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## Determination of Absolute Signs of Microwave Nonlinear Susceptibilities

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The sign of the microwave nonlinear susceptibility has been found for the first time for a number of acentric crystals. The method used determines the absolute sign without recourse to a comparison crystal. Using known signs of piezoelectric coefficients to specify crystal orientation, all of the nonlinear susceptibilities measured are negative. Predictions of signs and magnitudes of some coefficients in pyroelectric crystals are also made.

### INTRODUCTION

Complete specification of a nonlinear susceptibility requires not only that its magnitude be known but also that an algebraic sign related to a defined positive direction in the crystal be given. We describe here a method of finding the absolute signs of microwave nonlinear susceptibility coefficients ( $d^m$ ) and relate these to positive axes found by piezoelectric tests. We also present the sign results for some crystals in order to complement the recent<sup>1</sup> measurements of the  $d^m$  magnitudes. These results, together with recent determinations of the signs of electro-optic<sup>1-3</sup> ( $d^{\infty}$ ) and nonlinear optical<sup>3,4</sup> ( $d^o$ )

susceptibilities allow further characterization of materials in terms of Garrett's four-parameter anharmonic-oscillator model.<sup>1,5</sup> Additionally, in pyroelectric crystals, predictions can be made of magnitudes and signs of some tensor components of  $d^m$  other than those directly measured.

The determination<sup>4</sup> of  $d^o$  signs involves comparison with a known crystal. This, in turn, requires that the sign of  $d^{\infty}$  for at least one crystal be determined<sup>6</sup> and that its behavior be followed as the modulation frequency is increased through the lattice resonance region.<sup>7</sup> The  $d^{\infty}$  sign determination<sup>2</sup> is also a comparison using a crystal of known<sup>6</sup> sign. In our method of finding  $d^m$  signs, however, each

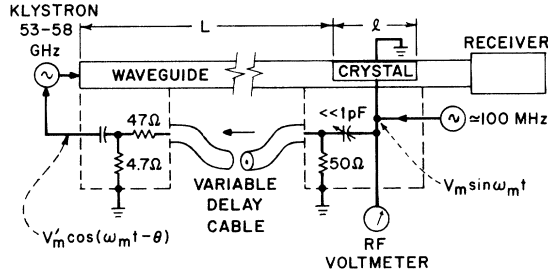


FIG. 1. Experimental arrangement for determining the absolute signs of microwave nonlinear susceptibilities.

measurement is an absolute one in itself.

#### EXPERIMENTAL METHOD

Both the magnitude and sign of  $d^m$  can be measured by generating sidebands, with a low-frequency ( $\sim 100$  MHz) modulating field, on a millimeter wave carrier (53–58 GHz) propagating in the crystal under test. The sidebands can be thought of as arising from sum and difference mixing of the carrier and modulating fields through the nonlinear susceptibility  $d^m$ . Equivalently, they are associated with phase modulation of the carrier, which results from a variation of the dielectric constant of the crystal induced through  $d^m$  by the modulating field. The magnitude of  $d^m$  can be determined from the sideband amplitudes.<sup>1</sup> Determination of the sign of  $d^m$  requires a comparison of the sideband phases with the phase of the modulating field. In our experiment, the phases of the sidebands produced in the crystal are measured by comparing them with equivalent frequency-modulation sidebands which are generated at the klystron carrier source by modulating its reflector voltage.

The apparatus used is similar to that described elsewhere.<sup>1,6</sup> It is shown schematically in Fig. 1, where the modifications necessary to this experiment are emphasized. The crystal is oriented so that a positive direction, found, for example, by piezoelectric tests, points toward the ground electrode. As shown in Fig. 1, a small portion of the modulating voltage  $V_m \sin \omega_m t$  applied to the crystal under test is used, after amplitude and phase adjustment, to modulate the reflector of the klystron. These adjustments are made to enable the sidebands produced at the klystron to cancel the sidebands produced in the crystal through  $d^m$ . It is experimentally convenient to adjust the amplitude of the sampled voltage by means of a voltage divider consisting of a very small variable capacitor ( $\ll 1$  pF) and a  $50\text{-}\Omega$  cable-terminating resistor. This divider also introduces a phase lead of  $\frac{1}{2}\pi$ , so that the resulting voltage  $V'_m \cos \omega_m t$  drives the matched variable-length coaxial line leading to the klystron. The phases of the sidebands produced at the kly-

stron are adjusted by varying the line length, making it imperative that the line be matched so that impedances seen at each end are constant. At the klystron end the coupling network has been designed to introduce virtually no phase shift.

After a variable delay  $\theta$ , introduced by the line, the modulating voltage applied to the reflector is  $V'_m \cos(\omega_m t - \theta)$ . The instantaneous klystron frequency is then given by  $\omega_t = \omega_0 - c_k V'_m \cos(\omega_m t - \theta)$ , where the electrical tuning parameter  $c_k$  is always positive. If care is taken to operate the klystron at the center of one of the reflector modes, it can be shown<sup>9</sup> that no added phase shifts are introduced.

The frequency-modulated output of the klystron then can be described by

$$(\pm 1)^n A J_n(\beta) e^{j[(\omega_0 \mp n\omega_m)t \pm \theta]},$$

where the modulation index  $\beta \equiv c_k V'_m / \omega_m$  is the argument of the Bessel's functions  $J_n$  and  $A$  is an amplitude. The phases of the modulation products are now completely specified because  $\beta$  is always positive. In the experiment we consider only the cancellation of the first sidebands at  $\omega_0 \pm \omega_m$  with similar sidebands produced at the nonlinear crystal. Since this sideband amplitude is small, the modulation index  $\beta$  is much less than unity and we can neglect terms in  $\beta^2$  and higher powers and use  $J_0(\beta) = 1$  and  $J_1(\beta) = \frac{1}{2}\beta$ . The carrier (C), upper sideband (USB), and lower sideband (LSB) fields incident on the crystal can then be written as

$$\begin{aligned} \text{C: } A_i^0 &= A e^{j(\omega_0 t - k_g L)}, \\ \text{USB: } A_i^+ &= -\frac{1}{2} A \beta e^{j[(\omega_0 + \omega_m)t - \theta - \gamma - k_g L]}, \\ \text{LSB: } A_i^- &= +\frac{1}{2} A \beta e^{j[(\omega_0 - \omega_m)t + \theta + \gamma - k_g L]}. \end{aligned} \quad (1)$$

In (1),  $k_g L$  is the phase length of the  $\omega_0$  wave component, which has a propagation constant  $k_g$  in the waveguide of length  $L$  between klystron and crystal. The phase lengths in the waveguide structure of the USB and LSB components are  $(k_g L + \gamma)$  and  $(k_g L - \gamma)$ , respectively, where  $\gamma \equiv k_0 k_m L / k_g$ . The quantities  $k_0$  and  $k_m$  are, respectively, free-space propagation constants of the  $\omega_0$  and  $\omega_m$  waves. Over the range of carrier frequencies used,  $k_0 / k_g$  is nearly constant, so that  $\gamma$  is only a function of  $\omega_m$ .

At the nonlinear crystal, the modulating voltage  $V_m$  produces a change in the microwave dielectric constant  $\epsilon$ , given by

$$\Delta\epsilon = 4 d_{eff}^m (V_m / b), \quad (2)$$

where  $b$  is the crystal height and  $d_{eff}^m$  is the element or combination of elements  $d_{ijk}^m$  appropriate to the point group of the crystal and the geometry used. The change in dielectric constant in turn causes a change  $\eta$  in phase length:

$$\eta = -2 d_{eff}^m (V_m / b) (k_0^2 / k_{gc}). \quad (3)$$

In (3),  $k_{gc}$ , the propagation constant in the crystal-

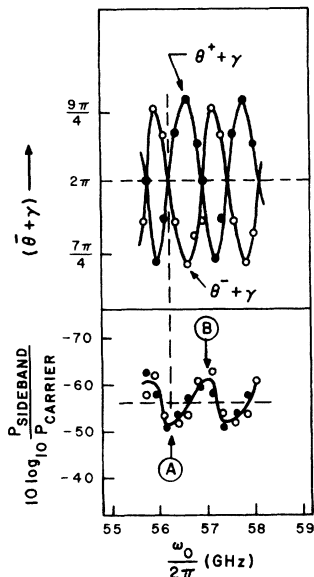


FIG. 2. Measured sideband-to-carrier power ratio and phase delay  $(\bar{\theta} + \gamma)$  as functions of carrier frequency  $\omega_0$ . Points for the upper sideband are represented by solid circles; those for the lower sideband by open circles. Points *A* and *B* occur at maximum and minimum transmission, respectively. Data are for the  $d_{333}^m$  coefficient of  $\text{LiNbO}_3$ :  $l = 1.5$  cm,  $b = 0.185$  cm,  $V_m = 150$  V<sub>rms</sub>,  $\omega_m/2\pi = 81.5$  MHz.

loaded guide, can usually be taken as  $\sqrt{\epsilon} k_0$ . The time-varying phase length then modulates the wave incident on the crystal. For clarity we consider first an *idealized* case in which the crystal is assumed lossless and matched to the guide. In this case, pure phase modulation is produced and  $\eta$  is the modulation index. The wave components transmitted through the crystal of length  $l$  are

$$\begin{aligned} \text{C: } & A_c^o = A' e^{j\omega_0 t}, \\ \text{USB: } & A_+^o = \frac{1}{2} A' e^{j(\omega_0 + \omega_m)t} (\eta - \beta e^{-j(\bar{\theta} + \gamma)}), \\ \text{LSB: } & A_-^o = -\frac{1}{2} A' e^{j(\omega_0 - \omega_m)t} (\eta - \beta e^{j(\bar{\theta} + \gamma)}), \end{aligned} \quad (4)$$

where

$$A' = A e^{-j(k_g L + k_{gc} l)}.$$

In deriving Eq. (4) all terms of second order or higher in  $\eta$  and  $\beta$  have been dropped and we have taken  $J_0(\eta) = 1$  and  $J_1(\eta) = \frac{1}{2}\eta$ . As noted earlier, the crystal is oriented with a positive direction pointing toward the ground electrode; reversal of the crystal changes the sign of  $\eta$  in (4).

In order to obtain cancellation of the  $(\omega_0 \pm \omega_m)$  wave components the magnitudes of  $\beta$  and  $\eta$  must be the same, as shown by (4). Recalling that  $\beta$  is always positive, we see that, if  $\eta$  is also positive, cancellation occurs when  $\theta$  is experimentally adjusted so that  $\bar{\theta} + \gamma = 2N\pi$ , where  $N$  is an integer and  $\bar{\theta}$  is the resultant experimental value of  $\theta$ . On the

other hand, if  $\eta$  is negative the null condition requires  $\bar{\theta} + \gamma = (2N + 1)\pi$ .

#### EXPERIMENTAL RESULTS

In the actual experiment the crystals had essentially the same cross section as the waveguide and, because of their high dielectric constants and generally non-negligible losses, were far from being matched. In such a case, the crystal acts as a dielectric resonator in the waveguide, and its transmission shows maxima at  $k_{gc}l = n\pi$  and minima at  $k_{gc}l = (n + 1/2)\pi$ . The measured ratio of sideband-to-carrier power, shown in Fig. 2 as a function of carrier frequency  $\omega_0$  for a typical crystal ( $\text{LiNbO}_3$ ), also exhibits resonant behavior. The sideband components now contain contributions from amplitude as well as phase modulation. In spite of this added complexity,  $|\eta|$  can be obtained directly, as analysis indicates that  $10 \log_{10}(|\eta|^2/4)$  equals the average of the logarithmic sideband-to-carrier ratios at the transmission maxima (point *A*) and minima (point *B*). The magnitude of  $d^m$  can then be obtained by using (3).

The phase condition on  $(\bar{\theta} + \gamma)$  for cancellation of the sideband components is also a function of carrier frequency in the resonant case (Fig. 2). In general, the phase delay required for cancellation of the upper- and lower-sideband components are different, and we denote them by  $\theta^+$  and  $\theta^-$ , respectively. However, at points *A* and *B*,  $\theta^+ = \theta^- = \bar{\theta}$ , and the cancellation condition reverts to the simple one in the ideal case above:  $(\bar{\theta} + \gamma) = 2N\pi$  if  $\eta > 0$ . If one departs, for example, from the  $k_{gc}l = n\pi$  condition (point *A*) by increasing  $\omega_0$ , cancellation requires an increase in  $\theta^+$  and a decrease in  $\theta^-$  (Fig. 2). The changes in  $\theta^+$  and  $\theta^-$  result both from phase-modulation shifts and from amplitude-modulation products. The difference between  $\theta^+$  and  $\theta^-$  is not small: We compute in a typical case that  $\theta^+ - \theta^- = \frac{1}{2}\pi$  for  $k_{gc}l = (2n + 1)\frac{1}{4}\pi$  if  $R e^{-2\alpha l} = 0.5$ , where  $R$  is the power-reflection coefficient at one crystal face and  $2\alpha$  is the power-attenuation coefficient. Our analysis shows, however, that for arbitrary  $k_{gc}l$  the null condition requires  $\frac{1}{2}(\theta^+ + \theta^-) + \gamma = 2N\pi$  for  $\eta > 0$ . Our measurements were made on both sidebands at a number of values of  $\omega_0$ , thereby varying  $k_{gc}$ . The experiment and analysis agree with regard to requirements on  $\theta^+$  and  $\theta^-$  as well as on amplitude cancellation requirements.

We have used piezoelectric tests in order to establish a direction to which the signs of the  $d^m$  could be related. Similar tests have been used in  $d^{90}$  (Ref. 2) and  $d^o$  (Ref. 4) sign determinations and have been related<sup>10</sup> to pyroelectric effect and spontaneous polarization in polar crystals as well as to atomic ordering. In all cases we have used the "parallel" geometry<sup>1</sup> in which modulating field and microwave field are parallel. Since the piezoelec-

TABLE I. Signs of piezoelectric and measured nonlinear microwave susceptibility coefficients.

Material	Point group	Tensor component <sup>a</sup> $d_{ijk}$	Piezoelectric sign	$d_{ijk}^m$ sign
BaTiO <sub>3</sub>	4mm	$d_{333}$	+	-
LiTaO <sub>3</sub>	3m	$d_{333}$	+	-
LiNbO <sub>3</sub>	3m	$d_{333}$	+	-
LiIO <sub>3</sub>	6	$d_{333}$	+	-
KH <sub>2</sub> PO <sub>4</sub>	$\bar{4}2m$	$\frac{1}{3}(2d_{231} + d_{123})$	+	-
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	$\bar{4}2m$	$\frac{2}{3}(2d_{231} + d_{123})$	+	-
ZnO	6mm	$d_{333}$	+	-
CdS	6mm	$d_{333}$	+	-
GaP	$\bar{4}3m$	$d_{123}$	-	-
GaAs	$\bar{4}3m$	$d_{123}$	-	-

<sup>a</sup>Apart from a multiplying factor for  $\bar{4}2m$  and  $\bar{4}3m$  crystals, these components are appropriate for longitudinal-piezoelectric and parallel-nonlinear coefficients.

tric tensors and  $d^m$  tensors have the same form, it is not surprising that this geometry is also one in which a "longitudinal" piezoelectric effect<sup>11</sup> exists: A compressional stress applied parallel to the field directions in the  $d^m$  experiments produces a change in polarization in the same direction. A positive [111] direction in the  $\bar{4}3m$  crystals or the positive [001] in the 6mm crystals are defined as the direction from cation to the nearest-neighbor anion lying in the appropriate direction. In Table I we list the piezoelectric signs used in identifying these axes. The positive  $c$ -axis direction in the pyroelectric crystals coincides with the sense of the spontaneous polarization. In the  $\bar{4}2m$  crystals both piezoelectric coefficients are taken as positive<sup>12</sup> and this allows one to find a positive axis.

Using positive axes described above, we find that all of the  $d_{ijk}^m$  we have measured are negative (see Table I).

#### DISCUSSION

In the II-VI and III-V compounds, the microwave nonlinearity appears to be closely related to atomic ordering, which determines the axis sense. The negative sign of the combination ( $2d_{231}^m + d_{123}^m$ ) found for the  $\bar{4}2m$  crystals probably<sup>13</sup> means that each of

the coefficients is negative, as one would expect from the Kleinman condition<sup>14</sup> allowing complete permutation of indices.

In LiNbO<sub>3</sub>, it is possible to predict the observed sign of  $d_{333}^m$  from the variation of dielectric constant with temperature. The constant-strain dielectric constants  $\epsilon_3^s$  and  $\epsilon_1^s$  both increase with increasing temperature.<sup>15</sup> If we assume that the entire change in  $\epsilon_i^s$  can be related to a change in spontaneous polarization  $\Delta P_s$ , acting through  $d_{i13}$ , we can write

$$\frac{\Delta\epsilon_i^s}{\Delta T} = \frac{4d_{i13}^m}{\epsilon_o(\epsilon_i^s - 1)} \frac{\Delta P_s}{\Delta T}, \quad (5)$$

where  $\Delta T$  is a temperature increment. Since  $(\Delta P_s/\Delta T) < 0$  and  $(\Delta\epsilon_i^s/\Delta T) > 0$ , then  $d_{i13}^m < 0$ . Thus, in addition to correctly predicting the observed negative sign of  $d_{333}^m$ , we also anticipate that  $d_{113}^m$  is negative. In using Eq. (4) one should note that constant-stress values of  $d_{i13}^m$  are actually more appropriate than the constant-strain value found in the microwave experiments. Also, differences between low- and high-frequency dielectric constants, volume changes, and temperature dependence of  $d_{i13}^m$  are neglected. Assuming that these factors affect  $\Delta\epsilon_1^s$  and  $\Delta\epsilon_3^s$  in a similar fashion, however, the ratio

$$\frac{(\Delta\epsilon_1^s/\Delta T)}{(\Delta\epsilon_3^s/\Delta T)} = \frac{d_{113}^m(\epsilon_3^s - 1)}{d_{333}^m(\epsilon_1^s - 1)} \quad (6)$$

can be used with the experimental values of  $\Delta\epsilon_i^s$  to predict that  $d_{113}^m \approx d_{333}^m$ . Uncertainties in the value of  $\Delta P_s$  are also eliminated by using (6).

Jerphagnon<sup>16</sup> has developed a relationship between the spontaneous polarization  $P_s$  and the vector parts of the optical and electro-optical nonlinear coefficients for pyroelectric crystals. It is possible to adapt this notion to the microwave nonlinearities, so that we can use the magnitudes<sup>1</sup> and newly measured signs of  $d_{333}^m$  to predict magnitudes and signs of  $d_{113}^m$ . Following Jerphagnon and defining<sup>17</sup>  $\delta_{333}^m \equiv d_{333}^m/(\epsilon_3^s - 1)^3$  and  $\delta_{113}^m \equiv d_{113}^m/(\epsilon_1^s - 1)^2(\epsilon_3^s - 1)$ , we can write, in the  $\delta$  formulation

$$\delta_{333}^m + 2\delta_{113}^m = KP_s. \quad (7)$$

The constant  $K$  can be evaluated from the data

TABLE II. Values of constant-strain dielectric constants, spontaneous polarization (in C/m<sup>2</sup>), microwave nonlinear coefficients (in 10<sup>-12</sup> m/V), and  $\delta$  coefficients (in 10<sup>-12</sup> m/V) for pyroelectric materials. Values of  $\epsilon_1^s$  and  $\epsilon_3^s$  are taken from current literature. The value of  $P_s$  for LiIO<sub>3</sub> has been estimated in Ref. 16, and the other values are tabulated there. Magnitudes of  $d_{333}^m$  are from Ref. 1.

Material	$\epsilon_1^s$	$\epsilon_3^s$	$P_s$	$d_{333}^m$	$\delta_{333}^m$	$\delta_{113}^m$	$d_{113}^m$
LiNbO <sub>3</sub>	43	25.5	0.71	-6700	-0.46	-0.16	-6700
LiTaO <sub>3</sub>	41	40	0.50	-16 000	-0.27	-0.14	-8700
BaTiO <sub>3</sub>	2300	57	0.26	-97 000	-0.55	+0.13	+3.9(10 <sup>7</sup> )
LiIO <sub>3</sub>	8	6.53	1.45	-177	-1.05	-0.27	-74

for  $\text{LiNbO}_3$  given in Table II, along with the above estimate that  $d_{113}^m \approx d_{333}^m$  for this material. We find that  $K = -1.1(10^{-12}) \text{ m}^3/\text{J}$ . Predicted values of  $\delta_{113}^m$  and  $d_{113}^m$  are given in Table II for some other pyroelectric crystals for which  $d_{333}^m$  is known. The positive sign and enormous magnitude anticipated for  $d_{113}^m$  in  $\text{BaTiO}_3$  are most interesting. All of

these predictions await experimental verification.

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## Dielectric Properties of Lithium Hydrazinium Sulfate<sup>†</sup>

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The dc conductivity and ac dielectric susceptibility of normal and deuterated lithium hydrazinium sulfate have been measured over a wide temperature range at frequencies up to 9.33 GHz. Over a very large temperature and frequency range the real and imaginary parts of the susceptibility are very large (up to  $\epsilon' \approx \epsilon'' \approx 10^6$ ) and vary with frequency somewhat as  $f^{-1/2}$ . This unusual behavior is shown to result from the nearly one-dimensional protonic conductivity and its extreme sensitivity to barriers caused by local structural defects. Etching studies indicate that the crystal is not ferroelectric, implying that the apparent hysteresis loops result from saturation of the ac conduction.

### I. INTRODUCTION

Lithium hydrazinium sulfate ( $\text{LiN}_2\text{H}_5\text{SO}_4$ ) has been generally considered to be a member of the ferroelectric sulfate family<sup>1</sup> because it exhibits what appear to be hysteresis loops, although no conclusive evidence for a ferroelectric phase transition has been found. At the same time, it exhibits unusually large protonic conductivity along the "ferroelectric"

$c$  axis.<sup>1,2</sup> It has been previously suggested that this crystal is not ferroelectric, and that its anomalous dielectric behavior is caused by protons in the hydrazinium chains which run along the  $c$  axis, but no detailed explanation was given.<sup>3</sup> We present herein a model which assumes partially blocked current flow along the hydrazinium ion chains and which predicts no hysteresis in the dc limit. Good qualitative agreement with our experimental results is ob-