PHYSICAL REVIEW VOLUME 174, NUMBER 3 15 OCTOBER 1968

Adjusting Poles and Zeros of Dielectric Dispersion to Fit Reststrahlen of $PrCl_3$ and $LaCl_3$

DWIGHT W. BERREMAN AND F. C. UNTERWALD
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 20 May 1968)

The dielectric dispersion function of a medium can be defined by the locations of the poles and zeros of that function in the complex-frequency plane. In this form the dispersion function is not restricted by special characteristics of any specific physical model from which dispersion might be derived. The locations of these poles and zeros are subject to several more or less fundamental physical restrictions which are described in this paper. The connections between the locations of the poles and zeros, the frequencies and damping constants of certain optical modes, and the Lyddane-Sachs-Teller relation are discussed. Adjustments of locations of poles and zeros, consistent with the physical restrictions, were performed to obtain least-squares fits of reststrahlen data from $PrCl_3$ and $LaCl_3$ using a small number of poles and zeros. In this way, approximate dispersion functions for the two dielectric tensor components of each crystal were obtained at room temperature and at lower temperatures.

INTRODUCTION

IN this paper we describe the fitting of some infrared reststrahlen reflectance data with dielectric dispersion functions of a very general form. We have avoided the usual custom of trying to fit the data with dispersion relations obtained theoretically from specific lattice dynamical models. Instead we only assume that, whatever the correct model is, the dispersion relation can be closely approximated by a function with only a few poles and zeros in the complex-frequency plane. The locations of these poles and zeros completely define the dispersion function. We have found the locations of a small number of poles and zeros that quite accurately describe the reststrahlen bands of $PrCl_3$ and $LaCl_3$ at temperatures of 293, 82, and 20°K. If a theoretical derivation of dispersion relations for these crystals from any specific model is carried out in the future, it should be a relatively small step to compute locations of the most significant poles and zeros and to compare them with our experimental results.

We place special emphasis on the method of analyzing data by adjusting the locations of poles and zeros in the dielectric dispersion functions because we believe that this is the first time that reststrahlen data have been fitted by this method. Reference to location of zeros and poles in previous analyses, if made at all, have usually been in the form of incidental remarks except in some papers by Barker.[1,2] In the past, data have generally been fitted with a dispersion relation derived from a model consisting of one or more uncoupled, harmonically damped modes of ionic vibration. Such relations are unnecessarily restrictive. Except when only one or two such modes are used as an approximation, more adjustable parameters may be required to get a good fit to data than are required if poles and zeros themselves are adjusted. Barker[2] has demonstrated that a better fit is obtained to certain reststrahlen data by using a dispersion relation written like the uncoupled oscillator expression but having a frequency-dependent damping term of a particular form that can be derived from a model with two coupled oscillators, than by using the same number of adjustable parameters in the classical uncoupled, harmonically damped oscillator relation. We will show that allowing poles and zeros to be adjusted independently is equivalent to allowing frequency-dependent complex parameters to appear in the uncoupled harmonic-oscillator relation. Both Barker's expression and the uncoupled-oscillator expression are restricted cases of the general pole and zero-dispersion relation. We will also discuss the relationship between the pole and zero-dispersion relation and the uncoupled classical oscillator relation. This is done so that readers familiar with the classical oscillator relation can readily interpret the physical significance of the locations of zeros and poles, and can recognize some of the advantages of the "pole and zero-" dispersion relation.

DISPERSION FUNCTION FORM

The following is a very general dispersion relation for each spatial component of a frequency-dependent dielectric tensor:

$$\epsilon=\prod_{m=1}^{M}(\omega-Z_m)/\prod_{n=1}^{N}(\omega-P_n). \tag{1}$$

In this expression, ω is the frequency of the incident radiation. The zeros Z_m and the poles P_n that we will determine have moduli or absolute values in the neighborhood of reststrahlen frequencies. Poles near the real axis and far from other poles may be taken to represent frequencies and damping constants of optically active or electrically polar TO phonon modes of long wavelength. Zeros near the real axis and well isolated from other zeros may be taken to represent frequencies and damping constants of electrically polar LO modes. If a pole and a zero are nearer to one another than they are to the real axis, they will show only a weak effect on

---

[1] A. S. Barker, Jr., Phys. Rev. **136**, A1290 (1964).

[2] A. S. Barker, Jr., in *Ferroelectricity*, edited by E. F. Weller (Elsevier Publishing Co., Amsterdam, 1967), p. 213ff, especially Eqs. (41) and (42).

the dispersion curves. Such pairs are characteristic of optical processes involving two or more phonons, which contribute small variations from the smooth curves that would be produced if only simple first-order optical resonances were present.

The dispersion relation (1) is the most general single-valued form of complex dispersion function not involving essential singularities or continuous lines of singularities. Numerator and denominator are polynomials in frequency ω. It is unlikely that any realistic dielectric dispersion function cannot be closely approximated, at least along the real axis, by a ratio of polynomials of rather low order. Some complex models from which dispersion functions are derived lead to localized clusters of poles and zeros in the complex-frequency plane. If such a cluster is far from the real axis compared to its diameter and contains equal numbers of poles and zeros, its effect on dispersion will be the same as if the cluster were replaced by a single pole and zero pair. Consider a cluster of N poles and N zeros near a point ω_1 in the complex-frequency plane. The location of poles (or zeros) will be represented by $\omega_1+\delta_{pi}$ (or $\omega_1+\delta_{zi}$), where the δ's are small. Then the contribution to the dispersion function by the whole cluster can be represented by

$$\prod_{i=1}^{N} \frac{\omega-\omega_1-\delta_{zi}}{\omega-\omega_1-\delta_{pi}} \approx \Big(\omega-\omega_1-\sum_{i=1}^{N}\delta_{zi}\Big)\Big/\Big(\omega-\omega_1-\sum_{i=1}^{N}\delta_{pi}\Big)$$

$$\approx 1-\sum(\delta_{zi}-\delta_{pi})/(\omega-\omega_1). \qquad (2)$$

[The approximation neglects terms of order $\delta^2/(\omega-\omega_1)^2$.] Hence a single pole at $\omega_1+\sum\delta_{zi}$ and a similarly expressed zero describe the effects of the whole cluster so long as $\omega-\omega_1$ is large compared to any δ in the cluster. The location ω_1 of the single pole-zero pair is not as critical in magnitude as its separation $\sum(\delta_{zi}-\delta_{pi})$ because ω_1 is a much larger quantity.

Probably the worst that might occur in any realistic model for dielectric dispersion is that N, the number of poles and zeros in a small cluster, may go to infinity in such a way that $\sum(\delta_{zi}-\delta_{pi})$ remains finite, so that the approximation can still be made.

With the provision that clusters of poles and zeros not too near the real-frequency axis are to be replaced by a single equivalent pole-zero pair, even the most complicated of realistic dielectric dispersion functions can probably be represented accurately with a moderate number of poles and zeros.

PHYSICAL RESTRICTIONS ON POLES AND ZEROS

Many of the results given here have direct analogs in the classical theory of passive two-terminal networks,[3] where, for instance, admittance over frequency can replace polarizability divided by the unit imaginary number i. Since electrical polarization $P=\chi E$ cannot occur in a medium in response to an applied electric field E before the field is applied, electrical polarizability χ is said to obey the principle of causality.[2,4] It has been shown that functions that obey the principle of causality can have poles only below the real axis, so that they are analytic functions on and above the real axis.[4] [We adopt the convention that time-periodic functions are of the form $\exp(-i\omega t)$. If the opposite sign convention were chosen, as in Barker,[1,2] poles would occur only above the real axis.] Since dielectric tensor components ϵ differ from polarizability components χ only by a real additive constant, ϵ must also have poles only below the real axis.

Another physically required property of the dispersion function for ϵ is that its zeros must also lie below the real axis. This follows from the fact that, if the crystal is polarized by any nonelectrical force, such as mechanical stress, an electric field $E=P/\chi$ will be caused by the polarization P. Since such an electric field cannot appear before the polarization is produced, $1/\chi$ must obey the principle of causality just as χ does. If $1/\epsilon$ had a pole above the real axis, then so would $1/\chi$, since χ and ϵ differ only by a real additive constant. Consequently, the zeros of ϵ as well as its poles must lie below the real axis.

If the electromagnetic behavior of a medium can be described by a scalar or a second-rank tensor dielectric function, propagation must be symmetric for positive and negative values of ω. Consequently, every pole and every zero not on the imaginary axis must have a mate with the same imaginary part but the opposite real part. That is, a map of the zeros and poles has "mirror symmetry" about the imaginary axis in most media (see Davidov[4]). For brevity we shall call this restriction the "symmetric" property.

Since ϵ approaches unity as ω approaches infinity for all substances, it is necessary that $N=M$ in Eq. (1). The infrared dispersive properties of crystals that are transparent and almost nondispersive in the optical-frequency region can be described quite accurately by lumping terms from zeros and poles at ultraviolet frequencies into a real multiplicative constant ϵ_{opt}. In order that ϵ may approach this constant at optical frequencies, which are much larger than the moduli of the poles and zeros in the reststrahlen region, it is also necessary that the number of zeros equal the number of poles in the reststrahlen region alone for such crystals.

Insulators can have only real values of ϵ at zero frequency. Consequently, insulators must have one zero on the imaginary axis for every pole on the imaginary axis, and vice versa. We will call this the insulator

---

[3] O. Brune, J. Math. Phys. **10**, 191 (1931); also, see recent textbooks on network analysis, such as P. E. Pfeiffer, *Linear Systems Analysis* (McGraw-Hill Book Co., New York, 1961), Chap. 9.

[4] See, e.g., J. Hilgevoord, *Dispersion Relations and Causal Description* (North-Holland Publishing Co., Amsterdam, 1960); A. S. Davidov, *Quantum Mechanics*, translated and edited by D. ter Haar (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1965), Sec. 112.

property. The Debye dispersion relation[5] represents the case in which a single zero and a single pole occur on the negative real axis. (In contrast, the Drude expression for the dielectric dispersion function of a metallic conductor has poles on the imaginary axis, but the corresponding zeros are not on the imaginary axis.) We found it unnecessary to include poles and zeros on the imaginary axis to fit our reststrahlen data.

Another physical requirement in the case of passive materials is that the imaginary part of ϵ should be positive for positive frequencies. Otherwise the crystal would have to contribute energy to a wave passing through it, as in a laser amplifier. We have found no tractable set of limitations on location of poles and zeros that assures compliance with this "passivity" requirement at all frequencies, although it is not hard to write two simple conditions on such locations that assure passivity at frequencies considerably larger than the largest modulus of a pole or zero and at frequencies considerably smaller than the smallest modulus. However, we found the use of such auxilliary equations unnecessary. (See the section on curve fitting.) Direct computation of ϵ from the adjusted dispersion relation at a few high and low frequencies beyond the range of the data revealed that the passivity condition was satisfied everywhere.

Finally, we will present two restrictions that seem to be very common but are more empirical than the fundamental physical restrictions already noted. We will considers crystals that have no purely imaginary poles or zeros and that are quite transparent in the visible and near-infrared regions, as many ionic crystals, including $PrCl_3$ and $LaCl_3$ are. The dielectric constant in the visible region is real and almost independent of frequency in such crystals. Hence we may represent the part of the dispersion function associated with poles and zeros at ultraviolet frequencies by a real multiplicative constant ϵ_{opt} so long as the function is only used for infrared frequencies. Recalling the symmetry property, we may write the infrared dispersion function for such crystals as follows:

$$\epsilon=\epsilon_{\mathrm{opt}}\prod_{j=1}^{N/2}\frac{[\omega-(Z_j'-iZ_j'')]}{[\omega-(P_j'-iP_j'')]}\frac{[\omega-(-Z_j'-iZ_j'')]}{[\omega-(-P_j'-iP_j'')]} \tag{3a}$$

$$=\epsilon_{\mathrm{opt}}\prod_{j=1}^{N/2}\frac{\omega^2+2iZ_j''\omega-(Z_j'^2+Z_j''^2)}{\omega^2+2iP_j''\omega-(P_j'^2+P_j''^2)} \tag{3b}$$

$$=\epsilon_{\mathrm{opt}}\prod_{j=1}^{N/2}\frac{\omega^2+2i\omega\omega_{zj}\sin\varphi_{zj}-\omega_{zj}^2}{\omega^2+2i\omega\omega_{pj}\sin\varphi_{pj}-\omega_{pj}^2}. \tag{3c}$$

Primes and double primes denote real and imaginary components, respectively. Form (3c) is an expansion of the polar form, in which, for instance, $Z=\omega_z\exp\times(-i\varphi_z)$. We have made use of the symmetry restriction to write ϵ in terms of $N/2$, rather than N, complex poles and complex zeros. Expanding numerator and denominator of Eq. (3a) in powers of $1/\omega$ for large ω we obtain, for the initial terms,

$$\epsilon=\epsilon_{\mathrm{opt}}\Big[\omega^N+\Big(2i\omega^{N-1}\sum_{j=1}^{N/2}Z_j''\Big)-O(\omega^{N-2})\Big]\Big/\Big[\omega^N+\Big(2i\omega^{N-1}\sum_{j=1}^{N/2}P_j''\Big)-O(\omega^{N-2})\Big] \tag{4}$$

$$=\epsilon_{\mathrm{opt}}\Big(1+\frac{2i}{\omega}\sum_{j=1}^{N/2}(Z_j''-P_j'')-O(\omega^{-2})\Big).$$

It is usually observed that the imaginary part of the dielectric constant falls off faster than $1/\omega$ at frequencies above the reststrahlen band. Most insulating crystals are quite transparent at less than twice the highest frequency in the reststrahlen bands and remain so into the visible region. Consequently, the sum of the imaginary parts of all the poles must be very nearly equal to the sum of the imaginary parts of all the zeros, so that the second term in the expansion is nearly zero. We will call this the near-infrared transparency condition.

COMPARISON WITH CLASSICAL OSCILLATOR DISPERSION

The classical Helmholz-Kettler uncoupled harmonic-oscillator dispersion relation[6–8] can be written

$$\epsilon=\epsilon_{\mathrm{opt}}-\sum_{j=1}^{N/2}\frac{\Delta\epsilon_j\omega_{pj}^2}{\omega^2+i\omega\gamma_{pj}\omega_{pj}-\omega_{pj}^2}, \tag{5}$$

where $N/2$ is the "number of independent oscillators." This relation has been used in one form or another by nearly every experimentalist since Rubins[9] to fit infrared reflectance or transmission spectra in the reststrahlen region. This relation can be derived from a model in which charges are subject to restoring forces proportional to their displacements and to damping forces proportional to their velocities. The relation satisfies the causality, passivity, reversibility, insulator, and near-infrared transparency requirements if γ_j, $\Delta\epsilon_j$, and ω_j are real and positive. Although the model is easy to visualize, the damping term, especially, is unrealistic. Attempts have been made to improve the accuracy of this or similar formulas by making γ_j and ω_j or $\Delta\epsilon_j$ into frequency-dependent parameters.[2,10–13] It is not trivi-

---

[5] P. Debye, *Polar Molecules* (Chemical Catalog Co., New York, 1929), Chap. 5.

[6] H. v. Helmholz, Pogg. Ann. **154**, 582 (1874).

[7] E. Kettler, Ann. Physik Chem. **30**, 299 (1887).

[8] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), Chap. II.

[9] H. Rubins, Ann. Physik Chem. **53**, 267 (1894); **54**, 476 (1895).

[10] M. Born and K. Huang (Ref. 8), Eq. (47.8).

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

[12] V. S. Vinogradov, Fiz. Tverd. Tela **4**, 712 (1962) [English transl.: Soviet Phys.—Solid State **4**, 519 (1962)].

[13] M. Lax, J. Phys. Chem. Solids **25**, 487 (1964).

ally easy to write a generalized harmonic-oscillator-like dispersion relation with variable parameters and still be sure that the fundamental physical restrictions are automatically satisfied. In fact, the function derived from quantum mechanics in Born and Huang[10] is not symmetric, and the one proposed on phenomenological grounds by Barker[2] does not necessarily obey causality, as he wrote it, unless the variables are restricted in a rather complicated, though not very stringent way. Some other dispersion relations written as sums that have been derived from quantum mechanics probably do satisfy all of the physical requirements.[11–13]

For a given number of poles and zeros, the Helmholz-Kettler dispersion function is more restrictive than the principles of physics require. If we expand the function into the pole and zero form, we get a special case. Conversely, if we try to reduce the pole and zero form to the classical oscillator form, we automatically get frequency-dependent terms for $\Delta\epsilon_j$ or else for ω_j and γ_j except in a special restricted case.

By way of illustration we will now obtain the frequency-dependent "constants" in the simple classical oscillator expression that make it equivalent to a dispersion relation with single pairs of poles and zeros ($N=2$). We will not adopt the near-infrared transparency condition that the sum of the imaginary parts of the poles should equal the sum of the imaginary parts of the zeros, but we will adopt the causality, symmetry, and insulator restriction. We can then write the pole and zero-dispersion relations in the polar coordinate form (3c) as follows:

$$\frac{\epsilon}{\epsilon_{\text{opt}}}=\frac{\omega^2+2i\omega\omega_z\sin\varphi_z-\omega_z{}^2}{\omega^2+2i\omega\omega_p\sin\varphi_p-\omega_p{}^2}=1-\frac{(\omega_z{}^2-\omega_p{}^2)[1+2i\omega(\omega_p\sin\varphi_p-\omega_z\sin\varphi_z)/(\omega^2{}_z-\omega_p{}^2)]}{\omega^2+2i\omega\omega_p\sin\varphi_p-\omega_p{}^2} \tag{6}$$

or

$$\epsilon=\epsilon_{\text{opt}}+\frac{\omega_p{}^2S(\omega)}{\omega^2+2i\omega\omega_p\sin\varphi_p-\omega_p{}^2}. \tag{7}$$

(Incidentally, causality requires φ_p and ω_p to have the same sign, and the same must be true of φ_z and ω_z.) This is equivalent to using a complex, frequency-dependent oscillator strength $S(\omega)$ in place of the real constant $\Delta\epsilon$ in the classical oscillator expression. Alternatively, if we define a variable oscillator frequency as

$$\Omega^2(\omega)=\omega^2{}_p\left(1+2i\omega\frac{\omega_p\sin\varphi_p-\omega_z\sin\varphi_z}{\omega_z{}^2-\omega_z{}^2}\right) \tag{8}$$

and a variable damping term as

$$\Gamma(\omega)=\frac{2\sin\varphi_p+(\omega_p\sin\varphi_p-\omega_z\sin\varphi_z)\omega_p/(\omega^2{}_p-\omega_z{}^2)}{[1+2i\omega(\omega_p\sin\varphi_p-\omega_z\sin\varphi_z)/(\omega_z{}^2-\omega_p{}^2)]^{\frac{1}{2}}}, \tag{9}$$

and use the Lyddane-Sachs-Teller relation,[1,2,14] which can be written

$$\Delta\epsilon=\epsilon_{\text{stat}}-\epsilon_{\text{opt}}=\epsilon_{\text{opt}}(\omega_z{}^2-\omega_p{}^2)/\omega_p{}^2, \tag{10}$$

then we may rewrite Eq. (6) in the form

$$\epsilon=\epsilon_{\text{opt}}-\frac{\Delta\epsilon\Omega^2(\omega)}{\omega^2+i\omega\Gamma(\omega)\Omega(\omega)-\Omega^2(\omega)}. \tag{11}$$

By some very complicated substitutions we have thus managed to write the simple dispersion relation for single independent pairs of poles and zeros in the form of the classical oscillator expression with frequency-dependent constants $\Omega(\omega)$ and $\Gamma(\omega)$. These constants are truly constant only if

$$\omega_p\sin\varphi_p-\omega_z\sin\varphi_z=0. \tag{12}$$

This is equivalent to a condition that the imaginary part of each pole equals the imaginary part of each zero in this single-oscillator model. When Eq. (12) is satisfied, that is, for the single classical damped oscillator, Eqs. (8) and (9) become

$$\Omega(\omega)=\omega_p \tag{8'}$$

and

$$\Gamma(\omega)=2\sin\varphi_p=\gamma_p \tag{9'}$$

[cf. Eq. (5)]. Thus we see that the classical harmonic-oscillator model forces compliance with the empirical restriction that the sum of imaginary parts of the zeros should equal the sum of imaginary parts of the poles in the case of a "single oscillator" ($N=2$). When more than one oscillator is required to fit data, the classical oscillator dispersion relation still forces rigid compliance with this empirical restriction. However, each additional classical oscillator adds another, generally much more complicated and unjustified, restriction on the positions of the poles and zeros. Hence the pole and zero-dispersion relation, with the *ad hoc* restriction that the sums of imaginary parts of zeros and poles must be equal or approximately equal, is much less restrictive than the classical uncoupled-oscillator relation with the same number of zeros and poles, except for the special unrealistically simple case when $N=2$.

The classical oscillator model also forces compliance with the passivity condition if all the damping terms γ_j are positive. However, we have found no difficulty in controlling the adjustment of pole and zero locations to satisfy that condition by the indirect computational method previously described if initial estimates of parameters are not too far off.

---

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

One possible reason that data can usually be fitted very well by using the Helmholz-Kettler classical oscillator dispersion relation with several oscillators is that, by appropriate choice of oscillator parameters, poles and zeros that are unnecessary to obtain a good fit may be made so close together that they have practically no effect on the resulting dispersion curve. The Helmholz-Kettler model is accurate enough to put the poles and zeros of the strongest or fundamental modes in the reststrahlen bands of simple ionic crystals in about the right places, but is it not very efficient for describing the finer features of such spectra. For example, a point made by Barker,[2] in his discussions of dielectric dispersion relations in $KTaO_3$ and $SrTiO_3$, was that much better fits could be obtained to observed infrared reflectance between about 5 and 40 μ using a dispersion relation derived from a special model with two coupled oscillators than from the Helmholz-Kettler model with two uncoupled oscillators used by earlier authors to fit the same data. To get as good a fit with the Helmholz-Kettler model would have required at least one and probably two additional oscillators, of three parameters each, whereas Barker used no additional parameters. (He might have used two more parameters since a complex coupling term appears in the most general two-coupled-oscillator model, but one of the damping constants was omitted and the coupling constant was made real in Barker's model.) Both models with two oscillators yield two poles and two zeros with positive real-frequency components. The extra poles and zeros that would appear if an equally good fit to these particular data were forced from the Helmholz-Kettler model by introducing more oscillators would cancel one another in such a way that only poles and zeros near the locations of those obtained from Barker's model would have appreciable effect. Both Barker's and the Helmholz-Kettler two-oscillator model use less parameters than are required to locate two poles and two zeros because the models contain implicit, special restrictions that may or may not be valid for a particular crystal. However, three or four Helmholz-Kettler oscillators would take more adjustable parameters than two poles and two zeros, and the most general two-coupled-oscillator model would take as many parameters as two poles and two zeros.

PHYSICAL INTERPRETATION OF POLE AND ZERO FUNCTION

In the general case where several pairs of poles and zeros are required to fit data, we find that each electrically polar TO phonon mode corresponds to a pole near the real axis and each electrically polar LO mode corresponds to a zero near the real axis. Higher-order effects correspond to pole and zero pairs close to one another and relatively far from the real axis.

The definition of the frequency of a phonon mode is somewhat arbitrary because of the finite lifetime of the mode. One way to define the real frequency of a TO mode is to identify it with the real parameter ω_j in the denominator of the classical oscillator dispersion relation, Eq. (5). This is exactly equivalent to identifying it with the distance of a pole from the origin (the modulus of the pole). [See Eq. (3b).] By direct analogy we may somewhat arbitrarily define the real frequency of a polar LO mode as the modulus of a zero in the dispersion function. (To show the physical significance of this definition we note that a pure, undamped LO mode would be one in which the electric field is entirely generated by polarization within the crystals, so that $E+P=O$ or $\chi=-1$ in rationalized cgs units, or $\epsilon=O$.[1,14,15])

Similarly, the lifetime of a TO mode is proportional to the reciprocal of the corresponding damping term $\gamma_j\omega_j$ in the classical oscillator relation. The dimensionless parameter γ_j, which might be called a "decay number," is the same as twice the sine of the absolute angle φ_p between the real axis and the pole [cf. Eqs. (3b) and (5)]. By direct analogy we may define the "decay number" of a LO mode as twice the sine of the absolute angle φ_z between a zero and the real axis. (Note that the peak in the polarization or in the damping of a phonon mode is not necessarily at ω_{zj} or at ω_{pj} unless the corresponding decay number is very small.)

The generalized form of the Lyddane-Sachs-Teller relation for several TO and LO modes is [1,2]

$$\epsilon_{\text{stat}}=\epsilon_{\text{opt}}\prod_{j=1}^{N/2}\frac{\omega_{zj}^2}{\omega_{pj}^2}, \tag{13}$$

where ϵ_{stat} is the static or very-low-frequency dielectric constant. This expression is an obvious result of allowing ω to approach zero in the pole and zero-dispersion relation with mirror symmetry about the imaginary axis [Eq. (3c)].

Once we understand the relations between the locations of poles and zeros in the dielectric dispersion relation and the frequencies and damping of modes and the Lyddane-Sachs-Teller relation, it seems somewhat pointless to try to maintain a semblance of the classical oscillator dispersion relations in describing experimental results, as experimenters have in the past. Theoretical expressions, as usually presented, involve sums of terms, as the classical oscillator model does, rather than products, as in the pole and zero expression, but some added physical insight might sometimes be gained by expanding such theoretical expressions into the pole and zero form.

PROPERTIES OF $PrCl_3$ AND $LaCl_3$

$PrCl_3$ and $LaCl_3$, along with other rare-earth chlorides, are of considerable current interest to solid-state spectroscopists because they have a number of long-

---

[15] D. W. Berreman, Phys. Rev. **130**, 2193 (1963); in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1963), p. 397.

lived excited electronic states over a wide range of frequencies. These states are associated, not with just a few impurity atoms but with the two rare-earth atoms in every unit cell. We hope to contribute to a better understanding of the role that phonons play in energy transfer among the rare-earth ions by learning more about the frequencies and lifetimes of the phonons themselves through study of the reststrahlen, or main infrared reflectance bands of these crystals.

$LaCl_3$, $PrCl_3$, and other rare-earth chlorides are trigonal crystals with three easy cleavage planes parallel to the threefold axis of symmetry. They belong to the space group C_{6h}^2 or $P^6\ 3/m$. Every rare-earth ion is enclosed in an almost regular, six-cornered cage of chlorine atoms.[16]

There are three long-wavelength modes of lattice vibration that result in oscillatory changes in polarization of each unit cell. Other modes exist but they do not result in such polarization and are therefore not infrared active in first order, though they may have small secondary effects. Of the three infrared-active modes, one, with A_u symmetry, is stimulated by infrared radiation with its oscillating electric-field component parallel to the threefold, or c-axis of symmetry. The other two modes, with E_{1u} symmetry, are stimulated by an oscillating electric field perpendicular to the c axis.[16]

The rare-earth chlorides are quite soft and are readily attached by water vapor. Consequently, in spite of our efforts to make smooth, clean samples by cleaving or polishing parallel to the (110) faces in a nitrogen atmosphere, there may be some decrease in reflectance near the tops of the reststrahlen bands caused by slight roughness of sample surfaces.[17] We found that such errors in measurement at the tops of reststrahlen bands would cause appreciable errors in fitting the locations of secondary poles and zeros but not in fitting the widely separated poles and zeros near the real axis that correspond to primary polar lattice modes.

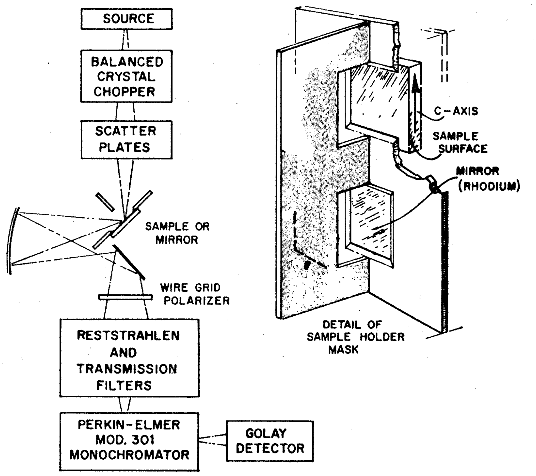

FIG. 1. Schematic drawing of optical system with inset drawing of sample holder, with shield, for measuring reflectance at right angles.

EXPERIMENT AND PRIMARY DATA

We mounted the samples in vacuum in a cryostat on the end of a cold finger. The cryostat had two polyethylene windows set at right angles to one another. The radiation was reflected by the sample or by a rhodium reference mirror at approximately 90° from the direction of incidence. The threefold or c axes of the crystals were always vertical, and perpendicular to the plane of incidence and reflection.

Measurements were made with a Perkin Elmer Model 301 grating spectrometer with a Golay cell detector. The sample chamber was altered to accommodate the cryostat and to return the reflected light back into the monochromator. The experimental setup is shown schematically in Fig. 1.

By making the threefold axis of the crystal perpendicular to the right angle of reflection, and by measuring reflectance of radiation with its electric field polarized parallel to the threefold or c axis, we obtained results only for the part of the dielectric tensor associated with vibrational polarization parallel to that axis. By turning the axis of polarization 90° without rotating the crystal, we obtained only the orthogonal component of the dielectric tensor. With the crystal oriented in that way, each of the two orthogonal components of polarized light obeys the standard Fresnel equations derived for reflectance of light at oblique incidence by an anisotropic crystal. When a trigonal crystal is oriented in that way the appropriate component of the dielectric tensor may be treated as a scalar in the Fresnel equations for each polarized component of the radiation. If the threefold axis had been oriented in any other direction, the simple Fresnel equations would not have been valid, at least for one component, because the electric-field vector of the incident radiation would have had components both parallel and perpendicular to the threefold axis.

The rare-earth chlorides are transparent to visible light. The refractive index n in the visible region was obtained by interposing a sample of known thickness between an objective lens of moderate numerical aperture in a microscope and a marked microscope slide. The vertical distance that the microscope barrel had to be moved to refocus the slide when the slab was interposed or removed, together with the slab thickness, give sufficient information to compute the refractive index. We found no measurable difference between the refractive index n, in the visible region, for light polarized parallel to the z axis and that for light polarized normal to it. The parameter ϵ_{opt} in the various dielectric dispersion relations is assumed to be equal to the square of the measured value of n. We assume that the

---

[16] J. Murphy, H. H. Caspers, and R. A. Buchanan, J. Chem. Phys. **40**, 743 (1964).

[17] D. W. Berreman, Phys. Rev. **163**, 855 (1967).

temperature dependence of n is negligible since the thermal-expansion coefficient is small.

The reststrahl reflectance bands for polarized radiation reflected at right angles from a thick flat crystal of $PrCl_3$ were measured at temperatures of about 300 and 82°K. The data are shown in Figs. 2 and 4. Similar data for $LaCl_3$ are shown in Figs. 3 and 5. A number of data points taken at 20°K lay almost exactly on the points taken at 82°K and are not shown.

CURVE FITTING

We used a computer program described elsewhere[18] to do the parameter adjustment for least-squares fitting and to compensate for the smearing effects of spectrometer slit width on the observed spectra. We used the Fresnel equations to compute reflectance of obliquely reflected radiation from values of ϵ derived from our dispersion relation. As usually written, the Fresnel reflectance equations contain an ambiguous sign on a square root. The sign is usually chosen so as to make the computed reflectance less than unity. This choice is equivalent to choosing the sign on the dielectric constant that makes its imagniary part positive to satisfy the passivity condition. However, if the poles and zeros in the general dispersion relation are not in appropriate locations, it may yield negative values of the imaginary part of ϵ. In order that the error in locations of poles and zeros would be "recognized" by the computer program that adjusted parameters for least-squares fitting of the data, we chose the root in Fresnel's equations that gave reflectance greater than unity when the dispersion relation gave negative values for the imaginary part of ϵ. We also had an option in the computer program to exaggerate the size of the imaginary part of ϵ if it came out negative. This feature augmented the misfit with experimental data and parameters were therefore adjusted away from improper values more rapidly. However, we found this option unnecessary if moderately accurate initial estimates of parameters were used. During the initial parameter adjustment we put in artificial data points of estimated reflectance at a very low and a very high frequency in order to make sure that the dispersion relation satisfied the passivity condition in the tails of the spectrum as well as in the range of the experiments. These two data points were not enough to affect the adjustment of parameters appreciably unless the passivity criterion failed at one of them, which it never did when good fits to the real data were obtained.

We tried using the real and imaginary parts of the poles and zeros on the positive side of the imaginary axis directly as adjustable parameters to do some of the curve fitting. This choice of adjustable parameters was satisfactory except that it did not allow us to impose the near-infrared transparency condition or to fix ϵ_{stat}. Another equivalent set of parameters was found to be just as stable in arriving at a good fit, and allowed direct control over ϵ_{stat} and the transparency condition.

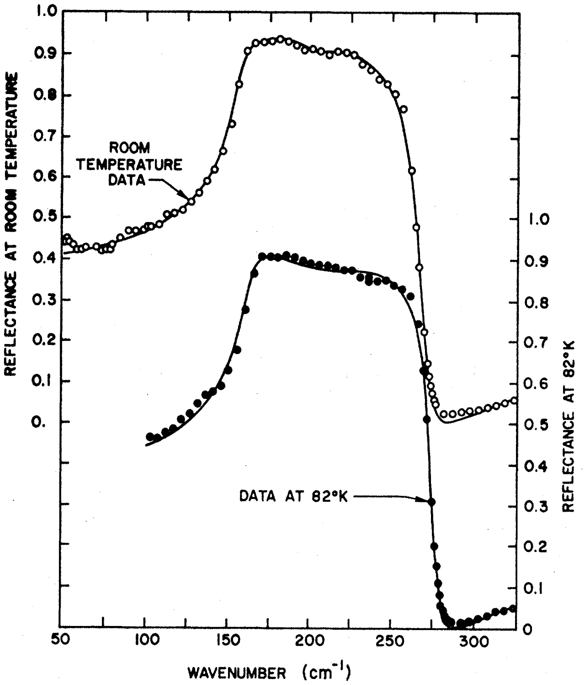

FIG. 2. Single reststrahlen band associated with A_u mode in $PrCl_3$ for radiation incident at 45° from normal, with curves computed from least-squares adjusted poles and zeros. Note displaced ordinates for curves at room temperature and at 80°K.

The alternative parameters used were ϵ_{opt}, $\epsilon_{\text{stat}}/\epsilon_{\text{opt}}$, $\sum Z_j''/\sum P_j''$, the $N/2$ parameters P_j'', the $N/2$ parameters ω_{pj}, the $\frac{1}{2}(N-2)$ parameters Z_j''/Z_1'' for $j>1$, and the $\frac{1}{2}(N-2)$ parameters ω_{zj}/ω_{z1} for $j>1$. This adds up to $2N+1$ adjustable parameters, which is the same number we would have had if we had used ϵ_{opt} and the two coordinates of each pole and zero in the positive real side of the complex plane.

The computer program that we used offers the possibility of fixing any of the parameters in the function to be fitted to data. In arriving at the pole and zero locations and curves given in the tables and figures we fixed the value of $\sum Z_j''/\sum P_j''$ at unity, which forces satisfaction of the near-infrared transparency requirement mentioned in the section on physical limitations. (Almost identical results were obtained when this paramater was left as a free variable.) We also set ϵ_{opt} equal to the values that we measured directly. If we had accurate measurments of ϵ_{stat} we could also fix the parameter $\epsilon_{\text{stat}}/\epsilon_{\text{opt}}$, but we do not.

EXPERIMENTAL RESULTS AND CONCLUSIONS

The data for σ-polarized radiation could be fitted moderately well with a single pair of poles and zeros near the real axis, or a simple classical oscillator model.

---

[18] D. W. Berreman, J. Appl. Opt. 7, 1447 (1968).

TABLE I. Locations of poles and zeros in the positive half-plane for the best two-pole-pair fit of σ-polarized reststrahlen data. (The electric field is parallel to the threefold axis.) ϵ_{opt} is fixed and ω is expressed in vacuum wavenumbers.

Temp. (°K)	Poles ω_p(cm^{-1})	$\sin\varphi_p$	Zeros ω_z(cm^{-1})	$\sin\varphi_z$	ϵ_{stat}
PrCl$_3$, $\epsilon_{\text{opt}}=3.184$					
293	156.2	0.0213	257.0	0.0137	10.26
	202.1	0.0477	201.5	0.0469	
82	163.1	0.0209	263.7	0.0104	9.45
	210.8	0.1883	205.1	0.1967	
LaCl$_3$, $\epsilon_{\text{opt}}=3.71$					
293	157.6	0.0211	256.3	0.0128	9.66
	203.1	0.0835	201.6	0.0849	
82	161.7	0.0158	261.6	0.0060	9.56
	205.7	0.1240	204.2	0.1297	

However, placing, on each side of the imaginary axis, an extra pole and zero that are close together and relatively far from the real axis improves the fit significantly. The results are shown in Table I and Figs. 2 and 3. The pole and zero near the real axis represent the main effect of the electrically polar TO and LO resonances, respectively, of A_u symmetry in the crystals. The pole and zero far from the axis and relatively close together may be thought of as representing a sort of average contribution of weaker, higher-order resonances in the crystal. However, the locations of the latter pair are probably further apart than they should be for an ideally smooth, clean sample because of the difficulty with sample surfaces mentioned earlier.

TABLE II. Locations of poles and zeros in the positive half-plane for best three-pole-pair fit of π-polarized reststrahlen data. (The electric field is normal to the threefold axis.)

Temp. (°K)	Poles ω_p	Poles $\sin\varphi_p$	Zeros ω_z	Zeros $\sin\varphi_z$	ϵ_{stat}
PrCl$_3$, $\epsilon_{\text{opt}}=2.814$					
293	164.0	0.0193	195.5	0.0155	8.688
	201.9	0.0178	257.0	0.0281	
	235.3	0.2458	233.9	0.2322	
82	169.2	0.0198	198.7	0.0081	8.665
	204.5	0.0128	260.0	0.0148	
	235.7	0.1523	237.8	0.1531	
LaCl$_3$, $\epsilon_{\text{opt}}=3.71$					
293	167.3	0.0169	191.0	0.0118	8.45
	195.6	0.0159	260.0	0.0262	
	234.7	0.2118	233.4	0.1995	
82	171.4	0.0155	193.6	0.0072	8.02
	198.1	0.0094	261.8	0.0127	
	237.4	0.1675	233.8	0.1694	

The data for π-polarized radiation could not be fitted very well with only two pairs of poles and two pairs of zeros, corresponding to the two E_{1u} modes. A single extra zero and pole on each side of the imaginary axis and close to one another improved the fit considerably. The extra pole and zero were not far enough apart or close enough to the real axis to suggest that they represent fundamental or "primary" lattice modes. A still better fit could be achieved by putting in another "correction term" (another closely spaced pole and zero pair) but the data are probably not sufficiently reliable to warrant such a fit. The two primary poles and zeros at each temperature with each sample are shown first in Table II and the third, secondary or cor-

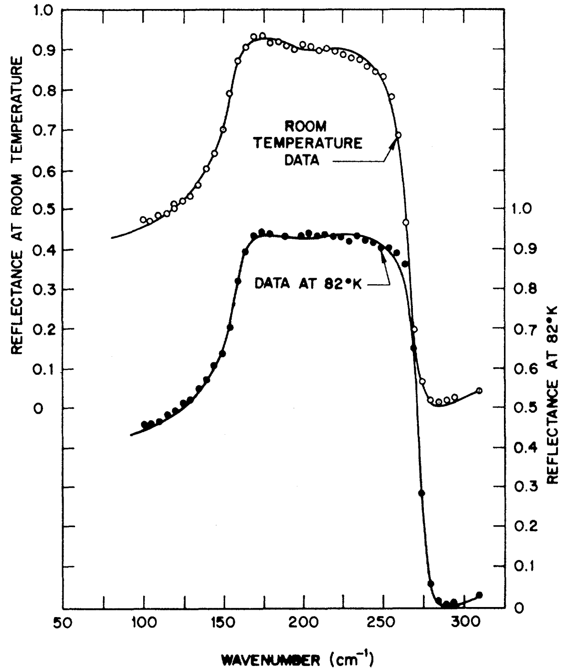

FIG. 3. Single A_u band for LaCl$_3$ plotted as Fig. 2 was plotted for PrCl$_3$.

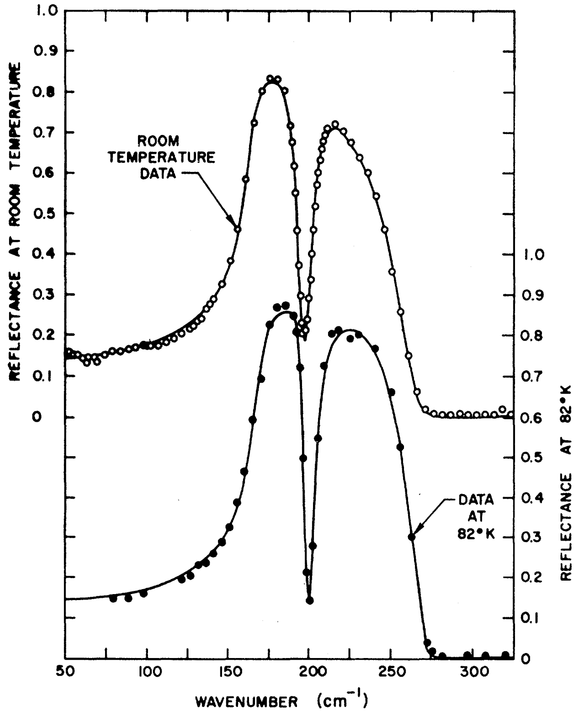

FIG. 4. Double reststrahlen band assoicated with E_{1u} modes in PrCl$_3$ plotted as in Fig. 2.

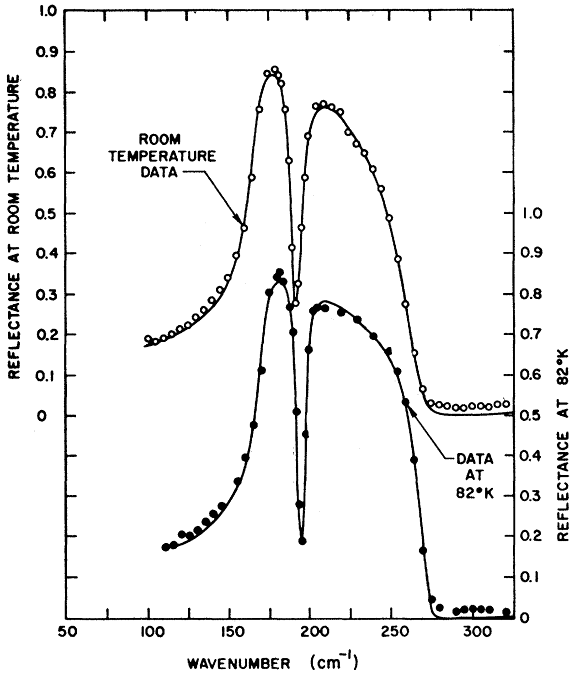

FIG. 5. Double E_{1u} band for $LaCl_3$ plotted as Fig. 4 was plotted for $PrCl_3$.

rection pole and zero are shown last. The data points and fitted curves are shown in Figs. 4 and 5.

There is a significant shift toward slightly lower-frequency moduli (ω_p and ω_z) and slightly larger damping or phase angles (φ_p and φ_z) in the locations of the primary zeros and poles when the temperature changes from ~82 to ~293°K. The lower-frequency moduli can be attributed to slightly lower atomic rigidity in the crystal which may be associated with thermal expansion. The higher damping is to be expected at higher temperatures because of the higher states of excitation in the phonon levels through which damping occurs. Neither shift is sufficient to suggest any radical change in the crystal, such as a phase transition, within or near this temperature range. We also obtain some data points at frequencies near poles and zeros at about 20°K. Those points lay almost exactly on top of the points obtained at nitrogen temperature. We therefore did not take sufficient data at liquid-helium temperature to warrant a separate determination of locations of zeros and poles by a separate curve fitting.

There is a striking similarity between $PrCl_3$ and $LaCl_3$ in both location and temperature dependence of location of poles and zeros. This confirms not only the similarity of the crystals but the reliability of the data and of the curve-fitting method adopted here. Readers familiar with the difficulty in eliminating higher orders of radiation in the far-infrared region with a grating spectrometer will not be surprised at the failure of most of the curves to reach the lowest reflectance computed from the fitted dispersion relations. The filtering was better in some of the later data, and better fits were obtained, but the parameters obtained for best fits seem to be remarkably insensitive to such difficulties. This insensitivity is in marked contrast to the great difficulties we encountered in attempting a direct Kramers-Kronig analysis of some of these data.

ACKNOWLEDGMENTS

The study of $LaCl_3$ and $PrCl_3$ was originally motivated by F. L. Varsanyi. Both he and B. Toth grew and gave us the single-crystal samples. We also had very helpful discussions with G. A. Baraff, A. S. Barker, Jr., and W. B. Joyce.