Optical Harmonic Generation in Single Crystal BaTiO$_3$

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Second-harmonic generation (SHG) of the Nd-doped CaWO$_4$ optical maser beam in ferroelectric BaTiO$_3$ has been investigated. Each of the three nonlinear coefficients which determine the magnitude of the SHG have been measured from room temperature to near the Curie temperature. It is found that all three coefficients have the same temperature dependence as the spontaneous ferroelectric polarization. The symmetry of the nonlinear coefficients required for a dispersionless, lossless SHG mechanism, namely, $d_{15}=d_{31}$ for BaTiO$_3$, applies over the entire measured temperature range. The effects on SHG due to antiparallel ferroelectric domains are described. The circumstances under which random as well as special antiparallel domain arrays can produce either an enhancement or a degradation of the second-harmonic intensity are discussed. Because of the dependence of SHG on the domain structure, the determination of the nonlinear coefficients requires single-domain crystals. A method for preparing suitable BaTiO$_3$ single-domain crystals is described. These crystals are also useful for investigations of the characteristics of ferroelectric domain growth.

INTRODUCTION

QUANTITATIVE studies of the second-harmonic generation[1] (SHG) of optical maser beams in ferroelectric crystals are interesting for several reasons. All ferroelectric crystals[2] have optical, electrical, and other properties that undergo large changes with temperature so that one might also expect the efficiency of SHG in these crystals to vary with temperature in some pronounced manner. In addition, ferroelectric crystals have a domain structure that can be influenced with an external electric field; and, as will be discussed, the ferroelectric domain structure can have a maked effect on the production of the second harmonic.[3-7] Neither the domain effects nor the marked temperature dependence of SHG will occur with the usual nonferroelectric piezoelectric crystal. Ferroelectric barium titanate is, in many respects, a good choice as a material for an investigation of these nonlinear effects. For example, suitable crystals are readily available, the point group (C_{4v}) is simple, it is among the most efficient nonlinear materials known,[6] the Curie temperature (120°C) is easily attained, its optical properties are well suited to SHG with at least one of the commonly used optical masers, and its domain dynamics are quite well understood.[2]

From the point group of BaTiO$_3$, it can be shown

that the second-order polarization $\bar{P}_{2\omega}$ has the form,[1,6]

$$\bar{P}_{2\omega} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_yE_z \\ 2E_xE_z \\ 2E_xE_y \end{bmatrix}. \quad (1)$$

In this equation, $\bar{P}_{2\omega}$ is the dielectric polarization at twice the maser frequency ω, d_{ij} are the nonlinear coefficients, and E_i are the optical electric fields in the medium. Inspection of Eq. (1) readily shows that c-domain ferroelectric plates, i.e., plates with the ferroelectric direction (z axis) normal to the major surfaces, are not very useful for a study of SHG. One would like to use a-domain plates, i.e., samples with the ferroelectric direction in the plane of the major surfaces of the plate, so that with appropriate use polarizers and analyzers, one can determine each of the three nonlinear coefficients. There is some indication in the literature that a-domain samples are difficult to prepare; and, furthermore, that they may be unstable.[8] In addition, since SHG is influenced by antiparallel ferroelectric domains,[6] one must prepare a-domain samples which are free of antiparallel domains, i.e., they must be single domain crystals. A method for preparing samples suitable for these SHG studies will be described.

The a-domain samples prepared for the SHG studies are also useful for another type of investigation. With electrodes along two opposite edges so that electric fields can be applied along the crystal z axis, one can study the domain dynamics of polarization reversal, i.e., the nucleation and growth of the antiparallel domains. In recent years, studies[2] of domain dynamics through the direct observation of the domains have been largely restricted to investigations of the sidewise motion of the 180° domain walls—the boundaries between antiparallel domains. With the a-domain sam-

[1] For a review on the subject of SHG, see P. A. Franken and J. F. Ward, Rev. Mod. Phys. **35**, 23 (1963).

[2] For a general review of the properties of BaTiO$_3$ and other ferroelectric crystals, the reader is referred to F. Jona and G. Shirane, *Ferroelectric Crystals* (The Macmillan Company, New York, 1962).

[3] R. C. Miller, quoted in Ref. 1.

[4] F. Brown, Bull. Am. Phys. Soc. **8**, 62 (1963).

[5] J. van der Ziel and N. Bloembergen, Bull. Am. Phys. Soc. **8**, 380 (1963), and N. Bloembergen, Proceedings of the International School of Physics "Enrico Fermi," Varenna, Como, Italy, 1963 (to be published).

[6] R. C. Miller, D. A. Kleinman, and A. Savage, Phys. Rev. Letters **11**, 146 (1963).

[7] R. L. Himbarger and J. L. Bjorkstam, Appl. Phys. Letters **3**, 109 (1963).

[8] P. H. Fang and W. S. Brower, J. Appl. Phys. **34**, 1516 (1963).

ples, one can for the first time observe in detail directly with a microscope the forward growth (growth in the direction of the spontaneous polarization) of the antiparallel domains under nearly ideal conditions. These phenomena, however, will not be described in this paper.

This paper discusses an analysis of some of the effects of antiparallel ferroelectric domains on SHG, the preparation of single crystals of $BaTiO_3$ suitable for studies of SHG and the forward growth of antiparallel domains, the determination of all the nonlinear coefficients as a function of temperature, and a brief discussion of these and other related experimental results.

EFFECTS OF FERROELECTRIC DOMAINS ON SHG

The effects which will be considered are those due to antiparallel domains. Effects which arise with twinned crystals due to mixed a- and c-domain configurations will not be discussed. Barium titanate will be treated in some detail, however, the phenomena to be described are not specific to $BaTiO_3$—they will occur with all ferroelectric crystals.

Consider what happens when an optical maser beam is at normal incidence on a $BaTiO_3$ crystal platelet. The maser beam fundamental produces a second har-
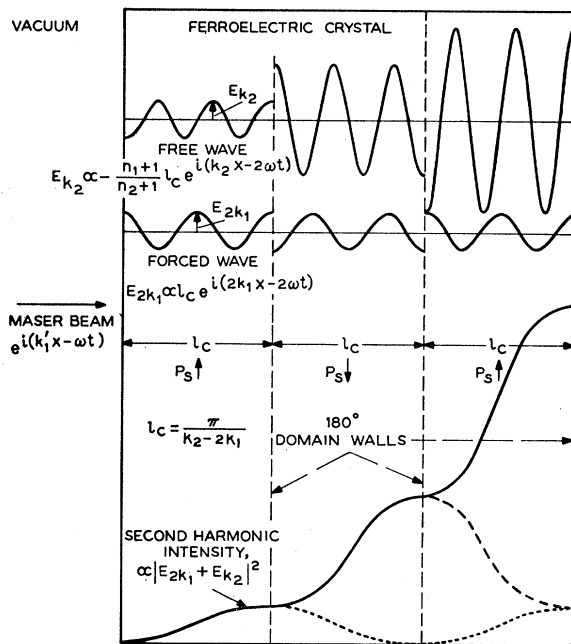

FIG. 1. Illustration of the enhancement of SHG due to antiparallel ferroelectric domains, one coherence length, l_c, thick. The forced and free second-harmonic waves are shown at the top of the figure and the resultant second-harmonic intensity at the bottom of the figure. At each domain wall the forced wave changes phase by π, and the free wave increases in amplitude by an amount equal to twice that of the forced wave. The dotted, dashed, and solid curves at the bottom of the figure show the effect on the second-harmonic intensity of zero, one, and two 180° domain walls.

monic forced wave[9,10] in the crystal as indicated in Fig. 1. This wave, which will be expressed as

$$E_{2k_1} \propto l_c \exp i(2k_1x - 2\omega t) \tag{2}$$

is tied to the fundamental maser light wave, $\exp i(k_1x - \omega t)$. In these expressions, ω is the frequency of the fundamental light wave, and k_1 the propagation constant in the medium. The quantity l_c is the coherence length,[1] which will be described in more detail in the next paragraph. The plane of polarization of the forced wave is determined by the nonlinear coefficient involved in the SHG process. For ease of presentation, the phenomenon to be described will be illustrated with the nonlinear coefficient d_{33} so that all polarizations, including the ferroelectric polarization, are in the same plane.

Boundary conditions imposed by Maxwell's equations, namely, the tangential components of E and H, must be continuous across the surface of the crystal, require that a free second-harmonic wave[9,10] also be present in the crystal. This wave, which is produced at the surface, is expressed by

$$E_{k_2} \propto -l_c \frac{n_1+1}{n_2+2} \exp i(k_2x - 2\omega t), \tag{3}$$

where k_2 is the propagation constant in the medium appropriate to the second-harmonic frequency. The quantities n_1 and n_2 are the indices of refraction at the fundamental- and second-harmonic frequencies, respectively. A reflected second-harmonic wave of small amplitude is also generated but will not be discussed further.[9,10] Since dispersion between the fundamental- and second-harmonic frequencies is usually present, $2k_1$ will not in general be equal to k_2 so that the forced and free waves, which are initially out of phase by π at $x=0$, travel with different velocities. The second harmonic intensity I_2 in the crystal is the result of the interference between these two waves, and can be approximated by

$$I_2 \propto |E_{2k_1} + E_{k_2}|^2. \tag{4}$$

Since $(n_1+1)/(n_2+1)$ is nearly unity, I_2 at $x=0$ is essentially zero compared to the maximum value of I_2 which first occurs at x equal to one coherence length l_c where the two waves are in phase; and then provided no domain walls are present, at successive odd multiples of l_c. The minima occur at even multiples of l_c. This oscillating phenomenon is illustrated near the bottom of Fig. 1. The coherence length l_c is given by

$$l_c = \pi/(k_2 - 2k_1) = \lambda/4(n_2 - n_1), \tag{5}$$

where λ is the free-space wavelength of the fundamental.

Now, consider what happens to these two second-harmonic waves when they traverse a 180° domain wall

[9] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. 127, 1918 (1962).
[10] D. A. Kleinman, Phys. Rev. 128, 1761 (1962).

where the normal to the wall is in the beam propagation direction. Since the z axes in two antiparallel domains are in opposite directions, Eq. (1) says that the phase of the second-order polarization wave $\bar{P}_{2\omega}$, and hence that of E_{2k_1}, will change by π on traversing the wall. The effect of the wall on the free wave is determined by the requirement that the tangential components of the E and H fields at frequency 2ω be continuous across the domain wall. For a wall at $x=x_0$, the free-wave changes from the form given in Eq. (3) to

$$-l_c\left[\frac{(n_1+1)}{(n_2+1)}-\frac{(n_1+n_2)}{n_2}\exp i(2k_1-k_2)x_0\right]$$
$$\times \exp i(k_2 x-2\omega t), \quad (6)$$

for $x>x_0$. Thus, in the case of the free wave, the domain wall in general introduces a change in amplitude as well as a change in phase. A reflected second-harmonic wave is also produced at the wall; however, since its amplitude is down from that of the transmitted second-harmonic wave by more than three orders of magnitude, the reflected wave will not be considered further. Assume as shown in Fig. 1, that a wall is at $x_0=l_c$, in which case the maximum increase in E_{k_2}, and hence I_2 is obtained. Setting $n_1\approx n_2$, i.e., small dispersion, one sees from Eq. (6) that the amplitude of the free wave increases by a factor of 3. Therefore, the maxima of the total second-harmonic intensity increase by a factor of 4 due to the first "properly" placed domain wall. In addition, the minima are no longer zero, but are equal to the maxima obtained in the absence of the 180° wall. Each properly placed 180° wall results in an increase of the amplitude of the free wave by $(n_1+n_2)/n_2\approx 2$ times the amplitude of the forced wave. With N properly placed walls, the part of I_2 which does not average to zero with x can be shown to increase by a factor equal $[1+(1+2N)^2]/2$. The largest enhancement one can obtain from this process occurs when the 180° walls are present at $x=l_c$, $2l_c$, $3l_c$, etc., up to the crystal thickness l. The effect is then to increase the coherence length from l_c to the crystal thickness l. With the Nd maser and BaTiO$_3$, $l_c=2.1\times10^{-4}$ cm for d_{33}[6] so that for a crystal of typical thickness, 2×10^{-2} cm, and with domain walls spaced l_c apart, one has $N_{max}=10^2$ or a SHG enhancement of 2×10^4, a very large effect.

For an array of N 180° domain walls situated randomly in the crystal, the resultant second-harmonic electric field is given by

$$E\propto l_c[(-1)^N e^{i2k_1 x}-e^{ik_2 x}(1-2\exp(-i\pi x_1/l_c)$$
$$+2\exp(-i\pi x_2/l_c)-2\exp(-i\pi x_3/l_c)+\cdots$$
$$+2(-1)^N\exp(-i\pi x_N/l_c))], \quad (7)$$

where the walls are placed at $x=x_1$, $x=x_2$, etc., and it is assumed that $n_1=n_2$ except in l_c. Then, for $2Nl_c<l$, Eq. (7) gives a second-harmonic intensity enhancement proportional to $(1+2N)$, where again only the part of

I_2 that does not average to zero with x is considered. The restriction that $2Nl_c<l$ is required so that in averaging the product of Eq. (7) and its complex conjugate one can permit each phase $\pi x_i/l_c$ to vary from 0 to 2π. Thus, even a random array of antiparallel domains can produce a substantial enhancement of the second harmonic in a ferroelectric crystal.

For $l_c\gg l$, i.e., when the free and forced waves propagate at very nearly the same velocity, Eq. (7) can be used to show that the intensity of the resultant SHG is proportional to the square of the difference between the total thickness of domains of one sign minus that for domains of the opposite sign. Since SHG for $l\gg l_c$ in the absence of domains[1] is proportional to l^2, antiparallel domains will have a serious degrading effect on SHG under "velocity matched" conditions.

In the case just treated, the crystal was assumed to consist of slabs of antiparallel domains with the normals to the walls parallel to the beam direction. If the wall normals are perpendicular to the beam direction the analysis given above does not apply. In the latter situation, one has second-harmonic coherent light beams emerging from the crystal with the phase of all the beams coming from domains polarized in one direction out of phase by π with those beams coming from domains polarized in the opposite direction. In an unfocused beam experiment with a few antiparallel domains present so that the cross sections of the radiating volumes are much larger than a wavelength, the emerging beams will be nearly parallel and will not interfere with each other and reduce the second-harmonic intensity below that which one would observe with a single-domain crystal. However, when diffraction effects become large, that is, when the cross sections of the radiating areas are comparable to a wavelength, the emergent beams are no longer nearly parallel to that they can interfere destructively with each other and reduce the second-harmonic output below that which one would observe with one or a few domains.

The optimum domain array for SHG is one where the crystal consists of sheets of antiparallel domains, each l_c thick, with the wall normals parallel to the beam direction. The question arises as to how one can produce such domain arrays. One possible method that would apply to crystals which undergo second or higher order ferroelectric phase transitions,[2] such as potassium dihydrogen phosphate (KDP), Rochelle salt, and triglycine sulfate (TGS), involves the formation of a domain pattern, as the crystal goes from the paraelectric to the ferroelectric phase, which is determined by the minimum free energy.[2] In the case of Rochelle salt, theory and experiment give a domain spacing obtained in this manner which is proportional to the square root of crystal thickness.[11] (This crystal thickness refers to the direction of the ferroelectric polariza-

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[11] T. Mitsui and J. Furuichi, Phys. Rev. 90, 193 (1953).

tion.) Thus, one may be able to produce a suitable array using this technique. This method will not work for crystals such as BaTiO₃ which undergo first-order phase transitions since the domain pattern formed on cooling through the phase transition is in this case determined by independent nuclei and not by the minimum free energy.[2]

It may be possible to produce desired domain arrays with electric fields. There is some evidence that the number of domains per unit area is determined by the magnitude of the field producing them,[12] so that with a suitable choice of the magnitude and the duration of the field, one may be able to produce useful domain patterns. A combination of electrical and thermal treatment may also be found useful.

Order of magnitude enhancements of the second-harmonic have been observed with both BaTiO₃ and TGS when antiparallel domains were known to be present. In these experiments, the ferroelectric domains had probably either circular, or approximately square, cross sections in the BaTiO₃; and probably lenticular, or circular, cross sections in TGS.[2] Thus, in neither case did the antiparallel domain configuration approximate the ideal slab structure. However, in no case was a decrease of the second harmonic observed when antiparallel domains were known to be present which shows that the enhancement effects of the 180° walls are larger than the degrading effects such as those due to small radiating areas.

A somewhat similar arrangement for enhancing SHG in quartz where $l_c < l$ was described earlier[1,9] and consists of stacking crystal plates in such a way so as to produce the effects shown in Fig. 1 and described in the text.

PREPARATION

Since no method of preparing samples suitable for the present experiments has been given in the literature, the techniques employed to produce the crystals will be described in some detail. Clear, undoped crystal plates of the order of 2×10^{-2} cm thick (grown by the Remeika method[13]) with clean smooth surfaces were selected and then etched in concentrated H₃PO₄ at 155°C sufficiently long to reduce the sample thickness by at least 5×10^{-3} cm. The samples were then rinsed in water, alcohol, and dc poled in distilled water with platinum electrodes. After poling, the specimens were examined with a polarizing microscope and only those samples which had large, unstrained c-domain areas were selected. Of these crystals, only those which had areas a millimeter or so on a side that were sufficiently plane parallel to give a few interference fringes with visible monochromatic light were used. These selected crystals were then cleaved, or broken, with a razor blade such that with much patience and some luck one obtained a c-domain

sample, rectangular in shape, several millimeters on a side, with the sides parallel to the a axes. Then air-drying silver-paste electrodes were painted on the more perfect two opposite edges and dc fields of a few kV/cm were applied to pole the sample a domain. The poling process was monitored with a polarizing microscope and the process usually hastened by heating the sample with a focused light beam to a temperature below but near the Curie temperature. When the poling process was complete, the light and field were removed and the resultant a-domain sample examined. At this point, the samples would in most cases be without antiparallel domains. If a few antiparallel domains did appear, they were usually readily eliminated with fields of a few hundred volts per centimeter. In the studies of SHG, a field of this magnitude was always kept on the sample while under investigation to insure that no antiparallel domains were present. However, even under these conditions, both twinning and antiparallel domains usually occur at temperatures above approximately 110°C. For this reason, coupled with the fact that going through the Curie temperature is frequently a destructive operation, almost all the studies were made at temperatures less than about 110°C. There was no indication that these a-domain samples were unstable, i.e., over periods of months, no changes in the domain structure were observed.

SHG STUDIES

Figure 2 shows a schematic drawing of the essential components of the experimental arrangement for studying SHG in BaTiO₃. For ease of analysis of the data, a careful alignment was made so that the polarization of the laser beam was in the xz plane of the crystal and at 45° to the x and z crystalline axes. Table I gives the nonlinear coefficients d_{ij} involved in SHG as determined from Eq. (1) for various orientations of the polarizer and analyzer with respect to the crystal z axis. As seen in the table, special orientations of the polarizing elements enable one to observe separately SHG from each of the three nonlinear coefficients. The polarizing elements in Fig. 2 are set to observe SHG due to d_{15}.
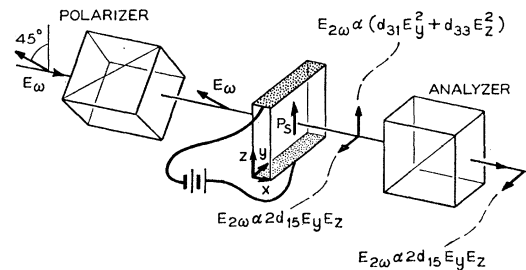
To make quantitative comparisons between nonlinear

FIG. 2. Schematic drawing showing the orientation of the BaTiO₃ sample with respect to the maser beam. The polarizing elements are set to measure the second harmonic due to d_{15}. The electric field is applied to insure that the sample remains single domain.

[12] H. L. Stadler and P. J. Zachmanidis, J. Appl. Phys. 34, 3255 (1963).
[13] J. P. Remeika, J. Am. Chem. Soc. 76, 940 (1954).

coefficients, it is necessary to consider the interference effects that occur between the second-harmonic forced wave produced by the maser beam, and the free second-harmonic light wave produced at the surface of the crystal. As mentioned in an earlier section, this interference effect, which was first demonstrated in quartz,[14] produces a second-harmonic wave whose amplitude varies in a periodic manner along the beam direction from essentially zero to some maximum value. For d_{33} in BaTiO₃ and a crystal of thickness l, the second-harmonic intensity, I_{33} generated by the fundamental intensity I_1 is given by

$$I_{33} \propto I_1{}^2 f(n) d_{33}{}^2 l_{33}{}^2 \sin^2(\pi l/2l_{33}), \qquad (8)$$

where $f(n)$ is a function of the indices of refraction, and l_{33} is the coherence length. The function $f(n)$ is given by

$$f(n) = \frac{n_2}{(n_1+1)^3(n_2+1)^3(n_1+n_2)}. \qquad (9)$$

In Eq. (8), the intensities are those measured outside of the crystal. Sufficient data on the indices of refraction of BaTiO₃ are not available to calculate the coherence length from Eq. (5) so that it must be determined experimentally from the data. The second-harmonic intensity is observed as the crystal is rotated about the z axis and then plotted as a function of angle. This rotation changes the path length of the beam in the crystal so that the periodic variation of the second harmonic is observed. These data on the angular dependence of I_{ij} are then used to determine l_{ij}, and are extrapolated to normal incidence to obtain relative values of d_{ij}. Room temperature determinations of d_{ij} and l_{ij} were given earlier,[6] but are also given here in Table II.

The temperature variation of the nonlinear coefficients is calculated from observations of the second harmonic intensity versus temperature. Figure 3 shows some of the data for the coefficient d_{31}. The oscillations present in the data occur due to changes in the magnitude of l_{31} through the temperature dependence of n_2-n_1.[6] Data on both the angular and temperature dependence of the second-harmonic intensity are required to determine directly the direction in which l_{ij}

TABLE I. Orientations of polarizer and analyzer to determine nonlinear coefficients in BaTiO₃.[a]

Polarizer	Analyzer	Nonlinear coefficient
0°	0°	d_{33}
90°	0°	d_{31}
90°	90°	none
45°	0°	d_{33} and d_{31}
45°	90°	d_{15}

[a] The angles are between the transmission direction of the electric field in the polarizing element and the z axis in the crystal.

[14] P. D. Maker, R. W. Terhune, M. Nisenoff, and C. M. Savage, Phys. Rev. Letters 8, 21 (1962).

TABLE II. Room temperature BaTiO₃ nonlinear coefficients and coherence lengths.

d_{ij}[a]	l_{ij}
$d_{15}=35\pm3$	$1.57\pm0.12\,\mu$
$d_{31}=37\pm3$	$2.90\pm0.14\,\mu$
$d_{33}=14\pm1$	$2.07\pm0.04\,\mu$

[a] The d_{ij} are relative to d_{36} for KDP where $d_{36}=1.00$.

changes with temperature. For example, in the case of d_{15}, it is found that $dI_{15}/d\theta$ is negative when dI_{15}/dT is positive so that l_{15} must be increasing with temperature. Similar considerations show that l_{31} and l_{33} both decrease with temperature. These experimentally determined temperature dependences for l_{ij} are in the direction one would predict from the limited data on the optical properties of the negative uniaxial BaTiO₃ crystal. The published data[2] show that the index of refraction for the ordinary ray is temperature-independent while the index of refraction of the extraordinary ray increases with temperature and becomes equal to the ordinary index of refraction at the transition temperature.

Since $f(n)$ in Eq. (9) is very nearly temperature-independent, the temperature variation of the amplitude of the maxima shown in Fig. 3 arises from changes in l_{31} and d_{31}. Since l_{31} is known from the room temperature data on the angular dependence of the second harmonic intensity, and each oscillation of the second harmonic shown in Fig. 3 represents the introduction of two additional coherence lengths, l_{31} can be determined as a function of temperature. The temperature variation of d_{31} can then be calculated from Eq. (8). Figure 4 shows data obtained in the manner just described on the temperature variation of each of the nonlinear coefficients for BaTiO₃. The relative values of d_{ij} were computed at the intensity maxima and are normalized so
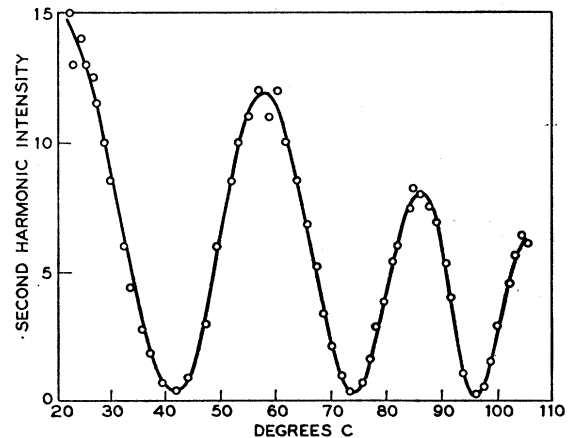

FIG. 3. Second harmonic intensity due to d_{31} as a function of temperature. The oscillations are due to changes in the indices of refraction with temperature. These data are used to calculate the temperature dependence of the nonlinear coefficient.
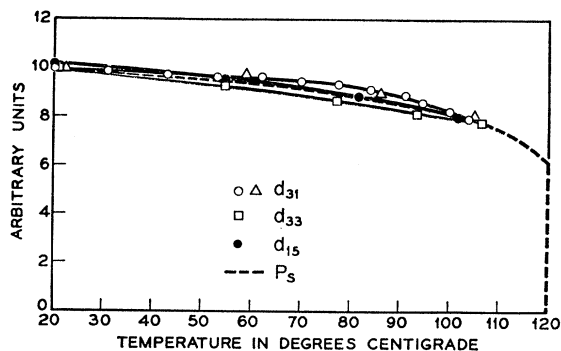
FIG. 4. The temperature dependence of the three nonlinear coefficients in $BaTiO_3$. All three have been normalized to 10 at 20°C. Within the experimental uncertainties of the measurements, all three coefficients vary with temperature as the spontaneous polarization which is also plotted in the figure and normalized to 10 at 20°C. The experimental points were calculated from the maxima of the second-harmonic intensity versus temperature data similar to that shown in Fig. 3.

that they all equal 10 at room temperature. All three coefficients were measured as a function of temperature with a crystal 2.48×10^{-2} cm thick, and in addition d_{31} was also measured with a second crystal 6.25×10^{-3} cm thick. In the case of the coefficient d_{15}, the curve shown in Fig. 4 is an average of six temperature runs. Although not shown in Fig. 4, it has been found that the d_{ij} decrease to zero discontinuously at the temperature where the crystal goes through a first-order phase transition from a ferroelectric phase into a nonpiezo-electric phase.[2] The discontinuous decrease of the second-harmonic intensity at the phase transition is consistent with the first-order phase transition. The temperature dependence of the spontaneous polariza-tion of $BaTiO_3$ (26 $\mu C/cm^2$ at 300°K) normalized to 10 at room temperature, is also shown in Fig. 4. Note that all d_{ij} vary with temperature within a few percent of each other and P_s. The temperature dependence of the d's will be discussed in the next section.

DISCUSSION

Attempts to describe the temperature dependence of the d_{ij}'s given in Fig. 4 in terms of $P_s(T)n$ show that $n=1$ results in the best over-all fit to the data. Empirical fits more "accurate" than that given by $d_{ij}(T) \propto P_s(T)$ can be obtained for d_{31} and d_{33}, however, these fits are in some cases not physically significant, e.g., d_{ij} does not go to zero as P_s goes to zero, and furthermore com-plicated empirical fits would not seem justified at this stage since within the experimental uncertainties of the measurements $d_{ij}(T)$ and $P_s(T)$ have the same temperature dependence. Therefore, the temperature dependence of each of the three nonlinear coefficients for $BaTiO_3$ from 20°C to about 105°C can be described by

$$d_{ij}(T) = \alpha_{ij} P_s(T) \qquad (10)$$

in which $P_s(T)$ is the temperature-dependent spon-taneous polarization, and α_{ij} is independent of tempera-ture. The question arises as to the significance of Eq. (10). At first glance there may be some objection to trying to describe a purely optical property such as d_{ij} in terms of P_s which is a dc or at most a low-frequency characteristic. However, there is at least one purely optical quantity whose temperature dependence is described by some power of P_s. Namely, in $BaTiO_3$ the birefringence is proportional to P_s^2.[15] Also in KDP, the temperature dependence of the change in birefringence consequent on passing through the ferroelectric phase transition is proportional to P_s^2.[16] Therefore, at this point one can say that it may not be simply fortuitous that Eq. (10) describes the temperature dependence of the d_{ij}.

There are few other data with which one can compare the present results or test the general validity of Eq. (10). SHG studies of KDP both above and below the Curie temperature, 123°K, have been described in two recent publications.[5,7] Since SHG occurs in KDP both above and below the Curie temperature (it is piezoelec-tric in both phases) the temperature dependence of SHG in KDP will be different from that of $BaTiO_3$. The onset of ferroelectricity in KDP involves a phase change from the point symmetry D_{2d} for the paraelectric form, to the point symmetry C_{2v} for the ferroelectric phase. This lowering of the crystal symmetry results in the introduction of one nonlinear coefficient, d_{33}, not present in the paraelectric phase. Therefore, the temperature dependence of d_{33} will be different from that of the coefficients which are also present in the high-temperature phase. If it turns out that Eq. (10) does indeed have some general validity, it would be reason-able to propose that the temperature dependence of the nonlinear coefficients for a ferroelectric crystal which is piezoelectric in the paraelectric phase, such as KDP, is given by

$$d_{ij}(T) = d_{ij}^0 + \alpha_{ij} P_s(T), \qquad (11)$$

where d_{ij}^0 is a temperature-independent nonlinear coef-ficient characteristic of the paraelectric phase. The change in the nonlinear coefficient in going through the phase change is described by $\alpha_{ij} P_s(T)$. For the new coefficient, d_{33}, which appears when the crystals be-comes ferroelectric, $d_{33}^0 = 0$.

Himbarger and Bjorkstam[7] observe no significant change in the second-harmonic intensity from KDP in going from room temperature, through the phase transi-tion, to 80°K. The data, which were obtained with a 0° ruby rod and therefore not a highly polarized maser beam, indicate that any discontinuity in the coefficients at the transition temperature is small. In terms of Eq. (11), these data would imply that $d_{ij}^0 \gg \alpha_{ij} P_s$ except for d_{33} and also that $d_{33} \ll$ all other d_{ij}. The coefficient d_{33}

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is reported by van der Ziel and Bloembergen[5] to be at least an order of magnitude smaller than the coefficients in the paraelectric phase. However, in disagreement with the data of Himbarger and Bjorkstam, van der Ziel and Bloembergen find that the nonlinear coefficients which are present in both phases change by factors ranging from about 3 to 0.2 as the crystal symmetry is lowered. Furthermore, except for the change in these coefficients at the phase transition, they are temperature-independent. The temperature dependence of d_{33} has not been determined. The discrepancy between the results of these two investigations on KDP could be due to effects arising from antiparallel ferroelectric domains; however, both groups were clearly aware of this complication. Discontinuities in the coefficients at the Curie temperature coupled with temperature-independent coefficients in the ferroelectric phase as reported by van der Ziel and Bloemberger are not consistent with Eq. (11).

Kleinman[17] has used a thermodynamic approach to show that if SHG arises from a nondispersive, nonlossy process, e.g., a high-frequency electronic mechanism, symmetry in addition to that required by the point group of the crystal will appear in the tensor which describes the second-order polarization coefficients. Data[6,18,19] on the Kleinman symmetry condition in a wide variety of crystals show that the additional symmetry is indeed present in the second-order polarization tensors. This symmetry condition requires for BaTiO₃ that $d_{15}=d_{31}$. As is evident in Table I, this condition is satisfied at room temperature within the approximately $\pm 10\%$ experimental uncertainties. The data shown in Fig. 4 demonstrate that the Kleinman symmetry condition is also satisfied over the entire measured temperature range.

A phenomenological theory[2] of ferroelectricity in which the Helmholtz free energy is expressed as a power series in the polarization has been quite successful, especially in the case of BaTiO₃ (Devonshire's theory), in explaining much experimental ferroelectric data. The validity of the Kleinman symmetry condition mentioned above, and the more general symmetry relations for nonlinear optical effects in lossless media derived using energy considerations by Pershan[20] both suggest that it may prove fruitful to extend the ferroelectric thermodynamic approach into the optical

region. This approach would give $d_{ij}(T)$ expressed as a power series in P_s with the coefficients of the various terms determined from the free-energy expression for the paraelectric phase. For BaTiO₃ only odd powers of P_s will occur in d_{ij}, while d_{ij} for KDP will involve all powers of P_s. Therefore Eq. (10) includes only the first term for BaTiO₃, and Eq. (11) the first two terms for KDP. However, dispersion does occur between the present optical frequencies and the frequencies at which the various coefficients in the free-energy expression have been determined. Therefore, coefficients for the free-energy expression at optical frequencies as well as clarification of the KDP second harmonic data and/or additional SHG measurements with other ferroelectric crystals are required before the full significance of Eqs. (10) and (11) can be ascertained.

Another phenomenon which will be discussed briefly is the possible effect on the SHG due to a temperature dependence of the absorption edge in the BaTiO₃ crystals. As the crystal is warmed, the absorption edge, about 4000 Å at room temperature, shifts to slightly longer wavelengths.[21] It has been suggested[22,23] that the efficiency of SHG should increase as the second-harmonic wavelength approaches that of the absorption edge; however, to date, no data supporting this suggestion have been presented. In fact, data[6] on SHG in CdS show that d does not change significantly when the absorption edge is moved thermally through the frequency of the second harmonic. In any event, this edge effect would if anything give an increasing d_{ij} with temperature, which is opposite to what is observed. Therefore, if the proximity of the edge to the second-harmonic frequency is affecting the temperature dependence of the present data, it is being dominated by a still larger effect which results in d_{ij} which decrease with increasing temperature.

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