Temperature Dependence of Optical Harmonic Generation in KDP and ADP Crystals*

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The temperature dependence of optical harmonics excited by a ruby laser in potassium and ammonium dihydrogen phosphate was investigated from 370°C down to the Curie temperatures. Both focused and unfocused laser beams were employed. The second harmonic intensity decreases slowly with decreasing temperature when a focused laser beam is employed. For an unfocused laser beam the second-harmonic intensity suffers a sharp decrease due to the destruction of the phase matching condition with changes in temperature. For KDP the phase matching angle was found to be a linear function of the temperature and no significant temperature dependence of the second-harmonic intensity was noted when the phase matching condition was satisfied. The temperature dependence of the second-harmonic generation may be explained in terms of the temperature dependence of the optical indices of refraction.

INTRODUCTION

WITH the advent of intense monochromatic light beams from optical masers, the possibility of observing nonlinear optical effects in matter became a reality. The observation of the second harmonic of the ruby laser line at $\lambda=6943$Å generated in crystalline quartz was first reported by Franken *et al.*[1] Since that time there have been several other investigations concerned with the experimental[2–7] and theoretical[8–14] study of the generation of optical harmonics. With the exception of the work of Bass[2] who found that no second harmonic is generated in triglycine sulfate when the crystal is heated to above its Curie temperature ($\sim$50°C) there seems to have been no experimental study of the temperature dependence of the generation of second harmonics, and it was thought to be worthwhile to undertake such an investigation. Since this work was started the theory of optical harmonics has become available.[8–14] Whereas the theoretical expressions do not give an explicit temperature dependence, such a dependence is contained implicitly through the dielectric constant of the material.[14]

This paper reports the experimental study of the temperature dependence of the generation of the second harmonic in potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) crystals. The results of this study are in qualitative agreement with the theoretical prediction.[12,14]

EXPERIMENTAL

A diagram of the experimental apparatus is shown in Fig. 1. The ruby laser consisted of an 0.05% Cr^{3+}-doped 90° c-axis ruby rod mounted on the axis of a GE FT-524 flash tube. The flash tube was fired with input energies of about 3200 J. The experiment was performed using a 15-mm focal length f:3 microscope objective to focus the laser beam in the crystal sample and also using a collimated laser beam without a focusing lens. For the collimated beam, a goniometer type arrangement was employed in order to facilitate the positioning of the crystal sample to obtain index matching.[3,4]

The KDP and ADP crystals used in this experiment were grown from an aqueous solution and only those crystals possessing the required optical quality and c-axis orientation were used. The crystals were mounted with their (101) face approximately perpendicular to the direction of the incident laser beam and their posi-

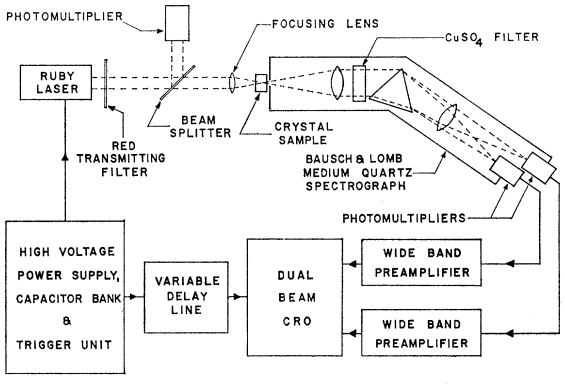

FIG. 1. Diagram of the experimental arrangement used for simultaneously detecting the fundamental and second-harmonic light pulses of the ruby R_1 line. The experiments were also performed with collimated light, without the focusing lens.

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[1] P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, Phys. Rev. Letters **7**, 118 (1961).
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[10] N. Bloembergen, Proc. IEEE **51**, 124 (1963).
[11] D. A. Kleinman, Phys. Rev. **125**, 87 (1962).
[12] D. A. Kleinman, Phys. Rev. **128**, 1761 (1962).
[13] R. Braunstein, Phys. Rev. **125**, 475 (1962).
[14] R. Loudon, Proc. Phys. Soc. (London) **80**, 952 (1962).

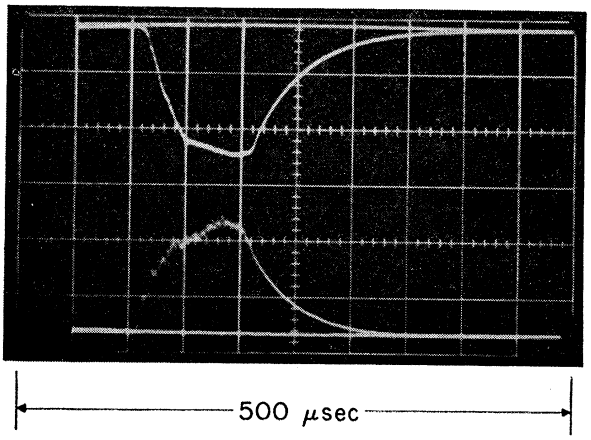

FIG. 2. Typical oscilloscope display as detected by the two photomultiplier tubes near the focal plane of the spectrograph. The upper trace shows the inverted fundamental pulse and the lower trace the second harmonic. Time increases from left to right.

tions were adjusted so as to maximize the second-harmonic signal.[3,4] The direction of polarization of the laser beam had to be perpendicular to the c axis of the crystal sample in order to generate the second harmonic, in accord with the findings of Savage and Miller.[7]

The crystals were clamped to the end of a $\frac{3}{8}$-in. copper rod. By changing the temperature of the copper rod the crystal could be either cooled or heated by conduction. A heating coil was wrapped around the copper rod and provision was made to immerse most of the rod in liquid nitrogen. In this way the temperature of the sample could be varied over a range of about 300°C. The temperature of the crystal was monitored by a thermocouple inserted in the copper rod near the crystal. To prevent the condensation of atmospheric water vapor on the crystal when it was cooled to low temperature the end of the rod on which the crystal was mounted was placed inside an evacuated fused quartz tube.

The crystal sample was placed at the slit of a Bausch and Lomb medium quartz spectrograph which was used to spatially separate the red and blue light beams. The fundamental and second-harmonic light pulses were detected by separate photomultiplier tubes placed behind the focal plane of the spectrograph. A filter composed of an aqueous solution of $CuSO_4$ was placed behind the collimating lens in order to attenuate the red light while transmitting most of the blue light. The concentration of the $CuSO_4$ solution was chosen such that red light scattered in the spectrograph could not be detected by that photomultiplier tube which measured the second harmonic radiation even for the highest gain settings on the preamplifier. The output signals from the two photomultiplier tubes were fed into identical wide-band (dc to 30 Mc/sec) preamplifiers and were then displayed on a Tektronix 555 dual beam oscilloscope. A low-voltage signal from the trigger pulse used to fire the laser was passed through a variable delay line and then triggered the sweep of the oscilloscope. Delay times of approximately 300 μsec were required in order to observe the photomultiplier pulses on the oscilloscope. A typical oscillogram is shown in Fig. 2.

It is important to note that the shape of the laser pulse is drastically changed upon passing through the $CuSO_4$ filter. The effect of this is shown in Fig. 3 which shows the same laser pulse (R_1 line) before and after transmission through the filter. The upper, inverted, trace shows the laser pulse reflected by the beam splitter without having passed through the filter and the lower trace shows the pulse as transmitted by the spectrograph and filter combination. The pulse shapes shown in Fig. 3 are interchanged when the filter is placed in the beam picked off by the beam splitter so that the distortion of the pulse shape is solely due to the passage through the filter, with the distortion contributed by the spectrograph being quite negligible. In this experiment, therefore, the distortions in the pulse shapes caused by the filter and spectrograph elements are assumed to be the same for the first- and second-harmonic pulses since these two light pulses followed the same optical path through the system. In the work of Savage and Miller,[7] the pulse shapes of the first and second harmonics are quite different. A quantitative comparison of these different pulse shapes would appear to be quite difficult in their case.

Oscillograms of the type shown in Fig. 2 were obtained for various temperatures of the crystal sample above the Curie point. No results can be reported for temperatures below the Curie point since there is a drastic change in the transparency of the crystals at the transition temperature rendering the crystals opaque.[15,16] The application of an electric field along

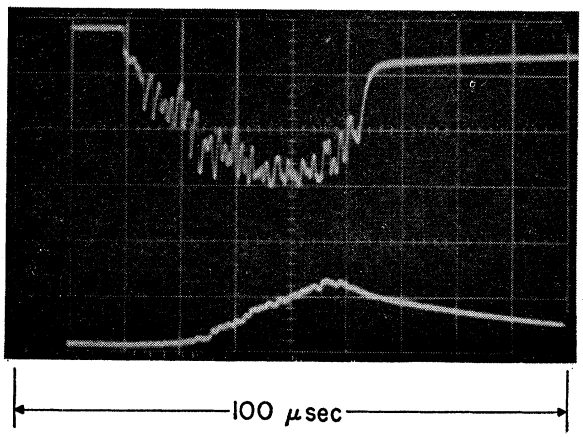

FIG. 3. Distortion of the ruby R_1 line caused by a $CuSO_4$ aqueous solution filter. The upper trace shows the laser pulse as reflected by the beam splitter while the lower trace displays the same pulse after having passed through the $CuSO_4$ filter and the spectrograph. Time increases from left to right.

[15] W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 98.
[16] A. R. Ubbelohde and I. Woodward, Proc. Roy. Soc. (London) **A188**, 358 (1946).

the c axis of the crystal could be used to eliminate the domain structure below the Curie point. To do this would require extensive modification of our apparatus and, therefore, we restricted the investigation to temperatures above the Curie point.[17] Moreover, it was found that the ADP crystals shattered at a temperature of approximately $-125°C$.[18]

The voltage amplitudes at various points along the pulse from the photomultiplier tube are directly proportional to the instantaneous power levels in the light beam impinging on the photocathode. Measurements were made of the pulse heights corresponding to the same instant of time along the decay portions of the first- and second-harmonic pulses. A plot of $\ln P_2^{1/2}$ versus $\ln P_1$, where P_1 and P_2 are the instantaneous power levels in the first- and second-harmonic pulses, yielded a straight line over the decay portions of single pulses in agreement with theory.[19]

As expected the slopes of these straight lines remained constant, independent of the temperature of the crystal. For a given power level P_1 on the decay portion of the first-harmonic pulse the corresponding power level P_2 was measured on the second-harmonic pulse for various crystal temperatures. The results of these measurements are shown in Fig. 4 which shows the temperature dependence of the power level of the second harmonic of the ruby R_1 line generated in ADP using a focused laser beam. The crystal sample was positioned such that index matching was obtained at room temperature and the orientation of the crystal was not changed as the temperature was varied. Measurements were also made using a collimated laser beam. It was found that for a collimated laser beam the matching angle was more sharply defined than when a focusing lens was used[20] and that this angle varied as a function of the crystal temperature. For a given temperature the crystal was then rotated about an axis perpendicular to the direction of the laser beam and the c axis of the crystal sample and the power level of the second harmonic was found to pass through a maximum as the crystal was rotated. By measuring the angular positions of the crystal for which these maxima occurred the change in the matching angle as a function of temperature was found. The results are shown in Fig. 5 for both KDP and ADP crystal samples. Over the temperature range that has been covered in this experiment the change in the matching angle with temperature seems to obey a linear relationship for KDP. The temperature gradient of the matching angle for KDP is, thus, found to be 0.0128 deg/°K. For ADP the change in the matching angle is more than twice as great as for KDP and its nonlinear behavior is depicted in Fig. 5.

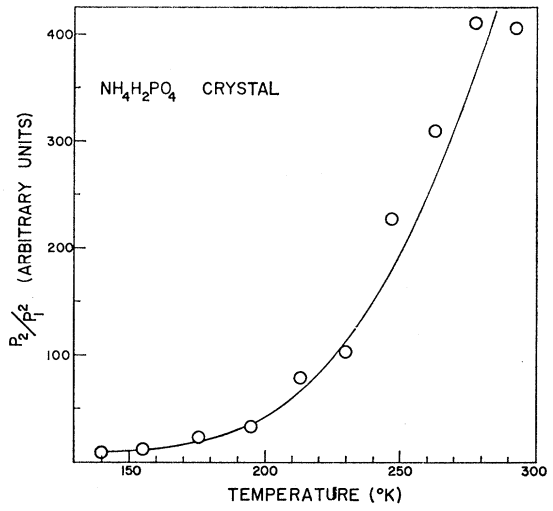

FIG. 4. Second harmonic output in ADP as a function of temperature. The crystal was illuminated with a focused laser beam and the angular orientation was held fixed. The temperature of the copper rod near the crystal sample was measured, not the actual temperature of the crystal sample. This accounts for the point on the graph at 140°K which is below the Curie temperature at 148°K.

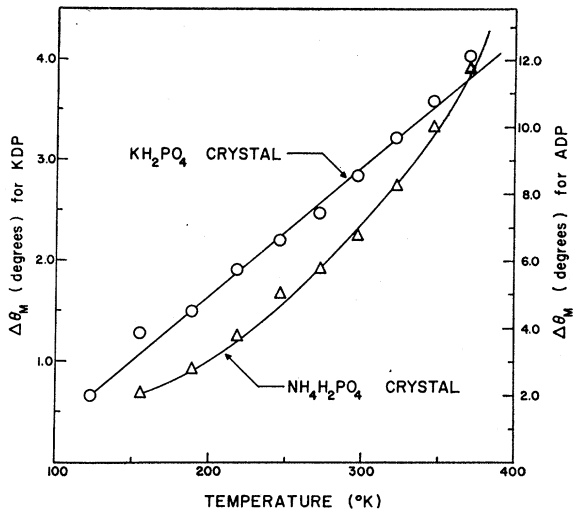

FIG. 5. Temperature dependence of the phase matching angle in KDP and ADP.

DISCUSSION

The theory of second-harmonic generation has been presented by several authors.[8–14] In the treatment given by Kleinman,[12] the expression for the intensity of the second harmonic inside a KDP crystal is given by[21] Eq. (1)

$$S = S_L^2 (32\pi^3\omega^2 l^2/c^3 n_0^3) d_{36}^2 \sin^2\theta_M F(\beta l\Delta), \qquad (1)$$

[17] During the course of revising this paper the work of J. van der Ziel and N. Bloembergen, Bull. Am. Phys. Soc. 8, 380 (1963) has come to our attention. These authors have been able to study the temperature effect below the Curie point by applying an electric field to the crystal.

[18] W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics* (D. VanNostrand, Inc., New York, 1950), pp. 147–148.

[19] See Ref. 12, Eq. (123).

[20] R. C. Miller and A. Savage, Phys. Rev. **128**, 2175 (1962), see Fig. 3.

[21] See Eq. (123) of Ref. 12.

where S_L is the laser intensity inside the crystal and the function $F(\beta l\Delta)$ is defined as

$$F(\beta l\Delta)=\langle(\sin^2\psi)/\psi^2\rangle, \quad (2)$$

where the brackets $\langle\ \rangle$ indicate an average over the narrow pencil of waves contained in the laser beam. The quantity ψ is given as

$$\psi=(\omega/2c)(n'\mathbf{s}_k-n\mathbf{s})\cdot\mathbf{r}, \quad (3)$$

where n' is the effective index of refraction of the polarization wave at the second-harmonic frequency and n is the refractive index for a wave freely propagating in the medium with frequency ω. For phase matching of the second-order polarization vector and the second-harmonic light wave vector the quantity ψ approaches zero and the factor $F(\beta l\Delta)$ in Eq. (1) tends toward unity. While Eq. (1) is strictly applicable only to the interior of the crystal, Kleinman has shown that it may also be used to relate the intensities of the laser beam and the second-harmonic radiation outside the crystal. An expression entirely equivalent to Eq. (1) has also been derived by Loudon.[14]

From Eq. (1) it is seen that there are three principal factors that are temperature-dependent, namely, $1/n_0^3$, where n_0 is the matching index of refraction, $\sin^2\theta_M$, where θ_M is the phase matching angle, and the function $F(\beta l\Delta)$. All three factors depend on the temperature through the indices of refraction. The third factor appears to be most sensitive to variations in the temperature since a small change in the refractive indices will not appreciably change the contributions from the factors $1/n_0^3$ and $\sin^2\theta_M$. Since the second-order polarization tensor is determined by the crystal structure the component d_{36} is assumed to be temperature-independent over the range studied in this experiment.[22]

The temperature dependence of the optical indices of refraction do not seem to have been studied over the temperature range covered in this experiment. The birefringence of KDP has been studied in the optical region as a function of temperature by Zwicker and Scherrer.[23] Their results show that the birefringence increases almost linearly as the temperature is lowered to the Curie point with a sharp drop occurring just below the Curie temperature. While the results of Zwicker and Scherrer are not directly applicable to the present problem they do suggest that the results of the present study as shown in Figs. 4 and 5 are accounted for by the temperature variation of the refractive indices at the fundamental and second-harmonic frequency. Thus, as the temperature of the KDP crystal is varied, the ordinary index at the fundamental frequency ${}_on_1$ and the extraordinary index of refraction at the second-harmonic frequency ${}_en_2$ change at different rates. This will destroy the index matching condition in the crystal as the temperature is changed. The gradual decrease in the second-harmonic output as shown in Fig. 4 is representative of a focused laser beam. The wave vectors of the fundamental light wave now possess different directions due to the focusing effect and as the index matching condition is violated for a particular direction in the crystal there are wave vectors of the fundamental light wave available to satisfy the matching condition in a new direction in the crystal. The decrease in the value of the function $F(\beta l\Delta)$ in Eq. (1) is then less rapid for a focused beam than for a collimated beam.[24] The matching angle θ_M has been expressed in terms of the refractive indices as[25]

$$\sin^2\theta_M=({}_on_1^{-2}-{}_on_2^{-2})/({}_en_2^{-2}-{}_on_2^{-2}). \quad (4)$$

The results of the measurements made with an unfocused laser beam are shown in Fig. 5 and indicate that the factor $\sin^2\theta_M$ in Eq. (1) changes only moderately with temperature. The temperature variation of the factor $1/n_0^3$ is expected to cause a moderate decrease in the intensity of the second harmonic as the temperature of the crystal is lowered to its Curie point. For temperatures above the Curie point, therefore, the effect of temperature changes upon the generation of second harmonics is then principally governed by the behavior of the function $F(\beta l\Delta)$. Attempts were made to make a quantitative study of the intensity of the second-harmonic output over the whole temperature range with an unfocused beam. These attempts were not successful since significant variations in the wave form of the laser pulse occurred during the course of the experiment.

ACKNOWLEDGMENTS

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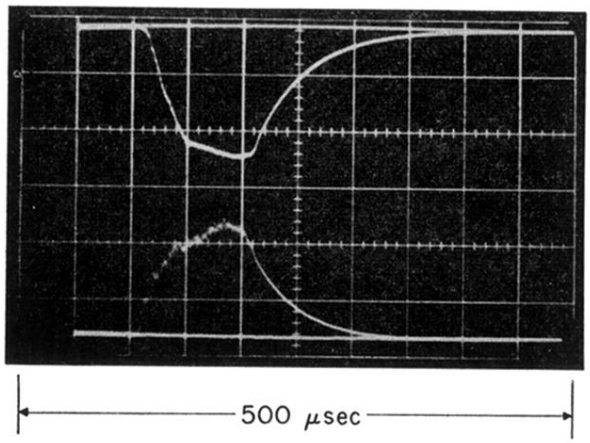
[22] This conjecture has been verified by the work of van der Ziel and Bloembergen, Ref. 17.

[23] B. Zwicker and P. Scherrer, Helv. Phys. Acta **17**, 346 (1944).

[24] Kleinman, Ref. 12, Sec. VIII gives a detailed discussion of second-harmonic generation in an isotropic medium when using focused beams.

[25] See Ref. 3 and Ref. 20, Eq. (3).



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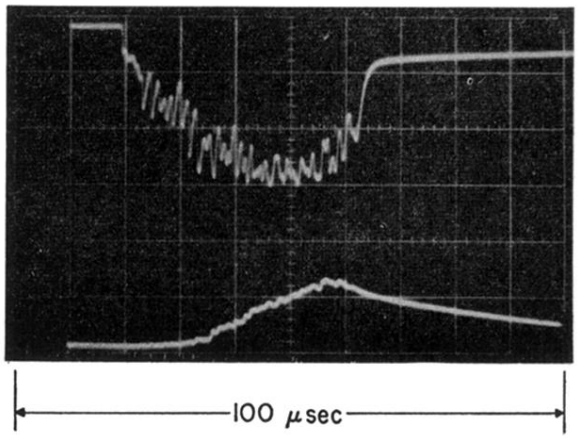

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