teristic frequency in transient phenomena.

In case some uncertainty is felt concerning the notion of magnetic resonance at zero frequency, we may recall that use of a rotating coordinate system allows the prediction of double-resonance phenomena in terms of the properties of resonance radiation in static fields. If we study the double-resonance experiment of Brossel and Bitter[5] in this way, we find no change in the form of the resonance curves as the frequency of resonance is reduced below the radiation width of the levels. This has recently been demonstrated experimentally.[6] There is no reason to suppose that the curves at zero frequency are not identical with those at high frequencies, provided that the incident radiation excites either $|a\rangle$ or $|b\rangle$ alone, but not a superposition of them. Again, magnetic resonance at zero frequency is well known in optical pumping experiments. When the longitudinal field is reduced through zero, a signal is often obtained which is indistinguishable from an ordinary magnetic resonance signal. This is due to stray fields which provide the transverse component H_1 exactly as required in the case detailed above.

Finally, we wish to comment on the remark of Eck, Foldy, and Wieder that the anticrossing signal vanishes when one of the states, say $|a\rangle$, is nonradiative. The explanation in terms of a double-resonance experiment is that, although the perturbation still induces transitions between the states, the atoms may only decay from that state to which they were excited, so that the steady-state signal will not depend on the probability of transitions between $|b\rangle$ and $|a\rangle$. However, there may be observable transient effects. The behavior of the excited atoms in a case similar to ours has been analyzed by Lamb.[7] We may readily derive an expression for the superposition state at time t of an atom excited at $t=0$ to state $|b\rangle$. The light emitted by such an atom may be calculated in terms of the modulus squared of the electric dipole operator between the superposition state and the ground state. The result includes terms exponentially damped at a rate intermediate between γ and $\frac{1}{2}\gamma$ (depending on the magnitude of $|V|$), and also damped, modulated terms. The frequency of modulation runs from $(\Delta^2+|2V|^2)^{1/2}$ when $|2V| \gg \frac{1}{2}\gamma$ to zero when $|2V| \leq \frac{1}{2}\gamma$ and $\Delta=0$. The limiting value, $|2V|=\frac{1}{2}\gamma$, is exactly that at which the ordinary repulsion of perturbed levels gives way to crossing, as pointed out by Lamb. The study of these transients would be technically difficult, but it makes possible, in principle, the experiment ruled out by Eck, Foldy, and Wieder.

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OBSERVATION OF CONTINUOUS OPTICAL HARMONIC GENERATION WITH GAS MASERS

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Nonlinear optical effects[1] have been observed on a continuous basis for the first time. Second-harmonic generation (SHG) was observed using the 1.1526-micron transition of the He-Ne maser with a focused and unfocused beam. The efficiency of SHG is found to be strongly dependent upon the transverse mode of the fundamental and is greatest for the lowest order transverse mode (TEM_{00q}).[2-5]

With the precision made possible by operating the gas maser in the lowest order mode, we have remeasured the nonlinear second-order polarization coefficient d_{36} for potassium dihydrogen phosphate (KDP) using unfocused light having a very small beam divergence angle. We find a value of 3×10^{-9} esu which is five times greater than the highest experimental value previously obtained.[6,7] Coherence lengths at least an order of magnitude greater than those obtained by previous workers have been used. The continuous output is a convenience in detection and makes direct visual observation of the harmonic light a useful technique for optimizing crystal orientation, focus, etc. Our threshold for detection of SHG from a focused

beam with a photomultiplier input to a scope is ~50 microwatts of fundamental power. This is about three orders of magnitude more efficient than our unpublished data on SHG using a multimode cw solid-state neodymium maser.

Previous workers[1,6,8,9] used pulsed solid-state masers which produce complicated multimode patterns and which have average beam divergence angles of about 1/4°. Some investigators[10,11] have begun to appreciate the complexities of the multimode data. Franken et al.[1] in their original work recognized that the gas maser may produce a larger coherence volume. Kleinman[7] has considered the effect of the beam diffraction angle in limiting the effective coherence length. Our own data on SHG with the cw neodymium maser led us to the conclusion that the multimode output of solid-state masers degrades the conversion efficiency and obscures the interpretation of the data.

By contrast the gas maser gives a much narrower spectral linewidth, a beam which is diffraction limited and easily capable of single mode operation. For the lowest order transverse mode (TEM_{00q}) our beam has a Gaussian intensity distribution $S_1 = S_0 \exp(-2r^2/w^2)$, where $w = 0.21$ cm and is defined[2,3] as the spot size. We define the half-beam divergence angle Δ as the half-beam angle at $r = w$. At the position of our sample for our beam, $\Delta = 2\times10^{-3}$ degree. By refocusing we can alter w and Δ at will. Higher order modes with larger beam angles and larger beam cross sections can be excited as well as combinations of modes.

With a 1.1526-micron parallel beam, optimum SHG occurs with the fundamental power P_1 in the TEM_{00q} mode at the index matching angle[6,9] θ_m (41° ± 1° with respect to the z axis). Varying the angle of the beam about the matching direction and assuming a parallel beam, we expect the harmonic power P_2 to be given by Kleinman's Eq. (123)[7] modified as

$$P_2 = \frac{P_1^2 32\pi^2\omega}{w^2c^3(n_1^0)^3} d_{36}^2(\sin^2\theta_m) l^2 \frac{\sin^2\psi}{\psi^2}, \qquad (1)$$

where ω is the harmonic frequency, l is the crystal length, and w is the spot radius, the appropriate average over the Gaussian intensity distribution having been taken as will be shown below. $\psi = \beta l\sigma$, where σ is the deviation angle from the matching direction in the plane formed by the optic axis and the beam. $\beta = (\omega n_1^0/2c)\sin\rho$, where ρ is the angle between the ellipse and sphere index surfaces at matching:

$$\tan\rho = \tfrac{1}{2}(n_1^0)^2\{1/(n_2^e)^2 - 1/(n_2^0)^2\}\sin 2\theta_m. \qquad (2)$$

If desired, (1) can be rewritten in terms of the coherence length $l_{coh} = \pi/\beta\sigma$ as defined by Kleinman[7] and Armstrong et al.[12]

Under the assumption of an essentially parallel beam, with $l = 1.23$ cm we compare the experimentally observed angular dependence of P_2 with Eq. (1). We expect the output to fall to zero at angles for which l is an integral number of coherence lengths. The comparison with experiment is shown in Fig. 1. The agreement indicates that essentially full coherence is occurring in the matching direction and that the beam angle and deviation of the crystal axis are indeed relatively small. The separation in angle of the minima is an experimental measure of β and thus the birefringence. Within the experimental error of 5% the results agree with the known birefringence.

To consider the effect of finite beam divergence when operating with very long samples in the index matching direction, Kleinman[7] shows by averaging $\sin^2\psi/\psi^2$ that there is an effective coherence length beyond which the harmonic output no longer varies as l^2 but as l. We find it convenient to define our effective coherence length as $l_{coh}' = \pi/\beta 2\Delta$ based on an average over our Gaussian beam. For $\Delta = 2\times10^{-3}$ degree, $l_{coh}' = 20$ cm. For an angular spread $\Delta = 1/4°$ (typical of solid-state masers), Kleinman estimates $l_{coh}' \sim 1$ mm. Thus our beam can give an effective coherence length more than two orders of magnitude longer than the solid-state maser beam. We have confirmed that the harmonic output varies closely as the square of crystal length for three different lengths up to 1.23 cm which is our thickest crystal.

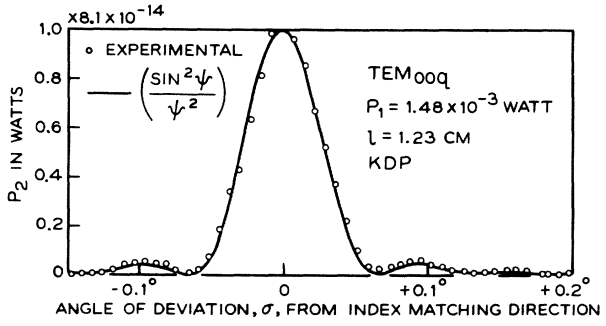

FIG. 1. Variation of second-harmonic power with σ, the angle between the fundamental beam in the lowest order mode and the phase-matching direction.

With the data shown in Fig. 1, we compute d_{36} from a second-harmonic power of 8.1×10^{-14} watt, the exact beam shape, crystal length (1.23 cm), and fundamental power of 1.48×10^{-3} watt. We find $d_{36}=(3\pm1)\times10^{-9}$ esu. Terhune, Maker, and Savage[13] estimated 3×10^{-10} esu, whereas Kleinman's estimate using Giordmaine's data[6,7] at the ruby wavelength was 6×10^{-10} esu. Our value includes small corrections for surface reflections[7] and absorption.

The beam, although all in the lowest order transverse mode, probably contains about three axial modes differing in frequency by about 67 Mc/sec. Analysis shows that harmonic power increases due to mixing by a factor $(2m-1)/m$, where m is the number of longitudinal modes between which a fixed amount of pump power is equally divided. This would cause an overestimate of d_{36}^2 by at most a factor of 2 for $m>4$, but is neglected here because the number and power distribution between longitudinal modes is not known for our beam. Bloembergen[10] has independently obtained this result for large m.

Progressively less SHG output was observed operating with higher order transverse modes in the phase-matched direction due to the differences in intensity distribution. Figure 2 shows the harmonic power P_2 plotted versus P_1^2 for the several modes. Theoretically we expect straight lines for each mode. The slope of curves 2 and 3 for the modes shown should be 0.75 and 0.56, respectively, of the slope of curve 1 for the lowest order mode. The ratio of the slopes is obtained by averaging the intensity relations $S_2=KS_1^2$ over the cross-sectional area thus:

$$P_2=KP_1^2\int S_1^2dA/[\int S_1dA]^2, \qquad (3)$$

where S_2 and S_1 are the theoretical intensity distributions and P_2 and P_1 are the total powers in the harmonic and fundamental beams, respectively. The slight discrepancy from theory may be due to small amounts of other transverse modes or to a change in the relative energy distribution between longitudinal modes.

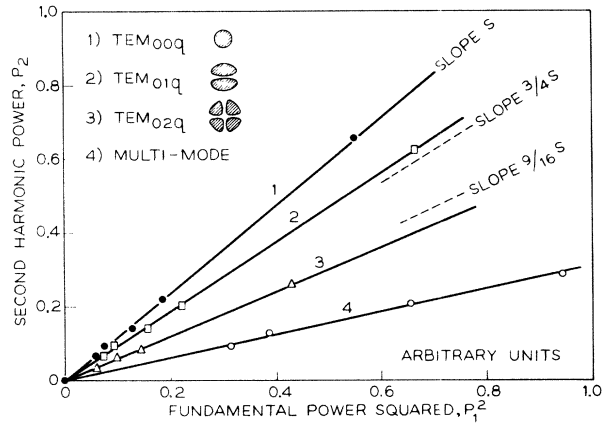

FIG. 2. Harmonic power P_2 versus fundamental power squared, P_1^2, for different transverse modes TEM_{plq} in cylindrical coordinates where the angular variation is $e^{il\varphi}$. The theoretical ratio of the slopes is 1:0.75:0.56. Curve 4 is a combination of transverse modes, predominantly TEM_{10q}, TEM_{01q}* (see reference 5), indicating the deleterious effects of multimode operation.

Working with focused light in the phase-matched direction, we found that the large output comes partly from the energy concentration and partly from coherence effects. In single-mode operation, however, we find by varying the focal length of the lens that coherence effects predominate. Thus, optimum SHG occurs when the beam is compressed or indeed magnified to the point where the beam angle is such that the effective coherence region is equal to the crystal length. For a 6-mm crystal length this occurs with about a 10-cm focal length lens and gives 5×10^{-12} watt of harmonic power for 0.7 milliwatt of fundamental. For a crystal about 20 cm long our unfocused beam has a comparable coherence length and would be expected to give a higher harmonic output. Still higher power could be obtained from a longer crystal and a magnified beam.

Photographs of the harmonic output follow all the fine details of the incident fundamental light such as interference fringes caused by reflections in filters, etc., and differences due to mode shape.

Further advantages of the single-mode technique will appear when resonant systems are used for enhanced harmonic generation or for studying parametric effects. Increased over-all efficiencies should be obtainable with the recent increases in gas-maser power[14] and with repetitive pulsing of gas masers.[15,16] Also, other aspects of second-harmonic generation can now be investigated in more detail, for instance, a more precise measurement of the accuracy of the frequency doubling and the linewidth of the harmonic light.

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ION PAIR ABSORPTION IN $PrCl_3$

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In experiments by Versanyi[1] it was demonstrated that in $PrCl_3$ one photon can excite simultaneously two Pr^{3+} ions to different excited levels, one of which was always $^3P_0$. This was shown by the appearance of fluorescence from $^3P_0$ with monochromatic excitation at frequencies where a single ion could not possibly absorb but which numerically corresponded to the sum of different absorption frequencies of the single ion.

Naturally fluorescence can occur only if there is absorption at the exciting frequency. We have now been able to obtain with suitable crystals of pure $PrCl_3$ under the proper experimental arrangements the absorption lines corresponding to ion pair absorption. The region most suitable for observing these absorption lines is that beyond the $^3P_2$ lines, as we know that there can be no absorption lines of the Pr^{3+} ion between 22 220 and about 50 000 cm^{-1}.

It turns out that in the region between 22 220 and 28 100 cm^{-1} there are about 90 weak but very distinct absorption lines, the frequencies of almost all of which can be written as the sum of two ordinary absorption frequencies. In this region one is sure that there are no single-absorption lines, and occasional impurity lines can be recognized by their greater sharpness.

Table I gives the wave numbers and classifications of the observed lines in a representative interval. The intensities are estimates from microphotometer traces, such as shown in Fig. 1. The

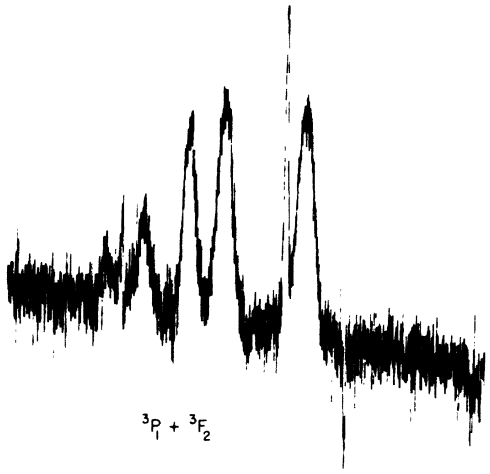

FIG. 1. Ion pair absorption lines of Pr^{3+} near 26 000 cm^{-1}. The sharp line is due to Nd^{3+}.

width of the lines is of the order of 6 cm^{-1}, considerably larger than that of the impurity lines. The lines are the sums of the two energy levels within the limits of experimental errors, which may here be more than 1 cm^{-1} for weak and crowded lines. The table shows that there are occasionally systematic deviations because the energy levels of concentrated $PrCl_3$, having to be derived from very broad lines, are not always accurately known.

Practically all sums of known levels which fall