Theoretical model to describe dispersive nonlinear properties of lead zirconate–titanate ceramics

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Frequency dependence of the first ultrasonic nonlinear parameter and the abnormally high third harmonic signals measured in lead zirconate–titanate (PZT) ceramics suggest the introduction of a revised theoretical model combining higher-order nonlinearity and generalized dispersion. The new nonlinear dispersive equation has been solved by perturbation theory. A solution is found in the form of a set of parameters whose magnitude is obtained from a fit of the experimental data. The parameters are independent of frequency and initial amplitude. The model is applied to four samples, and the results are discussed. The validity of the perturbation theory in these cases is tested. © *1996 Acoustical Society of America.*

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INTRODUCTION

Peculiarities of sound wave behavior in crystals is shifting the attention of scientists from the linear theory to more complicated models which describe phenomena like dissipation, dispersion, and/or nonlinear propagation. To describe sound propagation in solids in the linear approximation (Hooke's law approximation) one can write the longitudinal wave equation in the form

$$\rho_0 \frac{\partial^2 U}{\partial t^2} = M_2 \frac{\partial^2 U}{\partial a^2}, \tag{1}$$

where ρ_0 is the unstrained mass density, U is the longitudinal displacement, a is the distance measured along the propagation direction in the unstrained crystal, and M_2 is a linear combination of second-order elastic constants depending on the direction of propagation ($M_2 = K_2$, with K_2 as listed in Table I). This formulation is convenient because it allows one to account for a number of phenomena in a straightforward way. For **absorption**, one simply allows complex values of M_2.

To describe **nonlinearity** one can account for propagation in a pure mode direction (for cubic lattices one of the three principal directions), by writing the differential wave equation in the form[1]

$$\rho_0 \frac{\partial^2 U}{\partial t^2} = \frac{\partial^2 U}{\partial a^2}\left[M_2 + M_3 \frac{\partial U}{\partial a} + M_4 \left(\frac{\partial U}{\partial a} \right)^2 + \cdots \right], \tag{2}$$

where $M_3 = 3K_2 + K_3$ is a combination of both second- and third-order elastic constants, also depending on the direction of propagation (see Table I). Here, M_4 contains elastic constants up to the fourth-order ($M_4 = \frac{3}{2}K_2 + 3K_3 + \frac{1}{2}K_4$).

For **dispersion** one can modify Eq. (1) by inclusion of a fourth-order derivative with respect to the propagation distance

$$\rho_0 \frac{\partial^2 U}{\partial t^2} = M_2 \frac{\partial^2 U}{\partial a^2} + \Gamma_2 \frac{\partial^4 U}{\partial a^4}, \tag{3}$$

where Γ_2 is the dispersion constant.

The solution of Eq. (2) accounts for the generation of second harmonics (and higher harmonics) during the propagation of an initially sinusoidal wave of amplitude A. This solution can be obtained through use of a perturbation technique[2–4] or a more complicated Fourier analysis.[1] Such a solution has led to the introduction of the nonlinearity parameter, the negative ratio of the coefficient of the nonlinear term to that of the linear term in the nonlinear wave equation

$$\beta = -\frac{3K_2 + K_3}{K_2} = \frac{8A_2}{A^2 k^2 a}, \tag{4}$$

where A is the amplitude of the initially sinusoidal wave at the source and A_2 is the measured amplitude of the generated second harmonic at a propagation distance a; $k = 2\pi/\lambda$ is the propagation constant. If the amplitude of the initial ultrasonic wave is small enough, the amplitude of the third harmonic signal A_3 is expressed as[1]

$$A_3 = \frac{A^3 a^2 k^4}{32}\left(\frac{3K_2 + K_3}{K_2} \right)^2 \times \sqrt{1 + \frac{16}{9k^2 a^2}\left[1 - \frac{K_2(K_4 + 6K_3 + 3K_2)}{2(K_3 + 3K_2)^2} \right]^2}, \tag{5}$$

in which K_4 is a combination of fourth-order elastic constants. In Cu single crystals (and almost all other crystals) the amplitude of K_4 is of the order of $10K_3$. In experimental situations using ultrasonic frequencies, $k^2 a^2$ is generally of the order of 10^5, so that for most crystalline samples one can make the approximation

$$A_3 \cong \frac{A^3 a^2 k^4}{32}\left(\frac{3K_2 + K_3}{K_2} \right)^2. \tag{6}$$

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TABLE I. K_2 and K_3 for [100], [110], and [111] directions.

Direction	K_2	K_3
[100]	C_{11}	C_{111}
[110]	$\frac{C_{11}+C_{12}+2C_{44}}{2}$	$\frac{C_{111}+C_{112}+2C_{166}}{4}$
[111]	$\frac{C_{11}+2C_{12}+4C_{44}}{3}$	$\frac{C_{111}+6C_{112}+12C_{144}+24C_{166}+2C_{123}+16C_{456}}{9}$

Recently Na and Breazeale[5] found that the third harmonic measured in lead zirconate–titanate (PZT) samples was much too large to allow them to make the approximation given in Eq. (6). To satisfy their data they introduced a second nonlinearity parameter which was expressed in terms of measured quantities as

$$\beta_2=\frac{32}{a^2k^4}\frac{A_3}{A^3}. \tag{7}$$

For most crystalline solids this would mean that

$$\beta_2=\beta^2; \tag{8}$$

however, its definition allowed flexibility in data interpretation for PZT. Na and Breazeale stated that serious deviations from Eq. (8) in experimental data implies that K_4 no longer is negligible and/or that a nonlinear equation different from Eq. (2) must be used to describe the nonlinear wave propagation.

For single crystals, determination of the nonlinearity parameter from velocity measurements and harmonic generation yields values for the third-order elastic constants which agree with other methods.[6] The results are independent of frequency. Also, the relationship given by Eq. (8) is followed for single crystals whenever it has been tested.[3] This means that fourth order elastic constants in single crystals are indeed negligible.

When the nonlinear properties of PZT were investigated they were found to be considerably different from those of single crystals. Na and Breazeale used their measurements to report for the first time a frequency dependence of the nonlinearity parameter β at room temperature. In addition, they found that for their PZT samples the quantities β_2 do not satisfy Eq. (8) at 10 MHz. The observed third harmonic amplitudes were found to be much larger in PZT than one would calculate from Eq. (6).

In this paper we focus on the doubly anomalous behavior of PZT ceramics and propose a solution from theoretical analysis. The suggestions of Na and Breazeale about the role of large fourth-order elastic constants and/or the use of a different nonlinear equation have served as a starting point for this theoretical investigation. First, we formulate the model by combining the nonlinear equation of Thurston and Shapiro (in which we assume that K_4 is non-negligible) with a generalization of the dispersion equation. Then we use the perturbation method to find an approximate solution which we apply and discuss in connection with the physical properties of polarized and unpolarized $K1$ and $S1$ PZT samples (Table II). Finally, we examine the error made by using perturbation theory in our model.

I. THEORETICAL MODEL

A. Generalization of the differential equation

The third harmonic signals observed by Na and Breazeale[5] were too large to satisfy Eq. (8), in which the influence of K_4 is considered to be negligible. For the unpolarized $K1$ sample at 10 MHz they observed a value of $\beta_2=103.8$, whereas β^2 would be only 57.8. For the $S1$ polarized sample at the same frequency the ratio of β_2 to β^2 is even more strikingly different from unity: $\beta_2/\beta^2=127$.

Since both K_2 and K_3 are known from the measurement of the velocity and the nonlinearity parameter at low frequencies (e.g., $K_2=14.75\times10^{10}$ kg/ms^2 and $K_3=-156\times10^{10}$ kg/ms^2 for an unpolarized $K1$ sample), we can consider Eq. (5) as a function of K_4 only. Substituting this equation into Eq. (7), we obtain an expression for β_2 as a function of the fourth-order elastic constant. Knowing the experimental β_2 value, this relation can be inverted numerically for K_4 or one can estimate the fourth-order elastic constant from the intersection points of the graphs in Fig. 1. We have found that the experimental β_2 value for the $K1$ sample can only be reached for a value of K_4 which is at least three orders of magnitude larger than K_3. In an analogous way we have found that the values of K_4 for the other PZT samples must be even larger: almost five orders of magnitude for the polarized $S1$ sample.

As a consequence of these large K_4 values, the quantity M_4 $(=3/2K_2+3K_3+1/2K_4)$ in Eq. (2) must be large as well. This means that this term is the most important term in the expression for the third harmonic signal amplitude. In this situation we introduce an approximation that replaces Eq. (6):

$$A_3\cong\frac{ak^3A_1^3}{24}\frac{M_4}{M_2}. \tag{9}$$

TABLE II. Physical dimensions and properties of the $K1$ and $S1$ samples of PZT ceramic.

Sample	Velocity	Density	Thickness
$K1$-unpolarized	4334.1 m/s	7850 kg/m^3	9.03×10^{-3} m
$K1$-polarized	4577.2 m/s	7850 kg/m^3	9.07×10^{-3} m
$S1$-unpolarized	4320.0 m/s	8010 kg/m^3	9.07×10^{-3} m
$S1$-polarized	4523.1 m/s	8010 kg/m^3	8.82×10^{-3} m

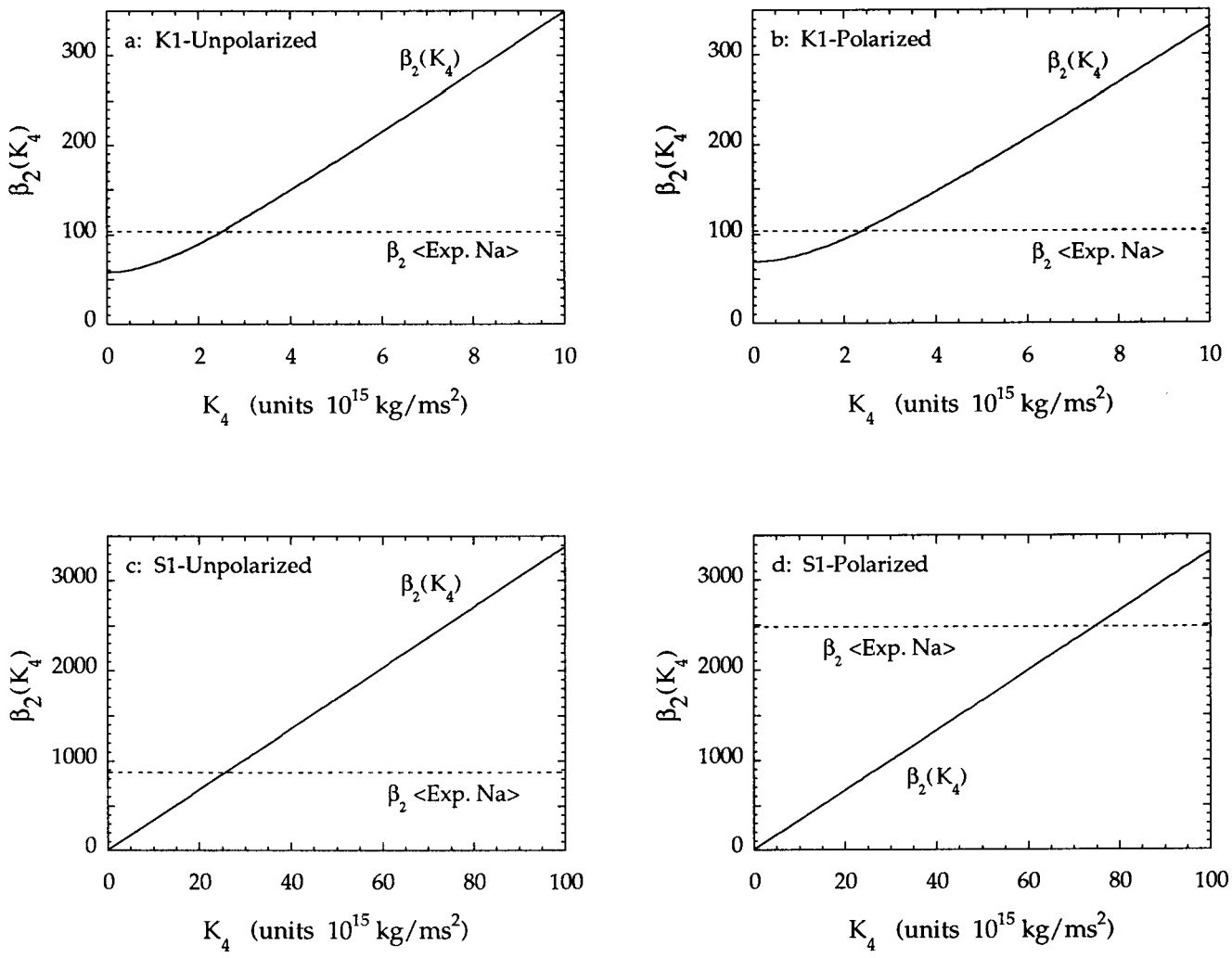

FIG. 1. The influence of K_4 on the second nonlinearity parameter β_2 [Eqs. (7) and (5)] for different samples of PZT. The intersection with the horizontal line (experimental value of β_2) gives an indication of the magnitude of the fourth-order elastic constant. (a) $K1$-unpolarized$\rightarrow K_4 \cong 2.5\times10^{15}$ kg/ms^2; (b) $K1$-polarized$\rightarrow K_4 \cong 2.3\times10^{15}$ kg/ms^2; (c) $S1$-unpolarized$\rightarrow K_4 \cong 25\times10^{15}$ kg/ms^2; (d) $S1$-polarized$\rightarrow K_4 \cong 75\times10^{15}$ kg/ms^2.

Indirectly, this expression calls for a new definition of β_2. This new definition, which is distinguished by a prime, is

$$\beta_2' = \frac{24}{ak^3}\frac{A_3}{A^3}. \tag{10}$$

This new definition makes it possible to obtain an approximate value of the fourth-order elastic constant in cases where its influence is non-negligible. The third harmonic signal measurements of Na and Breazeale have been analyzed in this way. They suggest that higher-order elastic constants should be taken into account in the nonlinear differential equation.

Consequently, to make further investigation we start with a generalized form of Eq. (2), the general nonlinear differential equation given by Thurston and Shapiro:[1]

$$\rho_0 \frac{\partial^2 U}{\partial t^2} = \frac{\partial^2 U}{\partial a^2} g\left(\frac{\partial U}{\partial a}\right), \tag{11a}$$

with

$$g\left(\frac{\partial U}{\partial a}\right) = \sum_{n=2}^{\infty} M_n \left(\frac{\partial U}{\partial a}\right)^{n-2} = M_2 + M_3 \frac{\partial U}{\partial a} + M_4 \left(\frac{\partial U}{\partial a}\right)^2 + M_5 \left(\frac{\partial U}{\partial a}\right)^3 + \cdots . \tag{11b}$$

In comparison with the linear equation, it is worthwhile to note that the multiplier of $\partial^2 U/\partial a^2$ is no longer a constant. It is a series expansion in the strain $\partial U/\partial a$.

The dispersion effects are included in a first approximation by modifying the linear wave equation with a term proportional to the fourth derivative of the displacement with respect to the propagation distance, in analogy with the generalization of the linear wave equation [Eq. (3)]. We have found that this still does not give an adequate nonlinear equation. Therefore, we have replaced Γ_2 in Eq. (3) by a series expansion in the strain $\partial U/\partial a$. The combination of

both nonlinear phenomena and dispersion effects lead to the following equation:

$$\rho_0 \frac{\partial^2 U}{\partial t^2} = g\left(\frac{\partial U}{\partial a}\right) \frac{\partial^2 U}{\partial a^2} + h\left(\frac{\partial U}{\partial a}\right) \frac{\partial^4 U}{\partial a^4}, \tag{12}$$

where

$$g\left(\frac{\partial U}{\partial a}\right) = M_2 + M_3 \frac{\partial U}{\partial a} + M_4\left(\frac{\partial U}{\partial a}\right)^2 + M_5\left(\frac{\partial U}{\partial a}\right)^3 + \cdots \tag{12a}$$

and

$$h\left(\frac{\partial U}{\partial a}\right) = \Gamma_2 + \Gamma_3\left(\frac{\partial U}{\partial a}\right) + \Gamma_4\left(\frac{\partial U}{\partial a}\right)^2 + \Gamma_5\left(\frac{\partial U}{\partial a}\right)^3 + \cdots . \tag{12b}$$

The purpose of our investigation is to determine the number and magnitudes of terms required in Eq. (12) for an adequate description of the behavior of PZT.

B. Approximate solution

Even though β, and especially β_2, can be large for PZT ceramics, the second and third harmonic amplitudes measured during the experiments are still small compared with the fundamental amplitude. This means that we are looking for small perturbations of an initially well-known waveform, so that we can use perturbation theory to find a solution to Eq. (12), and later check the validity of this approach.

We rewrite Eq. (12) in the form

$$\rho_0 \frac{\partial^2 U}{\partial t^2} - M_2 \frac{\partial^2 U}{\partial a^2} - \Gamma_2 \frac{\partial^4 U}{\partial a^4} = \left[g\left(\frac{\partial U}{\partial a}\right) - M_2\right] \frac{\partial^2 U}{\partial a^2} + \left[h\left(\frac{\partial U}{\partial a}\right) - \Gamma_2\right] \frac{\partial^4 U}{\partial a^4} \tag{13}$$

and propose a solution of this dispersive nonlinear equation in the form

$$U = U^0 + U^c \tag{14}$$

with U^0 the solution of the simplest dispersive linear equation:

$$\rho_0 \frac{\partial^2 U^0}{\partial t^2} - M_2 \frac{\partial^2 U^0}{\partial a^2} - \Gamma_2 \frac{\partial^4 U^0}{\partial a^4} = 0, \tag{15}$$

namely,

$$U^0 = A \sin(ka - \omega t) \quad \text{with} \quad \omega = \sqrt{\frac{M_2}{\rho_0}}\, k\left(1 - \frac{\Gamma_2}{M_2} k^2\right)^{1/2}, \tag{16}$$

in which A denotes the amplitude of the sinusoidal wave at input (zero propagation distance). Substituting Eq. (14) into Eq. (13) and taking into consideration only the largest contributions on the right-hand side (the zero approximation in terms of the small factors containing $U^c, \partial U^c/\partial a, \partial^2 U^c/\partial a^2, \cdots$), we find that the correction term U^c must satisfy

$$\rho^0 \frac{\partial^2 U^c}{\partial t^2} - M_2 \frac{\partial^2 U^c}{\partial a^2} - \Gamma_2 \frac{\partial^4 U^c}{\partial a^4} = \left[M_3 \frac{\partial U^0}{\partial a} + M_4\left(\frac{\partial U^0}{\partial a}\right)^2 + M_5\left(\frac{\partial U^0}{\partial a}\right)^3 + \cdots\right] \frac{\partial^2 U^0}{\partial a^2} + \left[\Gamma_3 \frac{\partial U^0}{\partial a} + \Gamma_4\left(\frac{\partial U^0}{\partial a}\right)^2 + \Gamma_5\left(\frac{\partial U^0}{\partial a}\right)^3 + \cdots\right] \frac{\partial^4 U^0}{\partial a^4}. \tag{17}$$

Substituting the zero approximation solution U^0 into Eq. (17), this can be written in the form

$$\rho_0 \frac{\partial^2 U^c}{\partial t^2} - M_2 \frac{\partial^2 U^c}{\partial a^2} - \Gamma_2 \frac{\partial^4 U^c}{\partial a^4} = \sum_{n=1}^{\infty} X_n \sin[n(ka - \omega t)], \tag{18}$$

where the X_n are

$$X_1 = -\sum_{l=1}^{\infty} \frac{(M_{2l+2} - k^2\Gamma_{2l+2})k^{2l+2}A^{2l+1}}{2^{2l}} \times \frac{1}{2l+1}\binom{2l+1}{l}, \tag{18a}$$

$$X_{2j} = -\sum_{l=j}^{\infty} \frac{(M_{2l+1} - k^2\Gamma_{2l+1})k^{2l+1}A^{2l}}{2^{2l-1}} \frac{j}{l}\binom{2l}{l-j}, \tag{18b}$$

$$X_{2j+1} = -\sum_{l=j}^{\infty} \frac{(M_{2l+2} - k^2\Gamma_{2l+2})k^{2l+2}A^{2l+1}}{2^{2l}} \times \frac{2j+1}{2l+1}\binom{2l+1}{l-j}. \tag{18c}$$

In Eqs. (18a), (18b), and (18c), the final factors in each term are binomial coefficients defined as follows:

$$\binom{n}{m} = \frac{n!}{m!(n-m)!}. \tag{19}$$

For example, if one considers only the coefficients M_n and Γ_n with $n \leqslant 6$, Eq. (18) becomes

$$\rho_0 \frac{\partial^2 U^c}{\partial t^2} - M_2 \frac{\partial^2 U^c}{\partial a^2} - \Gamma_2 \frac{\partial^4 U^c}{\partial a^4} = -\left[\frac{(M_4 - k^2\Gamma_4)k^4A^3}{4} + \frac{(M_6 - k^2\Gamma_6)k^6A^5}{8}\right]\sin[ka - \omega t] - \left[\frac{(M_3 - k^2\Gamma_3)k^3A^2}{2} + \frac{(M_5 - k^2\Gamma_5)k^5A^4}{4}\right]\sin[2(ka - \omega t)] - \left[\frac{(M_4 - k^2\Gamma_4)k^4A^3}{4} + \frac{3(M_6 - k^2\Gamma_6)k^6A^5}{16}\right]\sin[3(ka - \omega t)]$$

$$-\left[\frac{(M_5-k^2\Gamma_5)k^5A^4}{8}\right]\sin[4(ka-\omega t)]-\left[\frac{(M_6-k^2\Gamma_6)k^6A^5}{16}\right]\sin[5(ka-\omega t)]. \tag{20}$$

From Eq. (18b) one notices that the coefficients X_n for n even are influenced only by the nonlinear coefficients M_l and dispersive constants Γ_l having odd indices. Similarly Eqs. (18a) and (18c) show that X_n for n odd is affected by nonlinear and dispersive coefficients having even indices.

In acoustics dispersion usually is negligible. Thus Γ_2 is very small. If Γ_2 were identically zero, the exact solution of Eq. (18) would be

$$U^c=\sum_{n=1}^{\infty}\frac{aX_n}{2nkM_2}\cos[n(ka-\omega t)]. \tag{21}$$

Let us now assume that Γ_2 is very small, but not zero. In this case, we introduce a more general series expansion

$$U^c=\sum_{n=1}^{\infty}aB_n\sin[n(ka-\omega t)]+aC_n\cos[n(ka-\omega t)] \tag{22}$$

as a solution of Eq. (18). The coefficients B_n and C_n can be dependent on the propagation distance a, but we will assume that their derivatives with respect to distance is negligible. By using this substitution and approximation, we find closed expressions for the coefficients B_n and C_n:

$$B_n=\frac{-n^2(n^2-1)a\Gamma_2k^4X_n}{n^4(n^2-1)^2a^2\Gamma_2^2k^8+4k^2n^2(M_2-2n^2\Gamma_2k^2)^2}, \tag{23a}$$

$$C_n=\frac{2nk(M_2-2n^2\Gamma_2k^2)X_n}{n^4(n^2-1)^2a^2\Gamma_2^2k^8+4k^2n^2(M_2-2n^2\Gamma_2k^2)^2}. \tag{23b}$$

Using these expressions, one can write the amplitude A_n of the nth harmonic signal:

$$A_n=\frac{a|X_n|}{[n^4(n^2-1)^2a^2\Gamma_2^2k^8+4k^2n^2(M_2-2n^2\Gamma_2k^2)^2]^{1/2}}. \tag{24}$$

The amplitudes of the second and third harmonics generated by propagation of an initially sinusoidal wave over a distance a in a dispersive nonlinear medium can be evaluated from Eq. (24) by using $n=2$ or $n=3$ as follows:

TABLE III. Range of amplitudes (10^{-10} m) used in the experiments of Na.

Frequency	$K1$-unpolarized	$K1$-polarized	$S1$-unpolarized	$S1$-polarized
5 MHz	16.1–26.2 (21.15)	18–27.8 (22.9)	15.8–29.4 (22.6)	17.1–28.6 (22.85)
10 MHz	13.7–22.6 (18.15)	16.1–23.3 (19.7)	14.2–28.2 (21.2)	16.6–27.5 (22.05)
15 MHz	4.5–11.7 (8.1)	5.4–11.4 (8.4)	5.1–11.6 (8.35)	6.0–11.2 (8.6)
30 MHz	1.9–3.0 (2.45)	2.2–3.4 (2.8)	2.0–4.4 (3.2)	2.1–4.7 (3.4)

$$A_2=\frac{a|M_3-k^2\Gamma_3|k^2A^2}{8}\frac{\left|1+k^2A^2\dfrac{(M_5-k^2\Gamma_5)}{2(M_3-k^2\Gamma_3)}+\cdots\right|}{[(M_2-8\Gamma_2k^2)^2+9a^2\Gamma_2^2k^6]^{1/2}}, \tag{25}$$

$$A_3=\frac{a|M_4-k^2\Gamma_4|k^3A^3}{24}\frac{\left|1+k^2A^2\dfrac{3(M_6-k^2\Gamma_6)}{4(M_4-k^2\Gamma_4)}+\cdots\right|}{[(M_2-18\Gamma_2k^2)^2+144a^2\Gamma_2^2k^6]^{1/2}}. \tag{26}$$

Note that in the nondispersive case (when all Γ_n's are negligible) and when only M_2, M_3, and M_4 are to be taken into account, Eq. (25) reduces to

$$A_2=\frac{a|M_3|k^2A^2}{8M_2}, \tag{27}$$

which agrees with Eq. (4) used to define the nonlinearity parameter. Under the same conditions the third harmonic simplifies to

$$A_3=\frac{a|M_4|k^3A^3}{24M_2}, \tag{28}$$

which is the limit of Eq. (5) for the third harmonic amplitude given by Thurston and Shapiro for large values of the fourth order elastic constant K_4.

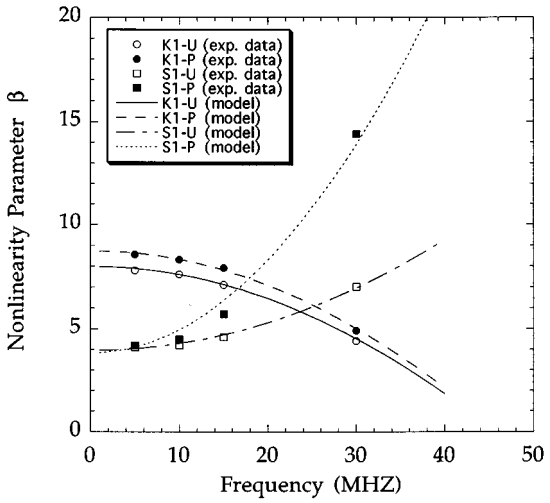

FIG. 2. Frequency dependence of the nonlinearity parameter β for different PZT samples. Data points represent experimental measurements. The lines are the theoretical prediction using the perturbation solution of the dispersive nonlinear differential equation with parameter values given in Table IV.

TABLE IV. List of elastic constants (kg/ms^2) and dispersion constants (kg m/s^2) for $K1$ and $S1$ samples.

Sample	K_2	K_3	K_4	Γ_2	Γ_3	Γ_4
$K1$-unpolarized	14.75×10^{10}	-162.0×10^{10}	3.015×10^{15}	2.0×10^{-3}	-2.70×10^{2}	?
$K1$-polarized	16.45×10^{10}	-193.0×10^{10}	3.190×10^{15}	2.0×10^{-3}	-3.60×10^{2}	?
$S1$-unpolarized	14.95×10^{10}	-104.0×10^{10}	25.830×10^{15}	2.0×10^{-3}	2.35×10^{2}	?
$S1$-polarized	16.39×10^{10}	-112.0×10^{10}	74.700×10^{15}	2.0×10^{-3}	9.50×10^{2}	?

The higher harmonics can be calculated in an analogous way. The presence of the factor ak^nA^n in the leading term of the expression for the nth harmonic means that the amplitudes of the harmonics decrease rapidly as n increases.

II. DISCUSSION

A. Application to PZT ceramic samples

Now that we have obtained an analytical solution for the dispersive nonlinear differential equation in terms of nonlinear constants M_n and dispersion constants Γ_n, we can adjust the numbers and find a set of theoretical parameters to match the experimental observations. The samples under consideration are $K1$ and $S1$ samples in both polarized and unpolarized form. The $K1$ samples had 45% PbTiO3 with a grain size approximately 5 μm; the $S1$ samples had 15% PbTiO3 with a grain size approximately 2.5 μm. The velocity, density and thickness are summarized in Table II. The experiments of Na and Breazeale have been performed at four different frequencies of an initially sinusoidal ultrasonic wave: 5, 10, 15, and 30 MHz. For each sample, the range of initial amplitudes used at these frequencies is listed in Table III. The mean value is written between brackets. We note that the applied amplitude diminishes drastically when higher frequencies are used. Experimental measurements of the second harmonic signal at the four frequencies used and application of Eq. (4) lead to the discrete values of the nonlinearity parameter β listed in Fig. 2. The nonlinearity parameter shows a frequency-dependent behavior. Using the solution derived in the previous paragraphs one can find a set of parameters per sample that fit each experimental data point. The values of these parameters are given in Table IV. For each sample these nonlinearity coefficients M_n and dispersion constants Γ_n are independent of applied frequency and amplitude. The nonlinearity parameter β becomes frequency dependent because of a nonzero magnitude of Γ_3. However, it should be noted that β remains independent of the input amplitude at any given frequency. The value of K_4 given in Table IV was necessary for the theoretical model to produce third harmonics as large as actually observed in the experiments. The definition of β_2' [Eq. (10)] instead of β_2 [Eq. (7)] guarantees that the theoretical value of the new second nonlinearity parameter is independent of frequency if Γ_4 is negligible. We also observe that the magnitudes of the first and this second nonlinearity parameter do not change significantly for values of K_5 between zero and 10^{18}.

The parameter sets in Table IV were used to make a theoretical calculation of the nonlinearity parameters for all four of the samples in the frequency range between 1 and 40 MHz. The results, using interpolation and extrapolation on the initial mean amplitudes, are shown in Fig. 2 as full lines. These theoretical curves fit the experimental data points with amazingly good agreement. It is necessary to allow both positive and negative values of Γ_3 in the model in order to match the experimental measurements for $K1$ and $S1$ samples, respectively. The link to a physical phenomenon to explain this behavior is not yet clear.

With this model one can calculate all constants (both nonlinear and dispersive) from experimental measurements: K_2 from velocity measurements; K_3 and K_4 from the first and second nonlinearity parameters β and β_2' at low frequencies; Γ_2 from the velocity dispersion; Γ_3 from the dispersion (frequency dependence) of the first nonlinearity parameter; Γ_4 from the dispersion of the second nonlinearity parameter, etc. Since at present there have been no measurements of the third harmonic signal at different frequencies, we have put a question mark at the position of the Γ_4 value.

B. Estimation of perturbation theory error

Use of perturbation theory always suggests that a number of terms are neglected and that only an approximate so-

TABLE V. Calculated relative amplitudes of second to seventh harmonics resulting from propagation over 9.03 mm in the $K1$-unpolarized sample. Amplitude of fundamental at input is given as well as its relative change at the receiver position; K_2, K_3, K_4, Γ_2, and Γ_3 as in Table IV; we assume $K_5=10^{18}$; $K_6, K_7, ...=\Gamma_4, \Gamma_5, ...=0$.

Frequency (MHz)	Amplitude A (10^{-10} m)	$\frac{A_1}{A}-1.0$	$\frac{A_2}{A}$	$\frac{A_3}{A}$	$\frac{A_4}{A}$	$\frac{A_5}{A}$	$\frac{A_6}{A}$	$\frac{A_7}{A}$
1.0	22.2000	0.149E-13	0.420E-04	0.575E-07	0.793E-11	0.375E-16	0.700E-22	0.642E-28
5.0	21.1500	0.192E-09	0.989E-03	0.653E-05	0.429E-08	0.966E-13	0.858E-18	0.375E-23
10.0	18.1500	0.666E-08	0.327E-02	0.385E-04	0.433E-07	0.168E-11	0.255E-16	0.191E-21
15.0	8.1000	0.301E-08	0.308E-02	0.259E-04	0.195E-07	0.503E-12	0.511E-17	0.253E-22
20.0	6.2167	0.586E-08	0.380E-02	0.361E-04	0.278E-07	0.727E-12	0.736E-17	0.355E-22
25.0	4.3333	0.528E-08	0.358E-02	0.342E-04	0.227E-07	0.502E-12	0.413E-17	0.155E-22
30.0	2.4500	0.161E-08	0.236E-02	0.188E-04	0.827E-08	0.116E-12	0.574E-18	0.129E-23
35.0	1.9750	0.172E-08	0.188E-02	0.192E-04	0.756E-08	0.891E-13	0.367E-18	0.715E-24
40.0	1.5000	0.127E-08	0.104E-02	0.162E-04	0.510E-08	0.459E-13	0.150E-18	0.242E-24

TABLE VI. Same as Table VII, for a propagation distance of 8.82 mm in the $S1$-polarized sample.

Frequency (MHz)	Amplitude A (10^{-10} m)	$\frac{A_1}{A}-1.0$	$\frac{A_2}{A}$	$\frac{A_3}{A}$	$\frac{A_4}{A}$	$\frac{A_5}{A}$	$\frac{A_6}{A}$	$\frac{A_7}{A}$
1.0	23.4000	0.679*E*-11	0.191*E*-04	0.123*E*-05	0.117*E*-10	0.399*E*-16	0.664*E*-22	0.584*E*-28
5.0	22.8500	0.965*E*-07	0.500*E*-03	0.146*E*-03	0.680*E*-08	0.113*E*-12	0.921*E*-18	0.396*E*-23
10.0	22.0500	0.536*E*-05	0.232*E*-02	0.109*E*-02	0.977*E*-07	0.314*E*-11	0.493*E*-16	0.409*E*-21
15.0	8.6000	0.141*E*-05	0.261*E*-02	0.560*E*-03	0.293*E*-07	0.552*E*-12	0.505*E*-17	0.243*E*-22
20.0	6.8667	0.322*E*-05	0.485*E*-02	0.846*E*-03	0.471*E*-07	0.938*E*-12	0.899*E*-17	0.446*E*-22
25.0	5.1333	0.384*E*-05	0.739*E*-02	0.923*E*-03	0.477*E*-07	0.872*E*-12	0.745*E*-17	0.317*E*-22
30.0	3.4000	0.221*E*-05	0.905*E*-02	0.698*E*-03	0.283*E*-07	0.392*E*-12	0.243*E*-17	0.731*E*-23
35.0	2.8500	0.275*E*-05	0.130*E*-01	0.773*E*-03	0.297*E*-07	0.371*E*-12	0.200*E*-17	0.533*E*-23
40.0	2.3000	0.260*E*-05	0.170*E*-01	0.742*E*-03	0.249*E*-07	0.256*E*-12	0.114*E*-17	0.265*E*-23

lution is found for the general problem. Therefore it is necessary to check whether the solution is being used within the range of applicability of the perturbation theory, and the magnitude of the approximation involved.

First, we can check the magnitude of the calculated amplitudes compared with the initial amplitude of the pure sinusoidal wave at input. Tables V and VI, calculated with the set of parameters listed in Table IV, and with K_5 equal to 10^{18}, shows that the fundamental amplitude A_1 does not change significantly from the applied input amplitude A at any given frequency. The generated amplitudes of the second and third harmonic signals appear to be measurable, and they are indeed considerably smaller than the fundamental amplitude, e.g., of the order of 2×10^{-3} for $K1$-unpolarized samples and 10^{-2} for $S1$-polarized samples at 30 MHz for the second harmonic. The higher orders have amplitudes which diminish uniformly for all frequencies.

A second check consists of investigating the error involved when we took into account only the zero approximation of the small factors containing U^c, $\partial U^c/\partial a$, $\partial^2 U^c/\partial a^2$, etc. as contributions to the right side of Eq. (13) after substitution of Eq. (14); i.e., instead of taking into account the complete right side

$$\left[g\left(\frac{\partial U}{\partial a}\right)-M_2\right]\frac{\partial^2 U}{\partial a^2}+\left[h\left(\frac{\partial U}{\partial a}\right)-\Gamma_2\right]\frac{\partial^4 U}{\partial a^4} \tag{29}$$

we considered only the first terms:

$$\sum_{j=1}^{\infty} M_{j+2}\left(\frac{\partial U^0}{\partial a}\right)^j\frac{\partial^2 U^0}{\partial a^2}+\Gamma_{j+2}\left(\frac{\partial U^0}{\partial a}\right)^j\frac{\partial^4 U^0}{\partial a^4},$$

$$\left(=\sum_{n=1}^{\infty} X_n\,\sin[n(ka-\omega t)]\right) \tag{30}$$

and assumed that the difference between the two is negligible.

The use of symbolic software enables us to estimate this difference. Table VII gives the percentage of relative error introduced by the truncation. We defined

$$\text{Estimated error }(\%)=100\cdot\frac{\text{Max}_1}{\text{Max}_2}, \tag{31}$$

where

$$\text{Max}_1=\text{Max}_{\text{period}}\left|\left[g\left(\frac{\partial U}{\partial a}\right)-M_2\right]\frac{\partial^2 U}{\partial a^2}+\left[h\left(\frac{\partial U}{\partial a}\right)-\Gamma_2\right]\frac{\partial^4 U}{\partial a^4}-\sum_{n=1}^{\infty} X_n\,\sin[n(ka-\omega t)]\right|$$

with

$$U=U^0+U^c$$

and

$$\text{Max}_2=\text{Max}_{\text{period}}\left|\sum_{n=1}^{\infty} X_n\,\sin[n(ka-\omega t)]\right|.$$

We note that the error never exceeds 5%, except for $S1$ polarized samples at 30 MHz. Looking again at Table VI, we observe that the second and third harmonic amplitudes for the $S1$-polarized samples are indeed substantial and that it might be inaccurate to apply the perturbation theory for higher frequencies. For the other samples we may conclude that the use of the perturbation theory is justified.

III. CONCLUSION

We propose a theoretical model which combines higher-order nonlinearity and generalized dispersion effects to interpret the results of experiments on PZT ceramics reported by Na and Breazeale. The new dispersive nonlinear differential equation has been solved by perturbation theory. It provides

TABLE VII. Estimated difference (%) between right-hand side of the complete dispersive nonlinear differential equation and the part considered using the perturbation method.

Frequency	Amplitude	$K1$-unpolarized	$K1$-polarized	$S1$-unpolarized	$S1$-polarized
5 MHz	25×10^{-10} m	0.96524	0.94616	0.72935	0.98461
10 MHz	20×10^{-10} m	3.03273	2.96520	2.90238	4.48704
15 MHz	10×10^{-10} m	3.16582	3.10470	3.08937	4.79720
30 MHz	3×10^{-10} m	2.40786	2.39183	4.35913	8.08418

an analytical expression for the harmonic amplitudes generated during propagation in the samples. We applied the model to $K1$ and $S1$ samples, both polarized and unpolarized, and found that the analytical solution can be fit to experimental data by means of one set of parameters in each case. The introduction of Γ_3 accounts for the measured frequency dependence of the first nonlinear parameter β. The abnormally high third harmonic signals can be explained by assuming values for fourth-order elastic constants. It is important to note that the set of parameters used in the model is independent of frequency and initial amplitude. Even though the physics behind the new differential equation and the real identity of the dispersive and nonlinear constants is not completely known at the moment, it is remarkable that this generalized dispersive-nonlinear model leads to such an extremely good fit of the data. The value of K_4 was arrived at under the assumption that the dispersion term does not contribute to the magnitude of the fourth-order elastic constant. We are investigating the validity of this assumption. Finally, we believe that the use of perturbation theory in these cases is justified since the generated amplitudes are small and because the relative error introduced by truncating the right-hand side of the differential equation generally is less than 5%.

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