

Anharmonicity and Millimeter-Wave Absorption in Alkali-Halide Crystals*

JAMES C. OWENS†

Harvard University, Cambridge, Massachusetts 02138

(Received 29 July 1968; revised manuscript received 26 December 1968)

The perturbation theory of infrared absorption in simple ionic crystals is extended by systematic consideration of higher-order anharmonic forces. It is shown that the effects of quartic anharmonicity may be comparable to or larger than the cubic contributions, although the effects of terms of still higher order are probably negligible. Measurements of the dielectric constant and loss tangent of LiF, NaCl, and KBr have been made at frequencies of 9.8, 35.4, and 116 GHz between 25 and 750°C, with some additional measurements at temperatures as low as -130°C. The results of these absorption measurements, and other published data, are in qualitative agreement with the temperature, frequency, and material dependence predicted by the theory, thus confirming the importance of the quartic effects. Finally, it is shown that the temperature dependence of the dielectric constant can be accurately described by a simple formula based on the classical theory of dielectrics.

I. INTRODUCTION

STARTING with the discovery of reststrahl radiation in 1897 by Nichols,¹ the dynamics and interactions with radiation of simple ionic crystal lattices have been investigated in great detail.² The results are usually given in terms of the ordinary dispersion formula

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 - (\omega/\omega_f)^2 - i(\omega/\omega_f)(\gamma/\omega_f)}, \quad (1)$$

where $\epsilon^* = \epsilon' + i\epsilon''$ is the complex dielectric constant, ϵ_∞ and ϵ_0 are its limiting values at high and low frequencies, respectively, ω_f is the resonance frequency, and γ/ω_f is the damping parameter. Although the use of a constant γ/ω_f in (1) leads to quite accurate predictions of the reflectivity of polar crystals, the absorption is poorly described except in the immediate vicinity of ω_f .³ Czerny's observations of nebenmaxima and anomalous frequency dependences of absorption in both wings of the resonance⁴ demonstrated that the damping parameter is in fact frequency dependent, and subsequent work has been largely directed toward explaining the frequency and temperature dependence of γ/ω_f .

It is known that there are three sources of absorption not included in the conventional harmonic theory: (1) third- and higher-order anharmonic terms in the potential energy,⁵ (2) second- and higher-order terms in the electric moment,⁶ and (3) boundary effects due

to the long-range Coulomb interaction.⁷ Although it has proven particularly difficult to evaluate the effects of proper boundary conditions, it appears that the use of periodic boundary conditions introduces little error except in special situations such as thin-film measurements with nonnormal incident radiation.⁸ A lengthy perturbation-theory calculation of absorption due to cubic potential and quadratic electric moment terms has been given by Born and Huang.⁹ Unfortunately, errors in this calculation invalidate the predicted temperature dependence in the wings of the main resonance.¹⁰ The most satisfactory calculation of this type, considering only the cubic potential, has been given by Kleinman.¹¹ Although quantitative calculations are possible only for certain special cases, it is clear that the cubic potential and quadratic electric moment terms give rise to an absorption proportional to the absolute temperature T at sufficiently high temperatures for equipartition of energy among the participating phonons to be assumed, while quartic potential and cubic moment terms lead to a T^2 dependence. The frequency dependence of the absorption is due primarily to the joint frequency distribution for each process; the nebenmaxima or "combination bands" correspond to singularities at critical points in the Brillouin zone. A number of many-body calculations, which confirm these conclusions, have also been carried out.¹²

In the present paper, Kleinman's direct perturbation calculation is extended to include the effects of both cubic and quartic potential energy. The resulting expressions for the extinction coefficient, the imaginary part of the complex refractive index $n^* = n + ik$, are

* Work supported by the Joint Services Electronics Program under Contract No. Nonr-1866(16). In addition, the author was a National Science Foundation Graduate Fellow, 1959-1963.

† Present address: ESSA Research Laboratories, Environmental Science Services Administration, Boulder, Colo. 80302.

¹ E. F. Nichols, *Wied. Ann.* **60**, 401 (1897).

² For a general historical survey as well as further details of this work, see J. C. Owens, thesis, Harvard University, 1964 (unpublished).

³ J. R. Jasperse, A. Kahan, J. N. Plendl, and S. S. Mitra, *Phys. Rev.* **146**, 526 (1966).

⁴ M. Czerny, *Z. Physik* **65**, 600 (1930).

⁵ M. Born and M. Blackman, *Z. Physik* **82**, 551 (1933); B. Szigeti, *Proc. Roy. Soc. (London)* **A258**, 377 (1960); J. Neuberger and R. D. Hatcher, *J. Chem. Phys.* **34**, 1733 (1961); D. W. Jepsen and R. F. Wallis, *Phys. Rev.* **125**, 1496 (1962).

⁶ M. Lax and E. Burstein, *Phys. Rev.* **97**, 39 (1955).

⁷ H. B. Rosenstock, *J. Chem. Phys.* **23**, 2415 (1955); A. A. Maradudin and G. H. Weiss, *Phys. Rev.* **123**, 1968 (1961); T. H. K. Barron, *ibid.* **123**, 1995 (1961).

⁸ D. W. Berreman, *Phys. Rev.* **130**, 2193 (1963); M. Hass and H. B. Rosenstock, *Appl. Opt.* **6**, 2079 (1967).

⁹ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954).

¹⁰ A. A. Maradudin and R. F. Wallis, *Phys. Rev.* **120**, 422 (1960).

¹¹ D. A. Kleinman, *Phys. Rev.* **118**, (1960).

¹² I. P. Ipatova, A. A. Maradudin, and R. F. Wallis, *Fiz. Tverd. Tela* **8**, 1064 (1966) [English transl.: *Soviet Phys.—Solid State* **8**, 850 (1966)]; *Phys. Rev.* **155**, 882 (1967).

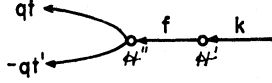


FIG. 1. Second-order cubic anharmonicity: representative diagram for summation terms.

compared to existing experimental data and to the results of new microwave and millimeter-wave measurements over a wide range of temperatures on three alkali-halide crystals. It is concluded that in the low-frequency wing of the reststrahl peak, away from the subsidiary resonances at nebenmaxima, the effects of quartic anharmonicity can be comparable to or larger than the cubic contributions. Just as the experimental work of Stolen and Dransfeld¹³ on a number of alkali halides gave convincing evidence for this conclusion in the wavelength range from 0.3 to 1.0 mm and temperature range from 15°K to room temperature, the present measurements do so in the ranges from 2.6 mm to 3.1 cm and 25 to 750°C.

II. THEORY

We shall follow Kleinman's excellent paper¹¹ closely in setting up the calculation, since we also are interested only in cubic crystals containing two kinds of atoms, and hence we may omit here all of the argument up to the extension beyond two-phonon summation processes. The use of ordinary time-dependent perturbation theory rather than the modified technique of Born and Huang⁹ is justified because we consider only the wings of the reststrahl peak. The use of an effective charge is equivalent to assuming rigid ions; the inclusion of nonlinear electric moments would require the use of the shell model. Aside from possible differences in the constants and the presence of a resonance denominator ($\omega_f^2 - \omega^2$), it can be seen by inspection of Kleinman's Hamiltonians that the multiphonon processes of a given order will have the same temperature dependence and the same general frequency dependence whether they are due to the anharmonic potential or to the nonlinear electric moment mechanisms. Hence we shall consider explicitly only the former. The anharmonicity is introduced using Kleinman's simple model, including terms in the potential energy which are cubic and quartic in the relative displacements of nearest-neighbor ions.

The calculation of the extinction coefficient due to a given type of multiphonon process is carried out by first evaluating the appropriate matrix elements of the interaction Hamiltonian \mathcal{H}^I and the anharmonic terms \mathcal{H}^{II} and \mathcal{H}^{III} , which can be done by inspection of the appropriate diagrams. From these matrix elements the total transition probability Ω for the process can be found. By invoking the correspondence principle,¹⁴ one

¹³ R. Stolen and K. Dransfeld, Phys. Rev. **139**, A1295 (1965).

¹⁴ Note that V^{-2} in Kleinman's Eqs. (26) and (27) should be V^{-1} . This does not change his results.

TABLE I. Summary of contributions to extinction coefficient.

Cubic anharmonic contributions:

$$\kappa_s = \frac{18A^2\hbar^2\hat{\rho}^2\pi^2}{V\epsilon_\infty^{1/2}m^2(\omega^2 - \omega_f^2)^2} \sum_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} \frac{|D_s(\mathbf{q}\mathbf{t}\mathbf{t}')|^2}{\omega_{\mathbf{q}\mathbf{t}}\omega_{-\mathbf{q}\mathbf{t}'}} \times (n_{\mathbf{q}\mathbf{t}} + n_{-\mathbf{q}\mathbf{t}'} + 1)\delta(\omega - \omega_{\mathbf{q}\mathbf{t}} - \omega_{-\mathbf{q}\mathbf{t}'})$$

$$\kappa_d = \frac{36A^2\hbar^2\hat{\rho}^2\pi^2}{V\epsilon_\infty^{1/2}m^2(\omega^2 - \omega_f^2)^2} \sum_{\mathbf{q}, \mathbf{q}', \mathbf{q}''} \frac{|D_d(\mathbf{q}\mathbf{t}\mathbf{t}')|^2}{\omega_{\mathbf{q}\mathbf{t}}\omega_{-\mathbf{q}\mathbf{t}'}} (n_{-\mathbf{q}\mathbf{t}'} - n_{\mathbf{q}\mathbf{t}})\delta(\omega - \omega_{\mathbf{q}\mathbf{t}} + \omega_{-\mathbf{q}\mathbf{t}'})$$

Quartic anharmonic contributions:

$$\kappa_I = \frac{144B^2\hbar^3\hat{\rho}^2\pi^2}{NV\epsilon_\infty^{1/2}m^2(\omega^2 - \omega_f^2)^2} \sum_{\mathbf{q}, \mathbf{q}', \mathbf{q}'', \mathbf{q}'''} \frac{|E_I(\mathbf{q}\mathbf{t}, \mathbf{q}'\mathbf{t}', \mathbf{q}''\mathbf{t}'')|^2}{\omega_{\mathbf{q}\mathbf{t}}\omega_{\mathbf{q}'\mathbf{t}'}\omega_{\mathbf{q}''\mathbf{t}''}} \times (n_{\mathbf{q}\mathbf{t}}n_{\mathbf{q}'\mathbf{t}'} + n_{\mathbf{q}\mathbf{t}'}n_{\mathbf{q}'\mathbf{t}''} + n_{\mathbf{q}\mathbf{t}''}n_{\mathbf{q}'\mathbf{t}'} + n_{\mathbf{q}\mathbf{t}'}n_{\mathbf{q}''\mathbf{t}''} + n_{\mathbf{q}''\mathbf{t}''}n_{\mathbf{q}'\mathbf{t}'} + 1) \times \delta(\omega - \omega_{\mathbf{q}\mathbf{t}} - \omega_{\mathbf{q}'\mathbf{t}'} - \omega_{\mathbf{q}''\mathbf{t}''})$$

$$\kappa_{II} = \frac{432B^2\hbar^3\hat{\rho}^2\pi^2}{NV\epsilon_\infty^{1/2}m^2(\omega^2 - \omega_f^2)^2} \sum_{\mathbf{q}, \mathbf{q}', \mathbf{q}'', \mathbf{q}'''} \frac{|E_{II}(\mathbf{q}\mathbf{t}, \mathbf{q}'\mathbf{t}', \mathbf{q}''\mathbf{t}'')|^2}{\omega_{\mathbf{q}\mathbf{t}}\omega_{\mathbf{q}'\mathbf{t}'}\omega_{\mathbf{q}''\mathbf{t}''}} \times (n_{\mathbf{q}\mathbf{t}'}n_{\mathbf{q}'\mathbf{t}''} - n_{\mathbf{q}\mathbf{t}''}n_{\mathbf{q}'\mathbf{t}'} - n_{\mathbf{q}\mathbf{t}''}n_{\mathbf{q}''\mathbf{t}'} - n_{\mathbf{q}\mathbf{t}'}n_{\mathbf{q}''\mathbf{t}''}) \times \delta(\omega - \omega_{\mathbf{q}\mathbf{t}} + \omega_{\mathbf{q}'\mathbf{t}'} + \omega_{\mathbf{q}''\mathbf{t}''})$$

$$\kappa_{III} = \frac{432B^2\hbar^3\hat{\rho}^2\pi^2}{NV\epsilon_\infty^{1/2}m^2(\omega^2 - \omega_f^2)^2} \sum_{\mathbf{q}, \mathbf{q}', \mathbf{q}'', \mathbf{q}'''} \frac{|E_{III}(\mathbf{q}\mathbf{t}, \mathbf{q}'\mathbf{t}', \mathbf{q}''\mathbf{t}'')|^2}{\omega_{\mathbf{q}\mathbf{t}}\omega_{\mathbf{q}'\mathbf{t}'}\omega_{\mathbf{q}''\mathbf{t}''}} \times (n_{\mathbf{q}\mathbf{t}''}n_{\mathbf{q}'\mathbf{t}'} + n_{\mathbf{q}\mathbf{t}'}n_{\mathbf{q}''\mathbf{t}''} - n_{\mathbf{q}\mathbf{t}'}n_{\mathbf{q}'\mathbf{t}''} - n_{\mathbf{q}\mathbf{t}''}n_{\mathbf{q}'\mathbf{t}'}) \times \delta(\omega - \omega_{\mathbf{q}\mathbf{t}} - \omega_{\mathbf{q}'\mathbf{t}'} + \omega_{\mathbf{q}''\mathbf{t}''})$$

can obtain the extinction coefficient κ , given by

$$\kappa = (\sqrt{\epsilon_\infty})\Omega/2\omega N_\omega, \quad (2)$$

where N_ω is the number of photons in the initial state. For the case $\kappa^2 \ll n^2$, the loss tangent ($\tan\delta = \epsilon''/\epsilon'$) is given by

$$\tan\delta = 2\kappa/\sqrt{\epsilon'}. \quad (3)$$

We first consider the contributions due to cubic anharmonicity, the two types of two-phonon terms. The summation terms are those in which a photon \mathbf{k} is destroyed and two phonons $\mathbf{q}\mathbf{t}$ and $-\mathbf{q}\mathbf{t}'$ are created, or vice versa (\mathbf{k} denotes the wave vector of the photon, $\mathbf{q}\mathbf{t}$ the wave vector and branch of the phonon), while the difference terms are those in which one phonon is created and one destroyed. For each type there are four diagrams representing photon absorption and four representing emission; in each set there are two diagrams in which \mathcal{H}^I precedes \mathcal{H}^{II} and two having the other order. The diagrams for the summation terms, as well as an example of the evaluation procedure, are given by Kleinman. In Fig. 1 we show only one of these diagrams.

The extinction coefficient κ_s due to the entire set of summation terms is given in Table I, in which the notation is the same as Kleinman's except for the symbols A and $D_s(\mathbf{q}\mathbf{t}\mathbf{t}')$. The first one, A , is the cubic potential energy parameter (Kleinman's G). The second is a sum over the j nearest neighbors (in our case 6) of a given ion, similar to Kleinman's $X_{\mathbf{q}\mathbf{t}\mathbf{t}'}$ but different because we choose to keep all constants explicit by normalizing the annihilation and creation operators for

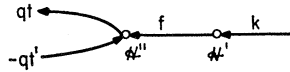


FIG. 2. Second-order cubic anharmonicity: representative diagram for difference terms.

photons as well as phonons to unit commutator, and by redefining the phonon polarization vectors $\mathbf{b}_{\sigma q t}$ so that no constants appear in the first of Kleinman's orthonormality relations (4). Hence our derivation begins with Kleinman's Eqs. (1) and (3), of course, but with the right-hand side of (1) multiplied by $(2\pi\hbar c^2/\epsilon_\omega\omega)^{1/2}$ and that of (3) multiplied by $(\hbar/2m_\sigma\omega_{q t})^{1/2}$ inside the summation. The factor $D_s(\mathbf{q}t t')$ then turns out to be

$$D_s(\mathbf{q}t t') = \sum_j (\mathbf{j} \cdot \mathbf{u}) C_{j q t} C_{j - q t'}, \quad (4)$$

where $C_{j q t}$ is given by

$$C_{j q t} = \mathbf{j} \cdot \left(\frac{\mathbf{b}_{j q t}}{\sqrt{m_j}} e^{i\rho \mathbf{q} \cdot \mathbf{j}} - \frac{\mathbf{b}_{\sigma q t}}{\sqrt{m_\sigma}} \right). \quad (5)$$

The evaluation of the difference terms, for which one diagram is shown in Fig. 2, is identical, except that we now have

$$D_d(\mathbf{q}t t') = \sum_j (\mathbf{j} \cdot \mathbf{u}) C_{j q t} C_{j - q t'}^* \quad (6)$$

rather than (4), and energy conservation permits us to write the nonredundant summation as $2 \sum_{t > t'}$ ⁽²⁾ to

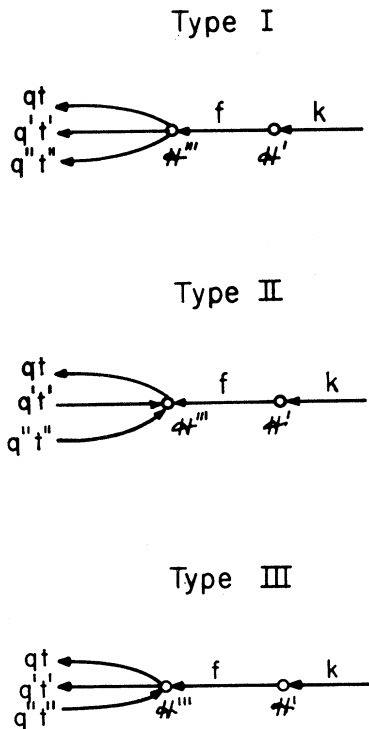


FIG. 3. Second-order quartic anharmonicity: representative diagrams for the three types of terms.

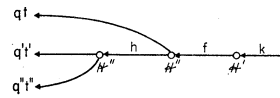


FIG. 4. Representative diagram in third-order perturbation theory.

indicate that the sum is taken only over those phonon pairs for which $\omega_{q t} > \omega_{-q t'}$. The resulting extinction coefficient κ_d is given in Table I.

We next consider the contributions due to quartic anharmonicity, involving matrix elements of \mathcal{H}^{IV} and \mathcal{H}^{CV} . The allowed combinations of terms are of three types: (1) summation terms, in which one photon is destroyed and three phonons are created (type I), (2) difference terms in which one photon and two phonons are destroyed and one phonon is created (type II), and (3) difference terms in which one photon and one phonon are destroyed and two phonons are created (type III). One diagram of the eight for each type is shown in Fig. 3, and the extinction coefficients κ_{I} , κ_{II} , and κ_{III} are given in Table I. In these expressions B is the quartic anharmonic energy parameter, and the factors E_{I} , E_{II} , and E_{III} are given by

$$E_{\text{I}}(\mathbf{q}t, \mathbf{q}'t', \mathbf{q}''t'') = \sum_j (\mathbf{j} \cdot \mathbf{u}) C_{j q t} C_{j q' t'} C_{j q'' t''},$$

$$E_{\text{II}}(\mathbf{q}t, \mathbf{q}'t', \mathbf{q}''t'') = \sum_j (\mathbf{j} \cdot \mathbf{u}) C_{j q t} C_{j' q' t'}^* C_{j q'' t''}^*, \quad (7)$$

$$E_{\text{III}}(\mathbf{q}t, \mathbf{q}'t', \mathbf{q}''t'') = \sum_j (\mathbf{j} \cdot \mathbf{u}) C_{j q t} C_{j q' t'} C_{j q'' t''}^*.$$

The summation in κ_{II} is restricted by the condition $\omega_{q t} > \omega_{q' t'}$, $\omega_{q'' t''}$, giving a redundancy factor of 3, while the condition for κ_{III} is $\omega_{q t}, \omega_{q' t'} > \omega_{q'' t''}$ and the factor is again 3.

Third and higher orders of perturbation theory must also be considered. A representative third-order diagram which gives the same over-all transition as the first diagram of Fig. 3 is shown in Fig. 4. The contributions from this diagram and its associated set are expected to be qualitatively similar to those of Fig. 3 but somewhat smaller, although quantitative evaluation is difficult. The convergence of perturbation theory for higher-order phonon processes usually depends on a delicate balance between magnitude of matrix elements and availability of phase space. It turns out that both for magnetic-spin-relaxation studies¹⁵ and anharmonic

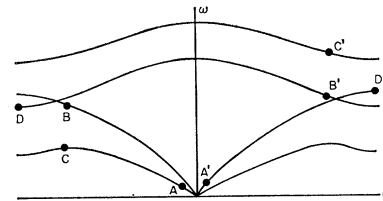


FIG. 5. Possible phonon pairs for cubic anharmonic terms.

¹⁵ N. Bloembergen, *Nuclear Magnetic Relaxation* (W. A. Benjamin, Inc., New York, 1961), p. 116.

phonon-collision processes¹⁶ the results for third-order perturbation theory are one or two orders of magnitude smaller than for second order, and hence we shall neglect them.

III. DISCUSSION OF THEORY

We now consider the temperature and frequency dependence of the calculated extinction coefficients in the low-frequency limit.

A. Two-Phonon Processes

The number of interactions allowed by \mathcal{H}'' , involving net changes in occupation numbers for two phonons, is severely limited by conservation of energy and crystal momentum. Several possible types of phonon pairs are indicated in Fig. 5 on a schematic representation of the dispersion curves for a crystal of the NaCl type. Except in special cases, only sum and difference processes involving pair $A-A'$, in which both phonons belong to the low-frequency acoustic branches near $\mathbf{q}=0$, can satisfy these conditions, and such pairs are expected to make the most important two-phonon contribution to the absorption at all frequencies other than the resonance frequencies of the reststrahl and nebenmaximum peaks. Pair $B-B'$, the only other possibility giving rise to continuous absorption at very low frequencies, is expected to be less important because of the small number of such branch crossings. In addition, such pairs can participate only in difference processes and will be unimportant at low temperatures. Umklapp processes similar to $B-B'$, but not requiring actual branch crossings since the vectors \mathbf{q} and \mathbf{q}' can be in different directions, can occur but will also be unimportant at low temperatures. Pairs $C-C'$ and $D-D'$, in which one or both phonons are at critical points, cannot contribute at arbitrarily low frequencies.

The temperature dependence of the absorption comes only from the occupation numbers through $n_{\mathbf{q}l} = (e^{\hbar\omega_{\mathbf{q}l}/kT} - 1)^{-1}$ if we neglect the small shifts in phonon frequency with temperature. For a photon frequency of 100 GHz, the frequencies of $A-A'$ phonons will be of the order of 50 GHz, and hence at room temperature the occupation numbers and the extinction coefficients for sum and difference processes will be proportional to the absolute temperature T . For the other three pairs the high-temperature approximation is not necessarily a good one at room temperature, however. We define a characteristic temperature θ by $k\theta = \hbar\omega_f$, and use it as a rough estimate of the characteristic excitation temperature of phonons near branch crossings. We find from the reststrahl frequencies¹⁷ that this temperature is 443°K for LiF,

236°K for NaCl, and 164°K for KBr. Hence, the contributions of these three types of phonon pairs to the extinction coefficient may show a stronger than linear temperature dependence, becoming linear only near the melting points of the crystals.

The frequency dependence of κ_s may be estimated, since only low-energy acoustic phonons are involved, by changing the sum to a double integral in reciprocal space and using an isotropic Debye model for the crystal. If we assume that $D_s(\mathbf{q}l'')$ is independent of ω , which is not unreasonable, we find κ_s to be proportional to ω^2 .

B. Three-Phonon Processes

It is well known that there is an important difference between the two-phonon and three-phonon processes: for the latter, the conservation rules are far less restrictive in that there are many more satisfactory combinations of phonons which can contribute to the absorption. Essentially, the whole Debye spectrum of acoustic phonons is now available, and optical phonons will contribute as well. A study by Maradudin¹⁶ of the density of final states for both types of processes, using a simple set of dispersion curves and actually counting the possible sets of phonons, has indicated that the density of states for quartic difference processes is between one and two orders of magnitude greater than that for the cubic ones. Thus, although the ratio of the corresponding matrix elements may be small, the quartic processes may nevertheless dominate the absorption at high temperatures.

The behavior of the extinction coefficient for three-phonon summation processes may be estimated in the same way as before. It can be seen by inspection that the temperature dependence of κ_{I} is quadratic at ordinary temperatures. If we assume that $E_{\text{I}}(\mathbf{q}l, \mathbf{q}'l', \mathbf{q}''l'')$ is independent of ω , we find that κ_{I} , like κ_s , is proportional to ω^2 . This analysis is not valid, however, for the difference terms, for which the most important contributions will probably be made by processes in which at least one of the phonons is of high energy and provides a large density of final states. For the extinction coefficient due to these processes we expect, first, a weak frequency dependence, because the phonon energies will in general be large, and hence the density of final states and the matrix elements will be insensitive to the photon energy. Second, the difference terms are expected to be more important than the summation ones because of their large number. Third, the limited validity of the high-temperature approximation will make the temperature dependence of κ_{II} and κ_{III} stronger than quadratic at ordinary temperatures. However, the ionic mass ratio and other factors affect the density of final states, and hence it will not necessarily be the case that the temperature dependence will be strongest in the crystal having the highest reststrahl frequency.

¹⁶ A. Maradudin (private communication).

¹⁷ *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Co., New York, 1963), 2nd ed., pp. 6-126.

TABLE II. Room-temperature dielectric properties of alkali-halide crystals.

Source	Frequency (GHz)	LiF			NaCl			KBr		
		ϵ'	$10^4 \tan\delta$	γ/ω_f	ϵ'	$10^4 \tan\delta$	γ/ω_f	ϵ'	$10^4 \tan\delta$	γ/ω_f
Present work	116	9.14	7.9	0.08	5.90	17.2	0.12	4.91	10.7	0.06
Genzel, Happ and Weber	100					28			7.5	
Dye	50	8.73	2.6		5.83	4.8		4.79	2.2	
Present work	35.4	9.14	4.1	0.14	5.90	4.9	0.12	4.91	4.5	0.09
Smith	24				5.90	2.9		4.85	1.3	
von Hippel	25				5.90	<5				
	10		1.8					4.90	2.3	
Present work	8.9	9.14	1.74	0.23	5.90	2.27	0.21	4.91	2.36	0.18

IV. EXPERIMENTAL PROCEDURES

In order to achieve high sensitivity in the measurement of these low-loss materials, a filled resonant cavity method was used at 10 and 35 GHz. The single-crystal blanks¹⁸ were ground to cylindrical shape with a 500-grit diamond wheel and then coated with an evaporated layer of silver to form the cavities. A simple frequency-insensitive gear-driven variable iris between the waveguide and the cavity permitted coupling adjustments to be made. The dielectric constant ϵ' can be found from the dimensions and resonant frequency ω_0 of the cavity using standard formulas¹⁹ after extrapolating ω_0 to zero iris diameter to eliminate cavity pulling effects. The loss tangent of the sample can be found from the measured unloaded Q of the cavity after wall losses are eliminated. Large cavities resonating in high-order high- Q modes such as TE_{013} and TE_{341} were used, but even so the wall losses were not negligible and required separate determination, which was done in two ways. First, cavity perturbation measurements were made at room temperature using small rod-shaped samples in TM_{010} and TM_{023} cavities. As is easily shown, the value of $\tan\delta$ obtained in this way is more accurate than the values of ϵ' and ϵ'' , and is independent of the cavity filling factor and any depolarization corrections as long as the general assumptions of the perturbation theory are satisfied. For a cavity filled with the same material at the same temperature, any decrease in Q below the previously measured value of $(\tan\delta)^{-1}$ must be due to wall losses. The ratio of measured to theoretical¹⁹ wall losses determines an effective resistivity for the cavity walls, and the known temperature dependence of the resistivity²⁰ can then be used to calculate the wall losses as a function of temperature and frequency. Second, the wall losses were independently determined from Q measurements on two different modes resonating at slightly different frequencies by assuming that for both modes the ratio of actual to theoretical loss was given by the same number. To facilitate the use of this method, the cavity shapes were chosen so that one high- Q and one low- Q mode fell reasonably close together.

A disadvantage in practice, but advantage in interpretation, of the filled cavity method is that the cavity resonance frequency decreases with increasing temperature and hence the temperature range over which a given mode can be followed in a given sample is determined by the tuning range of the oscillator. It can be seen easily from the dispersion formula (1) and the formula for cavity resonance frequency, however, that the ratio ω_0/ω_f remains approximately constant during the measurement. Thus what is measured is principally the change in absorption at fixed ω_0/ω_f due to increased damping, and the measurement is insensitive to the additional increase in absorption which would be observed at fixed ω_0 due to the decrease in ω_f with increasing temperature.

The measurements of ω_0 and Q at 10 GHz were made using a swept reflectometer circuit, standard except for the use of a special isolator and several tuners to suppress line resonances. The cavity bandwidths were measured using heterodyne marker pips generated in a variant of the well-known "cavity Q -meter" circuit.²¹ A new and simple method of directly measuring the unloaded Q of a reflection cavity, requiring only one universal graph and no reference short circuit even if there are series losses, was developed by extending Reed's analysis.²² At 35 GHz, a matched-magic-tee bridge circuit was used instead, one arm containing the sample in a transmission cavity and the other arm a precision attenuator and phase shifter. After balancing the bridge at ω_0 and measuring the cavity transmission, the reference arm power was reduced by 3 dB and the bridge rebalanced at the half-power points by adjusting the phase shifter. The same marker pip circuit as before was then used to determine bandwidth. From these measurements of loaded Q and transmission loss the unloaded Q could be determined.²³

Because the dielectric losses in these crystals increase more rapidly with frequency than do wall losses, a simpler method of measurement could be used at 116 GHz, requiring only measurements of transmission through a dielectric plug 70–80 wavelengths long which filled a section of waveguide. For dielectrics of fairly

¹⁸ Obtained from the Harshaw Chemical Co., Cleveland, Ohio.

¹⁹ *Technique of Microwave Measurements*, edited by C. G. Montgomery (McGraw-Hill Book Co., New York, 1956), Chap. 5.

²⁰ Reference 17, pp. 4–13.

²¹ Reference 19, p. 396.

²² E. D. Reed, Monograph No. 1953, Bell Telephone System, 1952 (unpublished).

²³ E. L. Ginzton, *Microwave Measurements* (McGraw-Hill Book Co., New York, 1957), p. 404.

TABLE III. Temperature dependence of ϵ' : parameters for Eq. (44).

	A (°C)	B (°C)	ϵ_∞
LiF, 10 and 35 GHz	2.15×10^4	3.01×10^3	1.940
NaCl, 10 and 35 GHz	6.86×10^3	1.98×10^3	2.385
KBr, 10 GHz	4.26×10^3	1.74×10^3	2.431
KBr, 35 GHz	4.63×10^3	1.89×10^3	2.431

low loss, ϵ' can be found from two successive frequencies at which the transmission is a maximum, and ϵ'' or $\tan\delta$ from the transmission at such frequencies. It was found that imperfect fit of the sample in the holder had little effect on the measured values of $\tan\delta$ because ϵ' and ϵ'' were similarly affected, although the errors in ϵ' could be as large as 10%. Once the total number of wavelengths in the sample had been determined at room temperature, further measurements could be made at fixed frequency by monitoring the sample transmission as the temperature was varied. Transmission maxima were recorded at intervals of 25–50°C. Wall losses in the sample holder contributed a correction of about 10% to the measured $\tan\delta$ values.

V. RESULTS AND DISCUSSION

A. Frequency Dependence of Dielectric Constant and Loss

The values of ϵ' and $\tan\delta$ measured at room temperature are listed in Table II along with other reported values.²⁴ No dispersion in ϵ' was expected or found. The present measurements of ϵ' at 10 and 35 GHz have an estimated error of 0.5% due to wavemeter and dimensional inaccuracies, while at 116 GHz the error may be as large as 10%. The values of $\tan\delta$ are believed to be accurate to within 10% at all three frequencies. The damping parameter γ/ω_f of classical dispersion

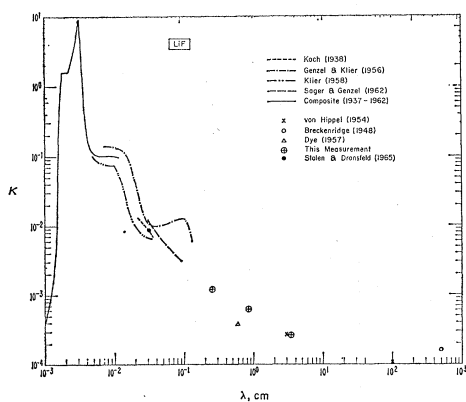


FIG. 6. Extinction coefficient of LiF at 25°C.

²⁴ L. Genzel, H. Happ, and R. Weber, Z. Physik **154**, 13 (1959); N. E. Dye, Laboratory for Insulation Research, Massachusetts Institute of Technology, Technical Report No. 114, 1957 (unpublished); G. C. Smith, Materials Science Center, Cornell University, Report No. 51, 1962 (unpublished); A. R. von Hippel, *Dielectric Materials and Applications* (Wiley-Interscience, Inc., New York, 1954), p. 301.

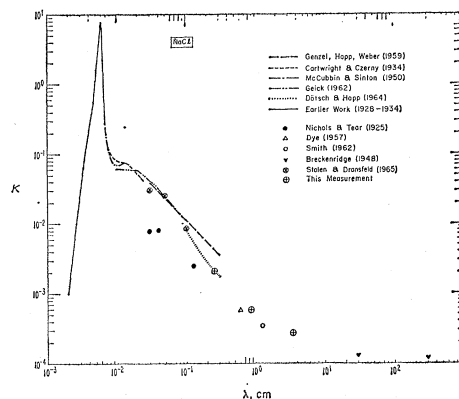


FIG. 7. Extinction coefficient of NaCl at 25°C.

theory, which can be shown to be related to the loss tangent for the case $\omega/\omega_f \ll 1$ by the simple expression

$$\frac{\epsilon'}{\epsilon' - \epsilon_\infty} \tan\delta = \frac{\omega \gamma}{\omega_f \omega_f}, \quad (8)$$

is also given in Table II.

A summary of the absorption measurements reported in the literature^{2,18,24,25} in the wavelength range from 10^{-3} to 10^3 cm is given in Figs. 6–8. The extinction coefficient decreases with decreasing frequency somewhat more rapidly than linearly in the far-infrared range beyond all distinct nebenmaxima, approximately linearly in the millimeter-wave region, and approaches a constant value of about 1×10^{-4} below 1 GHz. The origin of this constant “background” loss, which appears from the present work to be independent of temperature, is unknown, although it may be due to imperfections in the crystals. The weak frequency dependence

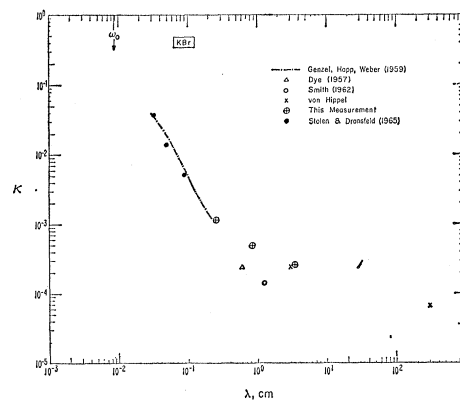


FIG. 8. Extinction coefficient of KBr at 25°C.

²⁵ R. G. Breckenridge, J. Chem. Phys. **16**, 959 (1948); C. H. Cartwright and M. Czerny, Z. Physik **90**, 457 (1934); H. Dötsch and H. Happ, *ibid.* **177**, 360 (1964); R. Geick, *ibid.* **166**, 122 (1962); L. Genzel and M. Klier, *ibid.* **144**, 25 (1956); M. Klier, *ibid.* **150**, 49 (1958); B. Koch, Ann. Physik **33**, 335 (1938); T. K. McCubbin, Jr., and W. M. Sinton, J. Opt. Soc. Am. **40**, 537 (1950); E. F. Nichols and J. D. Tear, Astrophys. J. **61**, 17 (1925); G. Seger and L. Genzel, Z. Physik **169**, 66 (1962).

suggests that the quartic difference processes, rather than the cubic processes, dominate the absorption in this frequency region. No significant change in frequency dependence with temperature was observed for temperatures high enough to make the background loss negligible.

B. Temperature Dependence of κ

The measured loss tangents were first corrected by subtraction of the loss due to ionic conductivity, given by

$$(\tan\delta)_{ic} = (1.13 \times 10^{13} / \epsilon' \omega_0) A e^{-B/T}, \quad (9)$$

in which the parameters²⁶ A and B for LiF and KBr are, respectively, 1.57×10^6 , 2.310×10^4 and 1.22×10^5 , 2.171×10^4 , while those for NaCl are $4.76 \times 10^8/T$, 2.194×10^4 . The corrected 10-GHz results may still be too high by a few per cent near 700°C due to uncertainty in this correction and to the effect of the relaxation of vacancy pairs. Next, the fixed-frequency 116-GHz data were made more directly comparable to the lower-frequency data through multiplication by $\omega_0(T)/\omega_0(25^\circ) = [\epsilon'(25^\circ)/\epsilon'(T)]^{1/2}$, the cavity frequency shift as a function of temperature observed at 10 and 35 GHz. This factor changes by about 9% in the range from 25 to 500°C . The data were then converted to values of extinction coefficient, the estimated background loss κ_0 subtracted, and the resulting values normalized by the remaining loss at 25°C . These normalized results are shown in Figs. 9–11. The three curves for each material are generally parallel, showing that the temperature dependence is similar at each frequency, although the 10-GHz LiF and 35-GHz KBr curves are somewhat anomalous.

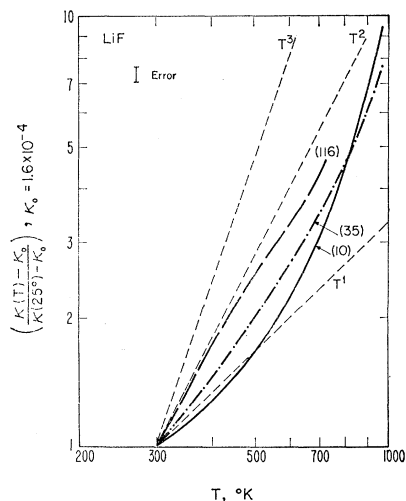


FIG. 9. Temperature dependence of normalized extinction coefficient of LiF. Experimental curves are labeled with nominal measurement frequency in parentheses. Dashed lines are guide lines corresponding to successive integral powers of temperature. Error bar indicates estimated experimental error.

²⁶ Reference 17, pp. 9–65; R. W. Dreyfus and A. S. Nowick, *J. Appl. Phys. Suppl.* **33**, 473 (1962).

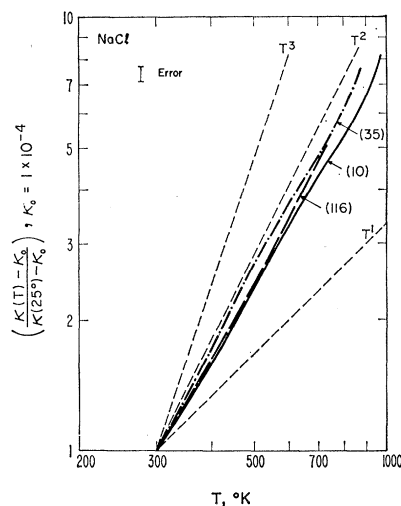


FIG. 10. Temperature dependence of normalized extinction coefficient of NaCl.

It is difficult to estimate the relative importance of the cubic anharmonic terms, the failure of the high-temperature approximation, the presence of anharmonicities of higher order than quartic, and the effects of incomplete experimental corrections in discussing the large deviations from the expected quadratic temperature dependence shown by some of the data. Several measurement runs were made at each frequency using different samples, and although the background loss varied somewhat from sample to sample, the general shape of the curves obtained was very similar. Nevertheless, it is believed that imperfect cancellation of the background loss rather than the presence of cubic anharmonicity is the reason why the lower-frequency curves for LiF and KBr are somewhat low and appear

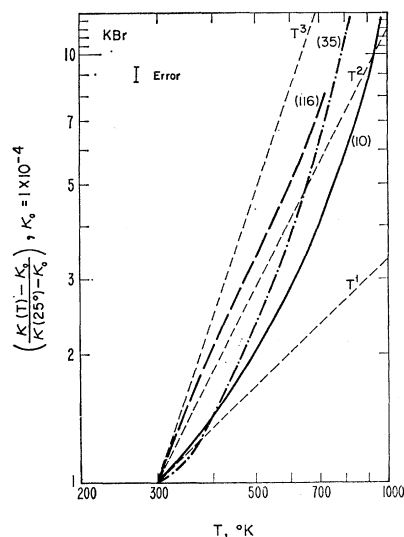


FIG. 11. Temperature dependence of normalized extinction coefficient of KBr.

to have a linear temperature dependence at low temperatures. Within the estimated error of 10% (which corresponds to a fixed vertical distance on these graphs) it is not possible to say whether the curves for a given material coincide quite well in slope or are really different, although it is believed that in this wavelength range, the curves should probably coincide except possibly at the highest temperatures, where ionic conductivity or vacancy-pair effects may cause the lower-frequency curves to turn upward.

The average temperature dependence of κ at the higher temperatures may be represented by T^δ , where the exponents δ for the three materials are 1.7–2.3 (LiF), 1.8–2.0 (NaCl), and 2.5–3.5 (KBr). The only other data to which these results may be directly compared are those of Smith,²⁴ who found the exponents at 24 GHz to be 2.5 for NaCl and 3 for KBr. The curve of $\kappa(T)$ which may be deduced from his data, however, is not parallel to the curves found in the present experiments at the two lower frequencies. Both sets of data agree, however, that the temperature dependence is not linear, as it would be if cubic anharmonicity were the dominant source of absorption, but quadratic or stronger, as predicted by the present theory. It seems probable that the deviations from $\delta=2$ unexplainable by experimental error are due at least in part to inadequate phonon excitation in the optical branches. The characteristic temperatures of the highest-energy phonons, which can be found from the earlier values θ by using the Lyddane-Sachs-Teller relation,⁹ are 973°K (LiF), 382°K (NaCl), and 235°K (KBr). We see that the high-temperature approximation is not a good one for all phonons in LiF even at the melting point, although it should be for KBr. This does not explain, of course, why the slopes are systematically larger in KBr than in LiF; it may be that in KBr there are significant anharmonic terms of higher order than quartic.

It was not possible to make reproducible loss measurements much below room temperature at 10 and 35 GHz, but such measurements were made at 116 GHz. These data showed no significant changes in the exponent δ at the minimum temperatures reached, -130°C (LiF), -100°C (NaCl), and -65°C (KBr), and could be extrapolated to zero at temperatures between -225 and -125°C for the three materials. Evidently, the exponent δ decreases at temperatures below those achieved in this work, when the cubic processes become dominant. Dötsch and Happ²⁵ have indeed found the temperature dependence of κ in NaCl at 3 mm wavelength to change from quadratic to linear to temperatures below -130°C . Similar behavior has been observed between 0.3 and 1.0 mm wavelength in a number of alkali halides by Stolen and Dransfeld,¹⁸ who noted that the quadratic temperature dependence was generally more marked at the longer wavelengths. This would be expected because the nebenmaxima, which are due to cubic processes and

much show a linear temperature dependence, become less important at long wavelengths relative to the nonresonant quartic absorption.

A further comparison with theory may be made by considering the relative absorption of the three materials at a given frequency. At low temperatures, NaCl exhibits the largest value of κ at all three frequencies. At high temperatures, NaCl remains highest only at 116 GHz, possibly due to a nearby nebenmaximum, while KBr has the largest absorption at the lower frequencies. It is understandable that LiF should have the lowest loss on the basis of both phonon excitation and ionic mass ratio, while the crossover of the NaCl and KBr curves is evidently due to a competition between these effects. We must, of course, also consider the ratios of the constant factors in the expressions for extinction coefficient of Table I. Using Szigeti's data,²⁷ the ratio of the factors $A^2(\hat{\epsilon})^2/V\epsilon_\infty^{1/2}(m\omega_f)^2$ for the cubic terms and $B^2(\hat{\epsilon})^2/\epsilon_\infty^{1/2}(m\omega_f)^2$ for the quartic may be shown to be $1.00A_L^2: 0.43A_N^2: 0.34A_K^2$ and $1.00B_L^2: 1.08B_N^2: 1.36B_K^2$, where A_L , A_N , and A_K are the cubic anharmonicity parameters and B_L , B_N , and B_K the quartic for LiF, NaCl, and KBr, respectively. If we assume that the sum over phonons is the same for all three crystals, which is reasonable for the cubic processes and the quartic summation processes and may even be satisfactory for the quartic difference processes, then if the cubic processes were dominant and $A_L=A_N=A_K$, the order of increasing κ would be KBr, NaCl, LiF, while if the quartic were dominant and the B constants equal, the order would be reversed and the differences smaller. The ratios of the observed values agree with the second case; if the cubic contributions were dominant it would be necessary to have $A_L < A_N$, A_K and at high temperature, $A_N < A_K$ as well. This order is inconsistent with the observations by Lax and Burstein⁶ and by Fuchs²⁸ that the width of the reststrahl band, the strength of the first high-frequency nebenmaximum, the deviation from the Cauchy relation, and the strain polarizability constant are consistent with cubic anharmonicity increasing in the opposite order. Hence, we again find a suggestion that the quartic effects are more important than the cubic in millimeter-wave absorption.

C. Temperature Dependence of ϵ' at 10 and 35 GHz

The value of ϵ' as a function of temperature at constant pressure is easily obtained from the cavity resonance condition and the linear coefficient of thermal expansion. It was found that the measured values could be fitted to within a few tenths of 1% by an

²⁷ B. Szigeti, *Trans. Faraday Soc.* **45**, 155 (1949); *Proc. Roy. Soc. (London)* **A204**, 51 (1950).

²⁸ R. Fuchs, Laboratory for Insulation Research, Massachusetts Institute of Technology, Technical Report No. 167, 1961 (unpublished).

TABLE IV. Temperature dependence of ϵ' .

		25°C ($\times 10^{-4}$)	75°C ($\times 10^{-4}$)	400°C ($\times 10^{-4}$)	600°C ($\times 10^{-4}$)
Present measurements of ($1/\epsilon'$)($d\epsilon'/dT$)	LiF	2.74	2.79	3.22	3.56
	NaCl	3.08	3.17	4.04	4.86
Smith	KBr ^a	2.86	3.01	4.04	4.98
	NaCl ^b		3.0	4.1	5.4
Eucken & Büchner	KBr ^b		2.9	4.6	5.6
	LiF	3.75			
Bosman & Havinga	NaCl	3.40			
	NaCl	3.24			
Panchenko	KBr	3.14			
	NaCl		3.1	10.0	
	KBr		3.2	10.0	

^a Average of X-band and K α -band values.
^b Smoothed values.

expression of the form

$$\epsilon' - \epsilon_{\infty} = A/(B - T), \quad (10)$$

for which the constants A , B , and ϵ_{∞} are given in Table III. An unexplained discrepancy between the 10- and 35-GHz values for KBr, ranging from zero at 25°C to 1½% at 500°C, was observed in repeated measurements.

It can readily be shown that this form for the temperature dependence of ϵ' is reasonable using classical theory. At frequencies much less than the reststrahl frequency the contribution to the dielectric constant from ionic motion is²⁷

$$\epsilon' - \epsilon_{\infty} = \left[\frac{1}{3}(n^2 + 2) \right]^2 \left[\frac{4\pi N (e^*)^2}{M \omega_f^2} \right], \quad (11)$$

where n is the optical refractive index, N is the number of ions pairs per unit volume, e^* is the effective charge, and M is the reduced mass. If the temperature is increased at constant pressure, both N and ω_f decrease. We may write the temperature dependence of ω_f as

$$\omega_f = (\omega_f)_0 (1 - \beta \gamma \Delta T), \quad (12)$$

where β is the volume coefficient of thermal expansion and γ is the Gruneisen constant. The temperature dependence of N is given by $N = N_0(1 + \beta \Delta T)^{-1}$. Substituting these into (11) and expanding the denominator to first order in $\beta \Delta T$, we find

$$\epsilon' - \epsilon_{\infty} = (\epsilon' - \epsilon_{\infty})_0 / [1 - \beta(2\gamma - 1)\Delta T], \quad (13)$$

which is easily changed to the form (10). For the alkali halides, the approximate values of the parameters at room temperature are²⁹ $\beta = 1.2 \times 10^{-4}$, $\gamma = 1.6$; with those values, the factors A and B are too large by about a factor of 2. However, if the proper value of γ for the fundamental mode of NaCl were 2.82 rather than 1.6, (47) would agree very well with the measured values.

The quantity $(1/\epsilon')(d\epsilon'/dT)$ obtained from the present measurements is tabulated in Table IV along with values from other sources.^{24,30}

E. Summary

It has been demonstrated by a systematic series of measurements of the frequency and temperature dependence of the dielectric constant and loss tangent of alkali-halide crystals in the microwave and millimeter-wave region, that simple theories of infrared absorption which consider only the lowest-order anharmonic effects are inadequate. A more complete theory is presented in which the effects of higher-order anharmonicity are systematically considered, using a simple model for the crystal, and it is shown that the contributions to the absorption due to quartic anharmonicity may be expected to be comparable to or larger than the contributions due to cubic terms. Although quantitative comparisons are not yet possible, the results of the present experiments are in general agreement with the predicted temperature, frequency, and crystal dependence of the absorption due to quartic anharmonicity, and strongly disagree with the behavior to be expected from cubic effects alone.

ACKNOWLEDGMENTS

The continuing interest and numerous suggestions of Professor N. Bloembergen, under whose supervision this research was performed, are gratefully acknowledged. Discussions with F. A. Collins were also most helpful. Finally, the services of S. Maurici in preparing all the samples were invaluable.

²⁹ C. Kittel, *Introduction to Solid State Physics* (Wiley-Interscience, Inc., New York, 1956), Chap. 6.

³⁰ A. Eucken and A. Büchner, *Z. Physik. Chem. (Leipzig)* **27**, 321 (1934); A. J. Bosman and E. E. Havinga, *Phys. Rev.* **129**, 1593 (1963); V. V. Panchenko, *Bull. Acad. Sci. USSR, Phys. Ser.* **24**, 141 (1960).