CP_0^2)$$

in which P_0 is the magnitude of the spontaneous polarization, occurring when F is at an absolute minimum, given by

$$A_0(T-T_0)+\frac{B}{\varepsilon_0}P_0^2 +\frac{C}{\varepsilon_0^2}P_0^4 = 0 \qquad (8)$$

satisfied by

$$P_0^2 = \frac{|B|+\sqrt{B^2 -4A_0(T-T_0)C}}{2C}\varepsilon_0 \qquad (9)$$

The other solution for P_0^2 (obtained by replacing the positive sign in Eq.(9) by a negative sign) corresponds to maxima in F and is therefore not chosen. We take axes with z along $\mathbf{P_0}$, and then P_0 is given by the positive square root of Eq.(9). However for the expressions of interest in this paper only even powers of P_0 appear: its sign is not important. The resonant response function in Eqs.(8) and (9) is

$$s(\omega) = -[\varepsilon_0(i\omega\gamma + m\omega^2 + f)]^{-1} \qquad (10)$$

where

$$f = -2P_0^2(B/\varepsilon_0^2 + 2CP_0^2/\varepsilon_0^3)$$

The soft mode frequency is defined by $m\omega_T^2 = f$; it decreases (softens) as $T \to T_0$.

4. NUMERICAL VALUES

Numerical estimates for the parameters m and γ pertaining to $PbTiO_3$ have been made from experimental data[8,9], as explained in Ref.[4]. They are

$$m = 5.15\times10^{-18} \text{ JmA}^{-2} \text{ and } \gamma = 2.43\times10^{-5} \text{ WmA}^{-2}$$

Also the numerical values used for the constants in Eq.(1) have been taken from published data[9] for $PbTiO_3$:

$$A_0 = 2.47\times10^{-6} \text{ K}^{-1}, \quad B = -1.27\times10^{-13} \text{ J}^{-1}\text{m}^3$$

and

$$T_c = 765 \text{ K}$$

5. DISCUSSION

Graphs showing the frequency and temperature dependence of χ_{zzzz}^{THG} and χ_{zzzz}^{IDRI} are shown in Figs.1 and 2. The main features are that the resonances are easily seen and the magnitudes increase as $T \to T_c$. The decrease in the resonance frequencies as $T \to T_c$ is also apparent. Note that, by extension of the usual interpretation of the imaginary part of the linear response function $s(\omega)$, the extrema occurring in the imaginary parts of the NLO coefficients correspond to the resonant frequencies of the coefficients; this is when absorption is high.
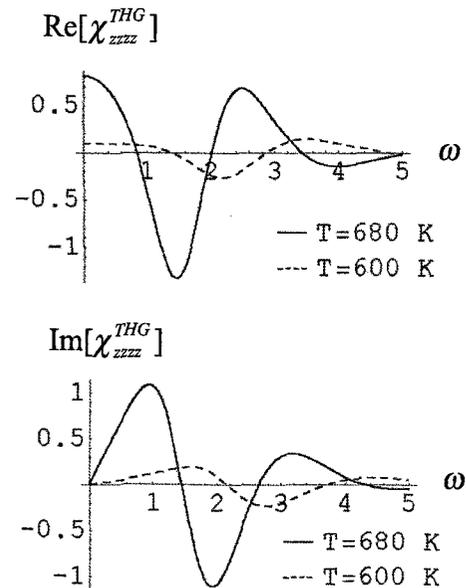

Fig.1: Real and imaginary parts of the THG coefficient plotted against angular frequency ω at the temperatures shown. Vertical scales are in units of $10^{-10}\text{m}^2\text{V}^{-2}$; units for ω are 10^{12} rad.s^{-1}.
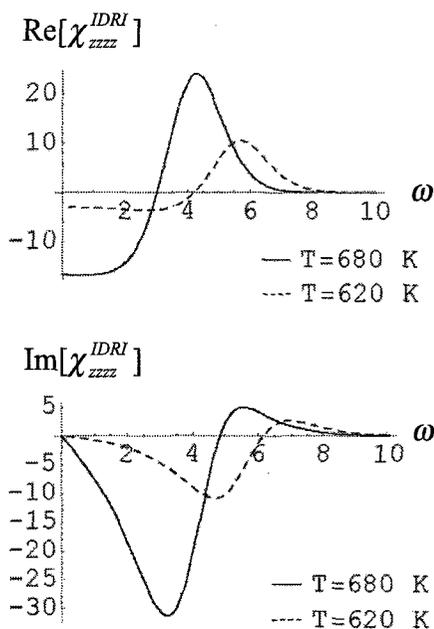
Fig.2: Real and imaginary parts of the IDRI coefficient plotted against ω at the temperatures shown. Vertical scales are in units of $10^{-12}m^2V^{-2}$; units for ω are the same as for Fig.1.

Measurement of the coefficients and possible applications (such as for terahertz-wave devices and parametric amplification), along with extensions and improvements to the theory have been discussed in Refs.[4,11–13].

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