the spring and dashpot people call a standard linear solid.

In the limit $\tau_c \to 0$, $\tau_c^{-1}\exp(-t/\tau_c)$ can be considered as a representation of $\delta(t)$ in the sense

$$\lim_{\tau_c\to 0}\frac{1}{\tau_c}\int_0^\infty dt\, e^{-t/\tau_c} f(t) = f(0)\,, \qquad \text{(A9)}$$

by a well-known property of Laplace transform theory. Therefore as $\tau_c \to 0$, the model approaches ordinary viscosity.

The relaxation function (A8) modifies the expressions (4.5) and (4.6) for the transverse and longitudinal attenuations by multiplying them by a factor $(1+\omega^2\tau_c^2)^{-1}$.

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Temperature Dependence of the Width of the Fundamental Lattice-Vibration Absorption Peak in Ionic Crystals. II. Approximate Numerical Results

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The results of numerical calculations of the temperature dependence of the width and position of the fundamental lattice-vibration absorption peak in NaCl and LiF are presented. The calculations are carried out in the high-temperature limit, on the basis of the Hardy-Karo deformation dipole model of these crystals. Cubic and quartic anharmonic terms are retained in the crystal Hamiltonian, but the approximation of neglecting the anharmonicity of the Coulomb forces has been made. The expressions for the Fourier-transformed anharmonic force constants have been approximated and simplified by a method suggested by Peierls. The results of the calculations show that the quartic anharmonic terms in the crystal potential energy make a contribution to the width of the fundamental absorption peak which is comparable in magnitude with the contribution from the cubic anharmonic terms, in agreement with the theoretical arguments of Gurevich and Ipatova. Since the quartic anharmonic contribution to the width is proportional to the square of the absolute temperature at high temperatures, these results provide an explanation for the experimental observations that the width increases with a power of the absolute temperature which is intermediate between the first and the second. Quantitatively, the theoretical results are in quite good agreement with the experimental data of Heilmann for the variation with temperature of the width of the fundamental absorption peak in LiF. In the case of NaCl, the agreement between theory and experiment is somewhat poorer, but the theoretical values are still within a factor of about 2 of the experimental values of Hass. The frequency dependence of the imaginary part of the dielectric constant of these two crystals has also been calculated, and is compared with experimental data.

1. INTRODUCTION

IN the first part of this series[1] a formal expression for the imaginary part of the dielectric constant of an ionic crystal of the rocksalt structure was derived. It has the form

$$\varepsilon_2(\omega)=\frac{4\pi\epsilon^2}{V_a}\frac{M_+ + M_-}{M_+M_-}\times\frac{2\omega_t\Gamma_t(\omega)}{[\omega^2-\Omega_t^2(\omega)]^2+4\omega_t^2\Gamma_t^2(\omega)}\,. \qquad (1.1)$$

In this expression ϵ is the first-order dipole-moment expansion coefficient, V_a is the volume of a primitive unit cell, and M_+ and M_- are the masses of the positive and negative ions, respectively. The frequency of the incident light is denoted by ω, and ω_t is the frequency of the transverse optical modes of infinite wavelength. Explicit expressions for the renormalized frequency $\Omega_t(\omega)$ and the damping constant $\Gamma_t(\omega)$ were obtained to second order in the cubic and quartic anharmonic force constants in I. It was shown there as well that the coefficient $(4\pi\epsilon^2/V_a)(M_+ + M_-)/M_+M_-$ can be identified with $(\varepsilon_0-\varepsilon_\infty)\omega_0^2$, where ε_0 and ε_∞ are the static and

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[1] 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)]. This paper will be referred to as I, and all references to equations from this paper will be prefixed by I.

high-frequency dielectric constants of the crystal, respectively, while ω_0 is the solution of the equation $\omega_0=\Omega_t(\omega_0)$, and is close to ω_t.

It is assumed in what follows that the reader is familiar with the contents of I. In the present paper we present the results of numerical calculations of the imaginary part of the dielectric constant (1.1) for NaCl and LiF. The principal motivation for the present calculations was a recent paper by Gurevich and Ipatova.[2] In this work largely qualitative arguments were presented to explain how the quartic anharmonic contribution to the width of the fundamental lattice absorption peak $[\approx 2\Gamma_t(\omega_t)]$ can be comparable to the cubic contribution, so that in the high-temperature limit the width is essentially proportional to the square of the absolute temperature, as is observed experimentally.[3,4] The present calculations were undertaken to confirm or disprove the theoretical arguments of Gurevich and Ipatova.

Numerical calculations of the quartic anharmonic contribution to the absorption spectra of LiF and MgO have been carried out by Mitskevich.[5] Because of the complexity of the expressions which have to be evaluated in such calculations, Mitskevich was forced to make rather gross approximations whose consequences it is not easy to assess. Nevertheless, his numerical results for LiF, if anything, give support to the arguments of Gurevich and Ipatova. Still, in the absence of detailed numerical calculations of the cubic and quartic contributions to the width of the fundamental absorption peak, such conclusions at best can have only a speculative character. In this paper, and in the third paper of this series, we present the results of such numerical calculations.

The principal source of difficulty in carrying out these calculations is the complicated forms of the Fourier transformed anharmonic force constants $\{V(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\cdots;\mathbf{k}_sj_s)\}$ which appear in the expressions for the functions $\Omega_t(\omega)$ and $\Gamma_t(\omega)$. Because of the complexity of the expressions for these coefficients and the computational difficulties to which it leads, it seemed to us to be desirable to determine the extent to which results for $\Omega_t(\omega)$ and $\Gamma_t(\omega)$ obtained on the basis of a simple approximation to the Fourier transformed anharmonic force constants reproduce the results of an exact calculation. In the present paper we describe a method for obtaining approximate expressions for the $\{V(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\cdots;\mathbf{k}_sj_s)\}$ and present the results of numerical calculations of $\Omega_t(\omega)$, $\Gamma_t(\omega)$, and $\varepsilon_2(\omega)$ based on them. In the next paper in this series we will describe the much more difficult calculations of these functions based on the exact expressions for the $\{V(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\cdots;\mathbf{k}_sj_s)\}$. Comparisons between the approximate and exact results will be given there.

2. THE ANHARMONIC FORCE CONSTANTS

In the lattice-dynamical model of alkali-halide crystals which underlies the numerical calculations of the imaginary part of the dielectric constant carried out in this paper, the short-range repulsive forces are assumed to be of the central-force type and to act only between ions which are nearest neighbors.

In our work we make the approximation of neglecting the anharmonicity of the Coulomb forces, and retain only the anharmonicity of the short-range repulsive forces. A rough justification for this approximation is the following argument. The short-range repulsive interaction can be taken to be of the form $ae^{-r_0/\rho}$, where r_0 is the nearest-neighbor separation. The total Coulomb energy per ion is $-\alpha e^2/r_0$, where α is the Madelung constant, 1.7476, and the total repulsive energy per ion is $6ae^{-r_0/\rho}$. The value of r_0 is determined from the equilibrium condition

$$\alpha e^2/r_0^2=6(a/\rho)e^{-r_0/\rho}. \tag{2.1}$$

The values of the third and fourth derivatives of the Coulomb energy and of the repulsive energy are

$$\text{3rd derivatives}\ \frac{6\alpha e^2}{r_0^4};\qquad \frac{-6a}{\rho^3}e^{-r_0/\rho}=-\frac{1}{\rho^2}\frac{\alpha e^2}{r_0^2}$$

$$\text{4th derivatives}\ \frac{-24\alpha e^2}{r_0^5};\qquad \frac{6a}{\rho^4}e^{-r_0/\rho}=\frac{1}{\rho^3}\frac{\alpha e^2}{r_0^2}. \tag{2.2}$$

The ratios of the magnitudes of the corresponding derivatives of the repulsive energy to the derivatives of the Coulomb energy are $(r_0^2/6\rho^2)$ and $(r_0^3/24\rho^3)$, respectively. Since r_0/ρ is of the order of 8 for the alkali halides, we see from these results that the contribution from the repulsive energy dominates the Coulomb contribution in calculations of higher derivatives of the potential energy.

If we denote the potential energy of interaction between a pair of ions κ and κ' situated a distance r apart by $\phi_{\kappa\kappa'}(r)$, then the Fourier transformed atomic force constants for an ionic crystal in the central force approximation can be written as

$$V(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)=\frac{1}{2}\frac{1}{s!}\left(\frac{\hbar}{2N}\right)^{s/2}(\omega_{j_1}(\mathbf{k}_1)\cdots\omega_{j_s}(\mathbf{k}_s))^{-1/2}$$

$$\sum_{ll'}\sum_{\kappa\kappa'}\sum_{\alpha_1\cdots\alpha_s}{}' \phi_{\alpha_1\cdots\alpha_s}(l\kappa;l'\kappa')U_{\alpha_1}(\mathbf{k}_1j_1;l\kappa;l'\kappa')$$

$$\times\cdots\times U_{\alpha_s}(\mathbf{k}_sj_s;l\kappa;l'\kappa'), \tag{2.3}$$

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[2] L. E. Gurevich and I. P. Ipatova, Zh. Eksperim. i Teor. Fiz. **45**, 231 (1963) [English transl.: Soviet Phys.—JETP **18**, 162 (1964)].

[3] G. Heilmann, Z. Physik **152**, 368 (1958).

[4] M. Hass, Phys. Rev. **117**, 1497 (1960).

[5] V. V. Mitskevich, Fiz. Tverd. Tela **4**, 3035 (1962) [English transl.: Soviet Phys.—Solid State **4**, 2224 (1963)].

where

$$\phi_{\alpha_1\cdots\alpha_s}(l\kappa;l'\kappa')=\frac{\partial^s}{\partial x_{\alpha_1}\cdots\partial x_{\alpha_s}}\phi_{\kappa\kappa'}(r)\big|_{r=|\mathbf{x}(l\kappa)-\mathbf{x}(l'\kappa')|} \quad (2.4)$$

and

$$U_\alpha(\mathbf{k}j;l\kappa;l'\kappa')=\frac{w_\alpha(\kappa|\mathbf{k}j)}{(M_\kappa)^{1/2}}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l\kappa)}-\frac{w_\alpha(\kappa'|\mathbf{k}j)}{(M_{\kappa'})^{1/2}}e^{2\pi i\mathbf{k}\cdot\mathbf{x}(l'\kappa')}. \quad (2.5)$$

The notation employed in writing these equations is that of I. The prime on the sums on the right side of Eq. (2.3) denotes that the terms with $(l\kappa)=(l'\kappa')$ are to be omitted.

A general property of the Fourier transformed atomic force constants is that they are completely symmetric in the indices $\{\mathbf{k}_ij_i\}$. Because $\phi_{\alpha_1\cdots\alpha_s}(l\kappa;l'\kappa')$ depends on l and l' only through their difference, it follows that $V(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)$ vanishes unless the sum of the wave vectors appearing in its argument equals a translation vector of the reciprocal lattice. We note further that $V(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)$ vanishes if we set $\mathbf{k}_i$ equal to zero and the corresponding j_i refers to an acoustic branch. This is because $w_\alpha(\kappa|0j)/(M_\kappa)^{1/2}$ is independent of κ for an acoustic branch,[6] so that $U_\alpha(0j;l\kappa;l'\kappa')$ vanishes. In fact, it can be seen from Eq. (2.5) that in the limit as $\mathbf{k}\to 0$ $U_\alpha(\mathbf{k}j;l\kappa;l'\kappa')$ is of $O(\mathbf{k})$, when j refers to an acoustic branch. On the other hand, $U_\alpha(0j;l\kappa;l'\kappa')$ does not vanish when j refers to an optical branch, because in this case $(M_+)^{1/2}w_\alpha(+|0j)=-(M_-)^{1/2}w_\alpha(-|0j)$.[6] The dependence of $V(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)$ on a particular wave vector $\mathbf{k}_i$ in the limit as $\mathbf{k}_i\to 0$ is therefore of the form $k_i/[\omega_{j_i}(\mathbf{k}_i)]^{1/2}$ when j_i refers to an acoustic branch, and is of the form $\text{const}/[\omega_{j_i}(\mathbf{k}_i)]^{1/2}$ when j_i refers to an optical branch. In either case the dependence on $\mathbf{k}_i$ is that of the function $[\omega_{j_i}(\mathbf{k}_i)]^{1/2}$ in the long-wavelength limit.

In the present paper we will be interested only in the cubic and quartic anharmonic coefficients, $V(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)$ and $V(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)$, respectively. In addition to the properties discussed above, these coefficients have the additional properties:

$$\begin{aligned}V(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)&=V^*(-\mathbf{k}_1j_1;-\mathbf{k}_2j_2;-\mathbf{k}_3j_3)\\&=-V(-\mathbf{k}_1j_1;-\mathbf{k}_2j_2;-\mathbf{k}_3j_3),\end{aligned} \quad (2.6a)$$

$$\begin{aligned}V(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)&\\=V^*(-\mathbf{k}_1j_1;-\mathbf{k}_2j_2;-\mathbf{k}_3j_3;-\mathbf{k}_3j_4)&\\=V(-\mathbf{k}_1j_1;-\mathbf{k}_2j_2;-\mathbf{k}_3j_3;-\mathbf{k}_4j_4),&\end{aligned} \quad (2.6b)$$

where the last equality in each case follows from the fact that every ion is at a center of inversion symmetry in crystals of the NaCl type. We see from these results that in this case $V(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)$ is purely imaginary, while $V(\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3;\mathbf{k}_4j_4)$ is real. It also follows that $V(0j;\mathbf{k}j';-\mathbf{k}j')$ vanishes, irrespective of whether j refers to an acoustic or to an optical branch.

We have discussed the properties of the V coefficients in some detail because these properties provide the basis for simple approximate expressions for them. We follow Peierls[7] in using these properties to rewrite $V(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)$ in the form

$$\begin{aligned}V(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)=&\frac{1}{2}\frac{1}{s!}\left(\frac{\hbar}{2N}\right)^{s/2}N\Delta(\mathbf{k}_1+\cdots+\mathbf{k}_s)\\&\times[\omega_{j_1}(\mathbf{k}_1)\cdots\omega_{j_s}(\mathbf{k}_s)]^{1/2}C(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s),\end{aligned} \quad (2.7)$$

where $\Delta(\mathbf{k})=1$ if $\mathbf{k}$ is a reciprocal lattice vector, and vanishes otherwise. Having extracted the factor $[\omega_{j_1}(\mathbf{k}_1)\cdots\omega_{j_s}(\mathbf{k}_s)]^{1/2}$, we expect the new coefficients $C(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)$ to have constant order of magnitude for all values of their arguments. [This cannot be strictly correct since we must have $C(0j;\mathbf{k}j';-\mathbf{k}j')=0$ when j is an optical branch.]

If in fact the coefficients $|C(0j;\mathbf{k}_1j_1;-\mathbf{k}_1j_2)|^2$ and $|C(0j;\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)|^2$, required in the calculation of $\Delta_j(\omega)=[\Omega_t^2(\omega)-\omega_t^2]/2\omega_t$ and $\Gamma_j(\omega)$ [given by Eqs. (I3.10) and (I3.11)], are slowly varying functions of their arguments, as a first approximation it is reasonable to replace them by constants which we denote by $|C_3|^2$ and $|C_4|^2$, respectively. With this approximation $\Gamma_j(\omega)$ takes the simple form in the high-temperature limit

$$\begin{aligned}\Gamma_j(\omega)=&\pi\frac{k_BT}{48}\omega\omega_j(0)|C_3|^2\frac{1}{N}\sum_{\mathbf{k}_1}\sum_{\pm j_1\pm j_2}{}'\,\delta(\omega+\omega_1+\omega_2)\\&+\pi\frac{(k_BT)^2}{384}\omega\omega_j(0)|C_4|^2\frac{1}{N^2}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{\pm j_1\pm j_2\pm j_3}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\\&\times\delta(\omega+\omega_1+\omega_3+\omega_3),\end{aligned} \quad (2.8)$$

where k_B is the Boltzmann's constant. At the same time, the expression for $\Delta_j(\omega)$ can be written as

$$\Delta_j(\omega)=\Delta_j+\tilde{\Delta}_j(\omega), \quad (2.9)$$

where Δ_j is the frequency-independent part of $\Delta_j(\omega)$,

$$\begin{aligned}\Delta_j=&\frac{k_BT}{8}\omega_j(0)\frac{1}{N}\sum_{\mathbf{k}_1j_1}C(0j;0j;-\mathbf{k}_1j_1;\mathbf{k}_1j_1)\\&-\frac{(k_BT)^2}{64}\omega_j(0)\frac{1}{N^2}\sum_{\mathbf{k}_1\mathbf{k}_3}\sum_{j_1j_2j_3}C(0j;0j;-\mathbf{k}_1j_1;\mathbf{k}_1j_2)\\&\times C(\mathbf{k}_1j_1;-\mathbf{k}_1j_2;\mathbf{k}_3j_3;-\mathbf{k}_3j_3),\end{aligned} \quad (2.10a)$$

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[6] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963), p. 14.

[7] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, England, 1956), p. 38.

and $\tilde{\Delta}_j(\omega)$ is the frequency-dependent part,

$$\tilde{\Delta}_j(\omega)=-\frac{k_BT}{48}\omega_j(\mathbf{0})|C_3|^2\frac{1}{N}\sum_{\mathbf{k}}\sum_{\pm j_1\pm j_2}{}'\frac{\omega_1+\omega_2}{(\omega+\omega_1+\omega_2)_P}$$
$$-\frac{(k_BT)^2}{384}\omega_j(\mathbf{0})|C_4|^2\frac{1}{N^2}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{\pm j_1\pm j_2\pm j_3}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)$$
$$\times\frac{\omega_1+\omega_2+\omega_3}{(\omega+\omega_1+\omega_2+\omega_3)_P}. \qquad (2.10\text{b})$$

In writing Eqs. (2.8) and (2.10b) we have used the notation $\omega_{j_p}(\mathbf{k}_p)\equiv\omega_p$, and the convention that $\omega_{-j}(\mathbf{k})=-\omega_j(\mathbf{k})$. In what follows the various contributions to $\Gamma_j(\omega)$, Δ_j, and $\tilde{\Delta}_j(\omega)$ will be distinguished by a superscript denoting their order in the dimensionless order parameter η introduced in Eq. (I3.3). The evaluation of the two terms on the right side of Eq. (2.10a) will be discussed below.

The primes on the first sums on the right of each of Eqs. (2.8) and (2.10b) mean that the terms with $|j_1|=|j_2|$ are excluded. This restriction follows from the fact that $C(\mathbf{0}j;\mathbf{k}_1j_1;-\mathbf{k}_1j_1)$ vanishes for the kinds of crystals we are studying.

It follows from Eqs. (2.8) and (2.10b) that $\tilde{\Delta}_j(\omega)$ and $\Gamma_j(\omega)$ are related by

$$\tilde{\Delta}_j(\omega)=\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\Gamma_j(\omega')}{(\omega-\omega')_P}d\omega'. \qquad (2.11)$$

This result is more general than the present analysis would indicate,[8] and will be of use in determining $\tilde{\Delta}_j(\omega)$.

It should be remarked that in their paper Gurevich and Ipatova[2] gave approximate expressions for the two contributions to $\Gamma_j(\omega)$ which differ from those given by Eq. (2.9) by the presence of factors of $[\omega_{j_1}(\mathbf{k}_1)\omega_{j_2}(\mathbf{k}_1)]^{-1}$ and $[\omega_{j_1}(\mathbf{k}_1)\omega_{j_2}(\mathbf{k}_2)\omega_{j_3}(\mathbf{k}_3)]^{-1}$ in the summands of the two expressions, respectively. It is felt that the present method of approximating the Fourier-transformed anharmonic force constants is more correct.

To determine the constants $|C_3|^2$ and $|C_4|^2$ we have proceeded in the following way. Comparing Eqs. (2.3) and (2.7) we obtain the result

$$\sum_{ll'}\sum_{\kappa\kappa'}\sum_{\alpha_1\cdots\alpha_s}{}'\phi_{\alpha_1\cdots\alpha_s}(l\kappa;l'\kappa')U_{\alpha_1}(\mathbf{k}_1j_1;l\kappa;l'\kappa')\cdots$$
$$\times U_{\alpha_s}(\mathbf{k}_sj_s;l\kappa;l'\kappa')=N\Delta(\mathbf{k}_1+\cdots+\mathbf{k}_s)$$
$$\times\omega_{j_1}(\mathbf{k}_1)\cdots\omega_{j_s}(\mathbf{k}_s)C(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s). \qquad (2.12)$$

On the basis of the assumption that $|C(\mathbf{0}j;\mathbf{k}_1j_1;-\mathbf{k}_1j_2)|^2$ and $|C(\mathbf{0}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)|^2$ are essentially constant, if we square the modulus of both sides of the equations defining these coefficients, Eqs. (2.12), and sum them over the free variables, we obtain, for example,

$$N^2\omega_j^2(\mathbf{0})|C_3|^2\sum_{\mathbf{k}_1}\sum_{j_1j_2}{}'\omega_{j_1}^2(\mathbf{k}_1)\omega_{j_2}^2(\mathbf{k}_1)$$
$$=\sum_{\mathbf{k}_1}\sum_{j_1j_2}\sum_{ll'}\sum_{\kappa\kappa'}\sum_{\alpha\beta\gamma}\sum_{l_1l_1'}\sum_{\kappa_1\kappa_1'}\sum_{\alpha_1\beta_1\gamma_1}\phi_{\alpha\beta\gamma}(l\kappa;l'\kappa')$$
$$\times\phi_{\alpha_1\beta_1\gamma_1}(l_1\kappa_1;l_1'\kappa_1')U_\alpha(\mathbf{0}j;l\kappa;l'\kappa')U_{\alpha_1}^*(\mathbf{0}j;l_1\kappa_1;l_1'\kappa_1')$$
$$\times U_\beta(\mathbf{k}_1j_1;l\kappa;l'\kappa')U_{\beta_1}^*(\mathbf{k}_1j_1;l_1\kappa_1;l_1'\kappa_1')$$
$$\times U_\gamma(-\mathbf{k}_1j_2;l\kappa;l'\kappa')U_{\gamma_1}^*(-\mathbf{k}_1j_2;l_1\kappa_1;l_1'\kappa_1'), \qquad (2.13)$$

with an analogous equation for $|C_4|^2$. Although in the sum on the left side of this equation we have explicitly omitted the terms with $j_1=j_2$, it is not necessary to do so on the right side, because such terms are identically zero and contribute nothing to the sum. The sums on the right hand side of this equation can be evaluated analytically if we assume that the short-range repulsive forces act only between nearest-neighbor ions. After some rather tedious calculations, we obtain the results

$$|C_3|^2=\frac{16}{\omega_j^2(\mathbf{0})S_3'}\frac{M_++M_-}{M_+^2M_-^2}[r_0^6B^2+6r_0^4BC+15r_0^2C^2], \qquad (2.14)$$

$$|C_4|^2=\frac{4}{\omega_j^2(\mathbf{0})S_4}\frac{(M_++M_-)^2}{M_+^3M_-^3}\left\{\frac{1}{M_+M_-}\frac{M_+^3+M_-^3}{M_++M_-}[4r_0^8A^2+24r_0^4A(2r_0^2B+3C)+60(4r_0^4B^2+12r_0^2BC+9C^2)]\right.$$
$$\left.+3[2r_0^8A^2+12r_0^4A(2r_0^2B+C)+6(16r_0^4B^2+20r_0^2BC+15C^2)]\right\}, \qquad (2.15)$$

where

$$A=\frac{1}{r_0^4}\left[\phi^{\text{IV}}(r_0)-\frac{6}{r_0}\phi'''(r_0)+\frac{15}{r_0^2}\phi''(r_0)-\frac{15}{r_0^3}\phi'(r_0)\right], \qquad (2.16\text{a})$$

$$B=\frac{1}{r_0^3}\left[\phi'''(r_0)-\frac{3}{r_0}\phi''(r_0)+\frac{3}{r_0^2}\phi'(r_0)\right], \qquad (2.16\text{b})$$

$$C=\frac{1}{r_0^2}\left[\phi''(r_0)-\frac{1}{r_0}\phi'(r_0)\right], \qquad (2.16\text{c})$$

and we have set $\phi_{+-}(r_0)=\phi_{-+}(r_0)=\phi(r_0)$. The sums

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[8] J. J. J. Kokkedee, Phys. Letters 4, 78 (1963); A. A. Maradudin, Westinghouse Research Laboratories Scientific Paper No. 63-129-103-P3, 1963 (unpublished).

S_3' and S_4 are defined by

$$S_3'=\frac{1}{N}\sum_{\mathbf{k}}\sum_{jj'}{}'\,\omega_j^2(\mathbf{k})\omega_{j'}^2(\mathbf{k})\,, \tag{2.17a}$$

$$S_4=\frac{1}{N^2}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}\sum_{j_1j_2j_3}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)\times\omega_{j_1}^2(\mathbf{k}_1)\omega_{j_2}^2(\mathbf{k}_2)\omega_{j_3}^2(\mathbf{k}_3)\,. \tag{2.17b}$$

The prime on the sum S_3' means that the terms with $j=j'$ are omitted. The phonon branch index j appearing in the expressions for $|C_3|^2$ and $|C_4|^2$ given by Eqs. (2.14) and (2.15) in all that follows refers to either of the two degenerate transverse optical branches.

We return now to the frequency-independent part of $\Delta_j(\omega)$ which is given by Eq. (2.10a). In the approximation of regarding $C(\mathbf{0}j;\mathbf{0}j;-\mathbf{k}_1j_1;\mathbf{k}_1j_1)$ and $C(\mathbf{0}j;\mathbf{0}j;-\mathbf{k}_1j_1;\mathbf{k}_1j_2)C(\mathbf{k}_1j_1;-\mathbf{k}_1j_2;\mathbf{k}_3j_3;-\mathbf{k}_3j_3)$ as constants C_4' and $|C_4''|^2$ which are independent of their arguments, Eq. (2.10a) takes the form

$$\Delta_j=\tfrac{3}{4}k_BT\omega_j(0)C_4'-(27/8)(k_BT)^2\omega_j(0)|C_4''|^2. \tag{2.18}$$

We can obtain approximate expressions for C_4' and $|C_4''|^2$ in the same way that the expressions (2.14) and (2.15) for $|C_3|^2$ and $|C_4|^2$, respectively, were obtained. In this way we find

$$C_4'=\frac{2}{3}\frac{1}{\omega_j^2(0)\mu_2}\left(\frac{1}{M_+}+\frac{1}{M_-}\right)^2\times[r_0^4A+10r_0^2B+15C], \tag{2.19a}$$

$$|C_4''|^2=\frac{8}{3}\frac{1}{\omega_j^2(0)\mu_2S_3}\frac{(M_++M_-)^2}{M_+^3M_-^3}\left\{\frac{M_+^2+M_-^2}{M_+M_-}\times(r_0^4A+10r_0^2B+15C)^2+[(r_0^4A+7r_0^2B)\times(r_0^4A+8r_0^2B+5C)+(r_0^2B+5C)\times(r_0^4A+10r_0^2B+15C)]\right\}, \tag{2.19b}$$

where

$$\mu_2=\frac{1}{6N}\sum_{\mathbf{k}j}\omega_j^2(\mathbf{k})\,, \tag{2.20a}$$

$$S_3=\frac{1}{N}\sum_{\mathbf{k}}\sum_{jj'}\omega_j^2(\mathbf{k})\omega_{j'}^2(\mathbf{k})\,. \tag{2.20b}$$

If the coefficients $C(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)$ are really constants, independent of their arguments, the relations $|C_4|^2=|C_4''|^2=(C_4')^2$ should hold. The degree to which these relations are satisfied is one indication of the validity of the approximations made in this section. This test will be discussed further in the next two sections.

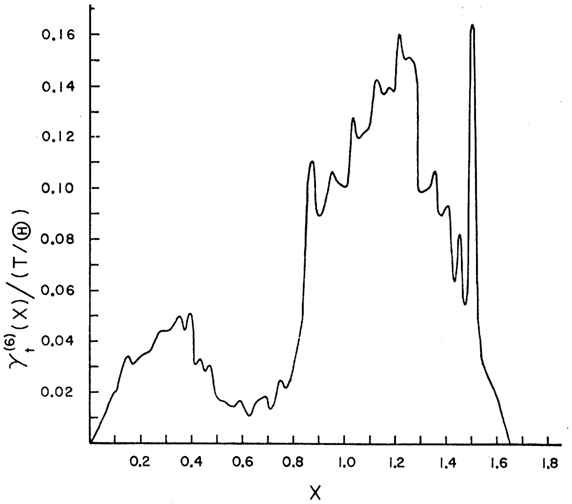

FIG. 1. The function $\gamma_t^{(6)}(x)/(T/\Theta)$ for NaCl.

3. NUMERICAL CALCULATIONS

The lattice dynamical model of an alkali halide crystal which describes the unperturbed or harmonic crystal in the present calculations is the deformation dipole model of Hardy.[9] This model has been discussed extensively in Refs. 9 and 10, and we will not describe it in detail here. In this model the short-range repulsive forces are of the central force type and are assumed to act between nearest-neighbor ions only. The potential energy of interaction between a pair of neighboring ions is given by

$$\phi(r)=ae^{-r/\rho}\,, \tag{3.1}$$

where r is the interionic separation. The parameters a and ρ are calculated from the room-temperature values of the equilibrium nearest-neighbor separation r_0 and

TABLE I. Data used in determining the parameters of the crystal models on which the numerical calculations reported in this paper are based, together with some derived quantities which characterize the crystals in the harmonic approximation. These data are from A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963), and from J. R. Tessman, A. H. Kahn, and W. Shockley, *ibid.* **92**, 890 (1953).

	NaCl	LiF
r_0	2.8138×10^{-8} cm	2.0087×10^{-8} cm
β	4.26×10^{-12} cm²/dyn	1.54×10^{-12} cm²/dyn
ε_0	5.62	9.27
ε_∞	2.25	1.92
α_+	0.255×10^{-24} cm³	0.029×10^{-24} cm³
α_-	2.974×10^{-24} cm³	0.759×10^{-24} cm³
M_+	38.16×10^{-24} g	11.52×10^{-24} g
$M-$	58.93×10^{-24} g	31.54×10^{-24} g
ρ	0.3283×10^{-8} cm	0.2989×10^{-8} cm
$ae^{-r_0/\rho}$	2.784×10^{-13} erg	4.974×10^{-13} erg
ω_L	4.848×10^{13} sec⁻¹	12.53×10^{13} sec⁻¹
Θ	370.3°K	957.0°K
$\lambda_t(0)$	0.644325	0.478866

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[9] J. R. Hardy, Phil. Mag. **7**, 315 (1962).

[10] A. M. Karo and J. R. Hardy, Phys. Rev. **129**, 2024 (1963).

the compressibility β using standard procedures.[11] The use of room-temperature values enables us, at least in part, to take into account the effects of thermal expansion on the atomic force constants and frequencies of our crystal model. As we are evaluating the high-temperature forms of $\Delta_j(\omega)$ and $\Gamma_j(\omega)$, corrections for the effects of thermal expansion should be made, and the present way of doing this, if not rigorous, is at least simple.

The values of the experimental interatomic spacings and compressibilities used in determining ρ and a, together with various quantities derived from these data are collected in Table I. The experimental values used are those quoted by Karo and Hardy.[10]

For a repulsive potential of the form given by Eq. (3.1) the coefficients A, B, C given by Eqs. (2.16) may be readily evaluated. The numerical values of these coefficients for NaCl and LiF are given in Table II.

The normal-mode frequencies $\omega_j(\mathbf{k})$ were computed for values of the wave vector $\mathbf{k}$ given by

$$\mathbf{k}=\frac{1}{2r_0}\left(\frac{p_x}{20},\frac{p_y}{20},\frac{p_z}{20}\right), \tag{3.2}$$

where p_x, p_y, p_z are three integers which are all odd or all even, and which satisfy the conditions

$$0\leqslant p_x\leqslant p_y\leqslant p_z\leqslant 20\,,\quad p_x+p_y+p_z\leqslant 30\,. \tag{3.3}$$

There are 262 sets of numbers of this type, and when all of their multiplicities are taken into account, they correspond to 8000 points inside the first Brillouin zone for the rocksalt lattice.

In carrying out the numerical calculations it was found convenient to introduce a characteristic temperature $\Theta=\hbar\omega_L/k_B$, and dimensionless frequencies $\lambda_j(\mathbf{k})=\omega_j(\mathbf{k})/\omega_L$ and $x=\omega/\omega_L$, where ω_L is the maximum frequency of the crystal. The values of ω_L and Θ yielded by our crystal model for NaCl and LiF are listed in Table I. The Θ values are somewhat larger than the values of the Debye characteristic temperatures, which for NaCl and LiF are 308°K [12] and 708°K,[13] respectively. The frequencies $\lambda_j(\mathbf{k})$ were stored on punched cards for use in the remainder of the calculation.

It should be kept in mind that in calculating the imaginary part of the dielectric constant the phonon-branch index j refers to either of the two degenerate transverse optical branches. The value for the dimensionless frequency of these modes at infinite wavelength is denoted by $\lambda_t(0)$ and is given in Table I.

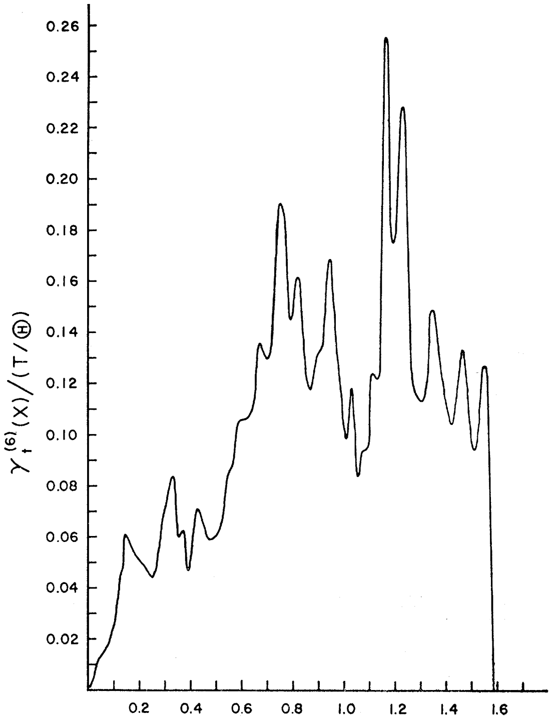

FIG. 2. The function $\gamma_t^{(6)}(x)/(T/\Theta)$ for LiF.

The frequency independent sums μ_2, S_3', S_3, and S_4 were evaluated by direct summation on a high-speed computer. The Δ-function restriction on the wave vectors in the last sum was treated by a standard method.[14] Wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are chosen systematically throughout the Brillouin zone. For each choice, the vector $-\mathbf{k}_1-\mathbf{k}_2$ is constructed and tested to see if it lies in the first Brillouin zone. If it does, it is called $\mathbf{k}_3$. If it does not, the unique translation vector of the reciprocal lattice which restores it to the first zone is added to this vector and the sum is called $\mathbf{k}_3$. The values

TABLE II. Quantities which arise in the calculation of the anharmonic properties of NaCl and LiF studied in this paper.

	NaCl	LiF
A	7.378×10^{51} erg/cm^8	87.125×10^{51} erg/cm^8
B	-4.915×10^{35} erg/cm^6	-34.791×10^{35} erg/cm^6
C	3.645×10^{19} erg/cm^4	15.859×10^{19} erg/cm^4
μ_2	$0.343915\ \omega_L^2$	$0.299182\ \omega_L^2$
S_3'	$3.294083\ \omega_L^4$	$2.29797\ \omega_L^4$
S_3	$4.265409\ \omega_L^4$	$3.243566\ \omega_L^4$
S_4	$8.78395\ \omega_L^6$	$5.78108\ \omega_L^6$
$\lvert C_3\rvert^2$	1.18152×10^{12} erg^{-1}	1.04451×10^{12} erg^{-1}
$\lvert C_4\rvert^2$	2.65708×10^{24} erg^{-2}	2.02998×10^{24} erg^{-2}
C_4'	2.0182×10^{12} erg^{-1}	1.398×10^{12} erg^{-1}
$\lvert C_4''\rvert^2$	0.77943×10^{24} erg^{-2}	0.26354×10^{24} erg^{-2}
$\hbar\omega_L\lvert C_3\rvert^2$	0.6038×10^{-1}	1.3787×10^{-1}
$\hbar^2\omega_L^2\lvert C_4\rvert^2$	0.69402×10^{-2}	3.5418×10^{-2}
$\hbar\omega_L C_4'$	0.10317	0.18467
$\hbar^2\omega_L^2\lvert C_4''\rvert^2$	0.2036×10^{-2}	0.4598×10^{-2}
$\hbar\omega_L\bar{C}_4'$	0.090101	0.22346

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[11] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, England, 1954), p. 25.

[12] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1953), 1st ed., p. 77.

[13] M. W. Holm, Bibliography, Phillips Petroleum Company Report No. IDO 16399, 1957 (unpublished).

[14] A. A. Maradudin and P. A. Flinn, Phys. Rev. **129**, 2529 (1963); P. A. Flinn and A. A. Maradudin, Ann. Phys. (N.Y.) **22**, 223 (1963).

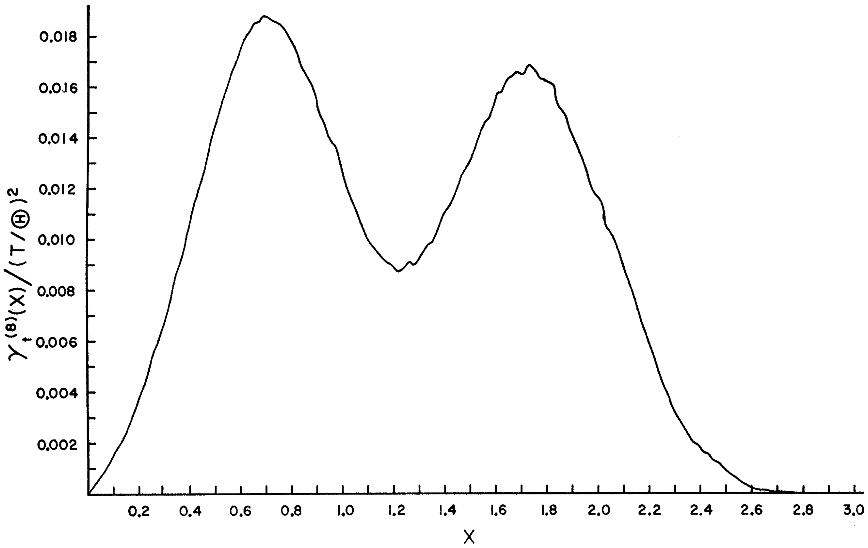

FIG. 3. The function $\gamma_t^{(8)}(x)/(T/\Theta)^2$ for NaCl.

of μ_2, S_3', S_3, and S_4 obtained in this way are presented in Table II together with the values of $|C_3|^2$, $|C_4|^2$, C_4', and $|C_4''|^2$ determined from them and the expressions (2.14), (2.15), (2.19a), and (2.19b), respectively.

With these sums in hand we can calculate the frequency independent part of the phonon frequency shift, $\delta_t=\Delta_t/\omega_L$. If we use the approximate expressions given by Eq. (2.18) we find that $\delta_t^{(4)}$, the contribution to δ_t of $O(\eta^4)$, is given by

$$\delta_t^{(4)}[\text{Eq. (2.18)}]=4.986\times10^{-2}(T/\Theta)\,,\quad \text{NaCl} \tag{3.4a}$$

$$=6.632\times10^{-2}(T/\Theta)\,,\quad \text{LiF}. \tag{3.4b}$$

[We remark parenthetically that the exact results for $\delta_t^{(4)}$ computed in a manner to be described in the next paper in this series are

$$\delta_t^{(4)}(\text{exact})=4.354\times10^{-2}(T/\Theta)\,,\quad \text{NaCl} \tag{3.5a}$$

$$=8.0255\times10^{-2}(T/\Theta)\,,\quad \text{LiF}. \tag{3.5b}$$

From these results we see that the approximate expression (2.18) yields values for $\delta_t^{(4)}$ which are within 20% of the exact values. We may have some confidence, therefore, in the results of the approximate calculations carried out in this paper.]

The values of $\delta_t^{(8)}$, the contribution to δ_t of $O(\eta^8)$, were computed only from the approximate expression (2.18). The results are

$$\delta_t^{(8)}=-0.4427\times10^{-2}(T/\Theta)^2\,,\quad \text{NaCl} \tag{3.6a}$$

$$=-0.7431\times10^{-2}(T/\Theta)^2\,,\quad \text{LiF}. \tag{3.6b}$$

In computing the frequency-dependent damping constant and frequency shift, it was the dimensionless functions $\gamma_t(x)=\Gamma_t(\omega_L x)/\omega_L$ and $\tilde{\delta}_t(x)=\tilde{\Delta}_t(\omega_L x)/\omega_L$ which were actually calculated. The function $\gamma_t(x)$ was computed first. The representation of the Dirac δ function used in the present calculation was

$$\begin{aligned}\delta(x)&=(1/2\epsilon)\quad -\epsilon<x<\epsilon\,,\\ &=0 \text{ otherwise}\,,\end{aligned} \tag{3.7}$$

where a value of 0.01 was chosen for ϵ. This method of calculation yields $\gamma_t(x)$ as a histogram. In calculating $\gamma_t^{(6)}(x)$, the contribution to $\gamma_t(x)$ of $O(\eta^6)$, the grid of 8000 points in the first Brillouin zone defined by Eqs. (3.2) and (3.3) was used. In the lengthier calculation of function $\gamma_t^{(8)}(x)$, the contribution to $\gamma_t(x)$ of $O(\eta^8)$, a grid of only 1000 points was used. This grid was obtained by replacing p_i by $2p_i$ in Eqs. (3.2) and (3.3).

In Figs. 1 and 2 we have plotted the functions $\gamma_t^{(6)}(x)/(T/\Theta)$ for NaCl and LiF, respectively. In Figs. 3 and 4 are plotted the functions $\gamma_t^{(8)}(x)/(T/\Theta)^2$ for NaCl and LiF, respectively. In Fig. 5 we have plotted $2\lambda_t(\mathbf{0})\gamma_t(x)$ for three values of (T/Θ) for NaCl. In Fig. 6

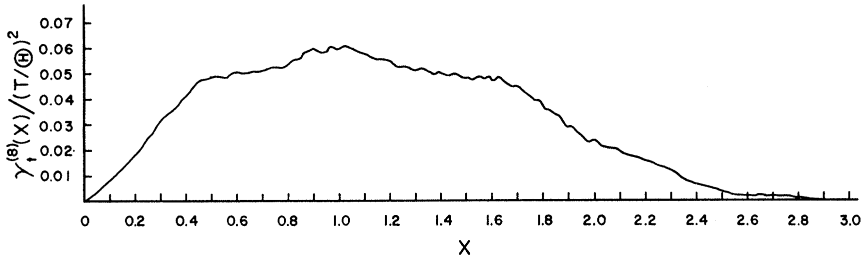

FIG. 4. The function $\gamma_t^{(8)}(x)/(T/\Theta)^2$ for LiF.

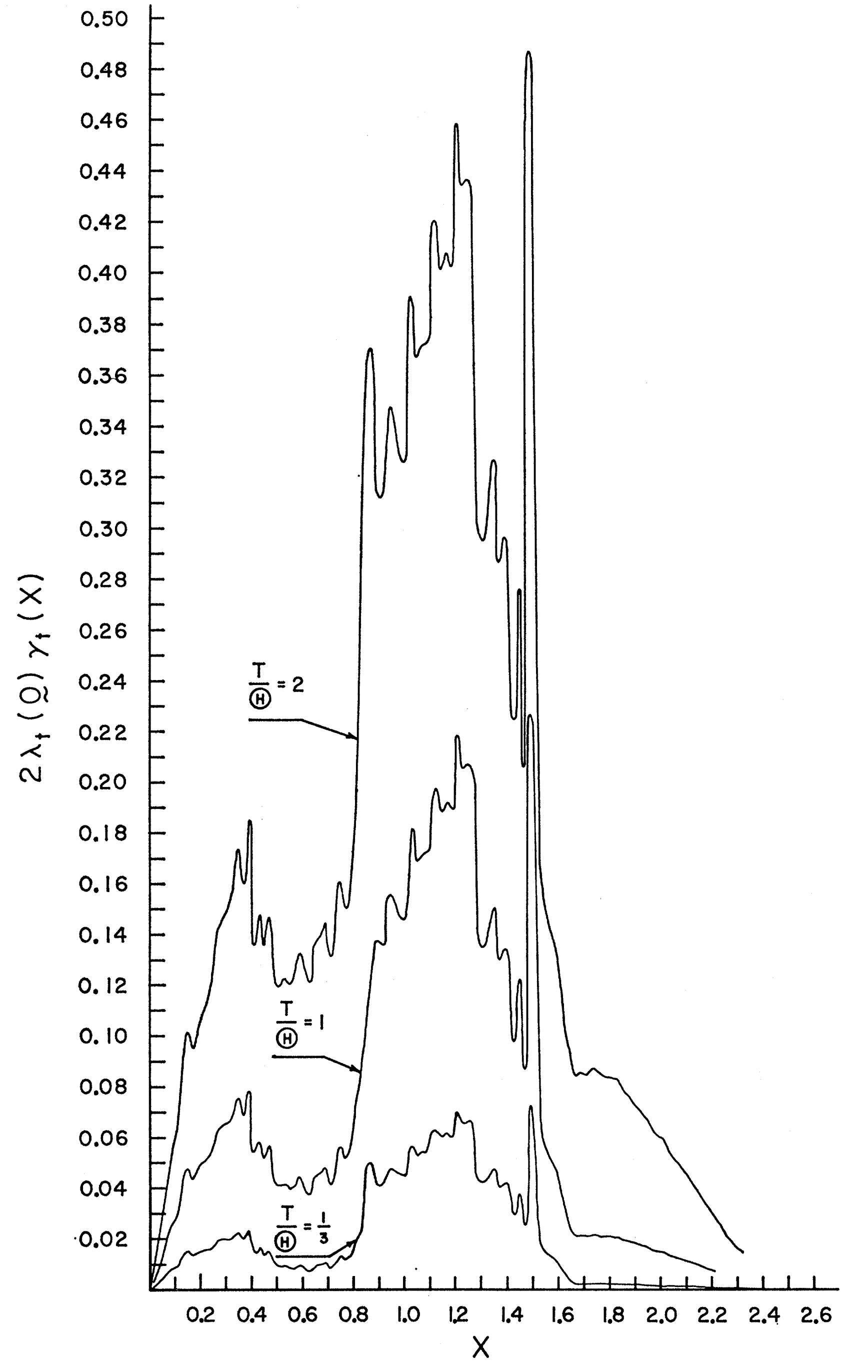

FIG. 5. The temperature dependence at elevated temperatures of the function $2\lambda_t(0)\gamma_t(x)$ for NaCl.

we have plotted the same function for two values of (T/Θ) for LiF. In each figure the rapid decrease in this function as x exceeds the value at which $\gamma_t^{(6)}(x)$ vanishes identically should be noted.

The frequency-dependent part of the frequency shift, $\tilde{\delta}_t(x)$, was computed by numerical integration from the results for $\gamma_t(x)$ on the basis of the following modification of the expression (2.11):

$$\tilde{\delta}_t(x)=\frac{1}{\pi}\int_{-l}^{l} dy\frac{\gamma_t(y)-\gamma_t(x)}{(x-y)_p}-\frac{1}{\pi}\gamma_t(x)\ln\left|\frac{l-x}{l+x}\right|. \quad (3.8)$$

In writing this expression we have used the fact that $\gamma_t^{(6)}(x)$ vanishes identically for $|x|>2$ and that $\gamma_t^{(8)}(x)$

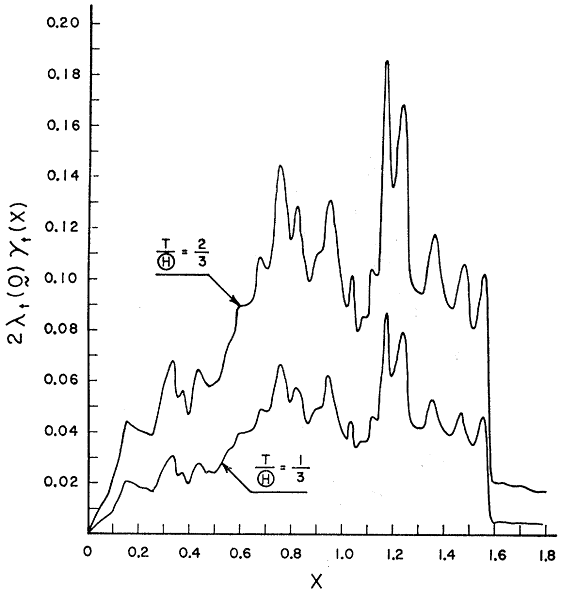

FIG. 6. The temperature dependence at elevated temperatures of the function $2\lambda_t(0)\gamma_t(x)$ for LiF.

vanishes identically for $|x|>3$, because the arguments of the Dirac δ functions in the expressions for these functions, Eqs. (2.8), cannot vanish for the indicated values of x. Therefore, the constant l in Eq. (3.8) is 2 for the evaluation of $\tilde{\delta}_t^{(6)}(x)$ and is 3 for the evaluation of $\tilde{\delta}_t^{(8)}(x)$.[15] We have added in and subtracted off the function $-\gamma_t(x)$ in the integral on the right side of Eq. (3.8) to make the integrand a smoothly varying function of y in the neighborhood of the point $y=x$.

In Figs. 7 and 8 we have plotted the functions $\tilde{\delta}_t^{(6)}(x)/(T/\Theta)$ for NaCl and LiF, respectively. In Figs. 9 and 10 we have plotted $\tilde{\delta}_t^{(6)}(x)/(T/\Theta)^2$ for NaCl and LiF, respectively.

The principal motivation for the work reported in this paper was the desire to determine the temperature dependence of the width of the fundamental absorption peak in NaCl and LiF. We can obtain an explicit expression for the width in the following way.

From Eq. (1.1) we see that the frequency ω_0, which is defined as the (positive) solution of the equation

$$\omega_0^2=\Omega_t^2(\omega_0)\,, \tag{3.9}$$

can be (and conventionally is) regarded as the position of the center of the fundamental absorption peak. [In fact, it is not quite the center because of the ω dependence of the function $\Gamma_t(\omega)$.] In the immediate vicinity of the frequency ω_0 the imaginary part of the dielectric constant can be written in the form

$$\varepsilon_2(\omega)\approx\frac{4\pi e^2}{V_a}\left(\frac{M_+ + M_-}{M_+M_-}\right)\frac{N_0}{\omega_0^2} \times\frac{(\gamma/\omega_0)}{[1-(\omega/\omega_0)^2]^2+(\gamma/\omega_0)^2}\,, \tag{3.10a}$$

where

$$N_0^{-1}=\left[1-\frac{d}{d\omega^2}\Omega_t^2(\omega)\right]_{\omega=\omega_0}\,, \tag{3.10b}$$

$$\gamma=2N_0\omega_t\Gamma_t(\omega_0)/\omega_0\,. \tag{3.10c}$$

If we compare the expression for $\varepsilon_2(\omega)$ given by Eq. (3.10a) with the expression which is obtained on the assumption of a damped harmonic oscillator,[16]

$$\varepsilon_2(\omega)=(\varepsilon_0-\varepsilon_\infty)\frac{(\gamma/\omega_0)(\omega/\omega_0)}{[1-(\omega/\omega_0)^2]^2+(\omega/\omega_0)^2(\gamma/\omega_0)^2}\,, \tag{3.11}$$

we find that for ω in the immediate vicinity of the frequency ω_0 the damping constant γ appearing in Eq. (3.11) is just that given by Eq. (3.10c). It is clearly the width of the fundamental absorption peak at half maximum. What is usually determined experimentally is γ/ω_0, and this according to Eq. (3.10c) is given by

$$\frac{\gamma}{\omega_0}=\frac{2N_0\omega_t\Gamma_t(\omega_0)}{\omega_0^2}\,. \tag{3.12}$$

Because $\Omega_t^2(\omega)$ is defined in terms of $\Delta_t(\omega)$ by

$$\Omega_t^2(\omega)=\omega_t^2+2\omega_t\Delta_t(\omega)\,, \tag{3.13}$$

we find that ω_0 differs from ω_t by terms of at least $O(\eta^4)$. Therefore, because $\Gamma_t(\omega_t)$ is already of $O(\eta^6)$, γ/ω_0 is given correctly to terms of $O(\eta^8)$ by

$$\frac{\gamma}{\omega_0}=\frac{2\Gamma_t(\omega_t)}{\omega_t}=\frac{2\gamma_t[\lambda_t(0)]}{\lambda_t(0)}\,. \tag{3.14}$$

Analytic expressions for γ/ω_0 for NaCl and LiF in the

TABLE III. Theoretical and experimental values of γ/ω_0 for NaCl and LiF at several elevated temperatures.

Crystal	T (°K)	γ/ω_0 (th.)	γ/ω_0 (exp)[a]
NaCl	300	0.0755	0.04
	460	0.1464	0.075
	640	0.2515	0.135
	820	0.3836	0.21
	985	0.5284	0.26
LiF	293	0.0943	0.08
	443	0.1569	0.12
	593	0.2292	0.15
	893	0.4030	0.35

[a] The experimental results for NaCl are due to M. Hass, Phys. Rev. **117**, 1497 (1960); the experimental results for LiF are due to G. Heilmann, Z. Physik **152**, 368 (1958).

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[15] We see from Figs. 1 and 2 that in fact $\gamma_t^{(6)}(x)$ vanishes identically for $|x|\gtrsim1.65$ in the case of NaCl, and for $|x|\gtrsim1.57$ in the case of LiF. That the upper limit in each case is smaller than 2 is a consequence of the fact that $|j|$ is not allowed to equal $|j'|$ in the first sum on the right-hand side of Eq. (2.8). Thus contributions from $\omega=\omega_1+\omega_2\approx2\omega_L$ are excluded from the sum for $\gamma_t^{(6)}(x)$.

[16] Reference 11, p. 121.

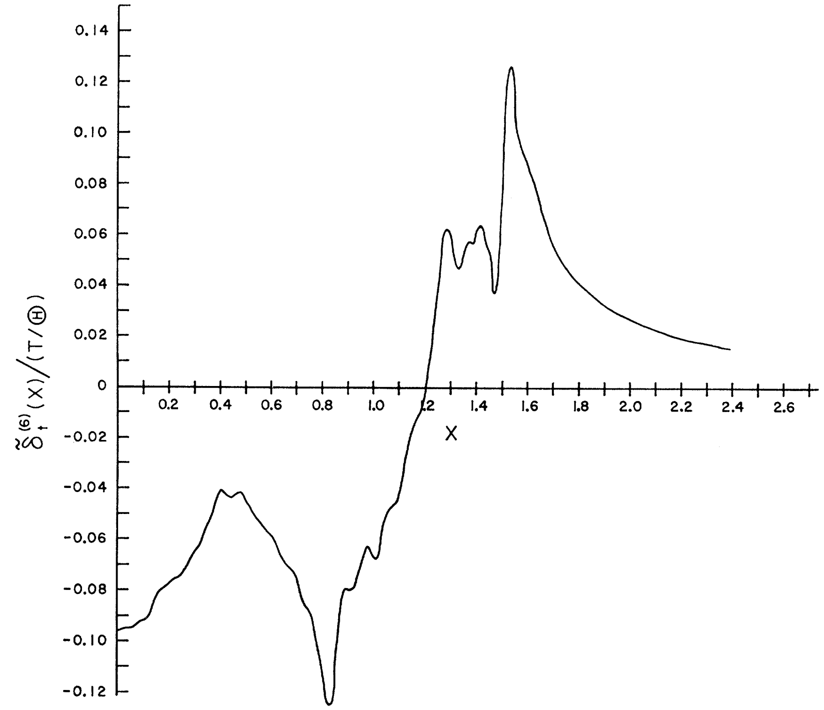

FIG. 7. The function $\tilde{\delta}_t^{(6)}(x)/(T/\Theta)$ for NaCl.

high-temperature limit obtained from Eqs. (2.8) and (3.14) are

$$\text{NaCl:}\quad \frac{\gamma}{\omega_0}=0.04699\left(\frac{T}{\Theta}\right)+0.05701\left(\frac{T}{\Theta}\right)^2 \qquad (3.15a)$$

$$\text{LiF:}\quad \frac{\gamma}{\omega_0}=0.2474\left(\frac{T}{\Theta}\right)+0.1977\left(\frac{T}{\Theta}\right)^2. \qquad (3.15b)$$

In Table III we give the values of γ/ω_0 for NaCl and LiF computed at several temperatures from Eqs. (3.15). In this table we have also quoted the experimental values of this function as obtained by Hass[4] and Heilmann,[3] respectively.

4. DISCUSSION

The first comment we can make about the results of the numerical calculations described in this paper is that they confirm the arguments of Gurevich and Ipatova in predicting that the quartic anharmonic contribution to the width of the fundamental absorption peak in NaCl and LiF is comparable with the cubic anharmonic contribution for $T \gtrsim \Theta$. The truth of this statement can be seen most directly from the analytic expressions (3.15), but also from the plots in Figs. 1–4. We see from these figures that for both crystals the comparable magnitudes of the cubic and quartic anharmonic contributions to the width of the fundamental

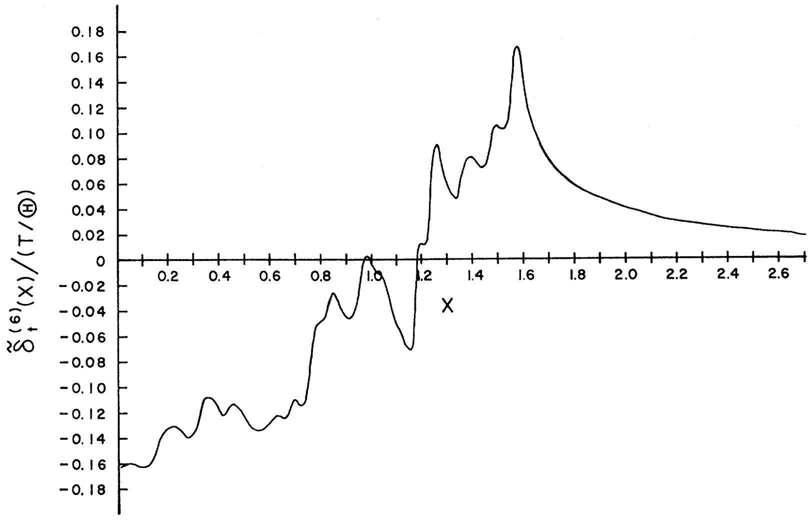

FIG. 8. The function $\tilde{\delta}_t^{(6)}(x)/(T/\Theta)$ for LiF.

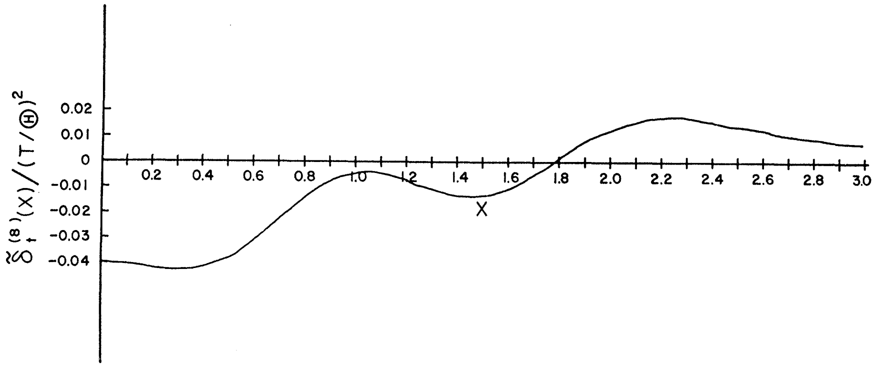

FIG. 9. The function $\underset{\sim}{\delta}_t^{(8)}(x)/(T/\Theta)^2$ for NaCl.

absorption peak are a consequence of the fact that $\gamma_t^{(6)}(x)$ has a local minimum for $x\approx\lambda_t(\mathbf{0})$, while $\gamma_t^{(8)}(x)$ has nearly its maximum value at this frequency. It is attractive to assume that the minimum in $\gamma_t^{(6)}(x)$ at $x\approx\lambda_t(\mathbf{0})$ is a reflection of that decrease in the number of phonon transitions contributing to this function (caused by the stringent wave vector and frequency conservation conditions) which, rather than any abnormally large values of $\gamma_t^{(8)}(x)$, leads to a parity between the contributions from these two functions.

It follows from these results that at elevated temperatures the width of the fundamental absorption peak in NaCl and LiF should increase more rapidly than as the first power of the absolute temperature, and this conclusion is in agreement with the experimental observations.[3,4] Because Θ for NaCl is so much smaller than Θ for LiF, our results suggest that in the temperature range in which the measurements were made (293–985°K), which lies below Θ_{LiF}, the width of the fundamental absorption peak in NaCl should vary more nearly as T^2 than should the width of the fundamental absorption peak in LiF. It is only at somewhat higher temperatures that a T^2 temperature dependence of γ/ω_0 is indicated for LiF. This conclusion contradicts the experimental results for these two crystals. Plots of the experimental points given in Table III show that on the basis of the results at the two highest temperatures for each crystal the temperature dependence of γ/ω_0 for LiF is more like T^2 than it is for NaCl. This result was explained by Gurevich and Ipatova[2] in the following way. In view of the greater relative separation between the acoustic and optical branches in LiF compared with NaCl (owing to the greater relative difference between the ionic masses in the former crystal), which makes more difficult the satisfaction of the frequency conservation condition for $\omega\approx\omega_0$, the cubic anharmonic contribution to γ should be suppressed to a greater extent, in comparison with the quartic, in LiF than in NaCl. The analytic expressions for γ/ω_0 given by Eqs. (3.15), however, disagree with this qualitative explanation. We see that Eqs. (3.15) indicate that the quartic anharmonic contribution to γ/ω_0, compared with the cubic, is larger in the case of NaCl than it is for LiF.[1] The argument of Gurevich and Ipatova, however, would be rigorously applicable only if the ratio of $|C_4|^2$ to $|C_3|^2$ were the same for the two crystals. However, reference to Table II shows that the ratio of $|C_4|^2$ to $|C_3|^2$ is somewhat larger for NaCl than it is for LiF, and this may partly overcome the relative suppression of the cubic anharmonic contribution to γ in LiF arising from the greater separation between the optical and acoustic branches. Moreover, it is also possible that while the qualitative conclusion that the cubic and quartic anharmonic terms in the crystal potential energy make comparable contributions to γ may well be insensitive to the approximations made in their evaluation, the relative magnitudes of these contributions in a given crystal may depend quite sensitively on these approximations. No firm conclusion on this point can be reached, however, until the results of exact evaluations of $\gamma_t^{(6)}(x)$ and $\gamma_t^{(8)}(x)$ become available. Finally, it should be kept in mind that the

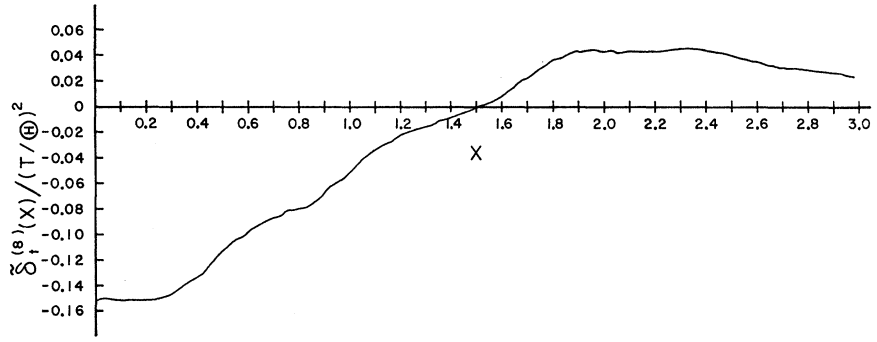

FIG. 10. The function $\underset{\sim}{\delta}_t^{(8)}(x)/(T/\Theta)^2$ for LiF.

disagreement between theory and experiment with regard to the question of for which crystal does the temperature dependence of γ/ω_0 more closely resemble proportionality to T^2 has its origin in experimental values of γ/ω_0 for LiF at essentially two temperatures in a temperature range in which according to our present results a T^2 dependence is not likely to be observed. More extensive measurements of the temperature dependence of γ/ω_0 at elevated temperatures for NaCl and LiF, particularly for the latter crystal, are also needed to settle this question.

Although we have established the essentially qualitative result that the quartic anharmonic contribution to γ/ω_0 is comparable to the cubic anharmonic contribution at elevated temperatures, we see from Table III that the quantitative agreement between the theoretical and experimental results is only fair. The agreement is better for LiF than it is for NaCl. In the latter case the theoretical results are within a factor of 2 of the experimental values, while the maximum error in the former case is only 50%.

Finally, in Figs. 11 and 12 we have plotted the imaginary parts of the dielectric constants of NaCl and LiF, respectively, as computed from the results of the present paper for a temperature of 300°K. In Fig. 11 we have also plotted the experimental results of Genzel *el al.*[17] and of Geick,[18] as combined by Burstein.[19] Similarly, in Fig. 12 we have also plotted the experimental results of Gottlieb[20] and of Genzel and Klier,[21] as combined by Burstein.[19]

We should remark at this point that the values of ε_0 and ε_∞ used in the present work are those obtained by Tessman, Kahn, and Shockely,[22] rather than the results of more recent investigations. This was done because it was these values which were used by Karo and Hardy[10] in setting up the deformation dipole model of ionic crystals which underlies the present numerical calculations. We may also point out that it has been established in Eq. (I.4.5) that the first-order dipole moment expansion parameter ϵ is given by

$$\epsilon=\frac{\varepsilon_\infty+2}{3}e^*, \qquad (4.1)$$

where e^* is the Szigeti effective charge,[23] and e is the magnitude of the electronic charge. Using the values of $e^*=0.74e$, $0.87e$ for NaCl and LiF, respectively, together with the values of ε_∞ given in Table I, we find that $\epsilon=1.05e$, $1.14e$ for NaCl and LiF, respectively.

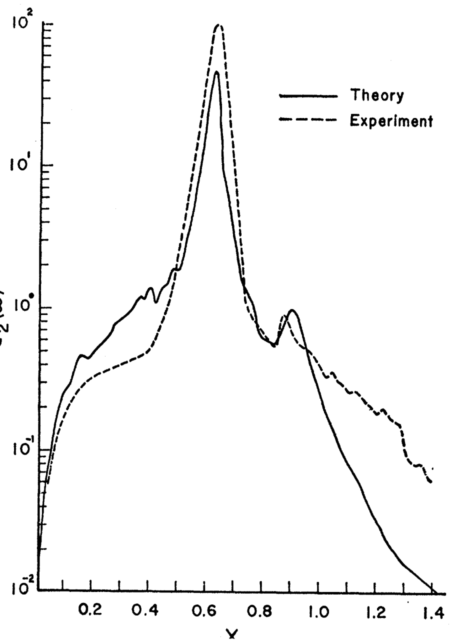

FIG. 11. Theoretical and experimental results for the imaginary part of the dielectric constant for NaCl at room temperature.

From Figs. 11 and 12 we see that there is reasonable qualitative agreement between the theoretical and experimental results for $\varepsilon_2(\omega)$ for both crystals. The theoretical results reproduce all of the qualitative features of the experimental curves such as the presence of a "shoulder" on the low-frequency side of the fundamental absorption peak, and the subsidiary maxima on

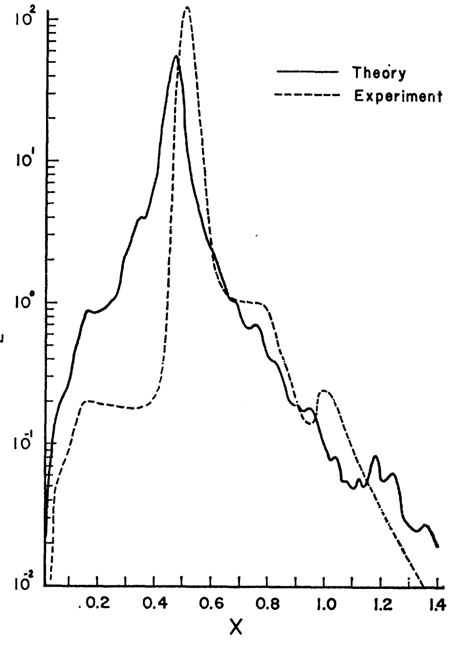

FIG. 12. Theoretical and experimental results for the imaginary part of the dielectric constant for LiF at room temperature.

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the high-frequency side. The quantitative agreement between the theoretical and experimental results for $\varepsilon_2(\omega)$ is somewhat better in the case of NaCl than it is for LiF. The frequencies at which the various structural features in $\varepsilon_2(\omega)$ occur are predicted quite accurately in our theoretical curve for NaCl, but the computed magnitude of $\varepsilon_2(\omega)$ is too large by about a factor of 3 on the low-frequency side of the fundamental absorption peak, and the height of the peak is too low by about the same factor. The most obvious difference between the computed and experimental curves of $\varepsilon_2(\omega)$ for LiF is that the former predicts values of $\varepsilon_2(\omega)$ which are too large by a factor of 5 to 10 on the low-frequency side of the fundamental absorption peak. In addition, the theoretical curve has more structure on the high frequency side of the peak, although the computed values of $\varepsilon_2(\omega)$ in this frequency range agree well with the experimental results. Some of this structure could be due to noise arising from our relatively coarse grid of points in the first Brillouin zone. It is a somewhat curious result that our calculations seem to reproduce the experimental curves for $\varepsilon_2(\omega)$ on the high-frequency side of the fundamental absorption peak much better than they do on the low-frequency side.

A possible explanation for the result that theoretical values for $\varepsilon_2(\omega)$ for LiF are much higher than the experimental values may have its origin in the fact that at room temperature $T/\Theta \approx 0.31$, i.e., room temperature is a low temperature for LiF. On the low-frequency side of the fundamental absorption peak it is the difference bands, i.e., those terms in the summand of $\Gamma_j(\mathbf{0};\omega)$ which are proportional to $[n_1-n_2]\delta(\omega+\omega_1-\omega_2)$ (see Eq. (I.3.6a)], which give the principal contribution to $\varepsilon_2(\omega)$. At high temperatures this factor is well approximated by $(k_BT\omega/\hbar\omega_1\omega_3)\delta(\omega+\omega_1-\omega_2)$, while at low temperatures it can be approximated by $[\exp(-\hbar\omega_1/k_BT)-\exp(-\hbar\omega_2/k_BT)]\delta(\omega+\omega_1-\omega_2)$. Our use of the high-temperature form in a calculation of $\varepsilon_2(\omega)$ at what is in fact a low temperature for LiF means that we are overestimating the contributions of the difference bands on the low-frequency side of the fundamental absorption peak. Because of the exponential dependence on temperature of the contribution of the difference bands to $\varepsilon_2(\omega)$, this overestimate can be appreciable at low temperatures.

Other discrepancies between the theoretical and experimental values for γ/ω_0 and $\varepsilon_2(\omega)$ can be attributed to several sources. One is certainly the simplicity of the assumed anharmonic interactions. These were derived from a nearest-neighbor, central-force, interionic potential function, which, when its two parameters are fixed by the values of the equilibrium interionic separation and the compressibility, has no additional adjustable parameters which can be varied to yield agreement between theory and experiment. Related to this point is the question of the adequacy of the deformation dipole model to describe anharmonic properties of ionic crystals. It is not our intention to address ourselves to this question except to note that inasmuch as it is a central-force model it is already incapable of accurately reproducing the harmonic forces between ions, in that it predicts the Cauchy relations among the elastic constants, which are known to be violated in NaCl and are strongly violated in LiF.

With respect to the simple approximations to the Fourier-transformed anharmonic force constants used in the present work, which are based on Eq. (2.7) we see from Table II that the three quantities $(|C_4|^2)^{1/2}$, C_4', and $(|C_4''|^2)^{1/2}$ agree among themselves to within a factor of about 2.5 for both NaCl and LiF. This result is in agreement with Peierls'[7] suggestion that $C(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)$ has a constant order of magnitude for all values of its arguments. The squares of these three quantities are in poorer agreement with each other, but even so, they still have a constant order of magnitude. If the exact result for the first term on the right-hand side of Eq. (2.10a) is written in the form given by the first term on the right-hand side of Eq. (2.18), the coefficient C_4' is replaced by a coefficient $\tilde{C}_4'$, whose value can be obtained from the results in Eq. (3.5), and which is quoted in Table II. The very good agreement between the values of $(|C_4|^2)^{1/2}$, C_4', and $\tilde{C}_4'$ also suggests that the method we have used in this paper to compute the constants by which we approximate $|C(\mathbf{0}j;\mathbf{k}_1j_1;-\mathbf{k}_1j_2)|^2$, $|C(\mathbf{0}j;\mathbf{k}_1j_1;\mathbf{k}_2j_2;\mathbf{k}_3j_3)|^2$, $\cdots$ for all values of their arguments gives reasonable results, at least for the frequency-independent sums. In addition, because in fact $C(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)$ is not a constant, independent of its arguments, we think that determining the constant-value approximation for $C(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)$ from the form of this coefficient that appears in the expression for the function being calculated, e.g., Δ_j, takes into account some of the (apparently weak) dependence of this coefficient on its arguments. In this way a better approximation to the desired function is obtained than would be if the approximate value of this coefficient were determined once and for all for all values of its arguments from the defining equation, Eq. (2.12).

Although one of the principal reasons for approximating the coefficients $\{C(\mathbf{k}_1j_1;\cdots;\mathbf{k}_sj_s)\}$ by constants in the calculations reported here was the desire to explore approximations which might render more tractable the difficult numerical calculations which arise in the evaluation of anharmonic properties of crystals, particularly frequency-dependent properties such as $\Delta_j(\omega)$ and $\Gamma_j(\omega)$, it must be admitted that even with this approximation the resulting numerical calculations are still by no means trivial to perform. This is particularly true of the calculation of $\gamma_t^{(8)}(x)$. It is perhaps an indication of the true extent of the computational difficulties posed by problems of lattice anharmonicity that preliminary results indicate that an exact calculation of $\gamma_t^{(8)}(x)$ takes about five times longer than the approximate calculations reported here, or about an hour to an hour and a half on an IBM 7094 computer.

Work still remains to be done on the problem of the absorption of light by alkali-halide crystals. Calculations of the functions $\gamma_t^{(6)}(x)$, $\tilde{\delta}_t^{(6)}(x)$, $\gamma_t^{(8)}(x)$, and $\tilde{\delta}_t^{(8)}(x)$ for the crystal model employed in the present work, but free from the approximations made here, are clearly desirable, and are in progress at the present time. The results of these calculations will be reported elsewhere.

In addition, we have chosen in the present work to order the magnitudes of the anharmonic terms in the crystal potential energy according to the prescription given by Eq. (I.3.3). In so doing we have omitted contributions to the phonon proper self-energy matrix, for example those associated with the diagrams in Fig. 13, which in the more usual ordering scheme[24] are of the same order of magnitude as the quartic anharmonic contribution to the damping constant we have retained. Moreover, and in the present context this may be even more important, these contributions are of $O(T^2)$ in the high-temperature limit. Inasmuch as we are interested in comparing the contribution of the terms of $O(T^2)$ to the damping constant with the contribution of the terms of $O(T)$, it would appear that the only rigorous way of doing this is to compute the contributions from *all* terms of $O(T^2)$, irrespective of the order in some coupling constant to which they are assigned by an ordering classification scheme. The neglect of many terms of $O(T^2)$ in the expression for the damping constant we have evaluated in the present work was dictated chiefly by the practical considerations that the number of such terms is large and that the expressions for their contributions would be very difficult to evaluate numerically at the present time. That their contributions cannot alter the qualitative aspects of the results we have obtained in this paper seems to be assured by the generally good agreement of the present theoretical results with experiment. Nevertheless it would seem to be worthwhile to study carefully the contributions of $O(T^2)$ which we have neglected here, and to try to estimate their magnitudes or at least to bound them from above.

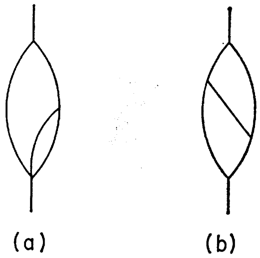

FIG. 13. Two diagrams which are associated with contributions to the width of the fundamental absorption peak of $O(T^2)$ in the high-temperature limit.

In any event, it appears to be clear from the results of the present paper that future theoretical calculations of the imaginary part of the dielectric constant, or of the absorption coefficient, of ionic crystals must take account of the quartic anharmonic contributions to the damping "constant" $\Gamma_t(\omega)$ in Eq. (1.1), if quantitatively reliable results are to be obtained.

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