It is evident that the evaluation of S_1 in either of these expressions has become exceedingly simple. In the form (A11) one has to evaluate only one single integral for each temperature T^*, while the form (A12) contains only three integrals. The volumes V_λ are easily obtained by adding up the elementary volumes associated with those $\mathbf{k}$ points of the fine mesh, which are omitted in the evaluation of S_2.

We conclude the Appendix by quoting two rational approximations for the integral $J(1/x)$ (A9). From Thacher's work[28] we derive that for the range $0 \leq x < 10$, $J(1/x)$ is very accurately approximated by the expression

$$\frac{3xe^{-x}}{e^{-x}-1}+4\left\{\frac{3953.632-800.6087x+85.07724x^2-4.43582x^3+0.0946173x^4}{3953.632+682.0012x+143.1553x^2+15.12149x^3+x^4}\right\}, \tag{A13}$$

in which the absolute error is smaller than 2.1×10^{-6}. For $x \geq 10$ we have used the expression

$$\frac{3xe^{-x}}{e^{-x}-1}+\frac{12}{x^3}\left[\frac{\pi^4}{15}-e^{-x}\{6+6x+3x^2+x^3\}\right], \tag{A14}$$

in which the fractional error is not larger than 5×10^{-6}. Expression (A14) has been obtained from a series expansion of the appropriate Debye function.[27]

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Polariton Spectrum of α-Quartz

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Mixed electromagnetic-mechanical excitations known as "polaritons" are observed in Raman forward-scattering experiments on α-quartz using an argon laser. Dispersion relations of the polariton frequencies are extended from the case of simple diatomic lattices to a more complex system, namely, α-quartz, which has nine atoms per unit cell. The dependence of frequency upon scattering angle observed for these mixed excitations in quartz is shown to be in very good agreement with that predicted. Polaritons associated with the transverse phonons at 1072, 797, and 450 cm^{-1} in α-quartz are discussed in the present work. The polariton associated with the 1072-cm^{-1} phonon mode is observed to range in frequency from 1072 to 822 cm^{-1}; the polariton associated with the 797-cm^{-1} phonon mode is observed at frequencies from 797 to 700 cm^{-1}; and that associated with the 450-cm^{-1} phonon mode is observed from 450 to 407 cm^{-1}.

INTRODUCTION

In the study of the optical properties of solids much interest is currently focused on the nature of interactions between optical phonons and other crystalline excitations. Among these are interactions between phonons and plasmons, phonons and cyclotron resonance excitations, and phonons and photons. Until now the study of these interactions has been almost entirely restricted to simple crystals possessing diatomic lattice structure and a single phonon mode.[1] In the present work we consider phonon-photon coupling in α-quartz, which has nine atoms per unit cell and eight TO phonons of species E which can couple with photons travelling through the crystal.

Transverse optical phonons in polar crystals interact strongly with electromagnetic waves when their energies and momentum vectors are nearly equal. The resulting mixed excitations, called "polaritons" by Hopfield,[2] were first observed in Raman experiments on cubic GaP by Henry and Hopfield[3] and on hexagonal ZnO by Tell *et al.*,[4] who made use of the uniaxial properties of the latter crystal to produce large shifts in the frequency of the excitation. A general theoretical discussion of polaritons has been given recently by Hopfield.[5]

While both GaP and ZnO have diatomic lattice structure with only one TO branch, the polariton effect is also expected in more complicated crystals. In the

[1] An exception is Barker's work on phonon-plasmon effects in $SrTiO_3$. A. S. Barker, Jr., in *Proceedings of the Internal Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1966).

[2] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).

[3] C. H. Henry and J. J. Hopfield, Phys. Rev. Letters **15**, 964 (1965).

[4] S. P. S. Porto, B. Tell, and T. C. Damen, Phys. Rev. Letters **16**, 450 (1966).

[5] J. J. Hopfield, in Kyoto Semiconductor Conference, Kyoto, Japan, 1966 (unpublished).

present study we consider polaritons in quartz and have been successful in observing over a wide frequency range the polaritons associated with three different phonon modes. We have made a simple extension of the polariton theory used before for diatomic lattices and find that the observed dependence of frequency upon scattering angle agrees very well with this theory. The theory employed is classical infrared dispersion theory, modified to include energy and momentum conservation for excitations in a uniaxial crystal. No adjustable parameters are involved; all input parameters are obtainable from conventional infrared measurements.

THEORY

For transverse infrared-active vibrational excitations in a crystal, the frequencies and momenta of the excitations are related by equations of the form[6,7]

$$\epsilon = k^2/\omega^2 = \epsilon_\infty + \sum_{i=1}^{m} S_i \omega_i^2 (\omega_i^2 - \omega^2)^{-1}, \quad (1)$$

where m is the number of vibrational modes; k is the magnitude of the polariton momentum; ω is 2π times the polariton frequency; ϵ is the dielectric constant, which is a function of ω; ϵ_∞ is the high-frequency dielectric constant; S_i is the dimensionless mode strength of the ith normal mode and can usually be determined numerically from infrared studies; and ω_i is 2π times the frequency of the ith normal mode for a purely mechanical excitation of the kind normally measured in right-angle Raman scattering experiments. ω, k, and ω_i are all given in cm^{-1} in Eq. (1), so the speed of light is essentially taken as unity here. Note that the definition of mode strength S_i used here has the result that $\epsilon(\omega=0)=\epsilon_\infty+\sum S_i$. We shall consider only vibrations of species E in α-quartz in this work; for such vibrations the polarization is in the xy plane, which allows us to consider a single scalar component of the tensor dielectric constant, as is done in Eq. (1). Equation (1), as applied in the present work, sums over only the species E modes.

Varga has shown[8] that the term $(-\omega_p^2\epsilon_\infty\omega^{-2})$ must be added to the right side of Eq. (1) for crystals containing free carriers; here ω_p is the plasma frequency. This term is essentially zero for quartz. In any event, a term of this form would shift only the LO frequencies and not the TO frequencies, and the latter are the subjects of the present paper. LO frequencies are given by the zeros of ϵ [see Eq. (1)]; TO frequencies are given by $\epsilon=k^2\omega^{-2}$, which for the usual physical situation where $k\gg\omega$ are essentially the same as infinities of ϵ.

In addition to the dispersion relations between ω and k considered above, we must take momentum and energy conservation into account. Conservation of momentum in the Raman scattering process requires that

$$\mathbf{k}=\mathbf{k}_L-\mathbf{k}_S \quad (2)$$

or

$$k^2=k_L^2+k_S^2-2k_Lk_S\cos\theta, \quad (3)$$

where $\mathbf{k}_L$ denotes the momentum of the incident photon from the laser; $\mathbf{k}_S$, that of the Stokes scattered photon; $\mathbf{k}$, the polariton momentum; and θ, the angle inside the crystal between incident and scattered photon propagation directions. Conservation of energy provides that $\omega_L=\omega+\omega_S$, where ω is 2π times the subscripted frequency ν, and ω or ν without a subscript refers to the polariton. We use this energy relationship and Eq. (4) below[9] and write Eq. (3) in somewhat different forms in Eqs. (5)–(7).

$$k_L=\omega_L n=\omega_L\epsilon^{1/2}, \quad k_S=\omega_S n=\omega_S\epsilon^{1/2}. \quad (4)$$

(Here n is the index of refraction and k and ω are defined in cm^{-1}.) For a uniaxial crystal having extraordinary incident radiation and ordinary scattered radiation (here designated "α_{zx} scattering"), substitution of Eq. (4) into Eq. (3) yields

$$k^2=[\omega_L(n_e-n_0)+\omega n_0]^2+2\omega_L(\omega_L-\omega)n_en_0(1-\cos\theta), \quad (5)$$

which, for small angles ($\theta\ll 1$ rad), is

$$k^2=[\omega_L(n_e-n_0)+\omega n_0]^2+\omega_L(\omega_L-\omega)n_en_0\theta^2. \quad (6)$$

Here the subscripts e and 0 denote extraordinary and ordinary.

For ordinary incident radiation and extraordinary Stokes scattered radiation (here designated "α_{xz} scattering"), the analogous form of Eq. (3) is

$$k^2=[\omega n_e-\omega_L(n_e-n_0)]^2+\omega_L(\omega_L-\omega)n_en_0\theta^2. \quad (7)$$

Since the index of refraction n is a function of frequency, i.e., $n_0=n_0(\omega)$ and $n_e=n_e(\omega)$, the term n_0 is actually $n_0(\omega_L-\omega)$ in Eq. (6) and $n_0(\omega_L)$ in Eq. (7), while n_e is $n_e(\omega_L)$ in Eq. (6) and $n_e(\omega_L-\omega)$ in Eq. (7). For the present study of quartz this distinction is unimportant and has been neglected; however, for some substances its neglect might introduce a larger error in the calculations, particularly for high-frequency vibrations or longer-wavelength laser radiation where $(\omega_L-\omega)\omega_L^{-1}$ is very different from 1, or in substances where

$$|n_e(\omega_L)-n_e(\omega_L-\omega)|, \quad |n_0(\omega_L)-n_0(\omega_L-\omega)| \geq |n_e(\omega_L)-n_0(\omega_L)|. \quad (8)$$

Equations (1) and (6) or (1) and (7) can be solved simultaneously, giving m roots $\omega(\theta)$. This is the procedure we have followed in the present work. Note that anisotropy can be neglected in Eq. (1), (i.e., ϵ and S_i assumed independent of direction) but not in Eqs. (6)

[6] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 17.
[7] A. S. Barker, Jr., Phys. Rev. **136**, A1290 (1964).
[8] B. B. Varga, Phys. Rev. **137**, A1896 (1965).
[9] N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, Inc., New York, 1965), p. 76.

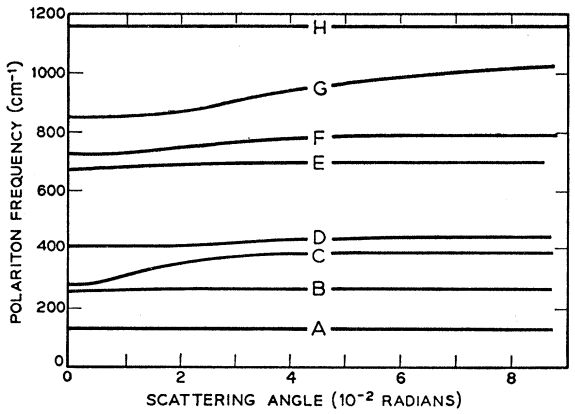

FIG. 1. Calculated dispersion curves for transverse optic vibrations of species E in α-quartz for incident light extraordinary and scattered light ordinary. θ is the angle between the y axis and the Stokes wave propagation direction, as measured in the yz plane, where z is the optic axis of the crystal and y is the direction of propagation of the incident light.

and (7) where the difference term (n_e-n_0) appears with a large coefficient.

For some crystals the constant term independent of θ in either Eq. (6) or (7) is very small. Whether this occurs in Eq. (6) or in (7) depends upon the sign of the term (n_e-n_0), i.e., upon whether the crystal is positive or negative uniaxial. Consider α-quartz, for example, which is positive. The quantity $[\omega n_e-\omega_L \times(n_e-n_0)]$ in Eq. (7) is nearly zero for laser radiation at 4880 Å and phonon frequency of 128 cm^{-1} (where one of the species E phonon modes occurs). For such a case

$$k\approx[\omega_L(\omega_L-\omega)n_0n_e]^{1/2}\theta, \tag{9}$$

or

$$k\propto\theta, \quad \text{(to a good approximation)}, \tag{10}$$

and so k is extremely small for near-forward scattering ($\theta\approx0$). For scattering in which both incident and scattered rays are ordinary,

$$k=[\omega^2n_0^2+\omega_L(\omega_L-\omega)n_0^2\theta^2]^{1/2} \tag{11}$$

and both k and the lowest phonon frequency ω can be made arbitrarily small by choice of sufficiently small θ. That is, for this orientation both k and ω become equal to zero at zero-degree scattering angle.

Frequencies of the eight transverse E-type vibrations were calculated by computer solution to Eqs. (1) and (6) and (1) and (7), with the values of ω_i obtained from our earlier work,[10] n_e and n_0 from the *Handbook of Chemistry and Physics* (1963), and S_i from Spitzer and Kleinman.[11] These calculations assume that there is zero coupling between modes of different symmetries. Figures 1 and 2 show the dispersion relations obtained: $\nu(\theta)$ is plotted versus θ for two cases: (1) incident light ordinary and scattered light extraordinary, and (2) incident light extraordinary and scattered light ordinary. The former shows the more marked dependence of ν upon θ. This is because the sign of (n_e-n_0) makes the θ-independent term in Eq. (7) nearly zero and hence results in a smaller phonon momentum k for a given θ. Consequently, the former scattering situation allows us to study a lower portion of the ν-versus-k dispersion curve. For example, for $\theta\approx0°$ we calculate $k\cong600$ cm^{-1} for polaritons associated with the 128 cm^{-1} phonon; this may be compared with $k\cong2400$ cm^{-1} for $\theta\approx0°$ and the scattering situation given in Eq. (6), and with $k\cong3\times10^5$ cm^{-1} for the same vibration at $\theta=90°$. Only the α_{xz} and α_{zx} scattering have been considered in detail in the present work. α_{xy} scattering (that with incident and scattered beams both ordinary) should allow scattering from even lower-frequency phonons, but detailed examination of very-low-frequency phonons requires scattering angles smaller than those used in the present experiment (1°–10°) and has not been included here.

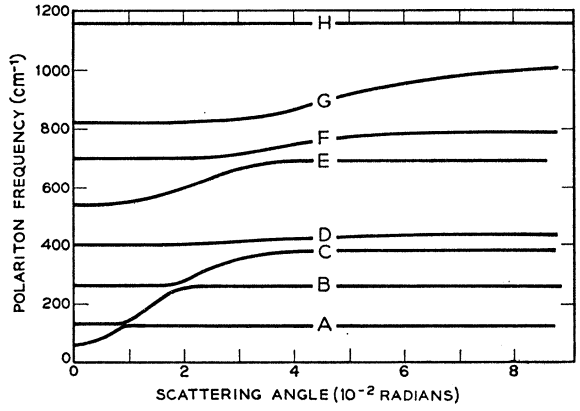

FIG. 2. Calculated dispersion curves for transverse optic vibrations of species E in α-quartz for incident light ordinary and scattered light extraordinary. θ is defined as in Fig. 1.

EXPERIMENTAL

The data used in this study were obtained with an argon ion laser emitting about 200 mW at 4880 or 5145 Å. A Spex tandem grating spectrometer was used as a monochromator, and detection was by means of a cooled EMI 6256 photomultiplier and a Keithley 610B electrometer. The sample was a 1-in. cube with the optic axis perpendicular to one face. The laser beam was focused very weakly so that its angle of convergence was always less than 1°, the smallest scattering angle used.

Figures 3–5 are photographs of the data. Figure 3 is a photograph of data from that part of the spectrum

[10] J. F. Scott and S. P. S. Porto, Phys. Rev. **161**, 903 (1967).

[11] W. G. Spitzer and D. A. Kleinman, Phys. Rev. **121**, 1324 (1961). After the present work was completed more accurate values of the S_i were published: E. E. Russell and E. E. Bell, J. Opt. Soc. Am. **57**, 341 (1967); however, the differences between the two sets of S_i are quite small and unimportant for our calculations.

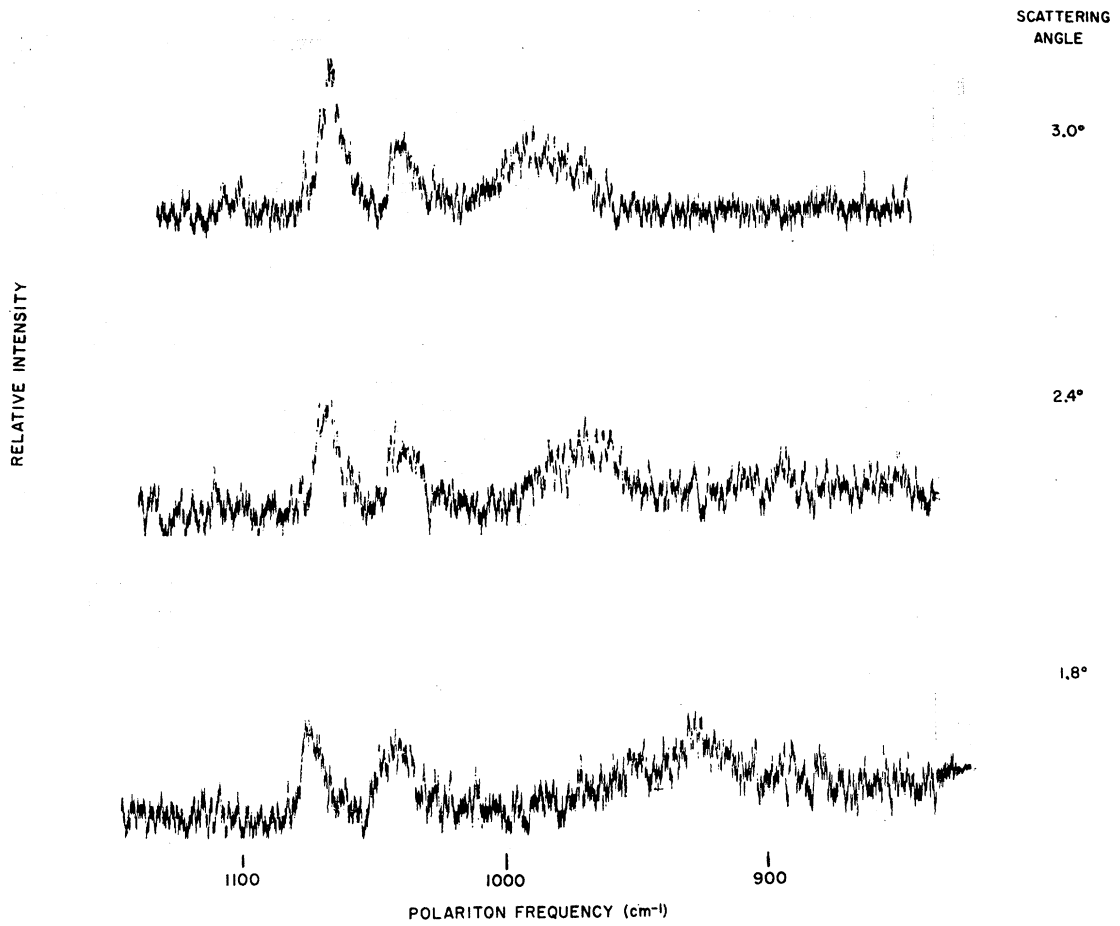

FIG. 3. Polariton spectrum of α-quartz for incident light extraordinary and scattered light ordinary. The three spectral lines which appear are, left to right; the 1072-cm^{-1} phonon, present here because of reflected back-scattered photons; an argon emission line; and the polariton associated with the 1072-cm^{-1} phonon.

of α-quartz which shows the polariton associated with the 1072 cm^{-1} mechanical excitation; this figure illustrates the α_{zx} scattering spectrum, i.e., that with incident beam extraordinary and scattered beam ordinary. Figure 4 shows the polariton associated with the 795-cm^{-1} mechanical vibration; scattering orientation is the same as in Fig. 3. Figure 5 illustrates the data from the other scattering arrangement, with incident beam ordinary and scattered beam extraordinary: α_{xz} scattering; polaritons associated with phonon modes at 1072, 795, and 450 cm^{-1} are all apparent in this figure. It is interesting to point out the fact that the 1072-cm^{-1} phonon is present in Fig. 3, along with its associated polariton; its occurrence is due to reflection of the back-scattered light in the crystal (i.e., scattering at 176–180° instead of 4–0°), and we were able to eliminate it by adjustment of the optics involved. All data were taken at about 300°K.

Some comment on the experimental difficulties encountered seems warranted. Adequate intensity required a finite acceptance angle of about 1°. In regions where ν changes rapidly as a function of θ and k, this acceptance angle resulted in broad lines. Since ν at 1° might be, say, 40 cm^{-1} less than ν at 2°, the spectral line detected at 1.5° with a 1° acceptance angle would be, for example, about 40-cm^{-1} wide (or about 10 Å in the 5000-Å region), while its integrated intensity would be no greater than that for the same acceptance angle and right-angle scattering. The result is a broader, flatter spectral line, which makes background noise more of a problem. The net effect of this factor is an uncertainty in the experimental value of ω or ν. An equally important uncertainty in our work is that in θ. Because of the optics used in our apparatus and to the finite beam width, it was difficult to measure the center of the scattered beam to much better than $\cong$0.5° absolute, although relative angles may be more accurate than that.

An additional difficulty encountered was that the intensity of the radiation entering the spectrometer

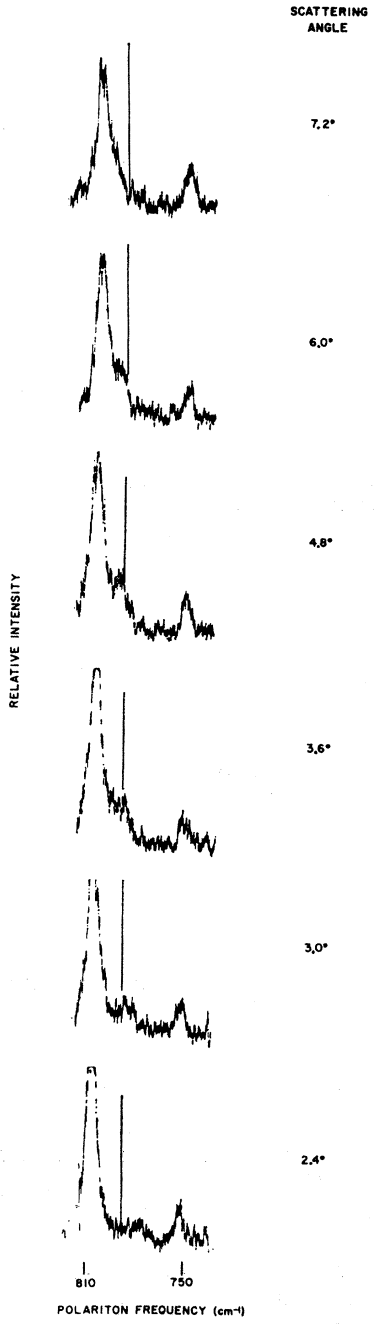

FIG. 4. Polariton spectrum of α-quartz for incident light extraordinary and scattered light ordinary. The intense line to the left is the associated LO (longitudinal component) at 807 cm^{-1}. The polariton line is seen as a weak shoulder on the LO which moves to lower frequencies as the scattering angle is reduced. The wide slit width required for adequate intensity in the near-forward scattering results in a blending of the LO-TO doublet; this doublet is easily resolved for conventional right-angle scattering (Ref. 10).

from spontaneously emitted argon lines increased as the scattering angle was reduced. At very small angles the Raman lines were sometimes masked by these argon lines; see Fig. 5.

Figures 6–8 are enlarged versions of Figs. 1 and 2 on a scale which allows us to show the detailed agreement between polariton theory and data. We had difficulty extending our measurements below 1° because of the reasons discussed in the previous section. Table I compares observed and calculated polariton frequencies; the disagreement in each case is less than that explainable by error of $\sim$1° in measured scattering angle.

DISCUSSION

For the eight vibrations of α-quartz which are both infrared and Raman-active, namely the transverse optic vibrations of species E, classical theory predicts a dependence of frequency upon momentum. In the present experiment we have made measurements of this dispersion relationship. Three of the phonon modes (at 1072, 797, and 450 cm^{-1}) exhibited large frequency shifts. One (at 1163 cm^{-1}) exhibited no shift. Two of the modes (697 and 394 cm^{-1}) are too weak in the Raman effect to allow reliable measurements at this time. And two (at 265 and 128 cm^{-1}) are expected to exhibit dispersion only at scattering angles smaller than those used in the present work.

Of the frequencies which were measured in our work, all agree fairly well with the calculated values. In addition to predicting frequencies well for a wide range of scattering angles, the classical oscillator theory used also explains the observed linewidths, which were primarily instrumental. Linewidths were observed to follow a dependence which can be predicted from Figs. 4 and 5. Lines were narrow at large angles, where the ν versus k (or θ) dispersion curve is nearly flat, wide at fairly small angles, where ν varies rapidly with k (and θ), and narrow again at very small angles, where the dispersion curves flatten out again. This behavior is attributable to the finite acceptance angle and is well illustrated in Fig. 3 for the polariton in the 1072–820-cm^{-1} region; all four traces in this figure were made with the same acceptance angle.

The calculations performed for this experiment may afford some insight into the physical behavior of the lattice modes, also. Figure 2 indicates a substantial mixing of wave functions, in addition to the dependence of ν upon θ and k it was designed to show. The predicted near level-crossings raise serious questions about the normal mode assignments usually made to describe the ionic motion. For the diatomic lattice treated by Loudon[12] this question does not arise; there is only one mode, and its frequency ν is a function of k, becoming essentially independent of k for k large compared to ω (both measured in the same units; otherwise, k large compared to ω/c). For more complicated crystals like quartz, mode assignments should be considered, however. Figure 2 suggests that for the α_{xz}-scattering it is the vibration observed at 450 cm^{-1} for right-angle

[12] R. Loudon, Advan. Phys. 13, 423 (1964).

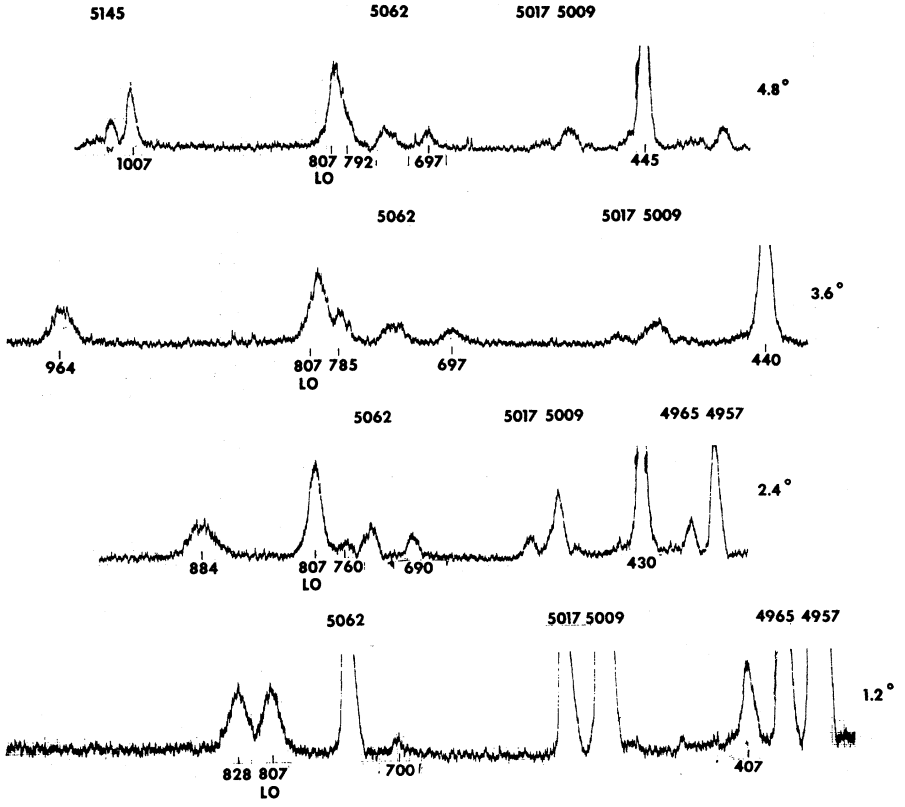

FIG. 5. Polariton spectrum of α-quartz for incident light ordinary and scattered light extraordinary. Polaritons associated with the phonons at 1072, 797 and 450 cm^{-1} are observed to shift to lower frequencies (written below each line) as the scattering angle is reduced. The other spectral lines present, which become increasingly intense as the scattering angle is reduced, are argon lines from the source and have their wavelength in angstroms written above them.

scattering which shifts all the way down to 55 cm^{-1} for $\theta=0°$, mixing with the phonon modes at 394, 265, and 128 cm^{-1} at scattering angles from 3 to 0.6°. Similarly, it would appear from Fig. 2 that the vibration observed at 1072 cm^{-1} for right-angle scattering shifts down to 546 cm^{-1} at 0°, mixing with the modes at $\sim$795 and 697 cm^{-1} at angles from 3° to 1.5°. Quantitative intensity measurements, which appear difficult at this time, are perhaps an additional source of experimental information on this hypothesized mode mixing at small k. We have observed, qualitatively, that the 90° scattering from the phonon at 1072 cm^{-1} is less intense than that of the phonon at 795 cm^{-1}.[10] As the scattering angles are reduced, the polariton line associated with the 1072-cm^{-1} phonon shifts in frequency down toward 820 cm^{-1} and *increases* in intensity (see Fig. 3), while the polariton line associated with the 795 cm^{-1} phonon shifts to lower frequencies and is greatly reduced in intensity

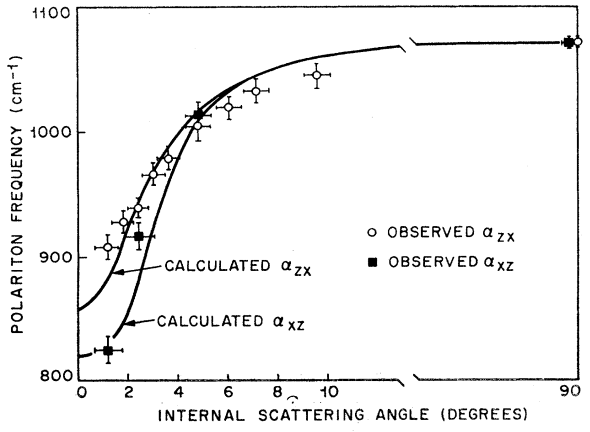

FIG. 6. Comparison of theoretical and observed polariton frequencies for the polariton associated with the phonon at 1072 cm^{-1} in α-quartz.

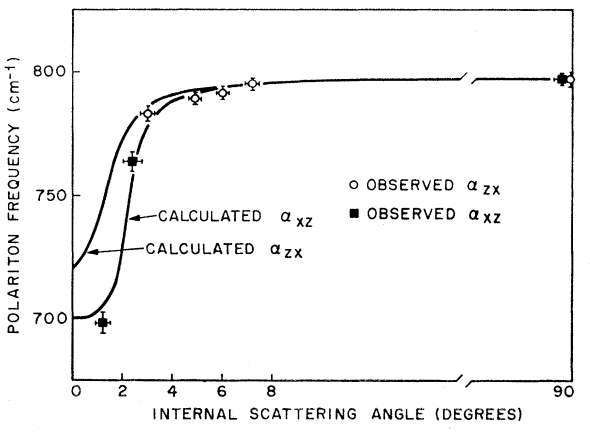

FIG. 7. Comparison of theoretical and observed polariton frequencies for the polariton associated with the phonon at 797 cm^{-1} in α-quartz.

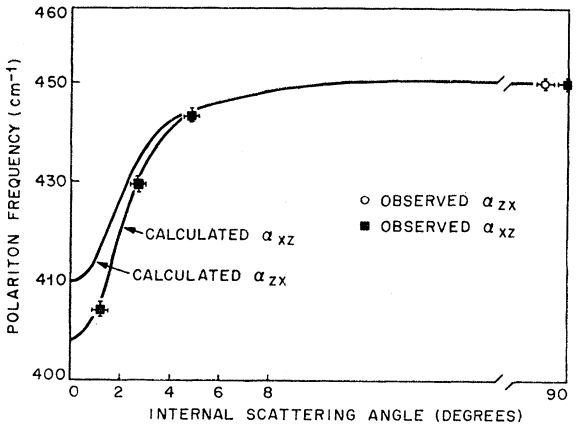

FIG. 8. Comparison of theoretical and observed polariton frequencies for the polariton associated with the phonon at 450 cm^{-1} in α-quartz.

from that observed at 90°. This suggests an intensity transfer, a virtual crossing of modes, and that the polariton associated with the 1072 cm^{-1} phonon retains its mode identity even at 546 cm^{-1} and 0°. Present data do not permit a more detailed discussion of intensities.

Our only observations in regard to α_{xy} scattering are that at very small angles ($<1°$) the 128-cm^{-1} line disappears, presumably into the wing of the laser line, and a new line appears at $\sim$140 cm^{-1} having an intensity approximately equal to that which the 128 cm^{-1} line has at larger angles. This line at 140 cm^{-1} is presumably the polariton associated with a higher frequency phonon, as discussed above. Detailed study of α_{xy} scattering is difficult at this time because the E vibrations which exhibit large dispersion have $\alpha_{xy} \ll \alpha_{xz}$, which is not coincidental,[10] and because the most interesting feature of α_{xy} scattering—generation of very-low-frequency phonons—requires very small scattering angles.

TABLE I. Polariton frequencies in α-quartz (cm^{-1}).

Internal scattering angle (degrees)	1072 cm^{-1} phonon mode		797 cm^{-1} phonon mode		450 cm^{-1} phonon mode	
α_{zz} Scattering[a]	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
90.0 (phonon)	1072[b]	1072	797[b]	797		
9.6	1056	1042				
7.2	1045	1031	795	795		
6.0	1034	1019	794	791		
4.8	1018	1004	792	789		
3.6	990	978	789	787		
3.0	969	966	785	783		
2.4	942	940	779	772		
1.8	911	928				
1.2	881	909				
α_{xz} Scattering[a]						
90.0 (phonon)	1072[b]	1072	797[b]	797	450[b]	450
4.8	1007	1013			444	443
2.4	884	918	758	764	430	430
1.2	828	822	704	697	408	407

[a] α_{zz} scattering denotes incident beam ordinary and scattered beam extraordinary; α_{xz} scattering denotes incident beam extraordinary and scattered beam ordinary.
[b] Forced agreement at 90° (large k).

CONCLUSIONS

The polariton spectrum of quartz has been analyzed and shown to agree with calculations. The phonon modes involved are those which are both infrared- and Raman-active. Since stimulated Raman emission has been reported recently for such a mode in quartz,[13] the possibility of stimulated Raman emission over a continuously tunable frequency range suggests itself.

ACKNOWLEDGMENTS

The authors would like to thank Mrs. M. L. Thomson, who programmed the simultaneous solution to Eqs. (1) and (6) and to (1) and (7). We also thank R. C. Mlller, who supplied the argon laser used. Helpful discussions with Dr. B. Tell initiated this work.

[13] P. E. Tannenwald and J. B. Thaxter, Bull. Am. Phys. Soc. 11, 813 (1966).