Absolute intensity measurements of Brillouin spectra of liquid and solid krypton, and determination of the elasto-optic constants*

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Values of the elasto-optic constants of krypton were determined from intensity measurements of the Brillouin spectra of liquid and solid krypton. Firstly, the relative intensity of the longitudinal Brillouin components of the liquid and solid was measured. Secondly, the absolute intensity of scattering in liquid krypton was measured, using the scattering from a Ludox solution as intensity standard; a value of $(2.0 \pm 0.2) \times 10^{-4}$ m^{-1} was obtained for the scattering efficiency of liquid krypton. This value together with the known ratios of the elasto-optic constants gave $p_{11} = 0.34 \pm 0.04$, $p_{12} = 0.34 \pm 0.05$, $p_{44} = 0.037 \pm 0.005$ for solid krypton at 115.5 K.

I. INTRODUCTION

The intensity of Brillouin scattering in a solid is dependent on the elasto-optic or Pockel's coefficients, and therefore, measured intensities can be used to evaluate these constants. Several such investigations have been carried out on ionic crystals,[1-3] crystalline quartz,[2] and calcite.[4] Recently, in a series of experiments in this laboratory on rare-gas single crystals, the relative intensities of transverse and longitudinal Brillouin components have been used to obtain values of ratios of the elasto-optic constants for xenon,[5] krypton,[6] argon,[7] and neon.[8] The data for krypton are considered to be the most accurate, and have been compared with the results of a recent theory of the elasto-optic constants for the rare-gas solids by Werthamer.[9]

In the present paper, we describe an extension of the experiments by Landheer *et al.*[6] on solid krypton to measurements of the absolute intensity of Brillouin scattering. First, a comparison was made of the intensities of the longitudinal components in solid krypton (at 115.5 K) and in the liquid (at 116.5 K). This was followed by a measurement of the absolute scattering intensity in liquid krypton using Rayleigh scattering of a Ludox solution for calibration.[10] Finally, these results together with values of the ratios[6] p_{12}/p_{11} and p_{44}/p_{11} were used to determine the three elasto-optic constants for solid krypton at 115.5 K, near the triple point.

II. BRILLOUIN SCATTERING EFFICIENCY IN LIQUIDS AND SOLIDS

The theory of Brillouin scattering from cubic crystals derived by Benedek and Fritsch[1] was used in the present investigation. They showed that the total scattering efficiency is given by

$$S=\left(\frac{\omega_0}{c}\right)^4 \frac{\epsilon^4}{(4\pi)^2}\left(\frac{kT}{\rho}\right)\sum_{\mu=1}^{3}\frac{|\xi^\mu|^2}{V_\mu^2}\ .$$

Here, ω_0 is the incident frequency, c is the velocity of light in vacuum, ϵ and ρ are the dielectric constant and density of the crystal, respectively, and the energy $kT \gg \hbar\omega$, where ω is the Brillouin frequency shift. The quantities ξ^μ for the three acoustic modes ($\mu = 1, 2, 3$) having velocities V_μ are given in terms of the crystal orientation and the Pockel's elasto-optic coefficients by Eqs. (36) and (37) of Ref. 1 (with the correction $2p_{44}$ in place of p_{44}). For the two longitudinal Brillouin components, the scattering efficiency $S_c(L)$ may be written

$$S_c(L) = \left(\frac{\omega_0}{c}\right)^4 \frac{\epsilon^4}{(4\pi)^2}\frac{kT}{\rho}p_{11}^2\mathfrak{F}(\theta, \phi, \chi;\ p_{12}/p_{11},\ p_{44}/p_{11}). \tag{1}$$

In this equation, p_{11} is one of the elasto-optic constants and is used as a normalization factor for these constants. The function $\mathfrak{F}$ is related to the Euler angles θ, ϕ, χ (describing the crystal orientation relative to the laboratory reference frame), to the ratios of the elasto-optic constants, and inversely to the square of the velocity of the longitudinal mode which in turn is determined from the elastic constants C_{11}, C_{12}, C_{44}. For a given crystal orientation, the function $\mathfrak{F}$ can be calculated in terms of known values of p_{ij}/p_{11} and C_{ij}. Thus, in principle, a measurement of $S_c(L)$ will lead to an evaluation of p_{11}^2 and therefore of p_{12}^2 and p_{44}^2.

However, a direct measurement of the absolute scattering intensity from a crystal (at cryogenic temperatures) is a much more difficult problem than the corresponding measurement from a liquid. For this reason, we have chosen to determine the absolute scattering from liquid krypton, and then to compare experimentally the scattering from the crystal and liquid.

For a liquid, the Brillouin scattering efficiency is known to be

$$S_l(L) = \left(\frac{\omega_0}{c}\right)^4 \frac{1}{(4\pi)^2}\left(\rho\frac{\partial\epsilon}{\partial\rho}\right)_s^2 kT\beta_s\ .$$

Here β_s is the adiabatic compressibility, and is given in terms of the density ρ and hypersonic velocity V_l by $\beta_s = (\rho V_l^2)^{-1}$. For a monatomic liquid, such as krypton, there is only one independent elasto-optic constant, $p_{11} = p_{12}$; and p_{11} is related to the adiabatic fluctuation in the dielectric constant with density by $(\rho \partial \epsilon / \partial \rho)_s = p_{11} \epsilon^2$. Thus the scattering efficiency becomes

$$S_l(L) = \left(\frac{\omega_0}{c}\right)^4 \frac{\epsilon^4}{(4\pi)^2} \frac{kT}{\rho} \frac{p_{11}^2}{V_l^2}. \tag{2}$$

A comparison of Eqs. (1) and (2) gives for the ratio of scattering efficiencies of crystal and liquid

$$R(\theta, \phi, \chi) = \frac{S_c(L)}{S_l(L)} = \frac{T_c}{T_l}\left(\frac{\epsilon_c}{\epsilon_l}\right)^4 \frac{\rho_l}{\rho_c}\left|\frac{(p_{11})_c}{(p_{11})_l}\right|^2 \times \mathfrak{F}(\theta, \phi, \chi; p_{12}/p_{11}, p_{44}/p_{11}) V_l^2. \tag{3}$$

Here, the subscripts c and l refer to the crystal and liquid values, respectively. This equation then leads to the ratio of the elasto-optic constants for crystal and liquid:

$$\left|\frac{(p_{11})_c}{(p_{11})_l}\right|^2 = \frac{T_l}{T_c}\left(\frac{\epsilon_l}{\epsilon_c}\right)^4 \frac{\rho_c}{\rho_l} \frac{1}{V_l^2} \frac{R(\theta, \phi, \chi)}{\mathfrak{F}(\theta, \phi, \chi; p_{12}/p_{11}, p_{44}/p_{11})}. \tag{4}$$

Equation (4) shows that a value for this ratio can be obtained from a measurement of the intensity ratio $R(\theta, \phi, \chi)$, and from the known constants and calculated value of the function $\mathfrak{F}$. Finally, if a value for $(p_{11})_l$ is determined, Eq. (4) can be used to obtain a value of p_{11} (and p_{12}, p_{44}) for the crystal.

III. EXPERIMENTAL METHOD AND RESULTS

As already mentioned in Sec. I, two different experiments were carried out in order to determine the absolute Brillouin scattering efficiency of solid krypton. One of these was the measurement of the relative intensity of the longitudinal components in the crystal and liquid, using the same apparatus. The other was the measurement of the absolute intensity of the longitudinal component in the liquid, using the Rayleigh scattering from a Ludox solution as intensity standard.

A. Relative scattering efficiencies of crystal and liquid

For this experiment, the apparatus described by McLaren *et al.*[8] and the method of crystal growth described by Landheer *et al.*[5] were used. Three different single crystals of krypton were grown and maintained at 115.5 K, just below the triple point. Their quality and orientation were determined by x-ray diffraction, and Brillouin spectra excited by 488.0 nm radiation from an argon ion laser were analyzed with a piezoelectrically scanned Fabry-Perot spectrometer. A typical spectrum showing the pair of longitudinal components and only one pair of transverse components is given in Fig. 1(b). For each crystal, three spectra were recorded, each spectrum consisting of about two spectral free ranges (and therefore containing three longitudinal and four transverse components). Thus, for each crystal, nine individual measurements of the area under the longitudinal Brillouin component were made in order to check the reproducibility of the measurements. The average values of these areas gave effective values of $S_c(L)$, the Brillouin scattering efficiency for the solid.

After recording the three spectra for each crystal, the temperature of the sample cell was slowly raised to melt the crystal. The liquid was maintained at 116.5 K (just 0.5 K above the triple point), and three Brillouin spectra were recorded for each of the three melts in the same way as for each crystal [Fig. 1(a)]. The areas of the Brillouin components gave effective values of $S_l(L)$. Since the intensity measurements with each crystal and liquid were carried out under identical experimental conditions, the ratio of the effective values $S_c(L)$ and $S_l(L)$ were used to obtain values of $R(\theta, \phi, \chi)$ of Eq. (3). These are listed in Table I. Also listed are the three values of the function $\mathfrak{F}(\theta, \phi, \chi; p_{12}/p_{11}, p_{44}/p_{11})$, calculated from the measured orientation of each crystal, using the known values[6] of the elastic constants and of the ratios of the elasto-optic constants. Finally, the three sets of data were used along with Eq. (4) to determine the ratio

TABLE I. Experimental intensity data for solid krypton.

Crystal	Orientation (θ, ϕ, χ)	$R(\theta, \phi, \chi)$	$\mathfrak{F}(\theta, \phi, \chi; p_{12}/p_{11}, p_{44}/p_{11})$ (10^{-6} m^{-2} sec^2)	$R/\mathfrak{F}$ (10^5 m^2 sec^{-2})
1	−62.3, 56.2, 131.1	0.56 ± 0.04	0.92 ± 0.14	6.1 ± 1.0
2	−69.1, −84.5, 132.9	0.58 ± 0.04	0.93 ± 0.13	6.2 ± 1.0
3	−29.1, 1.9, −157.5	0.48 ± 0.03	0.72 ± 0.09	6.7 ± 0.9
			Avg.	6.3 ± 1.1

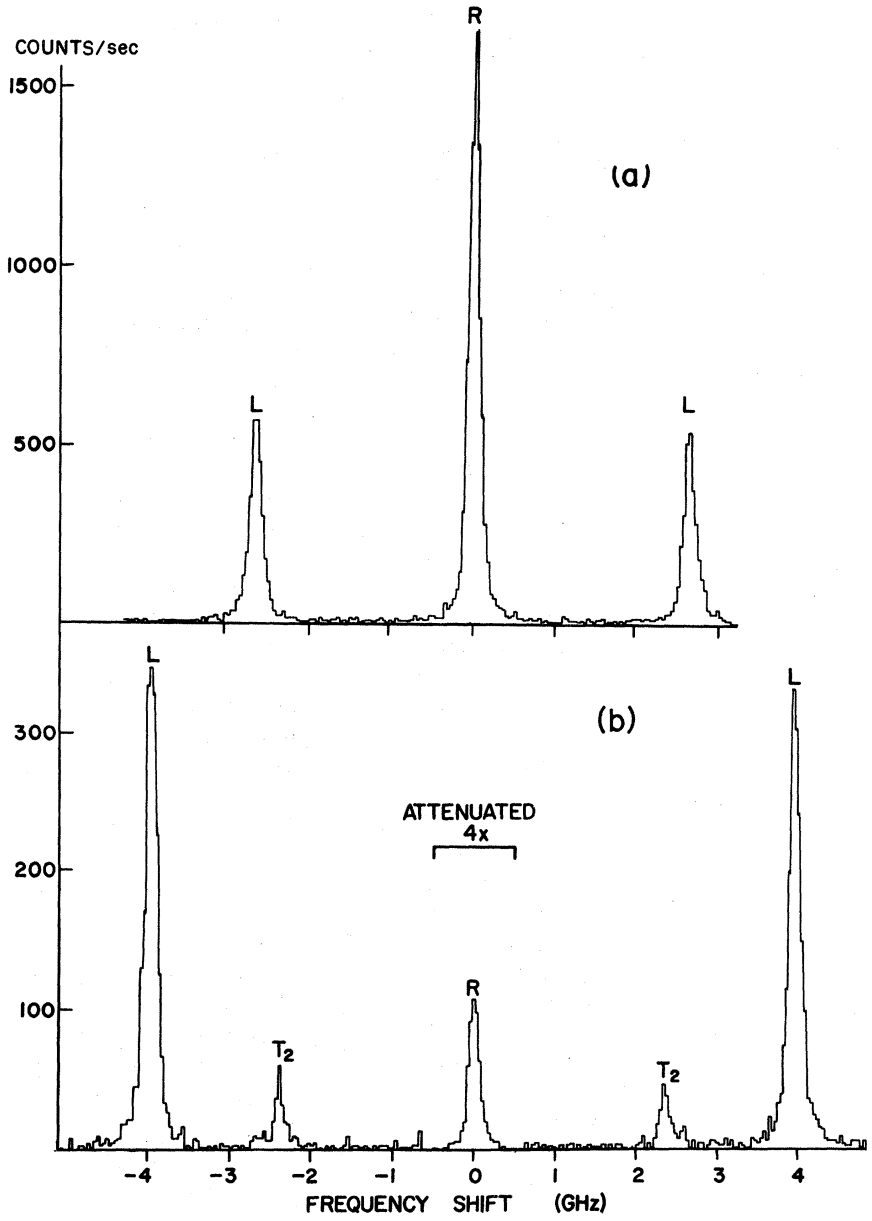

FIG. 1. Typical Brillouin spectra of (a) liquid, and (b) solid krypton.

$$\frac{(p_{11})_c}{(p_{11})_l} = 1.06 \pm 0.09 .$$

The quoted uncertainty is due to the variation of the three measurements of $R(\theta, \phi, \chi)$, and to the uncertainty of $\mathfrak{F}(\theta, \phi, \chi; p_{12}/p_{11}, p_{44}/p_{11})$ which arises from the errors given[6] for the ratios p_{12}/p_{11} and p_{44}/p_{11}.

B. Determination of absolute scattering efficiency of liquid krypton

The experimental arrangement for comparing the scattered intensity from liquid krypton and from a Ludox solution which served as an intensity standard is shown in Fig. 2. Liquid krypton was condensed in a cylindrical Pyrex cell (25 mm diam and 25 mm long) and maintained at a temperature of 116.5 ± 0.5 K. The Ludox solution (10% by weight in water) was contained in a rectangular glass cell (6 cm long × 2.0 cm × 2.5 cm). These dimensions were large enough so that the usual small, nonuniform distribution of silica particles near the walls did not affect the assumption of uniform attenuation along the cell length, the measured attenuation coefficient being 0.67 m^{-1}. The beam [λ(488.0 nm)] from an argon-ion laser was incident on both specimens during the experiment, and was polarized at right angles to the scattering plane. A long-focal-length lens $L_1(f = 1\ m)$ was used to reduce the beam size to 0.4 mm diam so

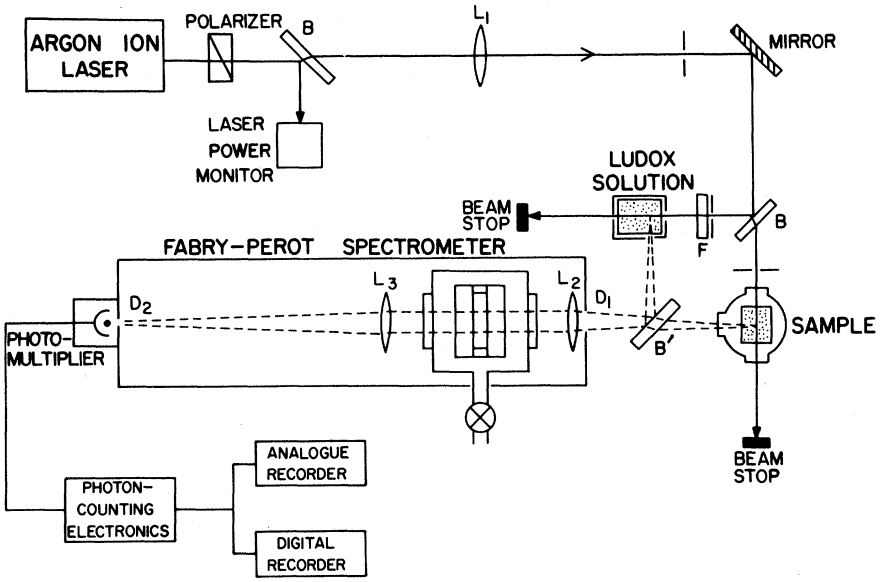

FIG. 2. Schematic diagram of apparatus for intensity measurements of liquids using a Ludox solution as intensity standard.

that the change in spot size due to refraction at air-to-sample interfaces was minimized. The beam splitter B' (in Fig. 2) was very carefully aligned so that the scattered beams from both samples had a common optical path through the Fabry-Perot spectrometer. A pressure-scanned interferometer was used with a 1.0-cm spacer and a finesse of 83. The transmittances and reflectances of all optical components which are necessary for calculating the Brillouin scattering efficiency were measured with an accuracy of ~1%. Also, a correction factor of 10% was applied for the different refraction of scattered light at liquid-to-air interfaces because of the different shapes of sample cells. This value was determined experimentally by comparing the scattered intensity from Ludox solution contained in a rectangular cell and in a cylindrical cell of 25 mm diam.

Spectra of the two samples were obtained by alternately blocking one of the scattered beams. Typical spectra are shown in Fig. 3. Four independent measurements of the Rayleigh scattering from the Ludox solution and of the Brillouin scattering from liquid krypton were made, leading to a value for the absolute scattering efficiency for liquid krypton,

$$S_l(L) = (2.0 \pm 0.2) \times 10^{-4}\ \mathrm{m}^{-1}.$$

This value together with the known physical properties of liquid krypton was then used in Eq. (2) to evaluate the elasto-optic constant of liquid krypton, giving

$$(p_{11})_l = 0.32 \pm 0.02.$$

Finally, by combining the values of p_{12}/p_{11} and p_{44}/p_{11} obtained by Landheer *et al.*,[6] and the values of $(p_{11})_c/(p_{11})_l = 1.06 \pm 0.09$ and $(p_{11})_l = 0.32 \pm 0.02$ obtained in the present experiments, the elasto-optic constants of solid krypton (at 115.5 K) are found to be

$$p_{11} = 0.34 \pm 0.04,$$

$$p_{12} = 0.34 \pm 0.05,$$

$$p_{44} = 0.037 \pm 0.005.$$

In making the above calculations, the following constants for solid krypton (at 115.5 K) and liquid krypton (at 116.5 K) were used: elastic constants,[6] $C_{11} = 2.657 \pm 0.030$, $C_{12} = 1.725 \pm 0.020$, $C_{44} = 1.261 \pm 0.015$, all in 10^{10} dyn/cm^2; elasto-optic constant ratios,[6] $p_{12}/p_{11} = 1.00 \pm 0.08$, $p_{44}/p_{11} = 0.11 \pm 0.01$; dielectric constants,[11] $\epsilon_c = n_c^2 = 1.820$, $\epsilon_l = n_l^2 = 1.702$; densities,[11] $\rho_c = 2.795$, $\rho_l = 2.448$ g/cm^3; and sound velocity $V_l = 694 \pm 5$ m/sec.

IV. DISCUSSION

Recently there has been considerable research activity in the elasto-optic properties of various materials, primarily because of interest in applications of acousto-optic devices. Values of elasto-optic constants for many amorphous and crystalline solids have been summarized by Pinnow.[12] The present values for krypton are the only ones available for a simple van der Waals solid, although as mentioned earlier values of ratios of the elasto-optic constants have been reported for xenon, argon, and neon. A comparison with tabulated values shows that the elasto-optic constants p_{11} and p_{12} for krypton are amongst the largest known.

Before making comparisons with theoretical values, some comment on the estimated accuracy

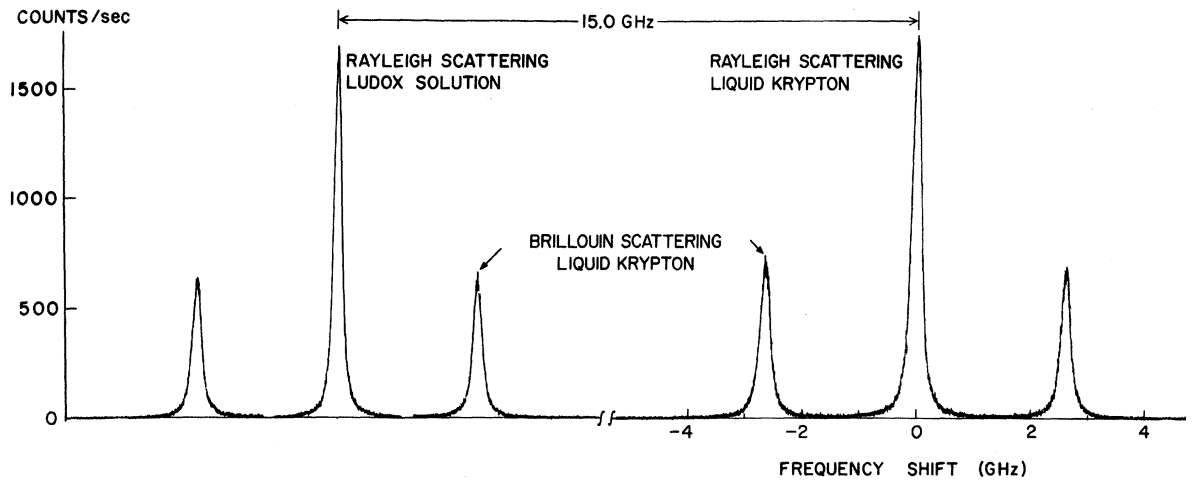

FIG. 3. Typical scan for measuring the relative intensity of Brillouin components of krypton to the Rayleigh scattering from Ludox solution. From left to right the components are B_K, R_L, B_K, B_K, R_K, B_K (where B_K represents Brillouin component from krypton, and R_L and R_K represent Rayleigh scattering from Ludox and krypton, respectively).

of the present data is in order. The use of Ludox solution as a standard for scattering intensity is well established, and in our investigations has given results for liquid toluene[13] in good agreement with published values. An accuracy of 10% for the absolute scattering efficiency of liquid krypton is estimated (being limited by the measurement reproducibility and by corrections for the change of solid angle due to refractive index changes from sample to glass to air). For solid krypton, the errors in the ratios p_{12}/p_{11} and p_{44}/p_{11} must also be included, leading to an accuracy of 10 to 15% in the derived elasto-optic constants. This value for a solid grown at low temperature is to be compared with a typical accuracy of ~ 5% obtained in modern acousto-optic experiments on solids at room temperature.

Recently, Werthamer[9] has developed a theory for the Brillouin scattering efficiency of rare-gas crystals. His theory is based on a dipole model in which neutral but polarizable atoms interact via van der Waals interatomic forces. According to this theory, the elasto-optic constants are given by

$$\begin{aligned} p_{11} &= \alpha + 2c\,(\alpha^2/a^3), \\ p_{12} &= \alpha - c\,(\alpha^2/a^3), \\ p_{44} &= -c\,(\alpha^2/a^3), \end{aligned} \tag{5}$$

(in the dimension of the polarizability α). Here c is a dimensionless constant, and a is the nearest-neighbor distance. An immediate result of Eqs. (5) is the relation $p_{11} - p_{12} + 3p_{44} = 0$. This, however, does not hold for solid krypton, as shown earlier by Landheer *et al.*[6] from the ratios of the elasto-optic constants. A similar discrepancy was also found for solid xenon.[5,9] The present values of p_{11} and p_{12} are the same within their experimental errors. Also, p_{44} is only ~ 10% of p_{11} and p_{12}, approximately the error in p_{11} and p_{12}. Thus, the first term, α, in the relations for p_{11} and p_{12} is the dominant term.

It should be noted that this first term arises from changes in density with strain, and thus provides the main contribution to the effects of longitudinal waves. This term may be estimated from the Lorentz-Lorenz model, which gives

$$p = (\epsilon - 1)(\epsilon + 2)/(3\epsilon^2),$$

where the dielectric constant ϵ equals n^2 (the square of the index of refraction). The measured values of n for liquid and solid krypton given by Sinnock and Smith[11] were used to calculate p, and the resulting values are listed in Table II for comparison with the present experimental values. The agreement is within the experimental accuracy.

The relation for p_{44} in Eq. (5), which gives an estimate of the contribution from the van der Waals interatomic forces, can be used to evaluate the parameter c. With α as the dominant term in p_{11}, c becomes $-(p_{44}/p_{11})\,(a^3/\alpha)$; and substitution of the values $p_{44}/p_{11} = 0.11$, $\alpha = 2.54\times10^{-24}$ cm^3, and $a = 4.115\times10^{-8}$ cm leads to a value $c = -2.9$. This is almost double the value estimated by Werthamer[9] (1.6 for face-centered-cubic crystal) and of oppo-

TABLE II. Elasto-optic constants for solid and liquid krypton.

	Crystal $T = 115.5$ K	Liquid $T = 116.5$ K
Expt.	$p_{11} = 0.34 \pm 0.04$ $p_{12} = 0.34 \pm 0.05$ $p_{44} = 0.037 \pm 0.005$	$p_{11} = 0.32 \pm 0.02$
Theor.	$p_{11} = 0.314$	$p_{11} = 0.297$

site sign.

An earlier and rather detailed theory for the elasto-optic constants of (ionic) cubic crystals was developed by Mueller, [14] in which he included changes in atomic polarizabilities of the constituent atoms and in the symmetry of the Lorentz cavity field, in addition to the above-mentioned changes in number density of atoms and in the short-range interatomic forces. While this theory is also applicable to nonpolar solids, the contributions to p_{11}, p_{12}, and p_{44} for krypton have not yet been evaluated.

V. CONCLUSION

The elasto-optic constants of krypton single crystals have been determined from measurements of the absolute intensity of Brillouin scattering. This is the first such determination for a rare-gas solid. A comparison of the present results with the available theories of the elasto-optic effect shows that there is qualitative agreement with the values expected on the basis of the Lorentz-Lorenz model. However, it appears that improvements in the present theories are necessary in order to explain the elasto-optic constants of krypton.

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[1]G. B. Benedek and K. Fritsch, Phys. Rev. 149, 647 (1966).

[2]P. E. Schoen and H. Z. Cummins, in *Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971), p. 460.

[3]L. Benckert and G. Bäckström, Phys. Rev. B 8, 5888 (1973).

[4]D. F. Nelson, P. D. Lazay, and M. Lax, Phys. Rev. B 6, 3109 (1972).

[5]W. S. Gornall and B. P. Stoicheff, Phys. Rev. B 4, 4518 (1971).

[6]D. Landheer, H. E. Jackson, R. A. McLaren, and B. P. Stoicheff (unpublished); H. E. Jackson, D. Landheer, and B. P. Stoicheff, Phys. Rev. Lett. 31, 296 (1973).

[7]S. Gewurtz and B. P. Stoicheff, Phys. Rev. B 10, 3487 (1974).

[8]R. A. McLaren, H. Kiefte, D. Landheer, and B. P. Stoicheff, Phys. Rev. B 11, 1705 (1975).

[9]N. R. Werthamer, Phys. Rev. B 6, 4075 (1972).

[10]S. H. Maron and R. L. H. Lou, J. Polym. Sci. 14, 29 (1954).

[11]A. C. Sinnock and B. L. Smith, Phys. Rev. 181, 1297 (1969).

[12]D. A. Pinnow, in *Laser Handbook*, edited by F. T. Arecchi and E. O. Schulz-DuBois (North-Holland, Amsterdam, 1972), Vol. I, p. 995.

[13]Y. Kato and G. A. Zdasiuk (unpublished).

[14]H. Mueller, Phys. Rev. 47, 947 (1935).