

Infrared Absorption at Longitudinal Optic Frequency in Cubic Crystal Films

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Thin flat films of cubic ionic crystals have sharp, strong infrared absorption bands at the frequencies characteristic of polar longitudinal optic modes of long wavelength in infinite crystals. The bands occur only when the incident radiation beam is not normal to the surface and only in the p -polarized component of the radiation. They occur not only in transmission through the films, but also in reflection when the films are deposited on thick metallic or dielectric substrates. Such a band was observed in films of LiF and was found to be in good qualitative agreement with, but somewhat stronger than, the band predicted from a dielectric dispersion curve obtained from other types of measurements by Bilz, Genzel, and Happ.

INTRODUCTION

A NUMBER of people have studied dielectric properties of alkali halides and similar cubic ionic crystals near the resonant frequency of polar *transverse* optic vibrational modes of long wavelength by measuring the transmittance of thin films for infrared radiation at normal incidence.¹⁻⁶ They appear to have overlooked the fact that in thin films of such crystals a strong absorption band also occurs at the frequency of polar *longitudinal* optic modes of long wavelength when the radiation is not incident normal to the surface.

It has often been assumed, without considering sample geometry, that absorption measurements in cubic ionic crystals will only give resonant peaks at the frequencies of long-wavelength transverse optic phonons or at frequencies corresponding to multiple phonon processes,^{3,7,8} unless there is some sort of coupling between longitudinal and transverse optic modes.^{5,6} It has been shown^{9,10} that electromagnetic waves, because they are transverse, cannot interact with longitudinal phonons in an *infinite* crystal. This fact may seem to imply that infrared absorption cannot be used to measure the frequency of long-wavelength longitudinal optic phonons. The apparent implication is false because of the boundary conditions in flat films.

Fray *et al.*⁵ actually observed absorption in GaAs at the longitudinal mode frequency limit and, in a note at the end of their paper, suggested that the structure of the vibration spectrum near zero propagation vector was strongly dependent upon the size, shape, and orientation of the specimen.

They appear to be the first experimentalists to have suspected effects of the sort to be described in this paper, but no explanation was given.

The fact that the equivalent of longitudinal optic modes in an infinite medium actually are stimulated in films and may cause considerable absorption of radiation when the angle of incidence is not exactly normal may account for some of the disagreement between authors¹⁻⁴ as to some of the details of the absorption spectra of films in the reststrahlen region.

It is possible for cubic crystals with more than two atoms per unit cell to have more than one transverse and one longitudinal polarized optic mode frequency limit at long wavelengths. The number of such pairs of frequencies can be obtained from the symmetry of the crystal. However, it is much easier to discuss the case of crystals with only one polarized long-wavelength transverse optic frequency limit, ω_t , and one polarized long-wavelength longitudinal optic frequency limit, ω_l . In the rest of this paper, it will be supposed that there is only a single ω_l and ω_t for each crystal. However, the arguments generally apply, with modification that will be mentioned where necessary, to more complicated cubic crystals.

Prior to this time, the polar longitudinal optic mode frequency limit, ω_l , has usually been obtained by one of the following four methods. First, the frequency limit of transverse optic phonons ω_t , and the values of the capacitance or dielectric constant at very low and at near infrared frequencies, ϵ_0 and ϵ_∞ , can be used to compute ω_l through the Lyddane-Sachs-Teller¹¹ relationship, $\omega_l = \omega_t(\epsilon_0/\epsilon_\infty)^{1/2}$. However, there is considerable uncertainty as to the values of ϵ_0 and ϵ_∞ to be used in many substances, especially those that are not good insulators and those that have low-energy electronic transition bands or more than one reststrahlen band.

A second method is to try to fit the observed reststrahlen reflectance curve using a dielectric dispersion relation in which ω_l is a variable parameter. This method lacks accuracy because dielectric dispersion formulas are not accurate unless they have several un-

¹ R. B. Barnes and M. Czerny, *Z. Physik* **72**, 447 (1931); R. B. Barnes, *ibid.* **75**, 723 (1932).

² R. L. Brown, thesis, Ohio State University, Columbus, Ohio, 1959 (unpublished).

³ G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, *Proc. Roy. Soc. (London)* **A261**, 10 (1961).

⁴ R. Geick, *Z. Physik* **166**, 122 (1962).

⁵ W. Cochran, S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, *Proc. Phys. Soc. (London)* **77**, 215 (1961).

⁶ S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, *J. Appl. Phys.* **32**, 2102 (1961).

⁷ W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howarth, *Phys. Rev.* **127**, 1950 (1962).

⁸ J. C. Willmot, *Proc. Phys. Soc. (London)* **A63**, 389 (1950).

⁹ R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, 1956), pp. 54-58.

¹⁰ J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960), p. 209.

¹¹ R. H. Lyddane, R. G. Sachs, and E. Teller, *Phys. Rev.* **59**, 673 (1941).

determined parameters.^{7,12} and the data may be fitted quite well with some range of values of ω_l .

A third method is to find the frequency at which the real part of the dielectric constant passes through zero, using measurements of reflectance and polarization measurements at various angles from thick crystals (Drudes' method or a modification of it). This method has not been used much because the instrumentation is difficult in the far infrared region and the process is laborious.

Finally, recent neutron diffraction studies of a few suitable alkali halides¹³ have yielded curves of longitudinal optic mode frequency at nonzero propagation vector that can be extrapolated to obtain a fairly accurate value of ω_l .

The infrared absorption bands at ω_l in cubic crystal films, to be described, are easily identified and measured, and their measurement should serve as a valuable supplement to the older methods of determining ω_l and the dielectric constant in the vicinity of ω_l .

PHYSICAL BASIS OF THE NEW EXPERIMENT

Plane transverse polar optic modes of long but finite wavelength in an infinite cubic crystal occur at a frequency, ω_t , such that the imaginary part, ϵ_i , of the capacitivity, ϵ , has a maximum value. Longitudinal polar optic modes occur at a frequency, ω_l , such that ϵ has a minimum absolute value. If the waves were not damped, the absolute values of ϵ would be infinite and zero, respectively, at ω_t and ω_l . This is true because undamped transverse waves have no electric field accompanying them, while longitudinal waves have no electric displacement accompanying them. The electric field produced by charge bunching in the longitudinal waves is equal and opposite to the polarization, in rationalized electrostatic units, so that $\epsilon=0$ if there is no damping. Similarly, without damping, the shearing motion of ions in the transverse modes produces no charge bunching, and hence no field, so that $|\epsilon| = \infty$.

A film of such crystal has two normal modes of polarized lattice vibrations having wavelength much greater than the film thickness. In one mode the vibrations are parallel to the film surface and the frequency is ω_t . In the other, vibrations are normal to the film surface and the frequency is ω_l . This is true because polarized vibrations parallel to the film surface produce no electric field, so that they occur when $|\epsilon|$ is very large, while polarized vibrations normal to the surface produce a surface polarization which results in an electric field normal to the surface equal to that component of polarization, and opposite in direction, so that $|\epsilon|$ is minimum.

If infrared radiation of frequency near ω_t , having an electric field component parallel to the film surface, is

incident upon the film, lattice vibrations parallel to the surface will have large amplitude, and an absorption band for the radiation associated with amplitude-dependent loss terms will occur. The large amplitude is a resonance phenomenon and may also be regarded as a consequence of the large value of ϵ , since internal and external components of electric field parallel to the film surface must match.

Similarly, infrared radiation of frequency near ω_l , having an electric field component normal to the film surface, will result in large amplitude lattice vibrations normal to the surface. This resonance may also be viewed as a consequence of the small value of ϵ , since internal and external components of electric displacement normal to the surface must match.

Amplitude-dependent loss terms in vibrations normal to the film surface will result in an absorption band around ω_l for the *p*-polarized component of infrared radiation not incident normal to the film surface. Measurement of this absorption band provides a direct, easy way to find ω_l and the absorption in the vicinity of ω_l , just as earlier measurements of the absorption of normally incident radiation in films have given accurate values of ω_l and absorption in that region.

If the cubic crystal is complex enough to have more than a single transverse and a single longitudinal polar optic mode frequency limit, the preceding physical arguments may be extended to show that each polar transverse mode occurs at a frequency such that $|\epsilon|$ is very large, and each polar longitudinal mode occurs when $|\epsilon|$ is very small.

TRANSMITTANCE OF THICK AND THIN FILMS

The following expressions for the fraction of the incident wave amplitude of the *s*-polarized and *p*-polarized components, respectively, of plane waves transmitted through a layer of isotropic material with plane parallel surfaces, were derived from Maxwell's equations, matching boundary conditions at the surfaces:

$$TA_s = \left\{ e^{i\delta \cos\theta} \left[\cos\delta J - \left(\frac{i}{2}\right) \left(\frac{J}{\cos\theta} + \frac{\cos\theta}{J} \right) \sin\delta J \right] \right\}^{-1}, \quad (1)$$

and

$$TA_p = \left\{ e^{i\delta \cos\theta} \left[\cos\delta J - \left(\frac{i}{2}\right) \left(\frac{J}{\epsilon \cos\theta} + \frac{\epsilon \cos\theta}{J} \right) \sin\delta J \right] \right\}^{-1}. \quad (2)$$

θ is the angle of incidence and ϵ is the (generally complex) dielectric constant. $J = (\epsilon - \sin^2\theta)^{1/2}$, and $\delta/2\pi$ is the thickness of the film, measured in vacuum wavelengths of the incident radiation.

¹² H. Bilz, L. Genzel, and H. Happ, Z. Physik **160**, 535 (1960).

¹³ A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. **119**, 980 (1960).

A first-order expansion of the absolute square of the transmitted amplitudes in powers of δ gives the following approximate expressions for transmittance of very thin films:

$$T_s = TA_s TA_s^* \approx 1 - \delta \epsilon_i / \cos \theta, \tag{3}$$

$$T_p = TA_p TA_p^* \approx 1 - \delta \left[\epsilon_i \cos \theta + \left(\frac{\epsilon_i}{\epsilon_r^2 + \epsilon_i^2} \right) \frac{\sin^2 \theta}{\cos \theta} \right]. \tag{4}$$

In these expressions, the complex dielectric constant is given by $\epsilon_r + i\epsilon_i = \epsilon$.

It will be noted that T_s and T_p both have minima when ϵ_i is maximum. This minimum occurs at the frequency of long-wavelength transverse optic phonons, ω_t . However, T_p also has a minimum when ϵ_i and ϵ_r are both very small, a phenomenon that occurs at the fre-

quency of longitudinal optic phonons of long wavelength, ω_l .

REFLECTANCE OF FILMS ON THICK SUBSTRATES

In some cases, it will be more practical to measure reflectance of a film deposited on a thick substrate than to measure transmittance of an unsupported film or a film on a substrate of negligible optical effect. There is an additional advantage to depositing the film on a metal substrate. A conductive metal practically eliminates the absorption by transverse modes without reducing the absorption band associated with the longitudinal modes. The reason for this is that almost no electric field can exist adjacent and parallel to a metallic surface. The following expressions are obtained for amplitudes of the polarized reflected wave components, relative to the incident amplitude components:

$$RA_s = \frac{\cos(\delta J)(1 - J_b/\cos \theta) - i \sin(\delta J)(J_b/J - J/\cos \theta)}{\cos(\delta J)(1 + J_b/\cos \theta) - i \sin(\delta J)(J_b/J + J/\cos \theta)}, \tag{5}$$

$$RA_p = \frac{\cos(\delta J)(1 - J_b/\epsilon_b \cos \theta) - i \sin(\delta J)(\epsilon J_b/J \epsilon_b - J/\epsilon \cos \theta)}{\cos(\delta J)(1 + J_b/\epsilon_b \cos \theta) - i \sin(\delta J)(\epsilon J_b/J \epsilon_b + J/\epsilon \cos \theta)}. \tag{6}$$

J_b is equal to $(\epsilon_b - \sin^2 \theta)^{1/2}$, where ϵ_b is the dielectric constant of the substrate. In these expressions, the phase is taken with respect to the first surface of the film.

Two interesting special cases appear when the film is very thin. If the substrate is a nonabsorbing dielectric with $\epsilon_b \geq 1.0$, the first-order approximations for reflectance become

$$R_s = RA_s RA_s^* \approx \left[\frac{J_b - \cos \theta}{J_b + \cos \theta} \right]^2 \left[1 + 4\delta \epsilon_i \left(\frac{\cos \theta}{\epsilon_b - 1} \right) \right], \tag{7}$$

and

$$R_p = RA_p RA_p^* \approx \left[\frac{J_b - \epsilon_b \cos \theta}{J_b + \epsilon_b \cos \theta} \right]^2 \times \left\{ 1 + 4\delta \left(\frac{\cos \theta}{\epsilon_b - 1} \right) \left[\epsilon_i J_b^2 - \left(\frac{\epsilon_i}{\epsilon_r^2 + \epsilon_i^2} \right) \sin^2 \theta \right] \right\}. \tag{8}$$

The reflectance, like the transmittance, shows irregularities at ω_1 and at ω_t , but at ω_t there is a reflectance maximum, while at ω_l there is a reflectance minimum.

If the substrate is a very conductive metal, so that the absolute value of ϵ_b is very large, practically no electric field can exist parallel and adjacent to the metal surface. Hence, transverse modes cannot be stimulated in a very thin film on the metal, and an absorption peak only appears at the longitudinal mode frequency in the p -polarized component at nonzero angle of incidence. In this case, the approximate reflectance equations are

$$R_s \approx 1.0, \tag{9}$$

and

$$R_p \approx 1 - 4\delta \left(\frac{\epsilon_i}{\epsilon_r^2 + \epsilon_i^2} \right) \frac{\sin^2 \theta}{\cos \theta}. \tag{10}$$

The validity of the last two equations near ω_t depends upon the supposition that $|\epsilon_b|$ is much larger than $|\epsilon|$ even at ω_t . The film must also be so thin that even when ϵ becomes very large, near ω_t , the film will be considerably thinner than one wavelength within the medium. If these conditions do not hold, a variation in reflectance appears near ω_t for both polarized components.

DISPERSION RELATIONS AND RESONANCES

A classical dielectric dispersion relation for cubic crystals with a single value of ω_t , obtained by using a fixed damping term, γ , proportional to the normal mode velocity in the optic mode of infinite wavelength, is^{12,14}

$$\epsilon = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \left(\frac{1}{1 - \Omega^2 - i\gamma\Omega} \right). \tag{11}$$

A similar dielectric dispersion formula based on a quantum-mechanical treatment with nonlinear coupling between modes may be written^{12,14}

$$\epsilon = \epsilon_\infty + \frac{f(\omega)}{2} (\epsilon_0 - \epsilon_\infty) \left(\frac{1}{1 - \Omega - i\gamma(\omega)} + \frac{1}{1 + \Omega} \right). \tag{12}$$

¹⁴ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1956), Eqs. (10.6) and (47.8).

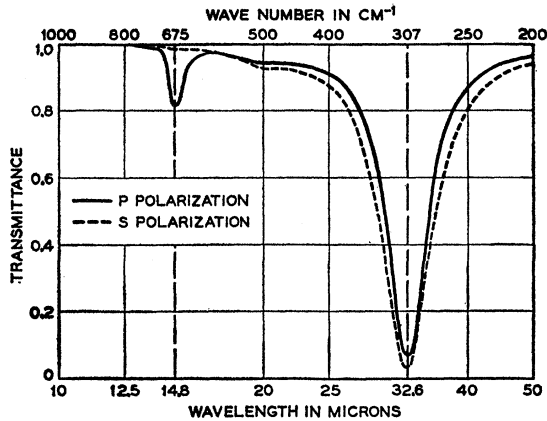


FIG. 1. Computed transmittance at room temperature of s -polarized and p -polarized radiation by a LiF film 0.20μ thick; radiation incident at 30 deg .

In both expressions, ϵ_0 is the dielectric constant at very low frequencies and ϵ_∞ is the dielectric constant at frequencies in the region of visible light. Ω is the ratio of frequency of incident radiation to the transverse optic phonon frequency. $\gamma(\omega)$ is a frequency-dependent damping term that has been computed from approximate theoretical phonon distributions for a few alkali halides and has also been derived from experimental values of the dielectric constant in these crystals.¹² $f(\omega)$ is a thermal correction factor on the oscillator strengths that is unity at absolute zero but becomes slightly dependent on frequency in the vicinity of ω_l at room temperature.¹²

Equation (11) is extended to include more than one value of ω_l in reference (7). The extension of Eq. (12) is analogous. In such complex crystals, each of the frequencies, ω_l , at which $|\epsilon|$ is minimum will depend strongly on the oscillator strengths and frequencies, ω_l , of all the transverse modes except very weak ones or ones with frequency very far from ω_l .

In both dispersion relations [(11) and (12)] the value

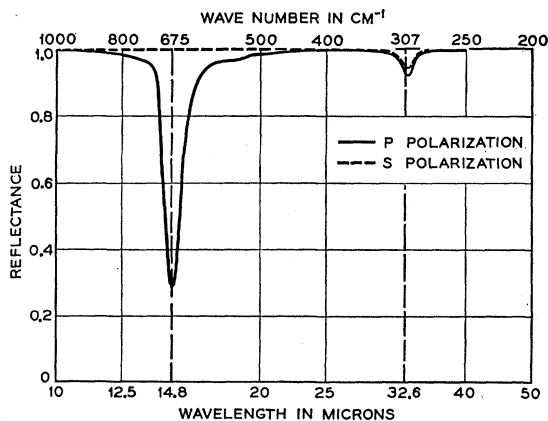


FIG. 2. Computed reflectance of s -polarized and p -polarized radiation by a LiF film 0.35μ thick deposited upon silver; radiation incident at 30 deg .

of ϵ_i is maximum when Ω is near unity, and the value of $\epsilon_i/(\epsilon_i^2 + \epsilon_r^2)$ is maximum when Ω is near $(\epsilon_0/\epsilon_\infty)^{1/2}$.

Upon expanding expressions from Eqs. (11) and (12) for ϵ_i about $\Omega=1$ and for $\epsilon_i/(\epsilon_i^2 + \epsilon_r^2)$ about $\Omega=\Omega_l = (\epsilon_0/\epsilon_\infty)^{1/2}$, one obtains the following Lorentzian resonance functions, assuming $f(\omega)$ is unity:

$$\epsilon_i \approx \left(\frac{\epsilon_0 - \epsilon_\infty}{2} \right) \left(\frac{G}{(\Omega - 1)^2 + G^2} \right), \quad (13)$$

and

$$\frac{\epsilon_i}{\epsilon_r^2 + \epsilon_i^2} \approx \left(\frac{1}{\epsilon_\infty^2 \Omega_l} \right) \left(\frac{\epsilon_0 - \epsilon_\infty}{2} \right) \left(\frac{H}{(\Omega - \Omega_l)^2 + H^2} \right). \quad (14)$$

In the elementary linear theory, $G=H=\gamma/2$, but in the nonlinear quantum-mechanical theory, $G=\gamma(\omega)$, while $H=\gamma(\omega)(\Omega_l+1)^2/4\Omega_l$.

NUMERICAL ILLUSTRATION

Equations (1), (2), (5), and (6) were used to compute the transmittance of a lithium fluoride film and the

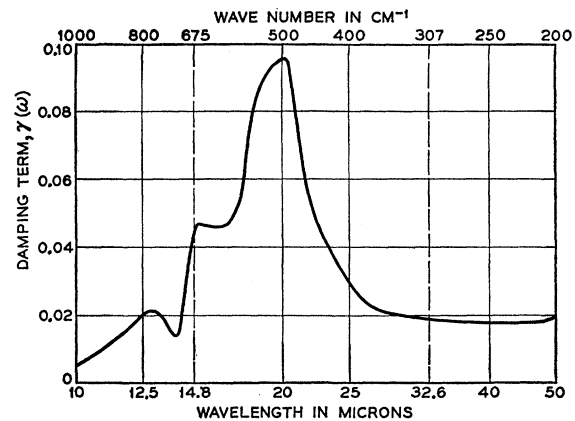


FIG. 3. The damping term, $\gamma(\omega)$, as a function of photon wavelength and wave number. Dashed lines at 14.8 and 32.6μ denote the assumed frequencies of longitudinal and transverse optic modes.

reflectance of a silver surface covered with a lithium fluoride film, assuming that the infrared radiation is perfectly collimated and plane polarized, and is incident at an angle of 30 deg from the normal. The results are shown in Figs. 1 and 2. The capacitance of LiF as a function of frequency was obtained from Eq. (12), using the values of $\gamma(\omega)$ shown in Fig. 3, which were obtained by Bilz *et al.*¹² from experimental data. The capacitance of silver as a function of frequency was computed from data and formulas published by Hodgson,¹⁵ although an infinite value would have given indistinguishable results at the frequencies of interest.

The asymmetry of the absorption band at ω_l (14.8μ) is due to the sudden change in $\gamma(\omega)$ at that frequency. The weak band at 20μ is associated with the peak in the

¹⁵ J. N. Hodgson, Proc. Phys. Soc. (London) **B68**, 593 (1955).

curve for $\gamma(\omega)$ there. The asymmetry and the extra band would be absent if the classical formula [Eq. (11)] with fixed γ were used. The thicknesses were chosen to be approximately the same as those used in the experiments to be described.

EXPERIMENTAL VERIFICATION

The following experiments were performed to verify the predictions represented in Figs. 1 and 2. A film of LiF 0.20μ thick was evaporated on a collodion film about 0.1μ thick that was at a temperature of about 25° . The ratio of intensities of polarized radiation transmitted at 30° from normal incidence through the sample and through a like piece of uncoated collodion are shown in Fig. 4. The transmittance of the uncoated collodion was over 95% at all wavelengths used.

A film of LiF 0.348μ thick was evaporated on a silvered segment of a microscope slide at about 25°C , and another LiF film 0.325μ thick was deposited on a similar substrate at 265°C . The microscope slides were optically flat and had freshly evaporated layers of silver about 0.1μ thick on them. The ratio of intensities of polarized radiation reflected from each sample of LiF film on silvered glass and from like pieces of uncoated, silvered glass are shown in Fig. 5. There was no measurable loss of intensity upon reflection from the silvered glass blanks.

The LiF film thicknesses were determined by evaporating LiF on a microscope slide placed beside the sample being formed for measurement. A straight-edged region with no LiF film was produced on the test slide by shielding part of the slide from the source of LiF with a piece of wire. The wire was removed, and a nearly opaque layer of silver was deposited over the LiF on the test slide. The height of the edge of the LiF film under the silver on the test slide was measured by placing a 90% reflecting silvered, transparent optical flat over the slide and measuring the steps in the Fabry-Perot

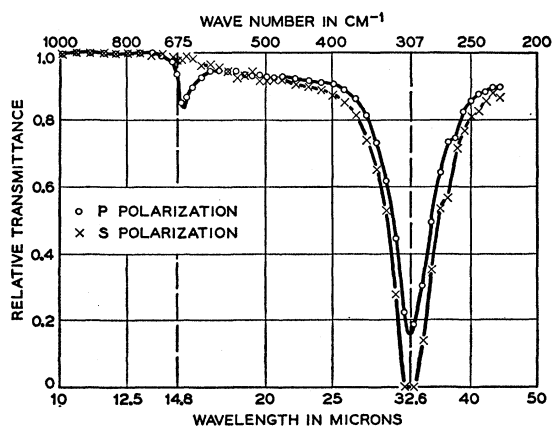


FIG. 4. Observed transmittance at room temperature of *s*-polarized and *p*-polarized radiation by a LiF film 0.20μ thick deposited at 25°C on collodion, relative to that by uncoated collodion. Radiation incident in a cone from 26 to 34 deg.

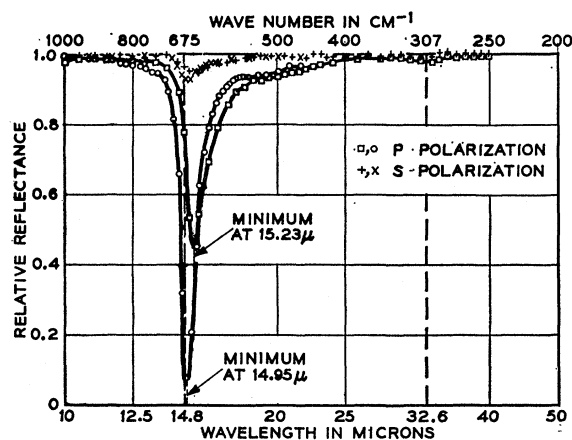


FIG. 5. Observed reflectance of *s*-polarized and *p*-polarized radiation by silvered glass slides with LiF films deposited on them, relative to that by silvered glass alone. Radiation incident from 26 to 34 deg. Circles and \times 's mark *p*- and *s*-polarized components for a film 0.325μ thick deposited on a substrate while it was heated to 265°C . Squares and $+$'s are for a film 0.348μ thick deposited on a substrate at 25°C .

interference fringes of monochromatic light from an Osram thallium vapor lamp with the aid of a metallographic microscope.

Infrared intensity measurements from 10 to 25μ were made using a 60 -deg CsBr prism in a Perkin Elmer Model 99 double-pass monochromator. Beyond 25μ a 27 deg CsI prism was used in the monochromator. There was a noticeable amount of scattered, partly polarized chopped radiation that produced either positive or negative signals at various points in the spectrum when the CsI prism was used. Part, but not all, of this was eliminated by placing an aperture at the image of the slit between the two mirrors adjacent to the chopper that return the beam for a second pass. In addition, the resolution was low with the CsI prism. Consequently, differences between calculated and observed reflectance or transmittance may not be significant in the region between 25 and 45μ . Neither difficulty was detected with the CsBr prism.

A sheet of pyrolytic graphite about 8μ thick,¹⁶ sandwiched between two CsI windows, was used as a polarizer. No corrections were made for incomplete polarization of the beam caused either by polarizer imperfection or by incomplete collimation of the beam. This fact accounts for the dip in measured reflectance of the *s*-polarized radiation at ω_1 .

The actual location of the peak of the absorption band around ω_1 was obtained by comparing continuous traces of transmitted or reflected beam intensity with and without the LiF films. The proximity of the band to a sharp atmospheric absorption band at 14.97μ due to CO_2 made possible very accurate determination of the wavelength. The minimum transmittance or reflectance

¹⁶ G. Rupprecht, D. M. Ginsberg, and J. D. Leslie, J. Opt. Soc. Am. 52, 665 (1962). (The pyrolytic graphite was a gift from the Raytheon Company.)

occurred at $15.23 \pm 0.05 \mu$ in films deposited on cold substrates and at $14.95 \pm 0.05 \mu$ in films deposited at 265°C .

INTERPRETATION AND CONCLUSIONS

The experimental results are in good qualitative agreement with the predictions based on the dielectric dispersion formula and data of Bilz *et al.* However, the films deposited on cold substrates show maximum absorption in the ω_l band at a significantly longer wavelength than was predicted, and the bands are more asymmetric than predicted. The film deposited on the heated substrate shows the absorption peak shifted to very nearly the predicted wavelength, but the absorption in all parts of the band, and especially at the peak, is greater than predicted.

It has been observed before² that LiF films deposited at room temperature do not give consistent infrared absorption spectra. Although spectra of films deposited on silver at room temperature at this laboratory were fairly consistent, they were not the same as the spectra of films deposited at 265°C . The reason for the difference is open to conjecture.

Films that are rough on the surface may be expected to have both absorption bands flattened, broadened, and slightly shifted toward frequencies intermediate between ω_s and ω_l . This is because the mean square electric displacement parallel to the surfaces would be increased and that normal to the surfaces would be decreased by irregularities in the surface polarization.¹⁷ CaF_2 films

evaporated on silvered glass at 25°C showed a large amount of such distortion of the absorption bands. Fabry-Perot interference fringes observed with the metallographic microscope when the film thickness was being measured were very broad over the CaF_2 films but sharp over the shadow left by the wire. This seems to confirm that the film surfaces were quite rough and granular. However, all of the interference fringes observed in measuring the LiF films were extremely sharp. This suggests that the asymmetry and shift of the band in LiF films deposited at 25°C is probably due, at least in part, to film properties other than surface irregularities, such as strains and grain boundary effects.

The absorption at the peak of the ω_l band by the LiF deposited on the heated substrate is greater than predicted by an amount that cannot be accounted for by correcting for the range of angles of incidence within the cone of the beam. Consistent large errors in measurement, giving too small film thickness, could account for most of the difference, but do not seem likely. The difference might be accounted for by supposing that the value of $\gamma(\omega)$ used at the peak of the band was quite a bit too large, but the higher absorption on the wings of the band suggest that $\gamma(\omega)$ is too small there. Thus, a rather violent fluctuation of $\gamma(\omega)$ is required to account for the absorption using the dispersion relation represented by Eq. (12). Altering $f(\omega)$ would shift the band frequency without changing its strength much. It seems likely that a more complicated dispersion relation¹⁸ is necessary to account for the observed band.

ACKNOWLEDGMENT

Much of the credit for setting up and performing the experiments on LiF films is due to R. H. Kaiser.

¹⁸R. F. Wallis and A. A. Maradudin, *Phys. Rev.* **125**, 1277 (1962).

¹⁷In the extreme cases when the "films" are composed of small isolated spheres on negligible substrates or hemispheres on metallic substrates, the two absorption bands move together to form a single band at an intermediate frequency such that $\epsilon \approx -2$. See H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, London, 1958), 2nd ed. [Eqs. (18.11) and (18.12)].