scattering it would be much larger—something like 3, and not so sensitive to temperature. The fact that all three noble metals show the same behavior in their Hall effects—both with alloying and with temperature—is good evidence for the p-state lying lowest in all three.

It would be interesting to apply the same arguments to the alkali metals, where the Fermi surface is not so distorted, and where, it seems, the s-state moves below the p-state as we pass from Na, through K, to Rb and Cs.[9] But we lack serious data on the Hall effect, and other manifestations of the anisotropy of τ, so that we should have little chance of making comparison with experiment. Another effect that might be calculated in the way we indicate here is the thermoelectric power, since this depends strongly on the way that $\tau(\mathbf{k})$ varies as we change the energy of $\mathbf{k}$. For example, is $\partial\tau(\epsilon)/\partial\epsilon$ negative on the belly simply because increasing the length of $\mathbf{k}$ reduces the value of $q_{\min}$, and thus allows many more U-processes? These, and many other questions in this field, remain to be answered.

ACKNOWLEDGMENTS

This paper was written while I was the guest of the General Electric Research Laboratory at Schenectady, New York. It is a pleasure to express my appreciation to Roland Schmitt, Walter Harrison, and others there, who provided the agreeable atmosphere in which this work was done.

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Infrared Lattice Bands of Quartz

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The infrared lattice bands of α quartz have been investigated at 297°K from 5 to 37μ in reflection and transmission with polarized light. Previously published measurements of the optical constants do not agree in this spectral range. It is shown that dispersion theory can fit the data within experimental error throughout the range, and accurate values of the dispersion parameters and the optical constants are obtained. This is the first accurate dispersion analysis of a complex spectrum. A study was made of the accuracy of the Kramers-Kronig method of analysis on this spectrum. The strength, width, and frequency of 14 optically active lattice vibrations are given, 4 of which have not previously been established. From a consideration of published Raman data, 10 of the resonances are assigned according to symmetry type as fundamental vibrations.

I. INTRODUCTION

QUARTZ was one of the first materials to be extensively investigated in the infrared. Because of its scientific and technological importance it has continued to be a frequent subject of investigation. Yet, its optical properties in the infrared remain largely unknown or uncertain. From an inspection of the existing literature one cannot obtain consistent values for the optical constants. The present work was undertaken with the purpose of providing a comprehensive and consistent account of the optical properties of α quartz in the region of its strong lattice absorption bands, 5 to 37 microns (μ). In order to achieve this purpose it was necessary to analyze the optical data according to classical dispersion theory. The success of this analysis demonstrates the applicability of this theory to very complicated lattice spectra such as that of quartz.

The reflectivity of α quartz (hereafter written simply "quartz") at room temperature (297°K) was measured in the range 5–$37\,\mu$ for the ordinary (O) ray and extraordinary (E) ray with plane polarized light. The transmission was measured in the range 7–27 μ for the O and E rays with polarized light. The sample thickness for the transmission was 0.00262 cm, which was sufficiently thin to afford considerable transmission between the main absorption bands. The range 5–37 μ includes all of the strong lattice absorption bands. Since a major aim of this work was to obtain a high degree of accuracy in the measurements, they were taken with great care and in many cases rechecked several times. Particular attention was paid to eliminating errors due to scattered light and incomplete polarization. A quantitative dispersion analysis was carried out with the aid of an IBM 704 computer on the reflectivity for both the O and E rays. From this analysis the optical constants for both rays were obtained over the entire spectral region studied. The extinction coefficients so obtained compare well in the regions between the strong absorption bands with the transmission measurements. The primary results of the dispersion analysis are the values of the dispersion parameters which describe the optically active lattice oscillators. The measurements and analysis are comprehensive as far as the reflectivity is concerned. All the information obtainable from the reflectivity is contained in the dispersion parameters. These parameters are also in agreement with the accepted values of the refractive index from 1 to 4 μ. The analysis was by the method of successive trials and adjustments of parameters. The technique of applying this method to a complicated spectrum is discussed. Its power is emphasized, and its limitations are specified. The Kramers-Kronig method of reflectivity analysis was critically investigated in regard to its accuracy. As data for the Kramers-Kronig method a calculated reflectivity was used which corresponded to exactly known optical constants. The exact and the Kramers-Kronig optical constants are compared.

According to the theory associated with the names of Helmholtz, Lorentz, and Drude, optical dispersion may be explained in terms of oscillators having the proper frequency and dipole moment. A review of classical dispersion theory, its historical development, and its experimental verification has been given by Wood.[1] In general, dispersion analysis may be defined as the full specification of the oscillators required to give agreement with reasonably accurate optical data extending over some wavelength range. Such analyses have been frequently applied to the refractive index in wavelength regions not containing strong reflection bands. In the early days of the theory Rubens and Aschkinass[2] were able to use an equation of the required form to represent the refractive index of quartz very accurately over the range 0.185 to 3.0 μ. In regions containing reflectivity bands, however, dispersion analysis is hardly practical even for the simplest spectrum without the use of high speed computing equipment. This has greatly hindered the use of dispersion analysis in the past, although a number of authors[3–11] have made qualitative use of dispersion theory to discuss the reflectivity of various substances, especially NaCl. Noteworthy is the work of Czerny[4] on NaCl, which was undertaken as a critical test of the theory. The qualitative agreement between theory and experiment demonstrated by Czerny was convincing evidence for the validity of the dispersion theory. Recently quantitative dispersion analyses by machine computation have been reported for SiC,[12] ZnO,[13] and GaP,[14] all of which have simple infrared reflectivity spectra consisting of a single band. In each case it was possible to fit the measured reflectivity within an experimental error of about 1%. It may be said that the validity of the theory for simple spectra has now been fully established. Dispersion theory has not heretofore been applied even qualitatively to very complicated spectra such as that of quartz.

For the most part the optical constants of materials have been obtained directly from optical data without the use of dispersion theory. Recent reviews of these methods have been given by Abeles and Mathieu[8] and by Fan.[15] Most of these methods require the measurement of two independent quantities as functions of wavelength. An exception is the method using the Kramers-Kronig relations,[16] which can yield the optical constants from a single measured quantity as a function of wavelength. This method has been recently employed[8,17–27] in discussing the reflectivity of a number of materials. Very little is known about the accuracy of the optical constants obtained by this method.[8]

There are definite reasons for undertaking a systematic investigation of the fundamental lattice bands of quartz. First is the continuing interest attached to quartz itself because of its basic importance in mineralogy and many optical and electrical applications. Second, in view of the discrepancies in the literature, there is an evident need for accurate infrared measurements and analysis. The discrepancies are discussed along with the results of the present work in Sec. IV. Third, there is the intriguing question of whether classical dispersion theory can account quantitatively for complex spectra such as that of quartz. As a material on which to test the theory, quartz is ideal,

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because excellent samples are readily available and a vast amount is already known about its properties. Fourth, the dispersion analysis provides the information needed for theoretical studies on such topics as the specific heat,[28] the infrared combination bands,[29] the electronic polarization accompanying nuclear motion,[30] the ionic charges in the lattice,[31,12] and the normal modes of vibration.[32] Fifth is the problem of the nature of vitreous silica.[33,28] A dispersion analysis of quartz is essential to a competent interpretation of the lattice dispersion of silica.

II. EXPERIMENTAL PROCEDURES

The room temperature reflectivity at near normal incidence was measured from 5 to 37 μ with a Perkin-Elmer single-beam double-pass spectrometer and prisms of NaCl, CsBr, and CsI. Measurements were made on four samples, three of which were *Z*-cut crystals of natural, synthetic, and rose quartz, and one was an *X*-cut crystal of natural quartz. The *X*-cut sample was rectangular in shape with one edge aligned with the optic axis. Spectroscopic analysis showed the major impurity of the rose quartz to be Al (0.088%) with much smaller amounts of Li, Na, Cu, Mg, Be, and Ti. The sample surfaces were prepared by standard optical polishing techniques[34] and the natural *Z*-cut crystal was etched in HF. The samples were sufficiently thick to be opaque over the range studied. The *Z*-cut samples were measured with unpolarized radiation within 6° of normal incidence. Within experimental error the three *Z*-cut samples gave identical results. During these measurements the wavelength calibration was checked several times, particularly in those regions where the reflectivity changes rapidly with wavelength. A sufficient number of points was taken to reveal clearly the shape of each band, and most of the points were checked and rechecked after remounting the sample. The result is the reflectivity for the *O* ray (electric field perpendicular to optic axis) shown by the points in Fig. 1(a).

The terms *O* ray and *E* ray are convenient for designating the reflectivities and optical constants obtained here under the conditions $E\perp C$ and $E\|C$, respectively, where E is the electric vector and C the optic axis. According to the usual terminology of the optics of uniaxial crystals, the ordinary ray is polarized perpendicular and the extraordinary ray parallel to the plane formed by the ray and the optic axis. In the degenerate case when the ray is along the axis the two rays are equivalent. All *O* rays have the same optical constants, and therefore a characteristic reflectivity can be defined. A characteristic reflectivity for the *E* ray can be defined in the sense that all *E* rays perpendicular to the optic axis have the same optical constants.

The instrument resolution in Fig. 1 varies from 0.016 μ at 8 μ to 0.15 μ at 27 μ. The accuracy of the measured wavelengths is limited by the ability to fix the positions of the calibration bands. Throughout the range these positions are uncertain to no more than 0.04 μ. The error due to spectrometer drift was eliminated by frequent recalibrations. Measurements on several portions of each sample showed no error due to surface irregularities. The random error in the reflectivity measurement includes fluctuations in the mounting and positioning of the sample as well as electronic noise in the detection system. From the reproducibility of measurements this error was estimated to be about 0.5% reflectivity independent of the value of the reflectivity. A systematic error can arise because of the presence of scattered light in the beam. If R_m, R, R_s, and the measured, true, and scattered light reflectivities, respectively, then $R_m=(R+\Delta R_s)/(1+\Delta)$, where $\Delta=I_s/I_0$ is the fraction of scattered light in the beam. From the transmission of a number of infrared filters it was determined that $\Delta\leq 1\%$ over the entire range; so we may write $R_m=R+\Delta(R_s-R)$. Since R_s, $R\leq 0.9$ the error term is less than 0.9%.

The *X*-cut sample was measured with polarized radiation. The polarizer consisted of a stack of plates (AgCl[35] for $\lambda<25$ μ, polyethylene[36] $\lambda>25$ μ) set at the polarizing angle. Since the spectrometer partially polarizes the beam, the polarizer was always kept in the position giving the maximum degree of polarization. Measurements were taken with the optic axis parallel and perpendicular to the plane of polarization. The latter measurements were in complete agreement with the reflectivity for the *O* ray shown in Fig. 1(a). The measurements with the axis parallel to the plane of polarization give the reflectivity for the *E* ray shown by the points in Fig. 1(b). That the polarizer was highly efficient at 19 μ is shown by the fact that the measured reflectivities for the *O* and *E* rays differ by a factor ~100 at this wavelength. Similar comparisons at 12.5 μ and 25.2 μ show that the polarizer efficiency was high throughout the range of study. A small error is introduced by the angle of incidence being 6°. The only effect of this error may be seen in Fig. 1(b) at 8.6 μ, where it was found that the small dip disappears when the angle of incidence is reduced to 3°. The dip at 19.7 μ in Fig. 1(b) is not sensitive to the angle of incidence. The depth of this minimum was found to be sensitive to the resolution, so the minimum reflectivity ~74% shown in Fig. 1(b) cannot be regarded as certain.

The room temperature transmission was measured on a single *X*-cut sample of thickness $(2.62\pm0.12)\times10^{-3}$

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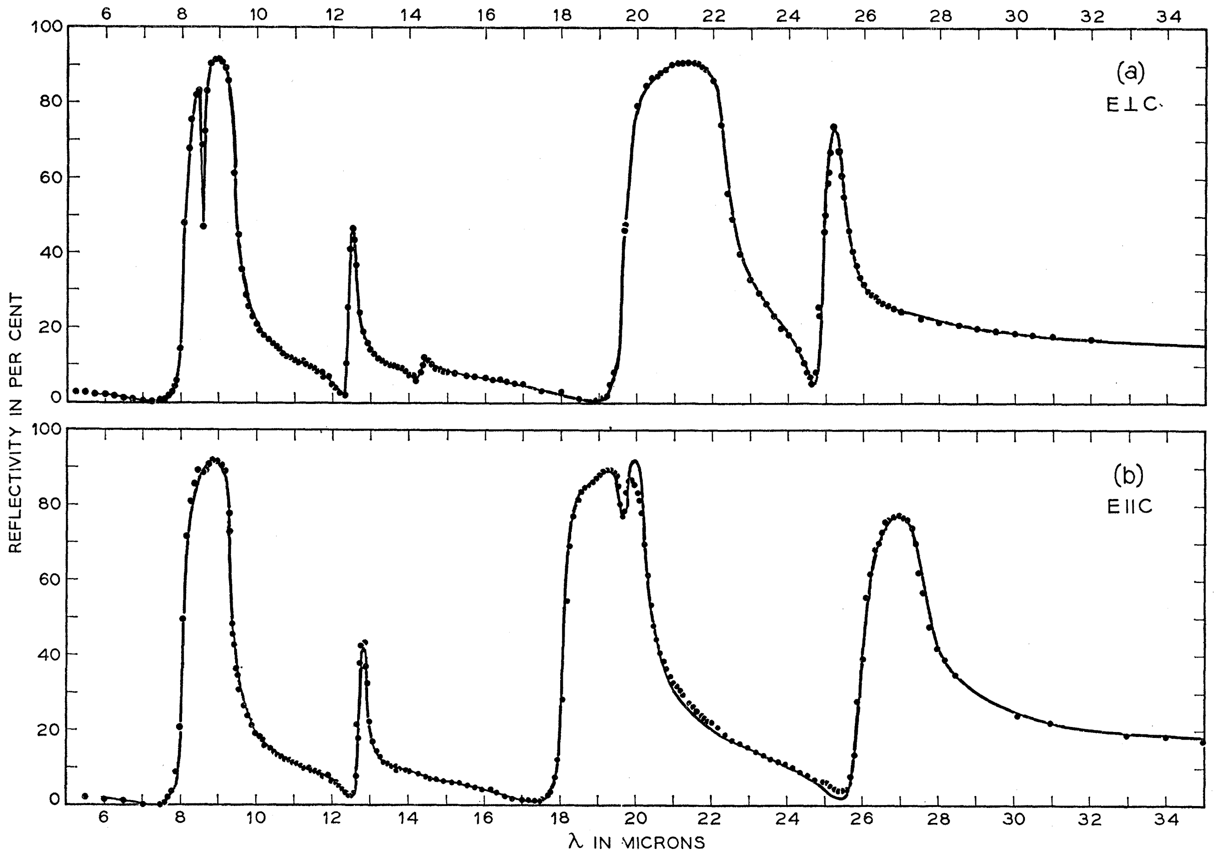

FIG. 1. The reflectivity of quartz for the ordinary ray (a) and the extraordinary ray (b). The data are shown by the points and the theoretical fit by the solid curves.

cm from 5 to 27 μ with polarized radiation. The results are shown by the points in Figs. 2(a) and 2(b) for the O and E rays. The sample was found to be opaque in those regions near the reflectivity peaks. The efficiency of the polarizer is again indicated by the transmission at 14.4 μ where the sample is nearly opaque to the O ray but transmits $\sim$62% of the E ray, and at 18.6 μ where the sample is opaque to the E ray and transmits 64% of the O ray.

III. DISPERSION ANALYSIS

According to the classical dispersion theory of crystals,[37] the refractive index n and extinction coefficient k are given by the equations

$$n^2-k^2=\epsilon_0+\sum_j 4\pi\rho_j\nu_j^2\frac{\nu_j^2-\nu^2}{(\nu_j^2-\nu^2)^2+\gamma_j^2\nu^2\nu_j^2},$$
$$nk=\sum_j 2\pi\rho_j\nu_j^2\frac{\gamma_j\nu\nu_j}{(\nu_j^2-\nu^2)^2+\gamma_j^2\nu^2\nu_j^2}, \tag{1}$$

where the summation is over the lattice oscillators. Each oscillator is described by its strength ρ_j, width γ_j, and frequency ν_j. The strength ρ in a diatomic crystal is simply related to the effective ionic charge,[12] or it may be defined in terms of an oscillator strength f by the relation

$$\rho_j=(Ne^2/4\pi^2m\nu_j^2)f_j,$$

where N is the concentration of unit cells and e, m are the charge and mass of the electron. The short-wavelength dielectric constant ϵ_0 describes the polarizability of the electrons with the atomic centers rigidly fixed. The long-wavelength dielectric constant is given by

$$\epsilon=\epsilon_0+\textstyle\sum_j 4\pi\rho_j. \tag{2}$$

The reflectivity at normal incidence,

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}, \tag{3}$$

can be calculated if the constants in (1) are known or assumed. These constants are called the *dispersion parameters* and the process of determining them is *dispersion analysis*. A dispersion analysis is successful if it fulfills the following requirements: (a) Within the wavelength region of interest the theory should fit the

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[37] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 17.

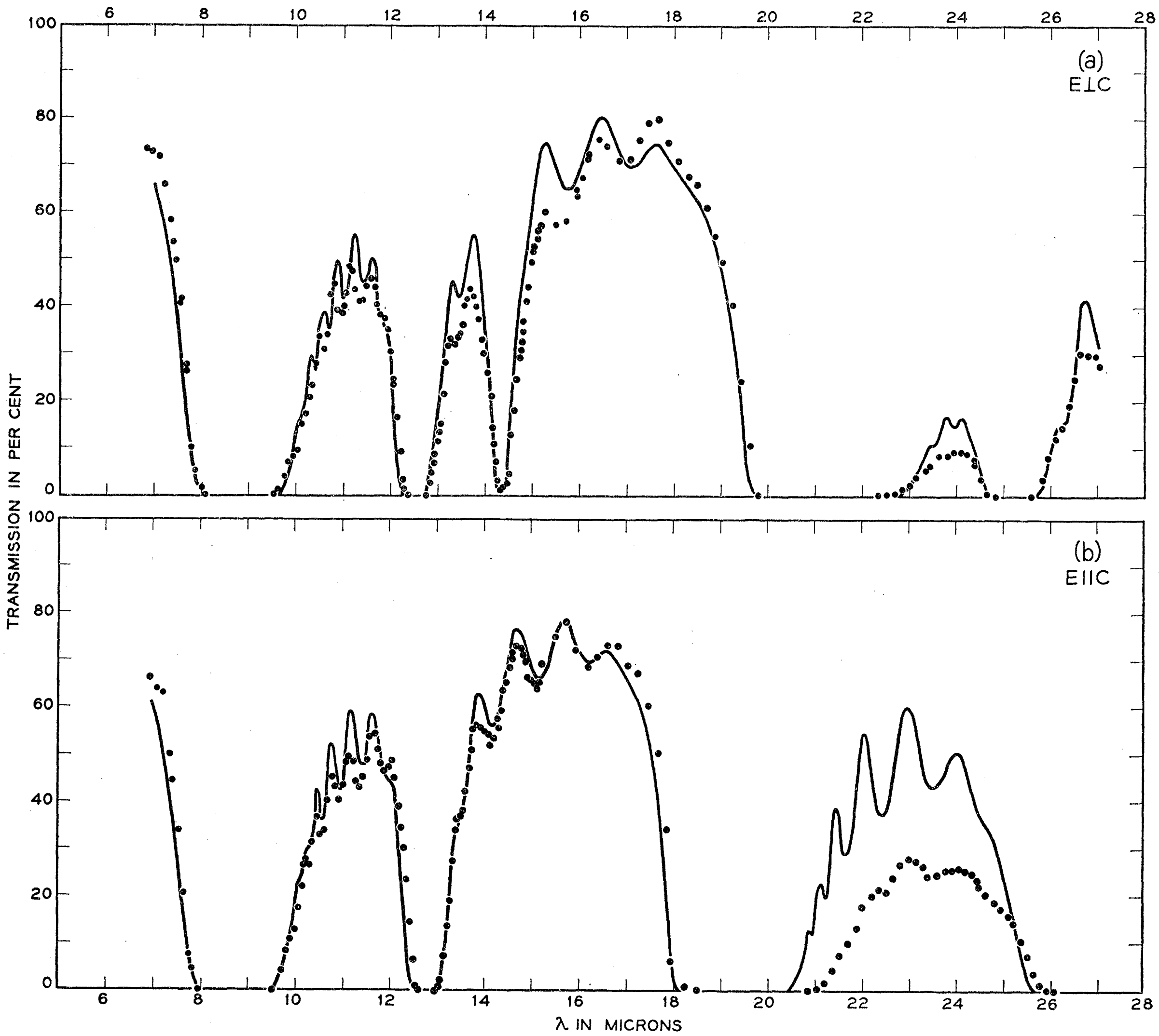

FIG. 2. The transmission of an 0.00262-cm thick X-cut quartz plate for the ordinary ray (a) and the extraordinary ray (b). The data are shown by the points and the theoretical fit by the solid curves.

data within reasonable estimates of the experimental error. (b) The number of oscillators used is the minimum number that the data requires. (c) The dispersion parameters are uniquely determined within reasonable uncertainties by the requirement of fitting the data. The analysis was carried out on the reflectivity of quartz by the method of successive trials and adjustments of parameters previously described[12] and successfully applied to SiC,[12] ZnO,[13] and GaP.[14] In this method reasonable values are chosen for the dispersion parameters, the reflectivity is then calculated by a high speed computer, and the parameters are adjusted until agreement is obtained with experiment. A glance at Figs. 1(a) and 1(b) shows four principal bands for both the O and E rays and several of the bands have structure. The dispersion analysis of quartz is therefore a much greater undertaking than the previous analyses. Nevertheless the analysis proved to be quite feasible, because reasonably good initial guesses could be made for most of the parameters from inspection of the data. Also ϵ_0 can be accurately ascertained from the refractive index[38] in the region 1–4 μ. The theoretical fit obtained is shown by the curves of Figs. 1(a) and 1(b).

It will be seen that for the O ray no discrepancy exists between the measurements and the analysis. But in the case of the E ray the following minor discrepancies may be noted: (a) The calculated peak at 20 μ is greater than the measured peak, (b) The analysis appears slightly low in the region 20.5 to 22.5 μ. The small dip measured at 8.6 μ is spurious as previously discussed, and was therefore omitted from the analysis.

Effects similar to that just noted at 20 μ have been observed in SiC [12] and GaP.[14] In these cases it was

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[38] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), Vol. 6, p. 23; also see reference 33, p. 591.

possible to ascribe the effect to a damaged surface layer, and this layer could be removed by etching. These damaged layers produced by polishing had thickness of approximately 1×10^{-4} cm. The measurements of Figs. 1(a) and 1(b) were taken after the removal of 3×10^{-4} cm by HF etching. Measurements taken prior to the etching (not shown) are in agreement with those shown except in the region 18.5 to 20.2 μ for the E ray where they are slightly lower. Therefore the discrepancy at 20 μ may be ascribed tentatively but not definitely to a damaged surface. The present situation differs in three respects from that of SiC and GaP: (a) It will be shown that the present case (the 18–20 μ band of the E ray) involves three resonances. (b) The strongest of the three is considerably weaker than the reststrahls of SiC or GaP. (c) The experimentally observed effect of etching is of much smaller magnitude.

The discrepancy in the region 20.5–22.5 μ coincides with a peak in the reflectivity of the O ray. Since the discrepancy is $<2\%$ it could very well be due to incomplete polarization.

The dispersion parameters obtained from the analysis are given in Table I(a) and (b) for the O and E rays, respectively. The first column gives the wavelengths of the resonances, the second column the corresponding frequencies in wavenumbers (cm^{-1}), the third column the resonance strengths, and the fourth column the widths. The notation is that of reference 12. Also listed are $\sum 4\pi\rho_j$ and $\epsilon_\perp$, $\epsilon_{\parallel}$. Most of the resonances listed are clearly distinguishable in the reflectivity, but not all in the same way. It is of course familiar that strong resonances give rise to bands of high reflectivity, as seen for example at 9.33, 22.20, and 25.35 μ in the O ray. It is not surprising that weaker resonances, if they are sharp, can produce smaller maxima as seen at 12.55 and 14.35 μ in the O ray and 12.85 μ in the E ray. However, when a sharp weak resonance lies close to a strong resonance at longer wavelength so as to fall within the high reflectivity band of the latter, it produces a *minimum* in the reflectivity. Examples of this may be seen at 8.6 μ in the O ray and 19.65 μ in the E ray. The very weak resonance at 18.9 μ produces only a suggestion of a minimum. This resonance and that at 19.65 μ have not been previously reported.

TABLE I. The dispersion parameters of quartz for the ordinary ray (a) and the extraordinary ray (b) obtained from the reflectivity.

		(a)	
$\lambda(\mu)$	$\tilde{\nu}$(cm^{-1})	$4\pi\rho$	γ
8.15±0.05	1227	0.009±0.002	0.11 ±0.04
8.60 0.02	1163	0.010 0.002	0.006 0.002
9.33 0.02	1072	0.67 0.02	0.0071 0.0003
12.55 0.02	797	0.11 0.01	0.009 0.001
14.35 0.02	697	0.018 0.002	0.012 0.004
22.20 0.02	450	0.82 0.02	0.0090 0.0005
25.35 0.02	394	0.33 0.02	0.007 0.001
		$\epsilon_0=2.356\pm0.002$	
		$\Sigma\, 4\pi\rho=1.97\pm0.04$	
		$\epsilon_\perp=4.32\pm0.04$	
		(b)	
8.20±0.05	1220	0.011±0.001	0.15 ±0.02
9.26 0.02	1080	0.67 0.01	0.0069 0.0003
12.85 0.03	778	0.10 0.01	0.010 0.001
18.9 0.10	539	0.006 0.001	0.04 0.01
19.65 0.10	509	0.05 0.02	0.014 0.003
20.20 0.10	495	0.66 0.02	0.0090 0.0003
27.45 0.15	364	0.68 0.02	0.014 0.0004
		$\epsilon_0=2.383\pm0.002$	
		$\Sigma\, 4\pi\rho=2.18\pm0.04$	
		$\epsilon_{\parallel}=4.56\pm0.04$	

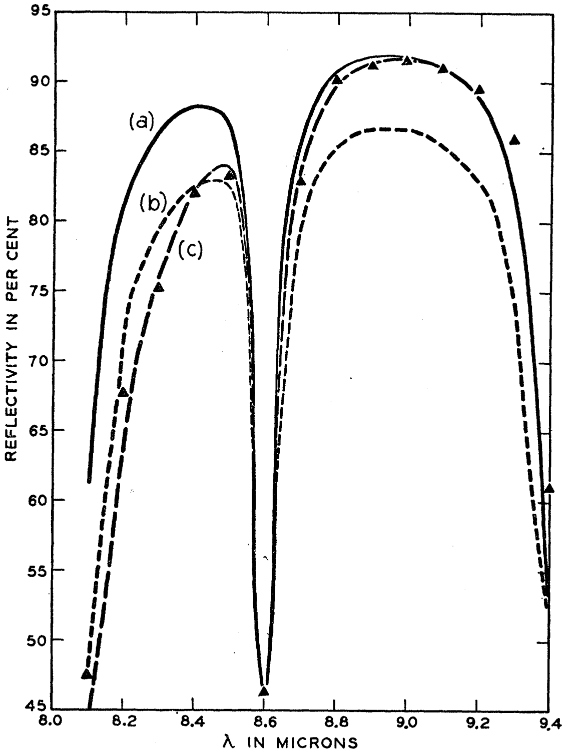

FIG. 3. The reflectivity near 9 μ for the ordinary ray showing the effect of the 8.15 μ resonance. For explanation of the three curves, see the text.

There is no dip, peak, or kink in the reflectivity for either ray to indicate a resonance near 8.2 μ, but these resonances are required by the shape of the short wavelength side of the 9-μ reflectivity bands. An enlarged view of the 9-μ band for the O ray is shown in Fig. 3 where the data is indicated by points. Curve (a) is calculated with the 8.15 μ resonance omitted and the other parameters as in Table I(a). The curve fits well except in the region 8.1–8.5 μ where it is too high. In curve (b) better agreement in this region is obtained by increasing γ for the 9.33 μ resonance from 0.0071 to 0.012, but this curve is poor at 9 μ. A thorough study has shown that the correct shape can be reproduced only by adding a resonance near 8.2 μ, although the parameters of this resonance cannot be determined with great accuracy. It will be seen that curve (c) which includes the 8.15 μ resonance fits the data well.

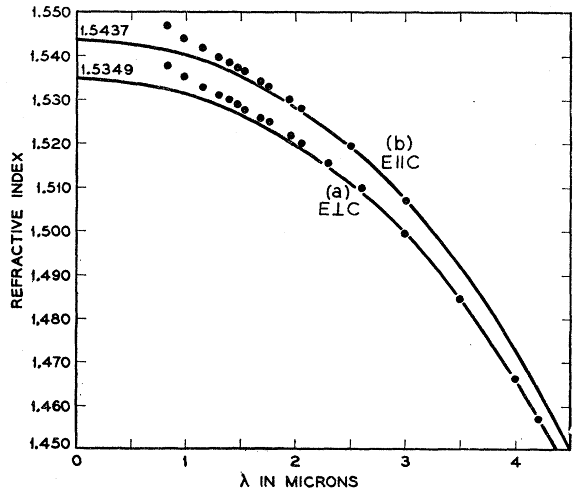

FIG. 4. The refractive index of quartz. The data[38] are shown by the points and the theoretical fit by the solid curves.

The 8.2 μ resonance in the E ray is required for the same reason.

The errors listed in the tables refer to the precision of the dispersion analysis. Most of the considerations concerning the accuracy of a dispersion analysis previously presented[14] for a simple spectrum also apply to the present case. In general the errors are estimated during the course of the analysis from the sensitivity of the results to the various parameters. Therefore the errors listed give the accuracy of fitting the data, but not the accuracy of the data itself. Except for the weak 8.2 μ resonances the listed errors in λ are no larger and in most cases much less than the experimental errors discussed in the previous section, showing that further precision in the analysis cannot be attained.

The high-frequency dielectric constant ϵ_0 was obtained from the refractive index[38] in the region 0.9 to 4 μ shown by the points in Fig. 4. The curves are calculated from the dispersion parameters, and only take into account the dispersion due to the infrared reflectivity bands. The increase of n above the curves for $\lambda<2$ μ is due to the fundamental absorption edge in the ultraviolet. The limiting values of the curves as $\lambda\rightarrow 0$ are $\epsilon_0^{\frac{1}{2}}$. To begin the analysis ϵ_0 was estimated from graphical extrapolations of $n(\lambda)$ to $\lambda=0$. It then proved possible to fit the reflectivity and obtain the other dispersion parameters. Finally ϵ_0 was slightly adjusted to obtain the best fit to $n(\lambda)$ as shown in Fig. 4. It did not prove necessary to readjust the other dispersion parameters. The asymptotic approach of $n(\lambda)$ for the O ray to the curve shows that ϵ_0 may be considered constant for $\lambda>3$ μ. The data for the E ray does not extend beyond 3.0 μ, but the asymptotic behavior appears to be the same as that of the O ray. The errors in ϵ_0 were estimated from the deviations of the curves from the data at 2.0 μ.

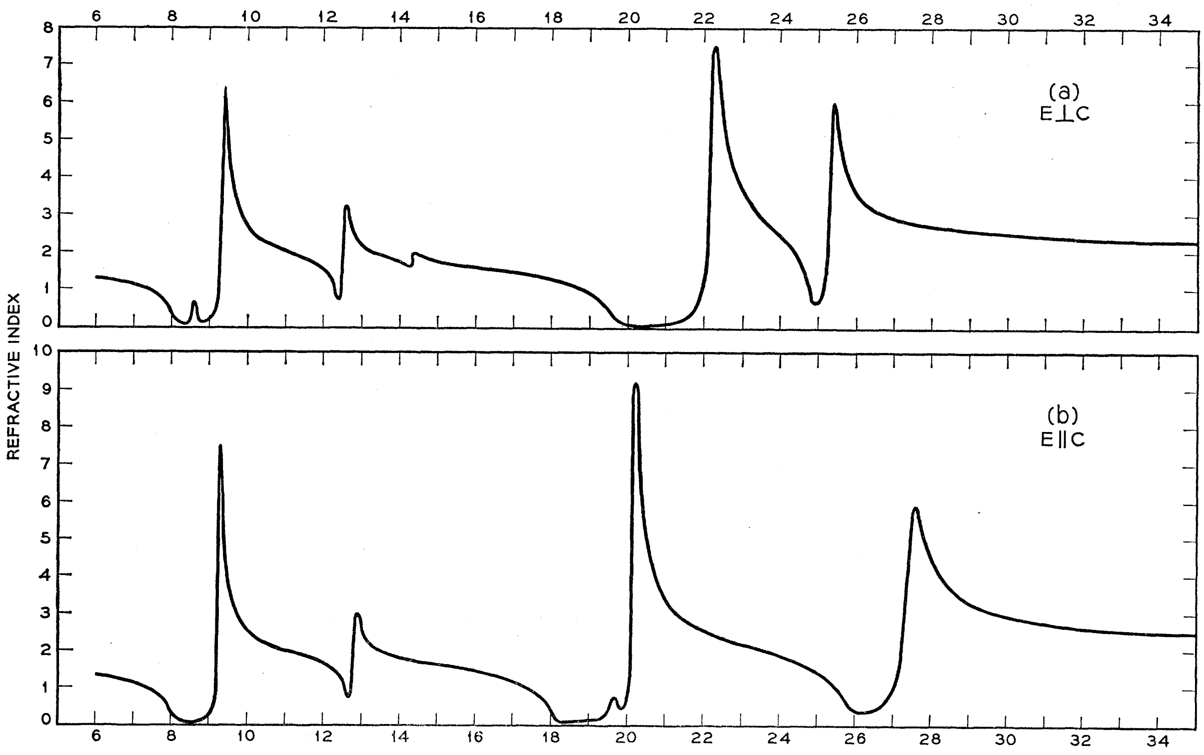

FIG. 5. The refractive index of quartz for the ordinary ray (a) and the extraordinary ray (b) as obtained from the dispersion analysis of the reflectivity.

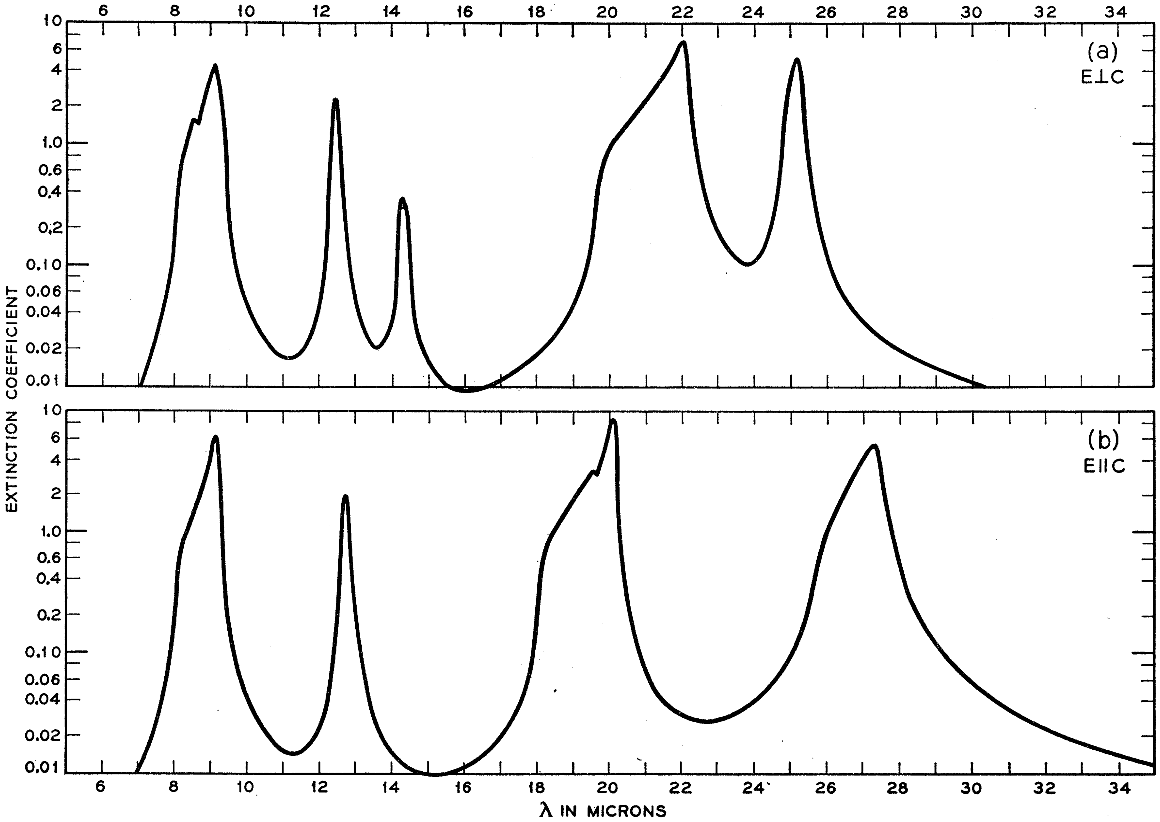

FIG. 6. The extinction coefficient of quartz for the ordinary ray (a) and the extraordinary ray (b) as obtained from the dispersion analysis of the reflectivity.

For many purposes the optical constants, n and k, are of interest rather than the dispersion parameters themselves. The refractive index from 4 to 35 μ is shown in Fig. 5 and the extinction coefficient in Fig. 6. It will be observed that k becomes quite small ~ 0.01 in the regions between the strong-reflectivity bands. This would predict that one should observe measurable transmission in these regions through samples of $\sim 10^{-2}$-cm thickness.

From the optical constants the transmission can be calculated for a sample of any thickness taking into account interference effects.[12] The results corresponding to the thickness of the measured sample are shown by the curves in Fig. 2. It will be realized that except for ϵ_0 the dispersion analysis is based entirely on the reflectivity. Furthermore, the analysis leans most heavily on the data within the reflectivity bands where the absorption is so high that the transmission measurements become impractical. Therefore a comparison of the measured and calculated transmissions provides a severe test of the dispersion analysis. With one exception the wavelengths at which the sample goes opaque are predicted within 0.1 μ. The regions of transparency exhibit a structure characteristic of interference effects which is closely reproduced by the theory. A total of 25 interference maxima are predicted correctly within 0.1 μ, indicating that the $n(\lambda)$ is given correctly by the theory to an accuracy of 1% or better in the regions of transparency. There is also good agreement in the level of transmission except in the windows at 23 μ. Here, especially in the E ray, the observed transmission is about half that predicted. This discrepancy is in the direction which would be expected, since some absorption could arise from combination bands. The transmission level of 25% at the top of the 23 μ window represents an additional absorption coefficient over that predicted by the dispersion analysis of $\Delta\alpha \sim 300$ cm^{-1}. Combination bands of about this strength have been observed in SiC [12] and GaP.[14] However an extra absorption coefficient of $\Delta\alpha \sim 1200$ cm^{-1} at 21 μ is needed to account for the opaqueness of the sample at that wavelength. If the extra absorption in the E ray from 20.6 to 25.3 μ is due to two phonon processes in which one of the phonons belongs to the same branch as the 27.45 μ resonance, the low-energy phonons would range in energy from 0.004 ev (31 cm^{-1}) to 0.015 ev (121 cm^{-1}). These are reasonable energies for acoustic phonons in a hard material.[39] It is also reasonable that the extra absorption would be greatest for the higher energy acoustic phonons.

It has been proposed[8,17–27] that the Kramers-Kronig

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[39] B. Brockhouse and P. Iyengar, Phys. Rev. **111**, 747 (1958).

(K-K) relation provides a powerful tool for analyzing the reflectivity spectrum. Recently Thomas and Hopfield[26] have analyzed the exciton spectrum of CdS by this method. If the reflectivity amplitude is written $re^{i\theta}$, where $r=R^{\frac{1}{2}}$, the K-K relation is[19]

$$\theta(\nu_0)=\frac{2\nu_0}{\pi}\int_0^\infty \frac{\ln r(\nu)}{\nu^2-\nu_0{}^2}d\nu. \tag{4}$$

The optical constants n, k can be readily obtained from the equation

$$re^{i\theta}=[(n-1)-ik]/[(n+1)-ik]. \tag{5}$$

The dispersion parameters are not given directly by the K-K method, but can be obtained from a dispersion analysis of k or of the imaginary part of the dielectric constant $-2nk$. If the resonances are sufficiently far apart the resonance strengths can be conveniently determined from the area under the nk curve by the relation[23]

$$\int nkd\nu=\pi^2\rho_j\nu_j. \tag{6}$$

According to Thomas and Hopfield[26] the accuracy of this procedure for estimating ρ_j is about 10–20%. If only the optical constants and not the dispersion parameters are desired the K-K method has the advantage of giving results with one machine calculation.

It is of interest to inquire into the accuracy of the K-K method as compared with that of dispersion analysis for determining the optical constants. This has been done by applying the K-K procedure to a hypothetical reflectivity obtained from a set of assumed dispersion parameters through Eqs. (1) and (3). The reflectivity was essentially identical with that of the E ray of quartz, so the results are indicative of what one obtains from a K-K analysis of quartz.

The program used was that of Thomas and Hopfield[26] for the IBM 704 computer. In this program the infinite integral in (4) is written as a finite integral over the available data plus a correction term. The correction term is expressed in the form $A+B\nu+C\nu^2$, and the three constants are evaluated by the machine so as to make $\theta(\nu)$ vanish at three appropriately chosen frequencies where k is known to be small. The finite integral is evaluated by representing $\ln r(\nu)$ by straight-line segments between the data points. The integral in (4) can then be evaluated exactly between each pair of data points by elementary integration. This procedure takes into account very accurately the contribution of the pole $\nu=\nu_0$.

The results for the extinction coefficient are shown in Fig. 7 where the exact values of k corresponding to the hypothetical reflectivity are indicated by crosses and the K-K results by open circles. The data were read into the machine for 160 wavelengths evenly spaced from 5 to 37 μ. The points of vanishing k were chosen to be 2.50, 5.62, and 50 μ where the exact k is 0.003 or less. These conditions are very favorable for accuracy because of the large number of data points, the absence of "error" in the data, the large wavelength range covered by the data, and advance knowledge of where the points of zero phase may be chosen. The correction term in the phase angle $\theta(\lambda)$ then turned out to be

$$\Delta\theta(\lambda)=-0.0224-0.0188(5/\lambda)+0.061(5/\lambda)^2, \tag{7}$$

where $\Delta\theta$ is in radians and λ in μ. On the basis of Fig. 7 it may be stated that the K-K procedure used here is accurate to better than 10% in k for $k>0.1$ on the more gradual short wavelength side of the absorption bands. Accuracy on the steep long wavelength side of the bands is somewhat less. For $k<0.1$ the accuracy tends to be poor. In these regions the phase angle is of the same order as the correction $\Delta\theta\sim 0.02$. In other regions of good agreement of k the refractive index n is also in good agreement. The K-K procedure is not a substitute for a dispersion analysis if accurate values for the optical constants are desired, especially in regions of low $k<0.1$.

IV. DISCUSSION

A comprehensive review of the most important experimental work on quartz and vitreous silica prior to 1922 has been given by Sosman.[33] An extensive bibliography of the early infrared work has also been given by Saksena.[32] The earliest work revealed strong reflectivity maxima for the O ray at 8.5, 9.0, 12.5, and 20.8 μ. The first detailed study of the reflectivity for both O and E rays by Reinkober[40] in the range 1 to 18 μ. In addition to the strong bands near 9 and 13 μ Reinkober found a number of minor peaks in these regions and a weak band in the O ray at 14.6 μ. Trowbridge and Wood[41] studied the shape of the 9 μ band in detail using a grating spectrometer of high resolution. They did not observe any of the minor peaks of Reinkober. The detailed shape was again studied at high resolution by Hardy and Silverman[42] who observed a great deal of small fine structure. This structure, however, cannot be identified with that of Reinkober. The reflectivity from 15 to 32 μ for both rays was measured by Liebisch and Rubens.[43] This work revealed strong bands for the O ray at 21.0 and 26 μ, and for the E ray at 19.7 and 27.5 μ. Simon and McMahon[44] have studied the reflectivity of quartz from 7 to 15 μ by the method described by Simon[45] in which the reflectivity is measured at two different angles of incidence. Using this method Reitzel[46] investigated the

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[40] O. Reinkober, thesis, Berlin, 1910 (unpublished); Ann. Physik **34**, 343 (1911).

[41] A. Trowbridge and R. W. Wood, Phil. Mag. **20**, 898 (1910).

[42] J. D. Hardy and S. Silverman, Phys. Rev. **37**, 176 (1931).

[43] T. Liebisch and H. Rubens, Sitzber. deut. Akad. Wiss. Berlin Kl. Gesellschaftswiss **198**, 876 (1919).

[44] I. Simon and H. O. McMahon, J. Chem. Phys. **21**, 23 (1953).

[45] I. Simon, J. Opt. Soc. Am. **41**, 336 (1951).

[46] J. Reitzel, J. Chem. Phys. **23**, 2407 (1955).

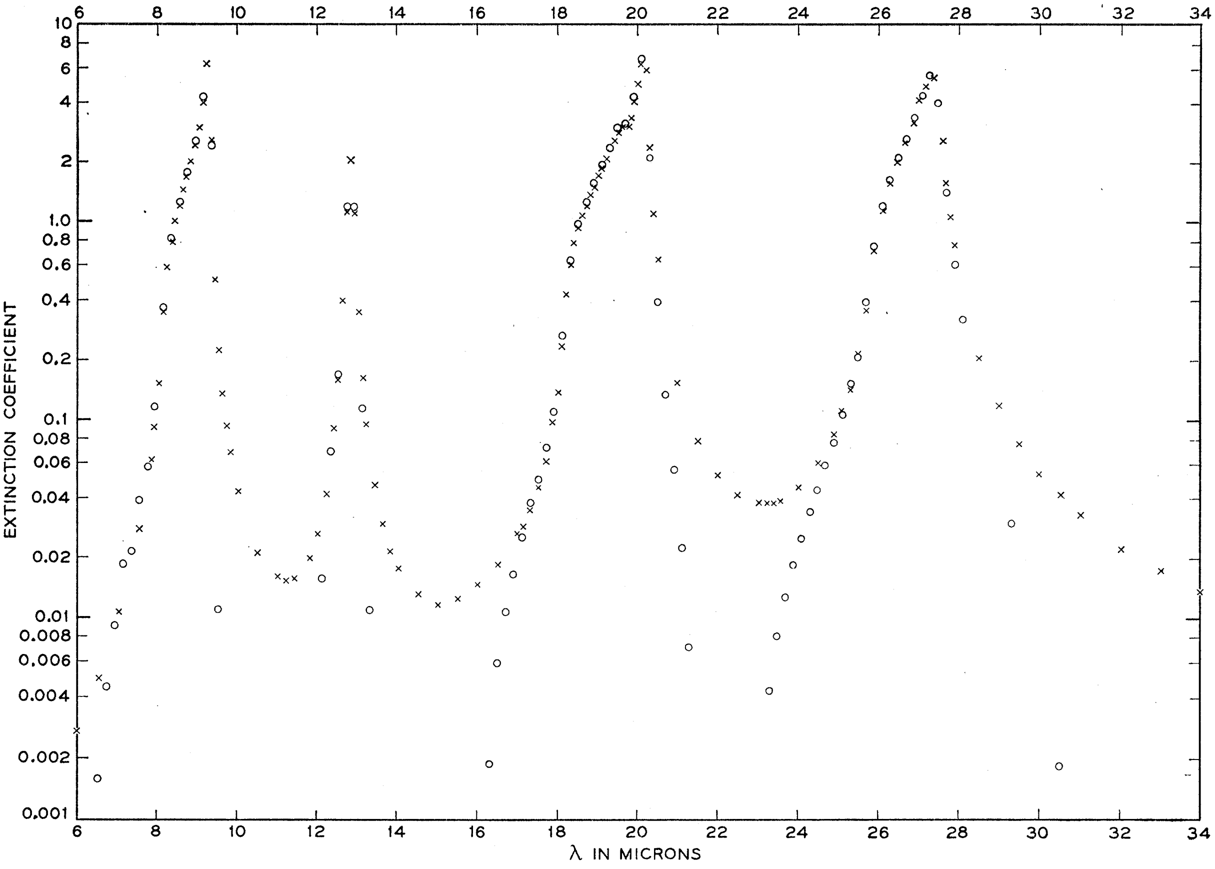

FIG. 7. The extinction coefficient calculated by the Kramers-Kronig method of analysis is shown by the open circles. The crosses show the extinction coefficient which corresponds to the theoretical reflectivity curve used as data. This theoretical reflectivity curve is nearly identical with the dispersion fit of Fig. 1(b).

region 16.5 to 25 μ. In principle[47] Simon's analysis gives the actual resonant frequencies of the lattice oscillators, which as pointed out by Havelock[48] are not the same as the reflectivity maxima.

Most of the early transmission work on quartz was in regions of relatively low absorption up to 5 μ or beyond 50 μ. The first to study a region of high lattice absorption was Nichols,[49] who measured the transmission of a thin sample (0.0018 cm) for the *O* ray in the region 4.5 to 8.1 μ. Rosenthal[50] measured the transmission of a 0.01 cm sample for the *O* ray from 3.5 to 20 μ, observing measurable transparency beyond 10 μ. Barnes[51] has studied both *O* and *E* rays in transmission from 20 to 135 μ. Barnes reports absorption bands at 38 (*O* ray), and 77, 105, 122 μ (both rays). The bands at 38 and 77 μ first seen by Czerny[52] are somewhat stronger than the other long wavelength bands, but very much weaker than the strong bands near 9, 13, 20, 26 μ. The region 1 to 7.8 μ has been remeasured more extensively by Drummond.[53] The most comprehensive transmission work in the region of strong lattice absorption is that recently reported by Saksena[54] from 4 to 15 μ. Using a transmission method Ramadier-Delbes[55] has measured the refractive index for the *O* ray between the strong absorption bands.

The Raman spectrum of quartz has been extensively

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[47] There appears to be difficulty in the application of Simon's method as described by Simon and McMahon for quartz. In applying this method to a uniaxial crystal care must be taken to insure that the light transmitted into the crystal is either an ordinary ray or else an extraordinary ray perpendicular to the optic axis. The only proper arrangement used by Simon and McMahon is shown in their Fig. 1(b), which measures the *O* ray. These authors suggest that in strong reflectivity bands the optical constants can be deduced by the use of an impedance chart, but it is not clear how much use was made of this method in obtaining their results. Also, as pointed out by T. S. Moss, *Optical Properties of Semiconductors* (Academic Press, Inc., New York, 1959), p. 16, the resonance frequency is given by the conductivity maximum rather than the ϵ'' defined by Simon.

[48] T. H. Havelock, Proc. Roy. Soc. (London) **A86**, 1 (1912); **A105**, 488 (1924).

[49] E. F. Nichols, Sitzber preuss. Akad. Wiss. Physik math Kl. 1183 (1896); see reference 33.

[50] H. Rosenthal, Ann. Phys. Chem. **68**, 783 (1899).

[51] R. B. Barnes, Phys. Rev. **39**, 562 (1932).

[52] M. Czerny, Z. Physik **53**, 317 (1929).

[53] D. G. Drummond, Proc. Roy. Soc. (London) **153**, 328 (1935).

[54] B. D. Saksena, Proc. Phys. Soc. (London) **72**, 9 (1958).

[55] Mme Ramadier-Delbes, J. phys. radium **12**, 954 (1951).

investigated, and a summary of the work prior to 1940 is given by Saksena.[32] There is excellent consistency between the various workers, who reported 17 lines between 8 and 80 μ. More recent work by Krishnan[56] which used longer exposures revealed 41 lines from 4 to 80 μ and is consistent with the earlier work. As a result the Raman spectrum is more accurately known than the infrared spectrum. In principle if both spectra are accurately known, including the polarization properties of the Raman spectrum, it should be possible to assign the fundamental lines to specific normal modes of vibration of the lattice. Saksena[32] had suggested assignments on the basis of a group theoretical analysis of the lattice vibrations and the available (1940) optical data. The data required from the reflectivity for such an analysis are the resonance frequencies which Saksena could only estimate[57] rather inaccurately from the reflectivity maxima.

We turn now to a more detailed consideration of the most recent work on the optical properties of quartz in the region of its strong lattice bands.[44,46,54] It is at once surprising that Saksena[54] reports a transmission of 2–3% between 8 and 9.7 μ which contains the well known strong 9-μ absorption band. This is the more surprising in view of the thickness of his samples which ranged from 0.003 to 0.011 cm. Upon comparing the absorption coefficients which he gives with those of Simon and McMahon,[44] one finds that the latter are larger by over an order of magnitude throughout most of the region 8–14 μ. For the *O* ray, the strong resonance in the 9-μ region is given by Saksena as 9.55 μ and Simon and McMahon as 9.39 μ; this discrepancy would seem to be outside of reasonable experimental error. In the 12.5-μ band of the *O* ray, Saksena reports peaks at 12.32 and 12.70 μ for a *Z*-cut crystal (sample plane normal to optic axis) and a single peak at 12.5 μ for an *X*-cut crystal (sample parallel to axis). Simon and McMahon report peaks at 12.47 and 12.58 μ for the *Z*-cut crystal in a quantity ϵ'' defined by them. However, their extinction coefficient, which is the quantity relevant to the transmission measurements of Saksena, shows only one peak at 12.5 μ. Although the double peak in a *Z*-cut crystal observed by Saksena may prove to be significant, it cannot be identified with the double peak in the ϵ'' of Simon and McMahon. It should be mentioned that if Saksena's observation is correct its explanation must be sought beyond the ordinary theory of crystal optics. Reitzel[46] extended the work of Simon and McMahon to 25 μ, but did not study the strong bands at 25 μ (*O* ray) and 27 μ (*E* ray). It is revealing[47] to note that he was unable to analyze the 19 μ-band in the *E* ray, since, as he states, no consistent values of the optical constants could be obtained. Also significant is the fact that the maximum reflectivity observed by Reitzel is $\sim$65%, whereas Liebisch and Rubens[43] observed $\sim$90%. Therefore, as asserted earlier, the optical constants of quartz throughout the range 8–30 μ are in doubt.

The resonance wavelengths found here from a dispersion analysis of the reflectivity of quartz have been listed in Table I. Previously Simon and McMahon[44] have reported resonances for the *E* ray ($E\|C$) at 8.01 not found here, 9.48 not in agreement with 9.26 found here, and 12.82 μ in good agreement with the present work. For the *O* ray ($E\perp C$) they find 8.12, 8.61, and 9.39 μ, all in good agreement with the present work, and 12.47 and 12.58 μ. The latter two are peaks in a quantity ϵ'' which they define. However, their *k* curve has a single maximum at 12.5 in satisfactory agreement with Fig. 6, but the magnitudes of *n* and *k* which they report are not in agreement with Fig. 6. Reitzel[46] reports a resonance at 22.0 μ for the *O* ray in poor agreement with 22.20 μ found here. Also the peak reflectivity (65%) at $\sim$21 μ reported by Reitzel is in disagreement with the present work (91%) and with the earlier work of Liebisch and Rubens[43] (90%). The extinction coefficient reported here agrees with the transmission measurements of Saksena[54] between 7.2 and 8.0 μ and with those of Barnes[51] at 35 μ. On the other hand the samples used by Saksena should have been completely opaque in regions of strong absorption. The reflectivity for the *O* ray in the range 8 to 14 μ at 20° from normal incidence reported by Simon and McMahon[44,47] in their Fig. 4 is in satisfactory agreement with the present work. The optical constants given by them are in qualitative and quantitative disagreement with Figs. 5 and 6. The measured reflectivity reported here is in general agreement with much of the earlier work reviewed in Sec. IV. The refractive index measurements of Ramadier-Delbes[55] in the transmission windows from 5 to 14 μ for the *O* ray are in good agreement with the present results.

The dielectric constant of quartz has been studied by a number of workers with somewhat varying results. It is certain that the dielectric constant $\epsilon_{\|}$ (electric field parallel to optic axis) is larger than $\epsilon_{\perp}$. By the liquid matching method Schmidt[58] obtained $\epsilon_{\|}=4.60$, $\epsilon_{\perp}=4.32$–4.36. Thornton[59] made very accurate measurements on the torsional period of long ellipsoids suspended in an electric field and obtained $\epsilon_{\|}=4.600$, $\epsilon_{\perp}=4.5485$. The most systematic study of $\epsilon_{\|}$ was by Jaeger[60] who obtained $\epsilon_{\|}=4.58$ as the average of many determinations by using the plate condenser method. A frequency effect[61] was observed by Doborzynski[62]

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[56] R. S. Krishnan, Nature **155**, 452 (1945).

[57] It appears from his text and Table II that Saksena has applied Havelock's formula for the shift in the wrong direction.

[58] W. Schmidt, Ann. Physik **9**, 919 (1902); see reference 33.

[59] W. H. Thornton, Proc. Roy. Soc. (London) **A82**, 422 (1909); see reference 33.

[60] R. Jaeger, thesis, Berlin, 1917 (unpublished); see reference 33.

[61] A frequency effect is to be expected in piezoelectric crystals if one compares dielectric constant measurements above and below a piezoelectric resonance. The limiting values far from the resonance are the clamped and free dielectric constants related by the expression $\epsilon_c/\epsilon_F=1-k^2$, where k is the electromechanical coupling factor (in quartz $k\sim 0.1$.) See W. P. Mason, *Piezoelectric*

who reported $\epsilon_{\parallel}=4.66$, $\epsilon_{\perp}=4.55$ at 50 cps and $\epsilon_{\parallel}=4.58$, $\epsilon_{\perp}=4.41$ at 5×10^6 cps. Rao[63] has reported $\epsilon_{\parallel}=4.50$–$4.60$, $\epsilon_{\perp}=4.40$–4.50, and has suggested that these variations are typical of apparently identical samples. Recently Stuart[64] has established that relaxation processes associated with impurity ionic conduction can produce large effects in $\epsilon_{\parallel}$. The existence of tunnels in the axial direction through which ions can migrate was pointed out by Gibson and Vogel.[65]

The values listed in Table I for the long-wavelength dielectric constants $\epsilon_{\perp}$, $\epsilon_{\parallel}$ are to be considered lower limits, since they do not include any resonances beyond 35 μ. However, it is known that there are no reflectivity bands out to 300 μ. Therefore the values

$$\epsilon_{\parallel}=4.56\pm0.04,\quad \epsilon_{\perp}=4.32\pm0.04,$$

may be considered a measurement of the static or low-frequency dielectric constant. This value of $\epsilon_{\parallel}$ is in agreement with Schmidt,[58] Thornton,[59] Doborzynski,[61] and Jaeger.[60] The value of $\epsilon_{\perp}$, however, is lower than most of the values previously reported, although it agrees with Schmidt.[58]

Saksena[32] has given an interpretation of the infrared and Raman spectra of quartz taking into account the selection rules arising from the crystal symmetry. He finds that the 24 normal modes of vibration of zero wave vector can be classified according to their symmetry properties as follows: 4 nondegenerate totally symmetric vibrations (Class A) active only in Raman spectra, 4 nondegenerate vibrations (Class B) active only in the infrared *E* ray, and 8 doubly degenerate vibrations (Class E) active in the infrared *O* ray and Raman spectra. The 4 Class B fundamental vibrations are most reasonably assigned to the *E* ray resonances having the largest $4\pi\rho$ which are at 9.26, 12.85, 20.20, and 27.45 μ. These assignments are the same as Saksena's except for more accurate values for the infrared wavelengths. The weak resonances at 8.20, 18.9, and 19.65 μ are therefore combination bands. The resonances in the *O* ray are compared with certain Raman frequencies reported by Krishnan[56] in Table II. The two long-wavelength resonances are from the transmission measurements of Barnes.[51] The agreement is good except for the 9.33-μ resonance which falls between Raman lines. The approximate strengths of the Raman lines are indicated in parentheses as reported by Krishnan; the infrared resonances are indicated simply as weak or strong. Since there can be only 8 fundamentals one of the resonances in Table II must be a combination band, and it is probably the 8.15-μ resonance which is weak in both spectra and relatively broad (large γ). All the other resonances are moderately strong in one spectrum or the other and an order of magnitude sharper.

TABLE II. A comparison of the ordinary ray resonances with Raman frequencies.

$\lambda(\mu)$	$\bar{\nu}$ (cm^{-1})	$\bar{\nu}$ Raman[a]
8.15 (*w*)	1227	1228 (3)
8.60 (*w*)	1163	1160 (7)
9.33 (*s*)	1072	1082 (4)
		1065 (3)
12.55 (*s*)	797	794 (5)
14.35 (*w*)	697	696 (4)
22.20 (*s*)	450	453 (2)
25.35 (*s*)	394	395 (5)
38 (*w*)[b]	265	267 (7)
78 (*w*)[b]	128	127 (20)

[a] See reference 56.
[b] See reference 51.

ACKNOWLEDGMENTS

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[62] D. Doborzynski, Bull. intern. acad. polon. sci., Ser A, No. 6-8A, 320 (1937).

[63] A.A.S.N. Rao, Proc. Indian Acad. Sci. **A25**, 408 (1947).

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