Microwave Nonlinear Susceptibilities Due to Electronic and Ionic Anharmonicities in Acentric Crystals

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A *microwave* nonlinear susceptibility analogous to the optical and electro-optical nonlinear susceptibilities is investigated in a number of acentric ferroelectric and semiconductor crystals. Contributions from ionic nonlinearities result in enormously larger nonlinear coefficients in some materials than any known for the optical or electro-optical effects. An interpretation is presented in terms of a relationship between the nonlinear coefficients and the electronic and ionic *linear* susceptibilities.

In this paper we correlate the little-studied microwave nonlinear susceptibility with the familiar optical and electro-optical nonlinear susceptibilities for three-frequency mixing. Our work includes the first measurement of the microwave nonlinear susceptibility coefficient[1] d^{m}, in a variety of acentric polar and nonpolar crystals (Table I). For some materials d^{m} exceeds the largest values of the optical nonlinear coefficient[2] d^{o} by many orders of magnitude. The much smaller differences between the electro-optic nonlinear coefficient[3] d^{eo} and d^{o} have been previously studied.[4,5] We interpret all these differences in terms of the values of the electronic and ionic linear susceptibilities, by means of a phenomenological model. We show how Kleinman's symmetry condition[6] for the d^{o} tensor coefficients also applies to d^{m} for some, but not all, materials. Finally we note that our macroscopic measure of nonlinearities is related to microscopic anharmonicities of the crystalline bonds and thus to other physical phenomena such as infrared absorption, pyroelectricity, and thermal expansion.

Optical nonlinearities (d^{o}) are purely electronic in origin since all frequencies are above the lattice mode frequencies. Values of d^{eo} and d^{m} differ from d^{o} because for d^{eo} one and for d^{m} all the frequencies lie below the optical lattice mode frequencies, so that ionic as well as electronic anharmonicities are present. The coefficient d^{m} is the most general of the various nonlinear coefficients in its dependence on these anharmonicities.

Miller[7] showed that d^{o} equals the product of linear susceptibility cubed (purely electronic in the optical region) and a frequency-independent, but somewhat material-dependent, parameter δ. Garrett[8] proposed a phenomenological model extending Miller's work to treat both electronic and ionic contributions to the nonlinear susceptibility. The nonlinear susceptibility is related to the linear electronic and ionic susceptibilities at each frequency by introducing four separate δ parameters. We interpret the listed values of d^{m}, d^{eo}, and d^{o} by a version of this theory.

Microwave nonlinearities have been reported before,[9-12] but primarily as a higher-order effect in the centric paraelectric state of ferroelectrics.[9,10] Limited measurements on acentric crystals[10-12] have been made but cannot be interpreted in terms of the coefficients discussed here.

Experimental technique.—The coefficient d^{m}, d^{eo}, or d^{o} is defined in mks units[2] by the relation between the induced-polarization-wave Fourier amplitude, $\mathcal{P}(\omega)$, and the electric-field Fourier amplitudes,[3,6] $E(\omega)$, as

$$\mathcal{P}_i(-\omega_3)=\epsilon_0 2d_{ijk}(-\omega_3,\omega_2,\omega_1)E_j(\omega_2)E_k(\omega_1), \quad (1)$$

where summation over repeated indices is implied. We adopt the convention (consistent with electro-optic usage) that the third index refers to the orientation of the modulating field. As defined in Eq. (1), the coefficient d^{o} is equivalent to the familiar optical second-harmonic-generation coefficient.[2] The factor of 2 in Eq. (1) arises because a mixing process rather than second-harmonic generation is being described. The third-rank tensor coefficient d_{ijk} differs from zero only in the acentric point groups, as does the piezoelectric coefficient.[13] Conservation of energy requires that $\omega_3=\omega_2+\omega_1$ and difference mixing occurs if $\omega_1 \to -\omega_1$.

The determination of d^{m} is analogous to that used for electro-optic coefficients.[14] A 56-GHz carrier (ω_2) is mixed with a 100-MHz modulation field (ω_1) in the crystal, which fills a section of RG-98/U waveguide (0.376 cm×0.188 cm), except for a 0.05-cm gap at each side. To find a constant-strain (clamped) coefficient, ω_1 is high enough to avoid piezoelectric resonances. The modulation voltage is applied by metal electrodes to two opposing faces of the crystal. Normally

Table I. Nonlinear susceptibilities and related parameters. n, value appropriate to the measurement of d^o. ϵ, values taken from current literature. α, absorption coefficient, measured at $\lambda = 5.3$ mm in the waveguide. r, electro-optic coefficients [values and signs from I. P. Kaminow and E. H. Turner, in "Handbook of Lasers" (Chemical Rubber Co., Cleveland, Ohio, in press); see also E. H. Turner, to be published, for details of the sign determination]. d, given in mks units where $d(\text{mks}) = (4\pi/3)10^{-4}d(\text{cgs})$ and $d(\text{cgs})$ is defined as in Eq. (1) with $\epsilon_0 = 1$ (Ref. 3). d^o, signs from R. C. Miller and W. A. Nordland, Opt. Commun. 1, 400 (1970), and to be published. For KDP see W. A. Nordland, to be published. Except as noted, magnitudes are from (i) Ref. 2; (ii) J. Jerphagnon and S. K. Kurtz, Phys. Rev. B 1, 1739 (1970); (iii) G. E. Francois, Phys. Rev. 143, 597 (1966); and (iv) J. E. Bjorkholm and A. E. Siegman, Phys. Rev. 154, 851 (1967). d^{eo}, value of n in the original work was used, where possible, to convert to the electro-optic nonlinear susceptibility coefficient d^{eo}. d^m, absolute signs have not yet been determined. δ_{AB}, sign is that of d^m. Where d^{eo} contributes significantly to d^m, two possible values of δ_{AB} are given.

							{ ←		10^{-12}m/V			→ }	
Material	Point Group	n	ϵ/ϵ_0	α cm^{-1}	χ^e	χ^i	r	d^o	d^{eo}	d^m	δ_D	δ_C	δ_{AB}	Measured d_{ijk}
$BaTiO_3$	4mm	2.29	57	1.7	4.25	52	+28	-6.8	-193	97,000	-0.08	-0.20	0.64	333
$LiTaO_3$	3m	2.14	40	1.0	3.58	35.4	+30.3	-20	-159	16,000	-0.44	-0.31	0.33	333
$LiNbO_3$	3m	2.16	25.5	0.48	3.66	20.8	+30.8	-40	-170	6,700	-0.82	-0.46	0.63	333
KH_2PO_4[a] (KDP)	$\bar{4}$2m	1.50 1.46	44 21	~0.9	1.24 1.13	41.8 18.9	-8.8	+0.48	+11	1,850[f]	+0.28	+0.36	0.053	123[f]
$NH_4H_2PO_4$[a] (ADP)	$\bar{4}$2m	1.51 1.47	58 14	~1.2	1.28 1.16	55.7 11.8	-5.5	±0.59	+7.2	970[f]	±0.31	+0.34 -0.40	0.024	123[f]
$LiIO_3$	6	1.72	6.53	0.4	1.96	3.58	+6.4	-4.3[b]	-14.5	±177	-0.57	-0.71	+2.7 -2.3	333
$NaNO_2$[c]	m2m	1.40	4.18	$\lesssim$0.1	0.97	2.21	<0.9	0.12[d]	<0.9	36	0.12	-	2.3	333
ZnO	6mm	1.96	8.7	<0.05	2.84	4.91	+2.6	-7.2	-10.7	±176	-0.27	-0.08	+1.0 -0.9	333
CdS	6mm	2.35	9.25	0.15	4.53	3.72	-2.7	+31	+18	±127	+0.25	-0.18	+1.0 -1.4	333
CdTe	$\bar{4}$3m	2.66	9.4	$\lesssim$0.1	6.07	2.3	-5.6	∓168	+73	±36	∓0.74	+2.7 -1.1	-0.8 -2.5	123
GaP	$\bar{4}$3m	2.95	10.75	0.1	7.70	2.05	-0.97	+78[e]	+20	±24	+0.16	-0.47	+0.1 -1.1	123
GaAs	$\bar{4}$3m	3.27	13.05	0.024	9.71	2.34	-1.5	+134[e]	+43	±51	+0.14	-0.41	+0.12 -1.4	123
Ag_3AsS_3	3m	2.52	21	~1.8	5.36	14.6	+0.9	-	-9	950	-	-	0.22	333

[a] Upper and lower values of n, ϵ, χ^e, and χ^i correspond to 1 and 3 axes, respectively.

[b] F. R. Nash, J. G. Bergman, G. D. Boyd, and E. H. Turner, J. Appl. Phys. 40, 5201 (1969).

[c] Polar 3 axis coincides with crystallographic b axis.

[d] K. Inoue, Jap. J. Appl. Phys. 9, 152 (1970).

[e] J. J. Wynne and N. Bloembergen, Phys. Rev. 188, 1211 (1969); also J. H. McFee, G. D. Boyd, and P. H. Schmidt, Appl. Phys. Lett. 17, 57 (1970).

[f] The listed value is the combination $\frac{1}{3}(2d_{231} + d_{123})$, which equals d_{123} if the Kleinman symmetry condition applies (see text). Account of double refraction requires that $\epsilon(\omega_3)$ in Eq. (2) be multiplied by $\cos^2\rho = (2\epsilon_{11} + \epsilon_{33})^2/3(2\epsilon_{11}^2 + \epsilon_{33}^2)$, where ρ is the double-refraction angle.

the electrodes are arranged so that $E(\omega_1)$ is parallel to $E(\omega_2)$, but some measurements in potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) were also made with $E(\omega_1)$ perpendicular to $E(\omega_2)$. Only the sidebands ω_3 generated with $E(\omega_3)$ parallel to $E(\omega_2)$ could propagate in the unfilled waveguide. At 56 GHz the coherence length for these parallel fields is several centimeters even in birefringent crystals. Two independent tensor coefficients were measured in KDP and ADP and one in the other crystals. A tunable narrow-band heterodyne receiver and precision attenuator are used to measure the power ratio P_3/P_2 of the upper or lower sideband at ω_3 to the carrier at ω_2. The value of d^m is deduced from this ratio and the modulation voltage at ω_1. In these high-dielectric-constant materials it was assumed that P_2 and P_3 propagate entirely within the crystal and that the field $E(\omega_1)$ is adequately uniform, as shown by potential-model studies. Microwave resonances are accounted for by measuring P_3/P_2 vs ω_3 over several free spectral ranges of the crystal and then deducing the nonresonant value of the power ratio.

The power ratio is calculated from the polarization wave, the peak Fourier amplitude of which is given by $\mathcal{P}(-\omega_3)=\epsilon_0 2d_{\mathrm{eff}}E(\omega_2)E(\omega_1)$. The relationship of the effective[3] nonlinear coefficient d_{eff} to the tensor coefficients $d_{ijk}{}^{\mathrm{m}}(-\omega_3, \omega_2, \omega_1)$ depends on the point group and orientation of the crystal and fields. For point groups $\bar{4}2m$ and $\bar{4}3m$ the three *parallel* fields are chosen with equal angles to the three crystallographic axes and $d_{\mathrm{eff}}=(2/\sqrt{3})(2d_{231}+d_{123})/3$ and $(2/\sqrt{3})d_{123}$, respectively. The fields are parallel to [001] and $d_{\mathrm{eff}}=d_{333}$ for the other point groups. The sideband-to-carrier ratio is given by[15]

$$\frac{P_3}{P_2}\approx\left(\frac{k_3}{\beta_3}\right)^2\frac{\omega_3{}^2 d_{\mathrm{eff}}}{c^2\epsilon(\omega_3)}\left(\frac{l}{b}\right)^2 V_1{}^2, \tag{2}$$

where k_3 is the plane-wave propagation constant in the dielectric; β_3, the filled waveguide propagation constant; c, the velocity of light; $\epsilon(\omega_3)$, the dielectric constant for $E(\omega_3)$; l, the crystal length; b, the crystal thickness *parallel* to the electric field $E(\omega_1)$; and V_1, the modulating-voltage amplitude. As an example, $P_3/P_2=5\times10^{-6}$ at $\omega_3/2\pi=56$ GHz in $\mathrm{LiTaO_3}$ with $l=1.0$ cm, $b=0.188$ cm, and $V_1=141$ V peak.

Interpretation of results.—Garrett suggests that $d_{ijk}(-\omega_3, \omega_2, \omega_1)$ can be generalized in terms of four Miller δ coefficients which are frequency independent and approximately equal in magnitude:

$$d(-\omega_3, \omega_2, \omega_1)=\chi_1{}^i\chi_2{}^i\chi_3{}^i\delta_A+\chi_1{}^i\chi_2{}^i\chi_3{}^e\delta_B+\chi_1{}^i\chi_2{}^e\chi_3{}^e\delta_C+\chi_1{}^e\chi_2{}^e\chi_3{}^e\delta_D. \tag{3}$$

The δ's can be related to coefficients of the crystal potential-energy terms cubic in the displacement of electrons and ions.[8] In Eq. (3) $\chi^e=n^2-1$ is the linear electronic susceptibility (n being the refractive index), $\chi^i+\chi^e=\epsilon/\epsilon_0-1$ (χ^i is the linear ionic susceptibility and ϵ the microwave dielectric constant), and subscripts indicate frequencies. The tensor nature of d and δ is not indicated. The large variation observed in d between materials is due to differences in values of χ's.

For d^{o} all $\chi_j{}^i=0$ and for d^{eo} only $\chi_1{}^i\neq0$. Consequently only the δ_D term is relevant for d^{o} while both δ_D and δ_C terms contribute to d^{eo}. For d^{m} all terms contribute. Neglecting dispersion in χ^e (from the optical to the microwave region) and in χ^i, one obtains

$$d^{\mathrm{o}}=(\chi^e)^3\delta_D, \quad d^{\mathrm{eo}}-d^{\mathrm{o}}=\chi^i(\chi^e)^2\delta_C, \quad d^{\mathrm{m}}-d^{\mathrm{eo}}=(\chi^i)^2(\chi^i\delta_A+\chi^e\delta_B)=(\chi^i)^2(\chi^i+\chi^e)\delta_{AB}. \tag{4}$$

The quantity δ_{AB} is introduced since we cannot separate the contributions of δ_A and δ_B. Equation (4) enables one to derive δ_{AB}, δ_C, and δ_D (Table I) from d^{m}, d^{eo}, and d^{o}. Akitt, Johnson, and Coleman[16] attempted to determine δ_B in CdTe from dispersion in d^{e} and d^{eo} data. Apart from this, values of δ_{AB} and δ_C have not been measured. For $\chi^i\gg\chi^e$ ($\mathrm{BaTiO_3}$ through $\mathrm{NH_4H_2PO_4}$), note that $\delta_{AB}\approx\delta_A$. The magnitudes of δ_D, δ_C, and δ_{AB} vary comparatively little, despite an extremely large range of d's. This is particularly impressive for materials with large χ^i. For a new material, using representative values of δ_{AB} and δ_C, one can predict d^{m} and d^{eo}. For many materials, Levine[17] has calculated δ_D from bond parameters and he obtains good agreement with experiment. For the III-V compounds Flytzanis[5] has extended Levine's calculation to include ionic displacements and has calculated the ratio of $d^{\mathrm{eo}}/d^{\mathrm{o}}$, from which it is possible to derive δ_C/δ_D. Theoretical values of δ_A and δ_B have yet to be found.

Depending on the point group of the material there are a number of independent tensor coefficients d_{ijk}. Kleinman[6] shows that in the optical region where $\chi^e\gg\chi^i$, certain symmetries of d^{o} apply beyond those of the piezoelectric coefficients.[13] Similarly, in materials where $\chi^i\gg\chi^e$ it would be expected that the same conditions hold for d^{m}. In KDP and ADP it would follow that $d_{231}{}^{\mathrm{m}}=d_{123}{}^{\mathrm{m}}$. A direct measurement of $d_{123}{}^{\mathrm{m}}$ was made in these materials with $E(\omega_1)$ *perpendicular* to $E(\omega_2)$ and $E(\omega_3)$. It was found that $d_{123}{}^{\mathrm{m}}=\frac{1}{3}(2d_{231}{}^{\mathrm{m}}+d_{123}{}^{\mathrm{m}})$ is obeyed for both materials, within experimental error, in agreement with the symmetry conditions. Where χ^i is *not* dominant then only two-index permutation (piezoelectric) symmetry will hold.

The δ's are closely related to the parameters describing other physical phenomena. For example, the pyroelectric coefficient has been derived in terms of parameters related to δ_A and δ_B.[8,18] Kleinman[19] has related the microscopic ionic anharmonicity of GaP by a local-field model to macroscopic quantities such as the strength and temperature shift of the infrared combination bands, the width of the fundamental lattice resonance, and the thermal expansion coefficient.[20] Our δ's are macroscopic parameters which can be similarly related to the microscopic ionic and electronic anharmonicities. A detailed comparison of our results with these phenomena has yet to be made.

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[1] The coefficient d^m $(=d^{\text{microwave}})$ describes nonlinear interactions at frequencies below the optic, but above the acoustic-resonance frequencies. This implies that d^m is the constant-strain or clamped value. The third-rank tensor nature of $d \equiv d_{ijk}$ is also implied, for all coefficients.

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Magnetic Transition in Thin Conducting Films

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When a thin conducting film in the quantum-size-effect region is placed in a strong magnetic field, the electronic motion becomes three-dimensionally quantized. Simple analyses are presented to show that the magnetization and the differential susceptibility may undergo unusual transitions between positive and negative values.

When an electron gas is confined in a metallic film whose thickness is comparable to the electron de Broglie wavelength, the electron motion in the direction of the film thickness becomes quantized. This is known as the quantum size effect (QSE).[1] It is conceivable that the magnetic properties of a metallic film under QSE conditions will differ significantly from those in bulk material. Furthermore, if a magnetic field is applied in the thickness direction so that the electron motion in the film plane is also quantized, it may be possible to find some unusual