129, 1911 (1963).

[4]L. T. Landau and E. M. Lifshitz, Statistical Physics (Pergamon Press, New York, 1958), p. 259 ff.

[5]We noticed these difficulties in connection with recent measurements of the sound velocity in ^{4}He near the critical point; we needed values of the density in order to calculate the adiabatic compressibility from the relation $\kappa_S^{-1}=\rho u^2$, and in the absence of direct density measurements we used the expression of EW to extrapolate the densities away from the coexistence curve. [C. E. Chase, R. C. Williamson, and L. Tisza, Phys. Rev. Letters 13, 467 (1964).]

[6]L. Cailletet and E. Mathias, Compt. Rend. 102, 1202 (1886).

[7]E. A. Guggenheim, J. Chem. Phys. 13, 253 (1945).

[8]It is a curious fact that in ^{4}He the orthobaric densities as measured by EW are indeed proportional to $t^{1/2}$ within the region indicated, although further away the dependence is more nearly $t^{1/3}$ as seems to be the case for most fluids. (See references 2 and 7.) If the former result is real, it might be attributed to the quantum corrections to the law of corresponding states. [J. de Boer, Physica 14, 139, 149 (1948); J. de Boer and R. J. Lunbeck, Physica 14, 509 (1948).] Similar behavior ought to be expected then in ^{3}He, and has in fact recently been observed [R. H. Sherman, Proceedings of the Conference on Phenomena in the Neighborhood of Critical Points, National Bureau of Standards, Washington, D. C., 1965 (to be published)].

[9]The straight line in the figure actually has a finite intercept on the abscissa, corresponding to +4.6 mdeg. This may indicate flattening of the coexistence curve close to the critical point, or be the result of errors in the measured temperatures in EW or in the assignment of T_c.

[10]M. H. Edwards and W. C. Woodbury, Can. J. Phys. 39, 1833 (1961).

[11]For a plot of these curves, see C. E. Chase and R. C. Williamson, Proceedings of the Conference on Phenomena in the Neighborhood of Critical Points, National Bureau of Standards, Washington, D. C., 1965 (to be published).

[12]The arguments in favor of this scheme far outweigh the slight inconvenience of using the chemical potential which, like the entropy, is measurable only indirectly. The compromise scheme p,ρ turns out to be impractical; this may be connected with the fact that these variables do not form a conjugate pair.

[13]L. Tisza, Ann. Phys. (N.Y.) 13, 1 (1961).

[14]T. D. Lee and C. N. Yang, Phys. Rev. 87, 410 (1952); see also C. N. Yang and C. P. Yang, Phys. Rev. Letters 13, 303 (1964).

RELATIVE PHASE MEASUREMENT BETWEEN FUNDAMENTAL AND SECOND-HARMONIC LIGHT*

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The nonlinear susceptibility describing the second-harmonic generation of light is real, when the medium is transparent at both the fundamental and the harmonic frequency. When the medium is absorbing at either or both of these frequencies, this nonlinear susceptibility is a complex quantity.[1] The nonlinear polarization has a phase shift with respect to the fundamental field. Measurement of the second-harmonic intensity only determines the absolute value of the nonlinear susceptibility. For some III-V and II-VI compounds, which are absorbing at the second-harmonic frequency, such measurements have been carried out in reflection.[2,3] In this note an experiment is described which determines the phase of the nonlinear susceptibility.

The experimental arrangement is shown in Fig. 1. A linear polarized laser beam from a Q-switched ruby laser enters an evacuated box and generates second-harmonic radiation by reflection from a nonlinear mirror of a crystal with $\bar{4}3m$ symmetry, whose complex nonlinear susceptibility must be determined. The laser beam subsequently generates an additional second-harmonic field in a potassium-dihydrogen-phosphate (KDP) platelet which serves as a reference signal. The second-harmonic fields generated in the two samples will have a definite phase relationship with respect to each other, as each has a specific relationship to the phase of the fundamental

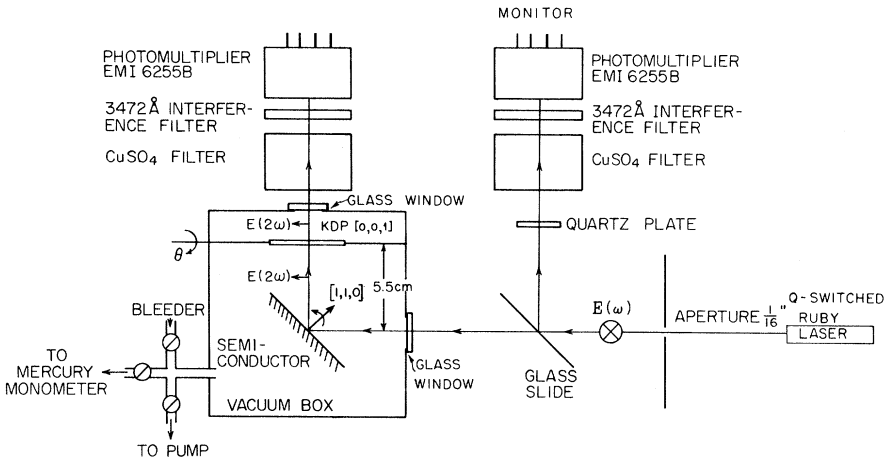

FIG. 1. Diagram of the experimental apparatus to determine the relative phase of the second-harmonic field, as described in the text. Each laser pulse is monitored by the harmonic production in quartz.

field squared. The total second-harmonic output is the result of the interference between the two second-harmonic beams. This interference can be made visible by admitting dry air into the box. The dispersion in air changes the relative phase between the fundamental and second harmonic in the 5.5-cm path between the reflection spot on the mirror and the KDP crystal. From tabulated dispersion data for air, a phase shift of 180° occurs for an air pressure equivalent to 22 cm Hg. The second-harmonic intensity emerging from the box is shown in Fig. 2 as a function of air pressure. It has the expected periodicity.

The KDP platelet is a (100) cut, and can be tilted around the (001) direction. The polarization of the laser beam is almost parallel to the (010) direction. In this manner the second-harmonic production in the platelet may be kept very small and made comparable to, but slightly larger than, the second-harmonic production in the mirror.

The nonlinear mirror may be turned around its (110) normal so that the laser field points along the (001) cubic axis. In this case no second harmonic is generated in the mirror.[4] The KDP platelet is then tilted, so that its second-harmonic output is a relative maximum.

Next the mirror is turned so that the fundamental field points along the (110) direction. The mirror then produces a second-harmonic field parallel to that generated in the KDP crystal. The interference pattern in Fig. 2 is observed, when the air pressure in the cell is increased. If the fundamental field points along the (111) direction of the crystal mirror, no

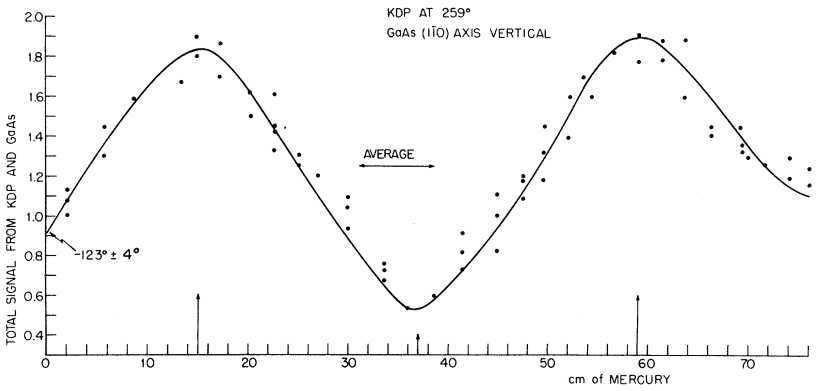

FIG. 2. The interference between the second-harmonic fields produced by the same laser beam in the GaAs mirror and the KDP platelet, as a function of the air pressure in the box shown in Fig. 1.

interference is observed because in this case the fields generated in the two samples are orthogonal.

The position of the first extremum in Fig. 2 is a measure for the phase relationship between the squared fundamental field and the second-harmonic field after reflection from the nonlinear mirror. From the angles for which zero harmonic production occurs in KDP, one can determine exactly the phase shift $\delta\varphi_{KDP}$ of the harmonic generated in KDP with respect to that of the harmonic from the nonlinear mirror. For our particular case $\delta\varphi_{KDP} = (\pi + 13°30')$ $\pm 3°30'$ when the KDP is tilted so that its second-harmonic output is a relative maximum.

The sign of the interference is reversed if either the $\bar{4}3m$ crystal or the KDP crystal is replaced by its piezoelectric antipode, or inversion image. All phases in the following discussion have therefore an ambiguity of 180°. This ambiguity of sign can only be eliminated if the sign of the piezoelectric tensor is measured and related to the absolute structure, both for KDP and the $\bar{4}3m$ crystals.

The experimental phase shift Δ between the position for zero pressure and the first extremum can be determined from Fig. 2 to be $-123° \pm 4°(+180°)$ for GaAs. For a mirror of InAs this phase angle was found to be $-90°$ $\pm 4°(+180°)$ and for ZnTe $0° \pm 4°(+180°)$. From these observations the phase angle φ_{NL} of the complex nonlinear susceptibility may be calculated from the relation

$$\Delta = \varphi_{NL} + \varphi(2\omega) - 2\varphi(\omega) - \delta\varphi_{KDP}. \quad (1)$$

The phase angle $\varphi(\omega)$ is the phase shift on reflection of the fundamental field, determined by the Fresnel formula for 45° angle of incidence,

$$\frac{E_R(\omega)}{E_i(\omega)} = \frac{1-\alpha(\omega)}{1+\alpha(\omega)} = r_1 e^{i\varphi(\omega)}, \quad (2)$$

where

$$\alpha(\omega) = \{2\epsilon(\omega) - 1\}^{1/2}.$$

The phase angle $\varphi(2\omega)$ follows from the nonlinear laws of reflection,[5] which for the geometry of Fig. 1 may be written in the form

$$E_R(2\omega) = E_i^2(\omega)\,|\chi^{NL}|\exp(i\varphi_{NL})\,r_2 e^{i\varphi(2\omega)},$$

with

$$r_2 e^{i\varphi(2\omega)} = \frac{32\pi}{\sqrt{2}} \frac{\alpha(2\omega)}{\{\alpha(\omega)+1\}^2\{\alpha(2\omega)+1\}^2\{\alpha(\omega)+\alpha(2\omega)\}}. \quad (3)$$

When the known values of the complex dielectric constants are inserted in Eqs. (1)-(3), the following phase angles for the nonlinear susceptibility are found: $\varphi_{NL} = -71° \pm 19°(+180°)$ for GaAs, $\varphi_{NL} = -37° \pm 20°(+180°)$ for InAs, and $\varphi_{NL} = 34° \pm 24°(+180°)$ for ZnTe. With the previously measured second-harmonic intensities[2,3] the estimated nonlinear susceptibilities relative to KDP become

$$\chi_{GaAs}^{NL}/\chi_{KDP} = \pm(165 - 475i),$$

$$\chi_{InAs}^{NL}/\chi_{KDP} = \pm(272 - 204i),$$

and

$$\chi_{ZnTe}/\chi_{KDP} = \pm(552 + 372i).$$

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[1]N. Bloembergen, Proc. IEEE 51, 124 (1963).

[2]N. Bloembergen, R. K. Chang, J. Ducuing, and P. Lallemand, Proceedings of the International Conference on Semiconductors, Paris, 1964 (Academic Press, Inc., New York, 1964).

[3]R. K. Chang, J. Ducuing, and N. Bloembergen (unpublished).

[4]J. Ducuing and N. Bloembergen, Phys. Rev. Letters 10, 474 (1963).

[5]N. Bloembergen and P. S. Pershan, Phys. Rev. 128, 606 (1962). Especially Eq. 4.13 of this paper is used with $\alpha + \theta_S = \pi/2$ and $\theta_R = \pi/4$.