Harmonic Generation and Mixing of $CaWO_4:Nd^{3+}$ and Ruby Pulsed Laser Beams in Piezoelectric Crystals

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Second harmonic generation (SHG) of the $CaWO_4:Nd^{3+}$ laser line (1.0582μ) has been observed in a variety of appropriately selected crystals. The pulsed beam (of the order of 30 W) is brought to focus within the crystal under investigation, and the second harmonic (5291 Å) is detected with a photomultiplier, photographic film, or occasionally with the eye. Crystals such as $BaTiO_3$ that are transparent in the visible but which could not be studied for nonlinear effects with the ruby laser due to absorption of the ruby laser second harmonic (3467 Å) can be conveniently investigated as harmonic generators using the $CaWO_4:Nd^{3+}$ laser. Ruby and $CaWO_4:Nd^{3+}$ laser beams have been mixed successfully in a number of crystals producing the sum frequency (4189 Å). In the geometry used, the two laser beams were made parallel to each other with a half-silvered mirror, and then brought to focus in the sample under investigation. In both the harmonic generation and the mixing experiments, potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) were the most efficient nonlinear crystals investigated. The crystallographic directions in KDP and ADP which give velocity matching of the second-order polarization wave and the corresponding light wave have been determined for SHG of the ruby and $CaWO_4:Nd^{3+}$ laser lines, as well as for mixing of these two laser lines. The SHG and mixing efficiencies are considerably enhanced when velocity matching occurs.

INTRODUCTION

MOST of the emphasis to date on the nonlinear interactions of optical maser beams with dielectric materials[1–7] has centered around the pulsed ruby laser. This is only natural since the first optical maser discovered was the ruby laser[8] and, in addition, it has provided more "monochromatic" laser output power (in the megawatt range) than that reported for other lasers currently in use. However, a number of interesting crystals cannot be investigated for nonlinear effects such as second harmonic generation (SHG) with the ruby laser (6934 Å) due to absorption within the crystal of the second harmonic light (3467 Å). One can avoid the problem of second harmonic absorption with crystals which are transparent in the visible, but opaque in the near uv, if one employs a laser operating in the vicinity of one micron. Consideration of the efficiency of frequency doubling of the ruby laser line in something like potassium dihydrogen phosphate (KDP)[4,7] shows that of the order of a fraction of a watt of pulsed optical maser power is required to produce an easily measurable second harmonic output. In this paper it will be shown that the pulsed $CaWO_4:Nd^{3+}$ laser[9] delivers sufficient power at a desirable wavelength, 1.06μ, so as to be very useful for the investigation of second harmonic generation (SHG) and other nonlinear effects in crystals which are not opaque in the visible at wavelengths longer than that of the second harmonic for this laser, namely, 5300 Å. In addition, the paper describes the mixing of two different optical masers in piezoelectric crystals. The sum frequency of the $CaWO_4:Nd^{3+}$ and ruby laser lines, 4189 Å, has been observed in a number of suitable materials.

In the case of KDP and ammonium dihydrogen phosphate (ADP), SHG, as well as mixing of the two lasers, have been studied as a function of crystal orientation. In particular, for these two materials, the crystallographic directions of the incident laser beam—or beams in the case of mixing—which give velocity matching[3,4,6] of the second-order polarization wave and the corresponding light wave have been determined. In these special directions, the nonlinear effects are greatly enhanced over those observed in other nonspecial directions.

EXPERIMENTAL

The confocal geometry[10] Nd-doped $CaWO_4$ rods were typically 5 cm long and about 0.25 cm in diameter. The cylindrical ruby rods were a standard geometry with plane parallel end faces. Each laser rod was mounted in a conventional maser head and optically pumped with an FT524 flashtube. A schematic of the experimental arrangement is shown in Fig. 1. In all the focused light experiments to be described, a 20-mm focal length lens of variable aperture was used to focus the incident light in the sample under study. For the investigation of effects due to sample orientation, the crystals (cut to near the desired orientations) were mounted on a rotatable head. In the mixing experi-

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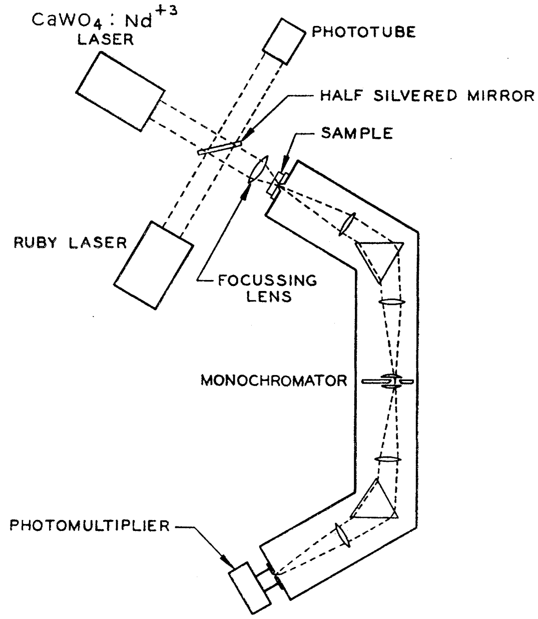

FIG. 1. Schematic drawing of experimental arrangement used for both the SHG of the $CaWO_4:Nd^{3+}$ and ruby laser lines, and the mixing of these two laser beams. The focusing lens is a 20-mm focal length lens of variable aperture. The phototube is used to detect a portion of the laser fundamental which is then compared with the nonlinear signal output on a dual beam oscilloscope.

ments, the two lasers are fired simultaneously and the beams made parallel to each other with a half-silvered mirror. The output signal is separated from the laser beam—or beams—and other unwanted light by a fast ($f/4.5$) double quartz prism monochromator and then detected with either a photomultiplier, photographic film, or with the eye.

RESULTS AND DISCUSSION

Frequency Doubling of the $CaWO_4:Nd^{3+}$ Laser Line

Figure 2 illustrates SHG in KDP generated by a focused ($f/2$) $CaWO_4:Nd^{3+}$ laser beam. The second harmonic and laser outputs are shown for three different oscilloscope sweep speeds. Careful inspection of these data shows that the second harmonic outputs are not consistently proportional to the square of the incident laser intensity. This must mean that either the coherence properties of the laser beam, and/or the direction of the laser beam, differ from one spike to another. A typical laser output of about 30 W is obtained with about 700-J input to the flash tube. In ADP, this level of laser power incident on the crystal in the [110] direction, produces of the order of 5×10^6 second harmonic photons, or of the order of 10^{-8} W. The second harmonic output of this magnitude is easy to detect with the eye and to photograph in color. When the sample is viewed directly with the unaided eye (through suitable filters to absorb the laser beam), the second harmonic light appears as a small, very bright, green flash.

Frequency doubling of the $CaWO_4:Nd^{3+}$ laser line in KDP has been observed with the laser operated at room temperature as well as at about 77°K. In general, at room temperature one or two lines (1.0582μ and 1.0652μ) may be present in the beam, while at 77°K, as many as five laser lines may appear.[9] Direct frequency measurements of the line or lines present in the $CaWO_4:Nd^{3+}$ laser beams employed in these experiments were not made. However, measurements on high resolution equipment of the wavelength of the second harmonic output observed with the laser operated at room temperature show that in this particular case, the second harmonic arises from the 1.0582μ line. The spectrum of the second harmonic observed when the laser is operated at about 77°K has not been investigated. It may prove possible to mix the various lines within the $CaWO_4:Nd^{3+}$ laser beam; however, this

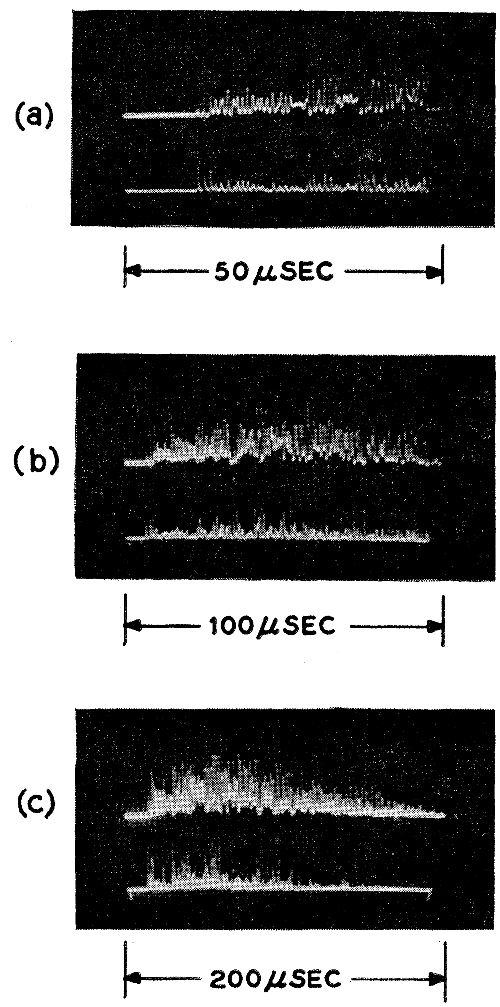

FIG. 2. Second harmonic generation of the $CaWO_4:Nd^{3+}$ laser beam in KDP. In each frame, the upper trace shows the fundamental, and the lower trace the second harmonic.

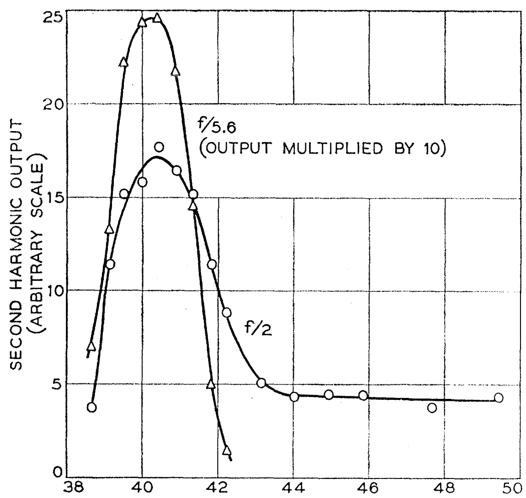

FIG. 3. Second harmonic output of the $CaWO_4{:}Nd^{3+}$ laser beam in KDP as a function of the angle θ between the optic axis in the crystal and the focused laser light cone. The value of θ at the intensity maximum is seen to be the same for the $f/2$ focusing lens as for the same lens stopped down to $f/5.6$.

mixing has not as yet been observed. *Note added in proof.* In a recent experiment with a $CaWO_4{:}Nd^{+3}$ laser beam which contained both the 1.0582 and 1.0652μ lines mentioned above, the second harmonic of each line, as well as the mixed sum frequency (5308 Å), were observed when the laser beam was focused in an ADP crystal.

Among the materials which are opaque to the ruby laser second harmonic but which exhibited frequency doubling of the $CaWO_4{:}Nd^{3+}$ laser beam are CdS, GaP, ZnO, $PbTiO_3$, and $BaTiO_3$.

Velocity Matching of the $CaWO_4{:}Nd^{3+}$ and Ruby Laser Beams in KDP and ADP

Giordmaine[3] and Maker *et al.*,[4] who have studied SHG of the ruby laser line in KDP, have shown the importance of proper phase matching of the second-order polarization and the second harmonic light wave vectors. In particular, when the second-order polarization wave vector $\mathbf{k}_2'$ which for parallel light,

$$\mathbf{k}_2'=2\mathbf{k}_1, \tag{1}$$

where $\mathbf{k}_1$ is the wave vector of the fundamental, is equal to that of the second harmonic light wave $\mathbf{k}_2$, large coherence volumes, and therefore enhanced second harmonic outputs are obtainable. The condition that

$$\mathbf{k}_2'=\mathbf{k}_2 \tag{2}$$

requires for parallel light that the indices of refraction for the fundamental and second harmonic light waves be equal—hence, Eq. (2) is equivalent to "index" or "velocity matching." For negative uniaxial crystals, this matching is possible,[3] provided that ${}_on_1$, the ordinary index of refraction at the fundamental frequency, is greater than the ${}_en_2$, the extraordinary index of refraction at the second harmonic frequency. In the case of KDP and ADP, matching of the appropriate wave vectors is possible for both lasers considered here. As has been verified during the course of the present experiments, this matching in a negative uniaxial crystal requires that the fundamental be an ordinary ray and the second harmonic an extraordinary ray.

SHG of both the $CaWO_4{:}Nd^{3+}$ and the ruby laser beams in KDP and ADP has been measured as a function of the polar angle θ between the crystallographic optic axis, z axis, and the axis of the focused light cone. The azimuthal angle Φ between the projection of the axis of the light cone on the x, y plane and the x axis was made 45°. This value of Φ optimizes the output with respect to Φ since the second-order polarization $P_2 \propto E_xEy$. Results given in Fig. 3 show the second harmonic output of the $CaWO_4{:}Nd^{3+}$ laser beam in KDP as a function of θ. These data are shown for the $f/2$ lens and also the same lens stopped down to $f/5.6$. It is to be noted that the position of the intensity maximum θ_0 is essentially unaffected by the speed of the lens. One effect on the second harmonic output of a laser light cone of large apex angle ($\approx 19°$ for the $f/2$ data) is to increase the relative level of the second harmonic for $\theta>\theta_0$ above that observed for a less convergent beam ($\approx 7°$ for the $f/5.6$ data). This relative enhanced output for $\theta>\theta_0$ is presumably due to contributions from nonparallel rays not present in the $f/5.6$ arrangement, mixing under matching conditions. The increase in SHG near θ_0 observed with the $f/2$ lens over that observed with the $f/5.6$ lens is believed to result largely from an increase in the electric field product E_xE_y at the focus of the lens.

The quantities θ_0 determined from data similar to those described above are given in Table I. In all cases, an $f/5.6$ lens was employed; however, the value of $41.9°\pm1°$ given for the Nd laser and ADP was also obtained with an unfocused laser beam. The uncertainty in $\theta_{0\ \mathrm{exp}}$ is an estimate of the precision with which the crystallographic orientation is known. Where possible, values of θ_0 calculated from the equation[3]

$$\sin^2\theta_0=\frac{{}_on_1^{-2}-{}_on_2^{-2}}{{}_en_2^{-2}-{}_on_2^{-2}} \tag{3}$$

are also listed. The indices of refraction used to calculate θ_0 from Eq. (3) were obtained from a compilation

TABLE I. Values of the angle between the optic axis in the crystal and the direction of the laser beam for velocity matching of the second harmonic polarization and corresponding light waves in KDP and ADP.

		KDP	ADP
Ruby laser	$\theta_{0\ \mathrm{calc}}$	50.2°	51.4°
	$\theta_{0\ \mathrm{exp}}$	50.4°±1°	51.9°±1°
$CaWO_4{:}Nd^{3+}$ laser	$\theta_{0\ \mathrm{exp}}$	40.3°±1°	41.9°±1°
	${}_on_{1\ \mathrm{exp}}$	1.495	1.506

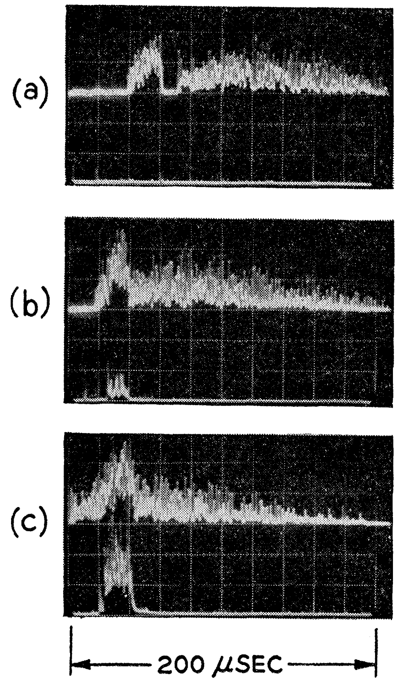

FIG. 4. Mixing of the pulsed ruby and $CaWO_4:Nd^{3+}$ laser beams in KDP. In each frame the upper trace shows the laser outputs and the lower the mixed sum frequency output at 4189 Å. In (a), the two lasers are out of phase timewise (the ruby laser pulse, approximately 20 μsec long, occurs first) and no mixed signal is generated. When the two lasers overlap timewise as in (b) and (c), a mixed signal output is observed.

(made by J. A. Giordmaine) of data from references 11–13 for KDP, and references 11 and 14 for ADP. Since sufficiently accurate values of ${}_on_1$ were not available at 1.06μ, values of ${}_on_1$ (required for later calculations) were obtained from $\theta_{0\ \mathrm{exp}}$ by means of Eq. (3). Values of θ_0 for SHG of the ruby laser line in KDP have been reported previously[3,4] and are in agreement with those given in Table I. Also, a value of θ_0 determined for the Nd glass optical maser[15] beam (centered on 1.063μ) in ADP has been obtained by Miles[16] and agrees with the present data.

Mixing of the $CaWO_4:Nd^{3+}$ and Ruby Lasers

Figure 4 shows typical data relevant to the mixing of $CaWO_4:Nd^{3+}$ and ruby laser beams in KDP. In Fig. 4(a), the two laser beams are out of phase (timewise) and no mixed signal is observed. When the two laser beams begin to overlap as shown in Fig. 4(b), a small mixed (sum frequency, 4189 Å) signal is observed. Finally, when the two beams are exactly in phase, Fig. 4(c) a large output is observed. For these data, the $CaWO_4:Nd^{3+}$ and ruby laser beams were 30 and 115 W, respectively, before reflection off the half-silvered mirror. No concernted attempt was made to optimize the mixed signal. One difficulty was that the two laser beams were not focused at exactly the same point along the direction of the beams—the $CaWO_4:Nd^{3+}$ laser beam was more divergent than the ruby beam. In any event, with the $f/2$ lens, of the order of 10^6–10^7 photons at 4189 Å could be produced in either ADP or KDP. This output is easily seen with the unaided eye at the exit of the monochromator.

The wavelength of the mixed signal has not been investigated with high-resolution equipment. However, since the $CaWO_4:Nd^{3+}$ laser was essentially the same in the mixing experiments as in the second harmonic generation experiment, we suspect that the important $CaWO_4:Nd^{3+}$ laser line is the one at 1.0582μ. Due to equipment limitations the difference frequency mixed signal at about 2μ, which should be generated with suitable materials, has not been investigated.

Mixing of these two laser beams has been carried out successfully in a number of different crystals. Among the more efficient crystals are KDP, ADP, $BaTiO_3$, and tourmaline. In both the SHG experiments and the mixing experiments, KDP and ADP were the most efficient nonlinear materials investigated.

Velocity Matching and Mixing of the Ruby and $CaWO_4:Nd^{3+}$ Laser Beams and ADP and KDP

The only case which will be considered here is that of the mixing of parallel rays in negative uniaxial crystals as illustrated in Fig. 5. Equation (1) is now

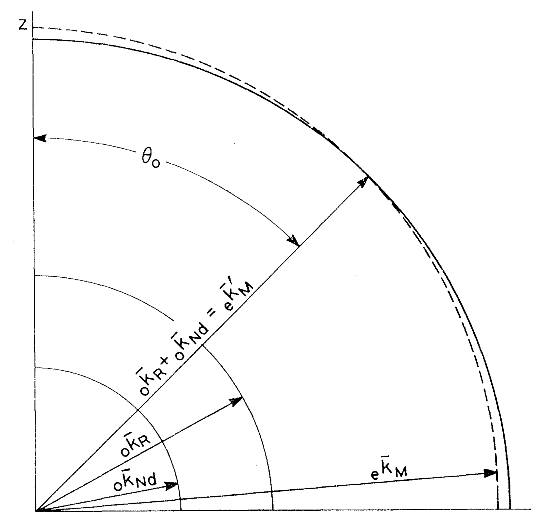

FIG. 5. Determination of the matching conditions for mixing of the ruby and $CaWO_4:Nd^{3+}$ laser beams in a negative unaxial crystal. The wave vectors ${}_o\mathbf{k}_R$ and ${}_o\mathbf{k}_{Nd}$ refer to the ruby and Nd laser fundamentals (ordinary rays), respectively. The wave vector of the mixed second-order polarization wave ${}_e\mathbf{k}_M'$ must equal that of the mixed second-order light wave (extraordinary ray) ${}_e\mathbf{k}_M$ to provide velocity matching of these two waves. For parallel laser beams, this occurs when the angle θ between the crystalline optic axis (z axis) and the direction of the fundamental laser beams, equals θ_0 as shown in the figure.

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[12] J. A. Giordmaine (private communication).
[13] *International Critical Tables of Numerical Data, Physics, Chemistry and Technology* (McGraw-Hill Book Company, Inc., New York, 1930), Vol. VII, p. 27.
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[16] P. A. Miles (private communication).

replaced by

$$ {}_{o}k_{R}+{}_{o}k_{Nd}={}_{e}k_{M}', \qquad (4)$$

where ${}_{o}k_{R}$ and ${}_{o}k_{Nd}$ refer to the propagation vectors of the ordinary ruby and $CaWO_4$:Nd^{3+} laser waves, rerespectively, and ${}_{e}k_{M}'$ refers to the extraordinary, mixed (sum frequency), second-order polarization wave. The condition for enhanced generation of the mixed signal, i.e., the velocity of the second-order polarization wave equal to that of the mixed light wave, gives

$$ {}_{e}\mathbf{k}_{M}'={}_{e}\mathbf{k}_{M}, \qquad (5)$$

where ${}_{e}\mathbf{k}_{M}$ is the propagation vector for the extraordinary, mixed, light wave. To calculate θ_0 for velocity matching in the case of mixing the laser beams, one uses the equation

$$\sin^2\theta_0=\frac{({}_{e}k_{M}'\lambda_M)^{-2}-{}_{o}n_M^{-2}}{{}_{e}n_M^{-2}-{}_{o}n_M^{-2}}, \qquad (6)$$

when ${}_{e}n_M$ and ${}_{o}n_M$ are the extraordinary and ordinary indices of refraction, respectively, at the frequency of the mixed signal $\lambda_M^{-1}=\lambda_R^{-1}+\lambda_{Nd}^{-1}$. Values of θ_0 calculated in this manner and those measured experimentally with an $f/5.6$ focusing lens are given in Table II.

As can be seen from the data in Tables I and II, the $\theta_{0\,\text{calc}}$ agree with the $\theta_{0\,\text{exp}}$ in the case of SHG as well as in the case of mixing. Although not unexpected, this agreement is especially gratifying in the case of mixing since these experiments were somewhat more complex than those encountered in SHG.

TABLE II. Calculated and experimental values of the angle between the optic axis of the crystal and the direction of the two parallel laser beams which provides matched conditions for the generation of the mixed light waves.

		KDP	ADP
Ruby and $CaWO_4$:Nd^{3+} mixed laser beams	$\theta_{0\,\text{calc}}$	42.6°	43.7°
	$\theta_{0\,\text{exp}}$	42.6°±1°	44.7°±1°

ACKNOWLEDGMENTS

The authors would like to take this opportunity to thank several of their colleagues for important contributions to certain phases of the present research: Dr. K. Nassau for the Nd-doped $CaWO_4$ laser rods, Dr. L. F. Johnson for information on their behavior, Dr. J. A. Giordmaine and Dr. D. A. Kleinman who were a constant source of inspiration and useful information throughout the research, and finally, other colleagues whose names are too numerous to mention for loans of the various lasers and other pieces of apparatus which made these experiments possible.

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Pressure Dependence of the Intrinsic Magnetization of Iron and Nickel*

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The relative change in the saturation flux, $\Delta\Phi_s/\Phi_s$, has been observed on Fe and Ni at room temperature in the range up to 11 000 kg/cm² in hydrostatic pressure. It decreases almost linearly as the pressure increases for both Fe and Ni. In the derivation of the pressure coefficient of the specific intrinsic magnetization, $\sigma_s^{-1}(\Delta\sigma_s/\Delta p)$, the demagnetizing field of the specimen was taken into consideration. The $\sigma_s^{-1}(\Delta\sigma_s/\Delta p)$ obtained is -3.04×10^{-7} (kg/cm²)$^{-1}$ for Fe and -2.38×10^{-7} (kg/cm²)$^{-1}$ for Ni.

IN a previous work,[1] the effect of hydrostatic pressure on the specific intrinsic magnetization σ_s was observed for Fe and Ni at about 6000 kg/cm² at room temperature, and for Fe it was found from the measurements at several points below 6000 kg/cm² that σ_s decreased almost linearly with increasing pressure.

This paper concerns observations of the pressure dependence of σ_s in the range up to about 11 000 kg/cm² for both Fe and Ni at room temperature, and remarks on the formula for the pressure coefficient of σ_s, $\sigma_s^{-1}(\Delta\sigma_s/\Delta p)$, in the presence of the demagnetizing field in the specimen.

The experimental procedure will be briefly described here again. The pressure is generated with the standard Bridgman press[2] with a nickel-chromium-molybdenum steel cylinder which was newly designed. The pressure-transmitting medium is petroleum ether and the pressure is determined from a change in the electrical resistance of manganin wire which is calibrated with the freezing pressure of mercury. The specimens are polycrystalline rods of Fe (99.8%) and Ni (99.8%), all 5.5 mm in diameter and 14.5 mm in length. The effect of pressure on the saturation magnetization M_s is obtained by making a measurement of the flux difference between two specimens, on one of which the pressure is applied.

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[2] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1958).

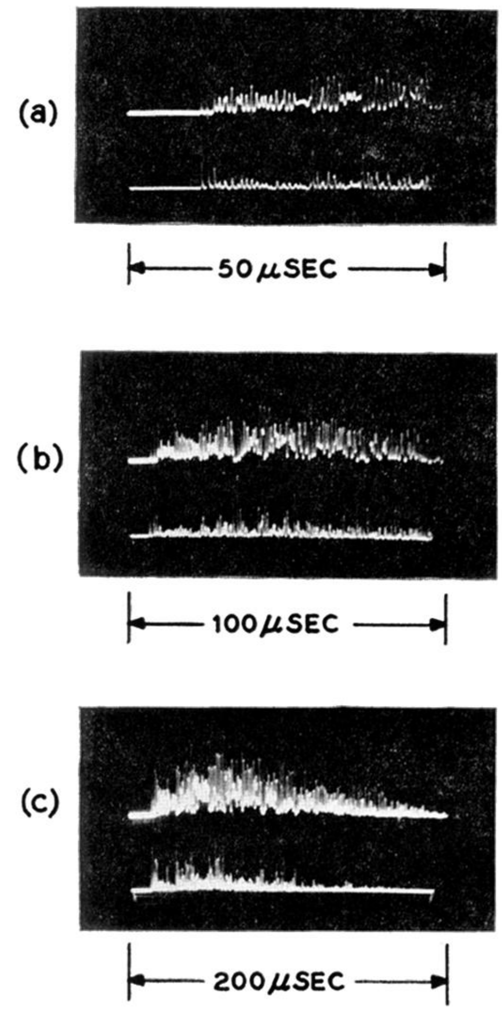

FIG. 2. Second harmonic generation of the $CaWO_4:Nd^{3+}$ laser beam in KDP. In each frame, the upper trace shows the fundamental, and the lower trace the second harmonic.

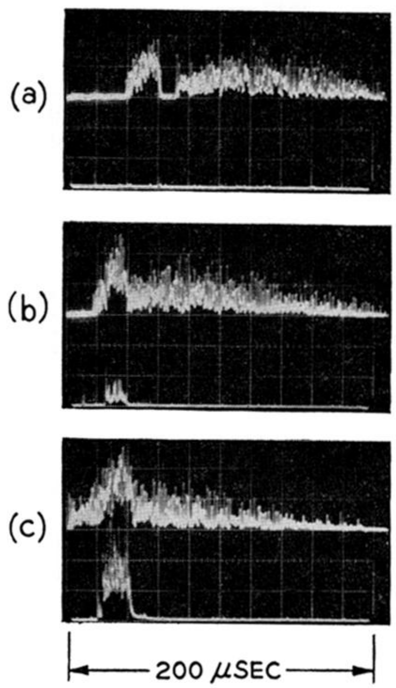

FIG. 4. Mixing of the pulsed ruby and $CaWO_4:Nd^{3+}$ laser beams in KDP. In each frame the upper trace shows the laser outputs and the lower the mixed sum frequency output at 4189 Å. In (a), the two lasers are out of phase timewise (the ruby laser pulse, approximately 20 μsec long, occurs first) and no mixed signal is generated. When the two lasers overlap timewise as in (b) and (c), a mixed signal output is observed.