

Theory of Infrared Optical Properties of Fluorite Crystals*

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This paper provides a theoretical background for, and some interpretation of, recent measurements of the infrared optical properties of fluorite crystals particularly CaF_2 , SrF_2 , BaF_2 , and CdF_2 . A quantum-mechanical derivation of the optical properties in the harmonic approximation is given. The most reasonable procedure for the phenomenological treatment of damping effects is described. The physical origin of damping effects is discussed and it is shown how the perturbation theoretic results may be simplified in the low-frequency limit. Damping functions for the above materials are presented as a function of frequency and temperature.

I. INTRODUCTION

Within the past few years, a good deal of accurate data have been obtained on the infrared optical properties of crystals having the CaF_2 structure. In particular, Bosomworth¹ has carried out infrared absorption and refractive index measurements on the long-wavelength side of the reststrahlen band for CaF_2 , SrF_2 , BaF_2 , and CdF_2 at temperatures from 4° to 300°K. Other recent measurements on these materials have been reported by Kaiser *et al.*² for CaF_2 , SrF_2 , and BaF_2 at 77° and 300°K, and by Fray *et al.*³ for CaF_2 at temperatures from 77° to 300°K. Reflectivity measurements on CdF_2 and PbF_2 at 300°K have been reported by Axe *et al.*⁴

The most natural way to analyze these data is in terms of a frequency- and temperature-dependent damping function, the method used in Ref. 4. This damping function is not simply related to the width of the reststrahlen absorption band but is introduced into the theory through a phenomenological generalization of formulae which are *exact* for a harmonic lattice of nondeformable ions. The pertinent theoretical expressions can be derived on a classical basis^{5,6} and are quite old. It is clear from the literature, however, that the logic of introducing damping effects in this manner has not always been appreciated. Moreover, a variety of nonequivalent results have been published dealing with the effect of damping corrections on various theoretical expressions such as the Lyddane-Sachs-Teller formula.^{6,7} For these reasons, and also because of some intrinsic interest, a quantum mechanical derivation of the theory is outlined in Sec. IIIA.

The physical origin of the damping function consists of two parts. The first part is the anharmonic nature of real crystals resulting in terms in the potential energy that are of cubic and higher order in the ionic displacements. The second part is the deformability of the ions resulting in terms in the dipole moment that are of quadratic and higher order in the ionic displacements. These effects have been extensively treated in the literature⁸⁻¹²; a succinct discussion may be found in Martin's recent review article.¹³ It is a quite straightforward task to derive formal expressions for the infrared absorption arising from such processes. However, it is probable that it will be some time before knowledge of interatomic forces and ionic deformabilities becomes precise enough to make it possible to extract reliable numerical results from the formalism. An indication that progress in this area is possible is provided by the calculations of phonon dispersion curves for CaF_2 by Ganesan and Srinivasan¹⁴ using a rigid ion model, with results in good agreement with inelastic neutron scattering data. The inclusion of deformability effects in this calculation by means of the shell model has been discussed by Axe.¹⁵ On the other hand, the recent calculations of Karo and Hardy¹⁶ of precise vibrational frequency distributions in NaCl demonstrate the sensitivity of the two-phonon density of states (which enters into the expression for the infrared absorption) to the detailed assumptions made about the dynamics. Furthermore, a great deal of computation is required due to the necessity of sampling a large number of points in the Brillouin zone.

Sections IIB and IIC contain discussions of the phenomenological treatment of damping effects and of the perturbation theoretic results, respectively.

In Sec. III, numerical values for the phenomenological damping function calculated from currently

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¹ D. R. Bosomworth (to be published).

² W. Kaiser, W. G. Spitzer, R. H. Kaiser, and L. E. Howarth, *Phys. Rev.* **127**, 1950 (1962).

³ S. J. Fray, F. A. Johnson, and J. E. Quarrington, in *Lattice Dynamics*, R. F. Wallis, Ed. (Pergamon Press, Inc., New York, 1965), p. 377.

⁴ J. D. Axe, J. W. Gaglianella, and J. E. Scardefield, *Phys. Rev.* **139**, A1211 (1965).

⁵ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), Chap. 2.

⁶ C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), Chap. 3.

⁷ R. H. Lyddane, R. G. Sachs, and E. Teller, *Phys. Rev.* **59**, 673 (1941).

⁸ M. Lax and E. Burstein, *Phys. Rev.* **97**, 39 (1955).

⁹ B. Szigeti, *Proc. Roy. Soc. (London)* **A252**, 217 (1959).

¹⁰ B. Szigeti, *Proc. Roy. Soc. (London)* **A258**, 377 (1960).

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

¹² M. Lax, *J. Phys. Chem. Solids* **25**, 487 (1964).

¹³ D. H. Martin, *Advan. Phys.* **14**, 39 (1965).

¹⁴ S. Ganesan and R. Srinivasan, *Can. J. Phys.* **40**, 74 (1962).

¹⁵ J. D. Axe, *Phys. Rev.* **139**, A1215 (1965).

¹⁶ A. M. Karo and J. R. Hardy, *Phys. Rev.* **141**, 696 (1966).

available data for CaF_2 , SrF_2 , BaF_2 , and CdF_2 , are presented and the experimental data are briefly discussed in connection with the theory of Sec. II.

II. SOME ELEMENTARY RESULTS

The CaF_2 structure is described in Ref. 17. The primitive cell contains a Ca^{2+} and two nonequivalent F^- ions; it is a rhombohedron of volume $2r_0^3$, where $2r_0$ is the lattice constant. The position of an ion in the unit cell is given by

$$\mathbf{R}_s = r_0(s-1)[111]/2, \quad (1)$$

where $s=1$ for the metal and $s=2, 4$ for the fluorines. Only the optical vibrations of essentially zero wave vector can interact directly with the infrared radiation. The displacements of the ions from their equilibrium positions \mathbf{r}_s in this case satisfy¹⁸

$$m_{\text{Ca}}\mathbf{r}_1 + m_{\text{F}}\mathbf{r}_2 + m_{\text{F}}\mathbf{r}_4 = 0, \quad (2)$$

$$m_{\text{Ca}}r_1^2 + m_{\text{F}}r_2^2 + m_{\text{F}}r_4^2 = 1, \quad (3)$$

where m_{Ca} and m_{F} are the masses of the calcium and fluorine ions, respectively. The first equation is simply the condition for the center of mass to remain at rest and the second equation arises from the orthonormality condition for the normal modes. The dipole moment per primitive cell for nondeformable ions is given by

$$\mathbf{P} = 2e^*\mathbf{r}_1 - e^*\mathbf{r}_2 - e^*\mathbf{r}_4, \quad (4)$$

where e^* is an effective charge which may be less than e due to covalent bonding. Equations (2) and (3) have two classes of solution. For the first class

$$\mathbf{r}_2 = -\mathbf{r}_4, \quad \mathbf{r}_1 = 0, \quad \mathbf{P} = 0.$$

These are the Raman-active modes. For the second class

$$\mathbf{r}_2 = \mathbf{r}_4 = -m^{1/2}/2m_{\text{F}}, \quad \mathbf{r}_1 = m^{1/2}/m_{\text{Ca}}, \quad (5)$$

$$\mathbf{P} = 2e^*/m^{1/2}, \quad (6)$$

where

$$m^{-1} = m_{\text{Ca}}^{-1} + (2m_{\text{F}})^{-1}. \quad (7)$$

These are the infrared active modes, in which the metal ions vibrate against the cage of the fluorines. For each class there are three directions of polarization. Infrared absorption occurs through the excitation of the infrared active mode having the polarization of the incident radiation.

The problem to be treated now is that of the interaction of a plane electromagnetic wave with an infinite ionic crystal. In practice, this means that the crystal dimensions must be large compared to a wavelength. For smaller crystals, the need to consider boundary

effects introduces considerable additional complication.¹⁹⁻²¹ Furthermore, it may be assumed that the wavelength is large compared to the lattice constant so that the dipole approximation is valid.

The Hamiltonian for the system is

$$H = H_C + H_F + H_{CF} + H_A + H_D, \quad (8)$$

where H_C is the Hamiltonian of the crystal in the harmonic approximation assuming nondeformable ions, H_F is the Hamiltonian of the electromagnetic field, H_{CF} represents the crystal-field interaction, H_A represents anharmonic terms in the crystal Hamiltonian, and H_D represents the additional interaction arising from ionic deformability. Consideration of the last two terms is deferred until Sec. IIC.

A. The Harmonic Approximation

The Hamiltonian for the radiation represents a monochromatic plane wave, of wave vector \mathbf{k} and frequency ω , propagating in the static lattice, i. e., in a medium of dielectric constant ϵ_∞ . This quantity is the electronic contribution to the dielectric constant at infrared frequencies, i.e., the limiting value of ϵ at high infrared frequencies but below the region of visible dispersion. Since the dielectric constant plotted as a function of frequency never actually becomes flat, some slight arbitrariness is generally involved in the choice of a numerical value for ϵ_∞ . At any rate, one has²²

$$H_F = (a_{\mathbf{k}}^* a_{\mathbf{k}} + \frac{1}{2}) \hbar \omega, \quad (9)$$

where $a_{\mathbf{k}}^*$, $a_{\mathbf{k}}$ are photon creation and annihilation operators, respectively.

Similarly, the Hamiltonian of the lattice vibrations may be written as¹⁸

$$H_C = \sum_{\mathbf{q}, t} (b_{\mathbf{q}t}^* b_{\mathbf{q}t} + \frac{1}{2}) \hbar \omega_{\mathbf{q}t}, \quad (10)$$

where $b_{\mathbf{q}t}^*$ and $b_{\mathbf{q}t}$ are creation and annihilation operators for phonons of wave vector \mathbf{q} and branch t and $\omega_{\mathbf{q}t}$ is the corresponding frequency.

The interaction energy is most conveniently calculated starting from the classical expression

$$H_{CF} = \frac{1}{3}(\epsilon_\infty + 2) \sum_{l,s} e_s^* \mathbf{E}(l,s) \cdot \mathbf{r}(l,s), \quad (11)$$

where E is the electric field, l is a cell index, s is an ion index, and the sum is over the entire crystal. The factor $(\epsilon_\infty + 2)/3$ arises from the use of a Lorentz correction to take into account the effect of the electronic polarizability, P_∞ , on the local field acting on

¹⁷ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1957), Chap. 1.

¹⁸ A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963), Chap. 2.

¹⁹ R. Fuchs and K. L. Kliewer, *Phys. Rev.* **140**, A2076 (1965).

²⁰ K. L. Kliewer and R. Fuchs, *Phys. Rev.* **144**, 495 (1966).

²¹ K. L. Kliewer and R. Fuchs, *Phys. Rev.* **150**, 573 (1966); R. Fuchs, K. L. Kliewer, and W. J. Pardee, *ibid.* **150**, 589 (1966).

²² W. Heitler, *The Quantum Theory of Radiation* (Clarendon Press, Oxford, England, 1954), Chap. 2.

an ion in a lattice of cubic symmetry. One has²³

$$E_{\text{loc}} = E + 4\pi P_{\infty}/3 = \frac{1}{3}(\epsilon_{\infty} + 2)E. \quad (12)$$

If, instead of using Eq. (11), one starts from the corresponding expression²⁴ containing the vector potential \mathbf{A} , one of course obtains exactly the same final results. One has to remember, however, to include the term in A^2 , in first order, when calculating the second-order energy shift discussed below.

The expansions of \mathbf{E} and \mathbf{r} in terms of annihilation and creation operators may be readily calculated from expressions derived in the references quoted.^{22,18} The usual normalization condition requires that in the expansion for \mathbf{E} one must multiply the corresponding expression for free space by $\epsilon_{\infty}^{-1/2}$, since the field energy per unit volume is multiplied by ϵ_{∞} . In evaluating the expression (11), only the transverse optic branch polarized parallel to \mathbf{E} contributes; the sum over l introduces δ functions expressing conservation of wave vector and the sum over s introduces the dipole moment given by Eq. (6). The final result is

$$H_{CF} = 2i\frac{1}{3}(\epsilon_{\infty} + 2)(\pi\hbar^2 e^{*2}\omega/v\epsilon_{\infty}m\omega_{\text{TO}})^{1/2} \\ \times (b_{\mathbf{k}}^* a_{\mathbf{k}} - b_{\mathbf{k}} a_{\mathbf{k}}^* - b_{-\mathbf{k}}^* a_{\mathbf{k}}^* + b_{-\mathbf{k}} a_{\mathbf{k}}), \quad (13)$$

where v is the volume of the primitive cell and ω_{TO} the frequency of the transverse optic vibrations at zero wave vector. The geometry of the fluorite structure has entered into the derivation only through the use of Eq. (6). Thus one may, for example, transcribe Eq. (13) and all subsequent results for the NaCl lattice by replacing e^* by $e^*/2$ and defining m as $m_{\text{Na}} m_{\text{Cl}}/(m_{\text{Na}} + m_{\text{Cl}})^{-1}$.

One may use the above expressions to calculate the absorption coefficient corresponding to the conversion of a photon into an optical phonon.²⁴ One calculates the corresponding transition probability Ω with first-order time-dependent perturbation theory subtracting the induced emission rate from the total absorption rate to obtain the net absorption rate. The absorption coefficient is found from the net absorption rate by dividing by the photon flux in the static lattice.

$$\alpha = \Omega \epsilon_{\infty}^{1/2} / n_{\omega} c, \quad (14)$$

where n_{ω} is the photon occupation number. The result is

$$\alpha = \frac{1}{3}(\epsilon_{\infty} + 2)^2 (4\pi e^{*2}/vmc^2) \epsilon_{\infty}^{-1/2} \delta(\lambda^{-1} - \lambda_{\text{TO}}^{-1}), \quad (15)$$

where λ_{TO}^{-1} is the wave number corresponding to the transverse optic frequency. Actually, this result has little significance since the harmonic model implies merely the continual interconversion of photons and optical phonons; true photon absorption is possible only when the terms H_A and H_D are included. Some signifi-

cance may be attached to Eq. (15), however, if one considers the case of a crystal that contains a very large anharmonic term H_A so that an optical phonon once formed can not be reconverted into a photon before it decays into other phonons. In this case, Eq. (15) is applicable provided the δ function is replaced by an appropriate Lorentzian. The considerations involved here are similar to those in the Weisskopf-Wigner theory of line shapes.²⁵

A result of more immediate interest is the calculation, by second order time-independent perturbation theory, of the energy shift arising from H_{CF} . In this calculation one drops the terms corresponding to spontaneous photon emission since these merely correspond to a vacuum self-energy of the crystal rather than an interaction energy with the applied electric field. The result defines the dielectric constant of the crystal at frequency ω through

$$\Delta E = -(\epsilon_{\omega} - \epsilon_{\infty}) \bar{E}^2 V / 8\pi, \quad (16)$$

where V is the volume of the crystal and \bar{E} the rms field strength. The energy gained by the crystal is equal to the energy lost by the field. The field strength is related to the photon occupation number by equating expressions for the total photon energy in volume V

$$n_{\omega} \hbar \omega = \epsilon_{\infty} \bar{E}^2 V / 4\pi. \quad (17)$$

The resulting expression for the dielectric constant is

$$\epsilon_{\omega} - \epsilon_{\infty} = \frac{1}{3}(\epsilon_{\infty} + 2)^2 (16\pi e^{*2}/vm) (\omega_{\text{TO}}^2 - \omega^2)^{-1}. \quad (18)$$

For $\omega = 0$, this result is known as the Szigeti formula.²⁶

If one formally introduces the longitudinal optic frequency⁶ by

$$\omega_{\text{LO}}^2 = \omega_{\text{TO}}^2 + \frac{1}{3}(\epsilon_{\infty} + 2)^2 (16\pi e^{*2}/vm\epsilon_{\infty}), \quad (19)$$

one immediately obtains

$$\epsilon_0/\epsilon_{\infty} = \omega_{\text{LO}}^2/\omega_{\text{TO}}^2, \quad (20)$$

which is known as the Lyddane-Sachs-Teller formula.⁷ The symbol ϵ_0 , introduced here, is defined analogously to ϵ_{∞} as the limiting value of ϵ at low infrared frequencies. This value is generally lower than the static or radio frequency value. At subinfrared frequencies the motion of lattice defects may make an important contribution to the polarizability and the theory developed here is not applicable.

The refractive index n_{ω} and wave vector \mathbf{k} in the medium are given by

$$\epsilon_{\omega} = n_{\omega}^2 = c^2 k^2 / \omega^2. \quad (21)$$

Hence one obtains the dispersion formula

$$c^2 k^2 (\omega_{\text{TO}}^2 - \omega^2) = \epsilon_{\infty} \omega^2 (\omega_{\text{LO}}^2 - \omega^2). \quad (22)$$

²³ See Chap. 7 of Ref. 17.

²⁴ R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press, Oxford, England, 1965), Chap. 3.

²⁵ See Chap. 5 of Ref. 22.

²⁶ B. Szigeti, *Trans. Faraday Soc.* **45**, 155 (1949).

This fundamental result is well known and can be easily derived on an entirely classical basis.^{5,6} An interesting quantum mechanical derivation based on a macroscopic description of the medium has been given by Hopfield.²⁷ The present treatment presents a quantum mechanical derivation based on an atomistic description of the medium. Although the dielectric constant has been derived here by perturbation theory, the result is actually exact. For a general mechanical system, higher-order terms in the perturbation expansion would give the nonlinear terms in the dielectric tensor. For a harmonic lattice, however, such nonlinearities can obviously not arise.

Equations (21) and (22) show that for $\omega < \omega_{\text{TO}}$ or $\omega > \omega_{\text{LO}}$ the refractive index is real and one has only dispersion. For $\omega_{\text{TO}} < \omega < \omega_{\text{LO}}$ the refractive index is imaginary and one has only attenuation. The attenuation coefficient is given by

$$\alpha = 2 \operatorname{Im} k = (2\omega/c) \epsilon_{\infty}^{1/2} [(\omega_{\text{LO}}^2 - \omega^2)/(\omega^2 - \omega_{\text{TO}}^2)]^{1/2}. \quad (23)$$

The integrated attenuation coefficient is given by

$$\int_{\omega_{\text{TO}}}^{\omega_{\text{LO}}} \alpha d(\lambda^{-1}) = (\pi^2/\lambda_{\text{TO}}^2) \epsilon_{\infty}^{-1/2} (\epsilon_0 - \epsilon_{\infty}), \quad (24)$$

a result which can also be obtained from Eq. (15) using Eq. (18).

All optical properties of the crystal can be calculated in terms of the real and imaginary parts of the refractive index

$$n = n_1 + in_2.$$

The reflectivity of a slab for normal incidence is given by

$$R = [(n_1 - 1)^2 + n_2^2] / [(n_1 + 1)^2 + n_2^2], \quad (25)$$

and is therefore 100% in the reststrahlen band, $\omega_{\text{TO}} < \omega < \omega_{\text{LO}}$, where $n_1 = 0$. The attenuation coefficient is given by

$$\alpha = 2\omega n_2/c, \quad (26)$$

yielding again Eq. (23).

B. Phenomenological Treatment of Damping

The harmonic approximation discussed in Sec. IIA is inadequate for the following reasons:

(1) Experimentally, one finds some absorption outside the reststrahlen band and less than 100% reflectivity within it.

(2) The Szigeti relation is not rigorously valid. If one inserts experimental values of ϵ_0 , ϵ_{∞} , and ω_{TO} one generally finds that the corresponding value of e^* is considerably lower than that calculated from the cohesive energy.²⁸ For instance, in CaF_2 at 300°K one requires $e^* = 0.82 e$ whereas the cohesive energy implies that the ions retain essentially their full formal charge.¹⁵

The L.S.T. relation, on the other hand, appears to be not inconsistent with the data. For CaF_2 at 300°K, one finds using Bosomworth's direct measurement¹ of ϵ_0 ,

$$\epsilon_0/\epsilon_{\infty} = (6.63 \pm 0.07)/2.04 = 3.25 \pm 0.03. \quad (27)$$

For ω_{TO} one has Cribier *et al.*'s²⁸ direct neutron inelastic scattering measurement of $258 \pm 2 \text{ cm}^{-1}$ in good agreement with other determinations.^{1,2} For ω_{LO} Cribier *et al.* measured $478 \pm 7 \text{ cm}^{-1}$ while Berreman,²⁹ using thin-film absorption at oblique incidence, found $475 \pm 3 \text{ cm}^{-1}$; a reasonable value therefore is $476 \pm 4 \text{ cm}^{-1}$. Thus, one finds

$$(\omega_{\text{LO}}/\omega_{\text{TO}})^2 = (476 \pm 4/258 \pm 2) = 3.40 \pm 0.12. \quad (28)$$

Any valid theory must give results consistent with the Krammers-Kronig relations.³⁰ If one defines the complex dielectric constant by

$$\epsilon_{\omega} = \epsilon_1(\omega) + i\epsilon_2(\omega), \quad (29)$$

One has

$$\epsilon_1(\omega) - \epsilon_1(\infty) = \pi^{-1} P \int_{-\infty}^{\infty} \frac{\epsilon_2(\omega')}{\omega' - \omega} d\omega', \quad (30)$$

$$\epsilon_2(\omega) = \pi^{-1} P \int_{-\infty}^{\infty} \frac{\epsilon_1(\omega') - \epsilon_1(\infty)}{\omega' - \omega} d\omega'. \quad (31)$$

In the present application of these equations, the quantities $\epsilon_2(0)$, $\epsilon_2(\infty)$ are to be interpreted as asymptotic values for low and high *infrared* frequencies as stressed in Sec. IIA. In fact, experiment indicates that $\epsilon_2(0) = \epsilon_2(\infty) = 0$. It is easily verified that if in Eq. (18) one makes the substitution, justified in the next paragraph,

$$(\omega_{\text{TO}}^2 - \omega^2)^{-1} \rightarrow P(\omega_{\text{TO}}^2 - \omega^2)^{-1} + i\pi \left[\frac{\delta(\omega - \omega_{\text{TO}})}{\omega + \omega_{\text{TO}}} + \frac{\delta(\omega + \omega_{\text{TO}})}{\omega - \omega_{\text{TO}}} \right], \quad (32)$$

then Eq. (30), with $\omega = 0$, is satisfied. Moreover, from Eq. (26) one may now directly obtain Eq. (15).

The simplest way to introduce a damping parameter is due to Huang,⁵ who added a damping term proportional to the velocity to the classical equation of motion for the long-wavelength optical vibrations. This yields instead of Eq. (22),

$$\epsilon_{\omega} - \epsilon_{\infty} = \epsilon_{\infty} [(\omega_{\text{LO}}^2 - \omega_{\text{TO}}^2)/(\omega_{\text{TO}}^2 - \omega^2 - i\gamma\omega)]. \quad (33)$$

The sign of the damping term is determined by the sign convention used in Eq. (29). By taking the limit $\gamma \rightarrow 0$ and using the usual definition of the ζ function²² one may easily check that Eq. (32) is correct

²⁸ D. Cribier, B. Farnoux, and B. Jacrot, *Phys. Letters* **1**, 187 (1962).

²⁹ D. W. Berreman in Ref. 2, p. 397.

³⁰ See, for example, C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), Chap. 2.

²⁷ J. J. Hopfield, *Phys. Rev.* **112**, 1555 (1958).

for the harmonic approximation. A constant γ , however, is inconsistent with the data for absorption or reflectivity. The obvious generalization is to allow γ to be frequency-dependent, a result which can be obtained from the classical theory by adding additional damping terms proportional to higher odd derivatives of the displacement. One now obtains

$$\epsilon_\omega - \epsilon_\infty = \epsilon_\infty \{ (\omega_{LO}^2 - \omega_{TO}^2) / [\omega_{TO}^2 - \omega^2 - i\gamma(\omega)\omega] \}. \quad (34)$$

This formula obviously enables one to fit either reflectivity or absorption data, though not necessarily both. As a practical matter, absorption can only be measured outside the reststrahlen band while the reflectivity is most sensitive to $\gamma(\omega)$ within the reststrahlen band. Accordingly, it is difficult to detect any inconsistencies in fitting the function $\gamma(\omega)$ to experimental data.

If one sets $\omega=0$ in Eq. (34) and assumes on physical grounds that $\gamma(0)$ is finite, one finds just the Szigeti and L.S.T. relations derived previously. Since the former is not rigorously valid, Eq. (34) must still be regarded as unsatisfactory; it is convenient, nevertheless, to use it as a means of correlating the experimental data.

The complex refractive index is determined from

$$(n_1 + in_2)^2 = \epsilon_\infty \{ [\omega_{LO}^2 - \omega^2 - i\gamma(\omega)\omega] / [\omega_{TO}^2 - \omega^2 - i\gamma(\omega)\omega] \}. \quad (35)$$

If one defines the quantities

$$\Omega_L = \omega_{LO}^2 - \omega^2, \quad (36)$$

$$\Omega_T = \omega_{TO}^2 - \omega^2, \quad (37)$$

$$\Gamma = \gamma\omega. \quad (38)$$

One finds the following results for n_1 and n_2 :

$$n_1 = [\epsilon_\infty / 2(\Omega_T^2 + \Gamma^2)^{1/2}] \times \{ [\Omega_L \Omega_T + \Gamma^2 + (\Gamma^2 + \Omega_L^2)^{1/2} (\Gamma^2 + \Omega_T^2)^{1/2}] \}^{1/2}, \quad (39)$$

$$n_2 = [\epsilon_\infty / 2(\Omega_T^2 + \Gamma^2)^{1/2}] \times \{ [-\Omega_L \Omega_T - \Gamma^2 + (\Gamma^2 + \Omega_L^2)^{1/2} (\Gamma^2 + \Omega_T^2)^{1/2}] \}^{1/2}. \quad (40)$$

By making use of Eqs. (26) and (20), one finds the following asymptotic results for the absorption coefficient:

$$\alpha \sim [(\epsilon_0 - \epsilon_\infty)\gamma(\omega) / c\epsilon_0^{1/2}] (\omega / \omega_{TO})^2 \quad \text{for } \omega \rightarrow 0, \quad (41)$$

$$\alpha \sim [(\epsilon_0 - \epsilon_\infty)\gamma(\omega) / c\epsilon_\infty^{1/2}] (\omega_{TO} / \omega)^2 \quad \text{for } \omega \rightarrow \infty. \quad (42)$$

The above results are for $\gamma(\omega)$ in angular frequency

units and α in cm^{-1} . If $\gamma(\omega)$ is in wave-number units, the right-hand sides of Eqs. (41) and (42) must be multiplied by $2\pi c$.

The Kramers-Kronig relations impose conditions on the function $\gamma(\omega)$. For instance, if one sets $\omega=0$ in Eq. (30) and uses Eq. (33) one finds the result

$$\int_0^\infty \frac{\gamma(\omega) d\omega}{(\omega_{TO}^2 - \omega^2)^2 + \gamma^2(\omega)\omega^2} = \frac{\pi(\epsilon_0 - \epsilon_\infty)}{2\epsilon_\infty(\omega_{LO}^2 - \omega_{TO}^2)}. \quad (43)$$

For a constant $\gamma(\omega)$, this equation merely reduces to the L.S.T. relation, Eq. (20).

C. Perturbation Theory

The various terms in Eq. (8) lead to a variety of diagrams in perturbation theory some of which are illustrated in Fig. 7 of Ref. 13. The term H_{CF} , Eq. (13), corresponds to vertices where a photon line meets an optical phonon line. H_A arises from terms of cubic or higher order in the atomic displacements and therefore corresponds to vertices where three or more phonon lines meet. H_D arises from terms in the dipole moment of quadratic or higher order in the atomic displacements, it therefore corresponds to vertices where a photon line meets two or more phonon lines. Thus, H_A leads to phonon decay or mechanical damping while H_D leads to photon decay or electrical damping. Note that while it is possible for mechanical damping to exist without electrical damping if $H_{CF}=0$ the presence of electrical damping always leads to mechanical damping in higher order. For instance, a phonon may transform into another phonon and a photon, the latter then transforming into two phonons.

The present discussion is concerned with ionic crystals where $H_{CF} \neq 0$. Furthermore, only the lowest-order contributions to H_A and H_D will be considered. There are then two mechanisms for photon absorption:

- (1) First order via H_D .
- (2) Second order via H_{CF} and H_A , the intermediate state being an optical phonon.

Two types of processes are possible:

- A. One in which two phonons of equal and opposite \mathbf{k} are created, i.e., a sum process.
- B. One in which one phonon is destroyed and another of higher energy but the same \mathbf{k} , is created, i.e., a difference process.

Process A and B lead two absorption coefficients. In each case, the amplitudes corresponding to mechanisms 1 and 2 must be added coherently since they lead to identical final states.

The algebra involved at this point is quite straight-

forward although laborious. The known results are,⁸⁻¹³

$$\alpha_{s,s'}^{\text{sum}} = \omega \int \delta(\omega - \omega_{ks} - \omega_{ks'}) \omega_{ks}^{-1} \omega_{ks'}^{-1} \times \left[F(\mathbf{k}, s, s') - \frac{e^* G(\mathbf{k}, s, s')}{\omega^2 - \omega_{\text{TO}}^2} \right]^2 \times [n(\omega_{ks}) + n(\omega_{ks'}) + 1] d^3k, \quad (44)$$

$$\alpha_{s,s'}^{\text{diff}} = \omega \int \delta(\omega - \omega_{ks} + \omega_{ks'}) \omega_{ks}^{-1} \omega_{ks'}^{-1} \times \left[F(\mathbf{k}, s, s') - \frac{e^* G(\mathbf{k}, s, s')}{\omega^2 - \omega_{\text{TO}}^2} \right]^2 \times [n(\omega_{ks'}) - n(\omega_{ks})] d^3k, \quad (45)$$

where

$$n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}, \quad (46)$$

and s, s' denote phonon branches. The functions F and G arise from H_D and H_A , respectively. As a practical matter they are not calculable at the present time. The factor e^* is included with G as a reminder that this term vanishes in a covalent crystal; F is in general still finite in such materials.

A general selection rule states that the two phonons involved in the final state can not belong to the same branch. Other selection rules are operative only at special points in the Brillouin zone.³¹

The terms in G , in Eqs. (44) and (45), become invalid when ω approaches ω_{TO} . This is because the photon-optical phonon coupling then becomes very strong and H_{CF} may no longer be treated as a perturbation. The correct procedure in this case is to diagonalize $H_C + H_F + H_{CF}$ exactly using essentially the procedure of Hopfield.²⁷ The resulting eigenstates, called polariton states, may then be used as the basis for a perturbation treatment of H_A and H_D .

In the low-frequency limit, some approximations which enable one to simplify Eqs. (44) and (45) seem reasonable. In general, the acoustic and optical phonon dispersion curves rarely cross. They do cross sometimes, for example, in CaF_2 along the $[111]$ direction.¹⁴ In the absence of such crossing, energy conservation requires that for $\omega \rightarrow 0$ only low-energy acoustic phonons can be involved in the final state. For such phonons one can write

$$\omega_{kl} = V_l k, \quad \omega_{kt} = V_t k, \quad (47)$$

where l and t indicate the longitudinal and transverse branches and V is the corresponding sound velocity, $V_l > V_t$. One also assumes isotropy, so that

$$d^3k = 4\pi k^2 dk = 4\pi \omega_{kl}^2 V_l^{-3} d\omega_{kl}. \quad (48)$$

³¹ S. Ganesan and E. Burstein, *J. Phys.* **26**, 645 (1965).

Some elementary manipulations now lead to

$$\alpha^{\text{sum}} \cong \frac{4\pi\omega}{V_l V_t (V_l + V_t)} \times \left[F\left(\frac{\omega}{V_l + V_t}\right) - \frac{e^* G[\omega/(V_l + V_t)]}{\omega^2 - \omega_{\text{TO}}^2} \right]^2 \times \left[n\left(\frac{\omega V_t}{V_l + V_t}\right) + n\left(\frac{\omega V_l}{V_l + V_t}\right) + 1 \right], \quad (49)$$

$$\alpha^{\text{diff}} \cong \frac{4\pi\omega}{V_l V_t (V_l - V_t)} \times \left[F\left(\frac{\omega}{V_l - V_t}\right) - \frac{e^* G[\omega/(V_l - V_t)]}{\omega^2 - \omega_{\text{TO}}^2} \right]^2 \times \left[n\left(\frac{\omega V_t}{V_l - V_t}\right) - n\left(\frac{\omega V_l}{V_l - V_t}\right) \right]. \quad (50)$$

Thus, α becomes large when the sum (or difference) of the slopes of the phonon dispersion curves approaches zero. This conclusion is actually valid for any ω since it simply expresses the requirement for the additive (or subtractive) 2-phonon density of final states to be large.

At high temperatures, one may expand the exponentials in the Bose-Einstein factors and obtain

$$\alpha^{\text{sum}} \cong \frac{4\pi k T (V_l + V_t)}{\hbar V_l^2 V_t^2} \times \left[F\left(\frac{\omega}{V_l + V_t}\right) - \frac{e^* G[\omega/(V_l + V_t)]}{\omega^2 - \omega_{\text{TO}}^2} \right]^2, \quad (51)$$

$$\alpha^{\text{diff}} \cong \frac{4\pi k T (V_l - V_t)}{\hbar V_l^2 V_t^2} \times \left[F\left(\frac{\omega}{V_l - V_t}\right) - \frac{e^* G[\omega/(V_l - V_t)]}{\omega^2 - \omega_{\text{TO}}^2} \right]^2. \quad (52)$$

These expressions become invalid at $T \gtrsim \theta_D$ when three phonon processes may become important.

As $T \rightarrow 0$ one finds

$$\alpha^{\text{sum}} \sim \frac{4\pi\omega}{V_l V_t (V_l + V_t)} \times \left[F\left(\frac{\omega}{V_l + V_t}\right) - \frac{e^* G[\omega/(V_l + V_t)]}{\omega^2 - \omega_{\text{TO}}^2} \right]^2, \quad (53)$$

$$\alpha^{\text{diff}} \sim 0. \quad (54)$$

III. DISCUSSION OF THE EXPERIMENTAL DATA

Bosomworth¹ has carried out measurements of the refractive index in the far infrared as a function of frequency and temperature for CaF_2 , SrF_2 , BaF_2 , and CdF_2 . Accurate measurements over a wide range of

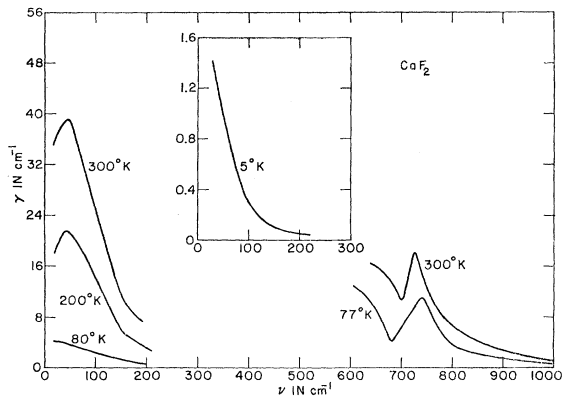


FIG. 1. The damping function for CaF_2 as a function of frequency and temperature.

frequencies were possible only at 80°K or lower where the absorption is small and nearly constant. At high temperatures accurate measurements could only be made in a limited low-frequency region. The harmonic approximation, Eqs. (18)–(20), gives

$$n_1(\omega) = \left[\frac{\epsilon_0 \omega_{\text{TO}}^2 - \epsilon_\infty \omega^2}{\omega_{\text{TO}}^2 - \omega^2} \right]^{1/2}. \quad (55)$$

The data were fitted very well to this expression and thus provided an accurate and convenient way of determining ω_{TO} at low temperatures. The effect of damping, using the experimentally determined $\gamma(\omega)$, is negligible.

Measurements of the absorption as a function of frequency and temperature are reported in Refs. 1–4. The results bear out the qualitative predictions implied by the theory of Sec. IIC. Thus, the absorption increases rapidly as ω approaches ω_{TO} . It increases with temperature more rapidly at low frequencies than at high frequencies. At low frequencies, it becomes roughly linear in T above 200°K indicating the predominance of two-phonon processes. The absorption shows considerable structure associated presumably with rapid

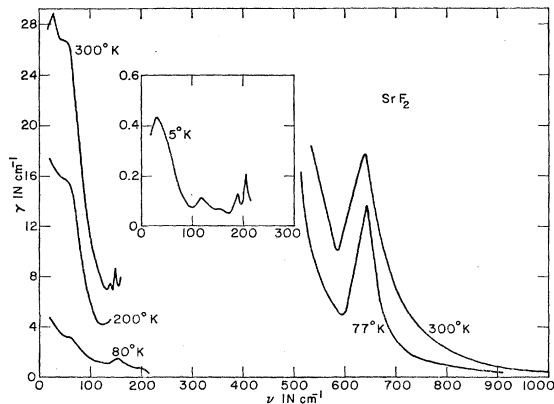


FIG. 2. The damping function for SrF_2 as a function of frequency and temperature.

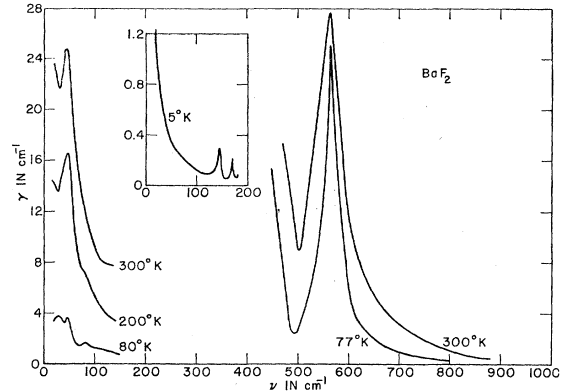


FIG. 3. The damping function for BaF_2 as a function of frequency and temperature.

variations in the density of states. Some peaks observed at higher temperatures sharpen on going to lower temperatures. Such peaks presumably are associated with sum processes and become sharper because the difference process contribution goes to zero at low temperatures. This is in accordance with the interpretation of Ganesan and Burstein³¹ of the data of Fray *et al.*³ It is reasonable also that those peaks that become less sharp at lower temperatures should generally occur at the lower frequencies where difference processes may be expected to be more important than sum processes.

The phenomenological damping function $\gamma(\omega)$ was determined from the data of Refs. 1 and 2, using Eqs. (39) and (40), with the aid of the RCA 601 computer. The calculations are most conveniently carried out by iteration.

The results are shown in Figs. 1 through 4. Numerical values corresponding to the high resolution data plotted in Ref. 3 were not available, but one should keep in mind that such data would lead to considerably more structure in $\gamma(\omega)$. The calculated damping functions all indicate a maximum at around 50 cm^{-1} which is not always apparent in the absorption. At higher

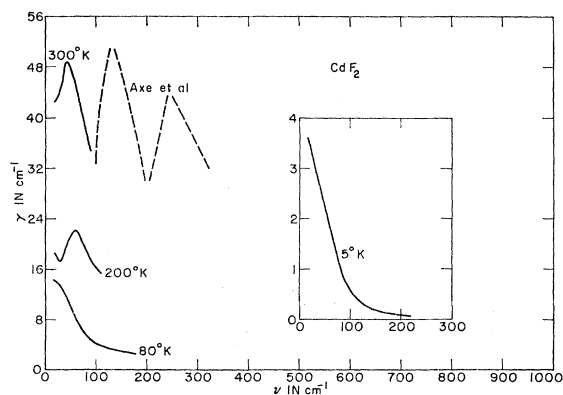


FIG. 4. The damping function for CdF_2 as a function of frequency and temperature.

frequencies $\gamma(\omega)$ generally decreases except for peaks corresponding to those in the data. The damping decreases with temperature more rapidly at low frequencies than at high frequencies. CdF_2 is more heavily damped than the other materials; here at 300°K the maximum value of $\gamma(\omega)/\omega_{\text{TO}}$ is about $\frac{1}{3}$. It is reasonable that associated with such large damping there should be large temperature-dependent frequency shifts so that one is not surprised to find that CdF_2 shows the largest temperature dependence of ω_{TO} and ϵ_0 .¹ In Fig. 4, the dashed curve represents the results deduced from reflectivity data by Axe *et al.*⁴ It is gratifying that these results join to those deduced from the absorption data of Ref. 1.

It is evident from the dispersion curves for CaF_2 ¹⁴ that the two-phonon (sum) density of states has a cutoff at $\omega_{\text{LO}} + \omega_{\text{R}}$. This particular phonon combination also satisfies the momentum and symmetry-based selection rules for infrared absorption.³¹ The value of this combination is about 790 cm^{-1} and it is gratifying to note that $\gamma(\omega)$ has a shoulder in this region. At higher frequencies, absorption must occur via a three-

phonon process and should therefore show an enhanced temperature dependence. Further inspection of the dispersion curves suggests that the peak at about 45 cm^{-1} can be assigned to a TO-TA difference process at the symmetry point X, the edge of the zone along the (100) direction. In the same way, the peak at about 725 cm^{-1} can be assigned to a LO+LA sum at the point X.

In conclusion, we mention two very recent papers in which anharmonic effects are treated by the powerful Green's function method.^{32,33}

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³² R. Wehner, *Phys. Status Solidi* **15**, 725 (1966).
³³ H. Hartmann, *Phys. Rev.* **147**, 663 (1966).

Scattering Theory of Absorption-Line Profiles and Refractivity*

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Attenuation processes are examined from the viewpoint of collision theory, and the optical theorem is used to connect attenuation cross section σ and refractive index n with diagonal elements of the T matrix. This approach provides resonance profiles (for "natural" lines shapes) of the form

$$\sigma(\omega) = C + \frac{(\Gamma/2)B + (\omega - \omega_0)A}{(\omega - \omega_0)^2 + (\Gamma/2)^2},$$

$$n(\omega) - 1 = \frac{Nc}{2\omega} \left[\frac{(\Gamma/2)A - (\omega - \omega_0)B}{(\omega - \omega_0)^2 + (\Gamma/2)^2} - D \right],$$

where the profile parameters $A, B, C, D, \Gamma, \omega_0$ are given in terms of atomic matrix elements.

Part I reviews the notion of resonances. Part II summarizes the relevant results of collision theory, stressing physical interpretation, and gives a definition for excited (or resonance) states based on a simple partition of basis states into two classes. Part III applies perturbation theory to the calculation of resonance profiles. Part IV applies these results specifically to the attenuation and refraction of photons by tenuous gases, with particular attention paid to the profiles of autoionizing lines. The effects of degeneracy (the extension of the bound-state Z^{-1} expansion theory) are noted.

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