

but c_{11} and c_{44} decrease which indicates a softening of the short-range repulsive forces. The result means that the short-range forces responsible for sound propagation are not connected with the dielectric properties.

Further evidence for this point is indicated by the behavior of the dielectric constant in the vicinity of the phase transition at 108°K. If the particular short-range lattice forces that determine the elastic properties are also connected with the forces that determine the frequency of the soft mode, a discontinuity of the dielectric constant would be expected. No discontinuity or even a change in slope of the dielectric constant is observed (Fig. 6).

It is surprising to us that such a marked change in the elastic properties can occur with little or no observable

effect on the dielectric properties. From the dependence of the elastic constants on electric field and on temperature, it appears that SrTiO₃ is not completely ionic. One possible interpretation is that the TiO₃ octahedra, which are the building blocks of the perovskite lattice, are partially covalently bound.¹³ At the transition temperature they undergo a slight rearrangement which cause the change in elastic properties. The soft mode, on the other hand, if assigned to the vibration of the strontium ion against the TiO₃ octahedron (Last), does not "notice" the rearrangement of the TiO₃ complex. The masses involved in this vibration and the total charge of the TiO₃ octahedron as seen by the strontium ion are not altered.

¹³ H. D. Megaw, *Acta Cryst.* **5**, 739 (1952).

Far Infrared Dielectric Dispersion in KTaO₃

ROBERT C. MILLER AND WILLIAM G. SPITZER*

Bell Telephone Laboratories, Murray Hill, New Jersey

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The room-temperature reflectivity of single-crystal KTaO₃ has been measured from 5000 to 77 cm⁻¹. These data have been analyzed by a Kramers-Kronig relation and by classical dispersion theory. The three infrared-active fundamental vibrations allowed by the lattice symmetry have been observed. The strength of the lowest frequency mode accounts for the large low-frequency dielectric constant of the material. The lattice band contribution to the microwave loss tangent at 3 cm is estimated to be about 2×10^{-3} . Attempts to fit the reflectivity data with dispersion theory show that a frequency-dependent damping constant for the low-frequency resonance is necessary in order to obtain a good fit between the calculated curve and the data. The required variation of the damping constant is by more than an order of magnitude. The present results are compared with similar measurements reported earlier on barium and strontium titanates.

INTRODUCTION

SEVERAL recent papers, both experimental^{1,2} and theoretical,^{3,4} have emphasized the essential role played by a single, long-wavelength, optical mode of vibration in accounting for the large values of the low-frequency dielectric constants observed in several materials containing the TiO₆-octahedra structure. In the case of the three crystals for which experimental data have been obtained, namely, BaTiO₃,² SrTiO₃,^{1,2} and TiO₂,² the low-frequency (microwave and lower frequency portions of the electromagnetic spectrum) dielectric constants ϵ_0 are of the order of hundreds or thousands, and the high-frequency or optical dielectric

constants ϵ_∞ are less than 10. Analyses^{1,2} of the near and far infrared reflectivity of these three crystals showed that of all the infrared-active vibrations allowed by symmetry, the lowest frequency mode in each case accounts for the large low-frequency dielectric constant. This mode is believed² to be primarily associated with TiO₆-octahedra vibrations. The unusually large damping constant characteristic of the low-frequency modes was consistent with the observed microwave loss tangents. For all three crystals investigated, attempts to fit the reflectivity data with classical dispersion theory were not completely satisfactory. The analyses suggested that to fit the experimental data accurately, a frequency-dependent damping constant was required for the low-frequency resonance.

Measurements and analyses similar to those described above have now been made on single-crystal KTaO₃. This material is in some ways quite similar to the titanates. Like SrTiO₃, it is cubic and paraelectric at room temperature.⁵ The ferroelectric Curie point is reported⁵

* Present address: Bell and Howell Research Center, Pasadena, California.

¹ A. S. Barker and M. Tinkham, *Phys. Rev.* **125**, 1527 (1962).

² W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth *Phys. Rev.* **126**, 1710 (1962).

³ W. Cochran, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960-61), Vol. 9, p. 387; Vol. 10, p. 401.

⁴ P. Anderson, in *Fizika dielektrikov*, edited by G. I. Skanavi (Akad. Nauk S.S.S.R. Fizicheskii Inst. im P. N. Lebedeva, Moscow, 1960).

⁵ J. K. Hulm, B. T. Matthias, and E. A. Long, *Phys. Rev.* **79**, 885 (1950).

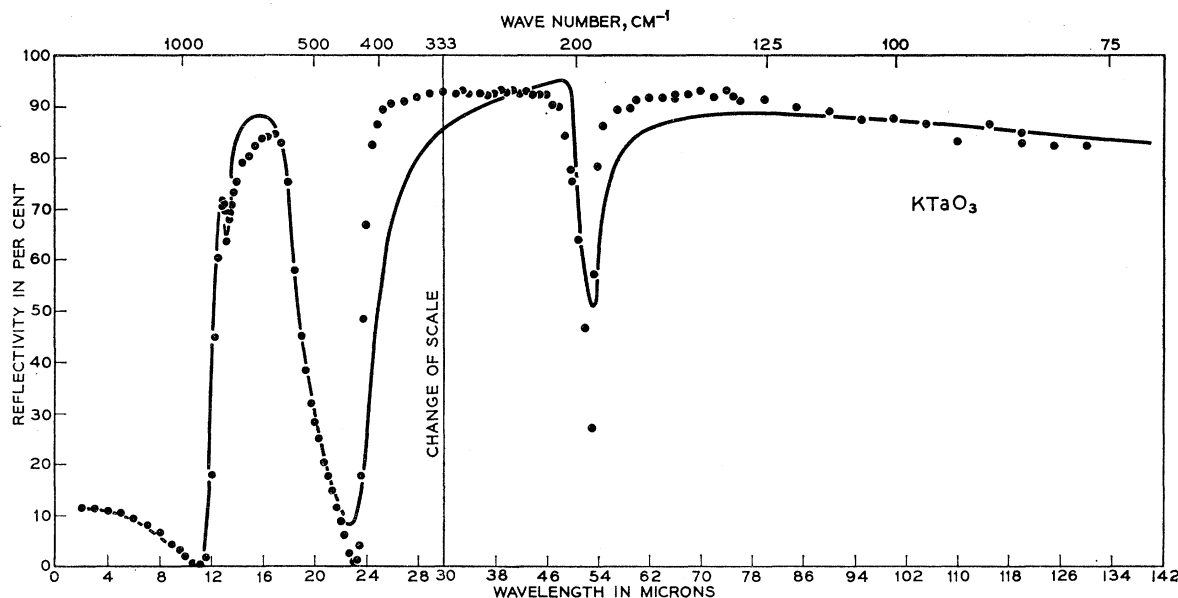


FIG. 1. Reflectivity of KTaO_3 . The solid curve was calculated using classical dispersion theory.

to be at 13.2°K . The values of the high- and low-frequency dielectric constants are about 4.5⁶ and 220,⁷ respectively. As in the case of SrTiO_3 and cubic BaTiO_3 , there will be three triply degenerate, infrared-active, normal modes of vibration.^{3,8} However, two of the ions in the tantalate lattice, namely, Ta and K, differ in mass and in valence from the two equivalent ions in the titanates. Therefore, significant differences between the fundamental lattice vibrations in KTaO_3 and the titanates might be expected. The above considerations led the authors to believe that the vibrational spectrum of KTaO_3 should be an interesting one to compare with that of the titanates.^{1,2}

In the present experiments, room-temperature reflectivity measurements have been obtained for KTaO_3 from 5000 to 77 cm^{-1} . These reflectivity data have been subjected to a Kramers-Kronig (hereafter referred to as K-K) analysis for the real and imaginary parts of the dielectric constant. Attempts were made to fit the reflectivity data with classical dispersion theory. It was found that a much improved fit to the data was obtained if the damping constant for the strong low-frequency resonance was allowed to vary as a function of frequency. Implications of this variation of the damping constant, which is greater than an order of magnitude, are discussed. A comparison of the present results with the earlier titanate work is also given.

EXPERIMENTAL

Measurements of the room temperature, normal incidence reflectivity between 5000 and 333 cm^{-1} , were

⁶ Unpublished result obtained during the course of the present experiments.

⁷ S. Wemple (private communication).

⁸ J. T. Last, Phys. Rev. **105**, 1740 (1957).

made on a double-pass spectrometer with NaCl and CsBr prisms. For frequencies between 333 and 77 cm^{-1} , a single-pass grating monochromator was used. The experimental techniques and equipment employed here are the same as those described in a previous study.²

The reflectivity was measured with unpolarized radiation for each of two polished KTaO_3 samples. The samples had a resistivity of about $1\ \Omega\text{-cm}$ at room temperature, were slightly blue in color, and transparent. One of the samples was measured to only 156 cm^{-1} due to its small size, while the other sample was measured over the full frequency spectrum. The reflectivity of the two samples agreed everywhere within the experimental accuracy of the measurement. The experimental results are shown by the points in Fig. 1.

ANALYSIS OF DATA

It is known from theoretical considerations^{3,8} and experimental measurements² that SrTiO_3 and cubic BaTiO_3 have three optically active normal modes of vibration. Since KTaO_3 is isomorphous with these materials, it will have the same number of fundamental infrared active lattice bands. In view of this similarity, and the high value of ϵ_0 , it is not surprising that the reflectivity measured for KTaO_3 is qualitatively similar to that observed for the two titanates. The reflectivity of each of the materials has a minimum between 10 and 15μ , another between 20 and 25μ , and a third between 50 and 60μ . In KTaO_3 , however, the structure, i.e., the depth and breadth of the minima, is considerably more pronounced than in either of the titanates, particularly in the case of the minimum near 50μ .

As in the case of the titanates, the present reflectivity data are first analyzed by employing a K-K relation.²

In the analysis, 11.5 and 76.8% were used for the high- and low-frequency limiting values for the reflectivity, respectively. The results of this calculation are shown in Fig. 2 where the imaginary part of the complex dielectric constant ϵ'' is given as a function of the frequency. As expected, three major resonances are clearly indicated with peaks in ϵ'' at 549, 201, and 90 cm^{-1} . The small dip in the reflectivity data at 755 cm^{-1} is too weak to show up as a peak in Fig. 2.

A second method,⁹ frequently used to study reflectivity data such as those obtained here, is classical dispersion analysis. The crystal dielectric behavior is approximated by a system, or systems, of damped oscillators, each system having a characteristic frequency and

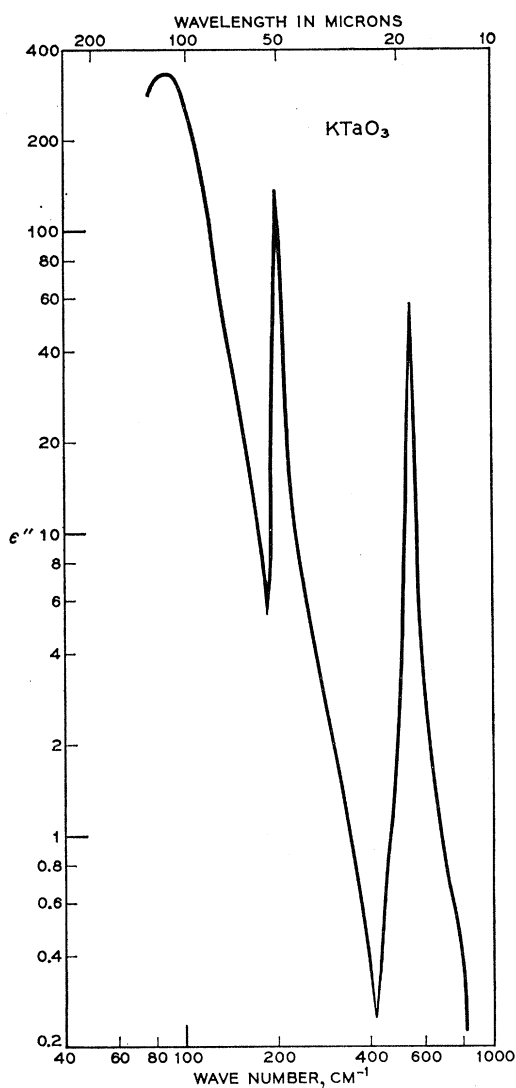


FIG. 2. Imaginary part of the dielectric constant of KTaO_3 calculated from the experimental data given in Fig. 1.

⁹ W. G. Spitzer and D. A. Kleinman, Phys. Rev. **121**, 1324 (1961).

TABLE I. Dispersion parameters calculated from the K-K analysis.^a

Resonance	1	2	3
ν_j	549+6 cm^{-1}	200.8 cm^{-1}	93.0±2.0 cm^{-1}
λ_j	18.2±0.2 μ	49.8 μ	107.5±2.0 μ
$4\pi\rho_j$	2.4 ±0.5	7.6±1.5	163 ±33
γ_j/ν_j	0.043±0.009	0.055±0.011	0.5±0.1

^a The uncertainties quoted here are those estimated from the uncertainties encountered in obtaining the various quantities from the K-K analysis and are therefore simply lower limits on the reliability of figures given.

dipole moment. The dispersion is quantitatively described by the high-frequency dielectric constant ϵ_∞ and three parameters for each resonance. These parameters are the resonance frequency ν_j , strength $4\pi\rho_j$, and damping constant or width γ_j . The real and imaginary parts of the dielectric constant, ϵ' and ϵ'' , as functions of frequency may be expressed in terms of the dispersion parameters. The reflectivity is given by the optical constants, refractive index and extinction coefficient, which are obtained from ϵ' and ϵ'' . This type of analysis was used for the titanates,² and it was found that the dispersion parameters estimated from the K-K results did not accurately reproduce the experimental reflectivity. While changes in the dispersion parameters produced minor improvements in the calculated reflectivity curves, the data still could not be fitted accurately. As in a number of calculations for other materials,¹⁰ it was assumed that the damping constant γ_j is frequency independent and it was suggested that this assumption was the major difficulty in obtaining good fits to the data.

Following the method employed for the titanates, estimates of the dispersion parameters are obtained from the K-K analysis for each of the three resonances indicated in Fig. 2. The parameters are given in Table I. These values were then adjusted in an attempt to improve the fit to the data and a fourth weak resonance ν_c was added at 13.20 μ to account for the dip in reflectivity at this wavelength. The best fit obtained to date is shown by the solid curve in Fig. 1 and the dispersion parameters are given in Table II. A comparison of the experimental points and curve of Fig. 1 shows

TABLE II. Dispersion parameters for the best fit to the reflectivity data.

Resonance	c^a	1	2	3
ν_j	758 cm^{-1}	549 cm^{-1}	198.8 cm^{-1}	85.1 cm^{-1}
λ_j	13.20 μ	18.2 μ	50.3 μ	117.5 μ
$4\pi\rho_j$	0.0075	2.4	5.0	209.4
γ_j/ν_j	0.025	0.043	0.012	0.600

^a Resonance c is a weak combination band and not a fundamental.

¹⁰ W. G. Spitzer, D. Kleinman, and D. Walsh, Phys. Rev. **113**, 127 (1959); W. G. Spitzer, D. Kleinman, and C. J. Frosch, *ibid.* **113**, 133 (1959); R. J. Collins and D. Kleinman, J. Phys. Chem. Solids **11**, 190 (1959); D. A. Kleinman and W. G. Spitzer, Phys. Rev. **118**, 110 (1960).

that while the curve reproduces the general features of the experimental data, there are several regions of serious disagreement. During the process of adjusting the dispersion parameters for the curve of best fit, it was observed that large changes in γ_1 and γ_2 influenced the calculated reflectivity very little except in certain spectral regions in the vicinity of the ν_1 and ν_2 resonances, respectively. For example, the sharp edge in the data near 23μ , and the sharpness of the 53μ band, could not be reproduced by variations in γ_1 or γ_2 . However, it was also observed that changes in γ_3 have a pronounced effect on the calculated reflectivity and in fact allow a good fit to the data throughout the entire frequency range. Figure 3 shows γ_3/ν_3 as a function of frequency for the case where the calculated and experimental reflectivities are in good agreement, and all other dispersion parameters are the same as those given in Table II.

INTERPRETATION OF RESULTS

As in the case of the titanates, both the K-K and the classical dispersion analyses show that KTaO_3 has three strong infrared-active lattice vibrations. These three resonances, listed in Table II, are at 549, 198.8, and 85.1 cm^{-1} . As predicted by Cochran, the lowest frequency resonance has an extremely large strength³ and accounts for $\sim 95\%$ of the low-frequency dielectric constant, $\epsilon_0 = \epsilon_\infty + \sum_j A_j \rho_j = 221$. This value of ϵ_0 is equal to that obtained from other measurements⁷ indicating that the choice made here for the low-frequency limiting reflectivity, 77%, is a reasonable one. The limiting value for the high-frequency dielectric constant, $\epsilon_\infty = 4.35$, is somewhat less than that measured⁶ in the yellow region of the visible, i.e., $\epsilon \approx 4.5$. This difference, however, is reasonable since the present analysis does not take into account the dispersion in the visible arising from the fundamental absorption edge at a higher frequency.

It may be noted that a fourth set of dispersion parameters for a resonance at ν_c has been included in Table II. This resonance, at 758 cm^{-1} , is very weak and is probably a two-phonon combination band. The values $\nu_c = 758 \text{ cm}^{-1}$ and $\nu_1 + \nu_2 = 748 \text{ cm}^{-1}$ are quite close. It should be pointed out, however, that ν_1 and ν_2 are transverse optical mode frequencies for zero wave number, $q_1 = q_2 = 0$, whereas ν_c represents the sum of frequencies for which $\mathbf{q}_i + \mathbf{q}_j = 0$ but \mathbf{q}_i and \mathbf{q}_j are not necessarily each zero.

The normal mode assignments for KTaO_3 are assumed to be the same as those proposed earlier² for the titanates. This assumption is supported not only by the considerations previously indicated, but also by the close similarity in the dispersion parameters themselves, particularly between KTaO_3 and SrTiO_3 . According to this model, the resonance at $\nu_2 = 199 \text{ cm}^{-1}$ involves a cation-type vibration with respect to the TaO_6 octahedra. The ν_1 and ν_3 resonances are described as modes which involve TaO_6 bending and TaO_6 stretching, respectively. A comparison of the ν_2 frequencies of 178 cm^{-1} for SrTiO_3 ² and 199 cm^{-1} for KTaO_3 shows that

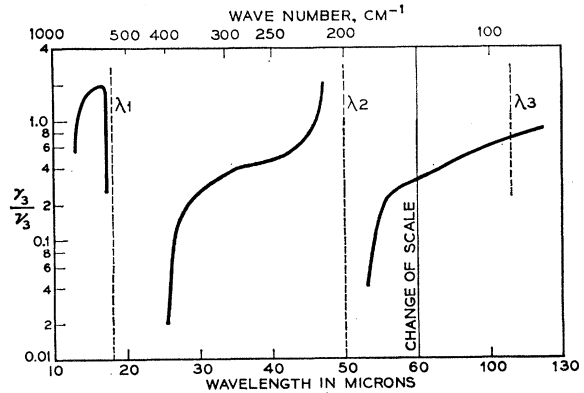


FIG. 3. The damping constant γ_3/ν_3 for the low-frequency resonance as a function of frequency. The solid curve gives the values of γ_3/ν_3 required to fit the experimental reflectivity data. Other than for γ_3/ν_3 , the dispersion parameters used in the calculation are given in Table II.

the observed frequency shift of 21 cm^{-1} is approximately $\frac{2}{3}$ of that predicted from the change in reduced mass assuming that the TiO_6 and TaO_6 octahedra vibrate as a unit. A similar comparison of the ν_2 frequency of 183 cm^{-1} for BaTiO_3 ² with that for SrTiO_3 shows that the frequency shift of 18 cm^{-1} calculated in the manner described above is opposite in direction to that observed. These results serve to emphasize that accurate comparisons cannot be made without detailed knowledge of the normal modes and the force constants for the crystals considered.

It is of interest to note that an approximate value may be given for the contribution of the lattice vibrations to the loss tangent in the microwave region. Following the method employed for the titanates,² the lattice band contribution to the loss tangent comes almost completely from the strong low-frequency resonance ν_3 and is given by $\tan \delta \approx \gamma_3 \nu / \nu_3$. At 3-cm wavelength, this gives a room temperature $\tan \delta \approx 2.3 \times 10^{-3}$ which is within a factor of 3 of the experimental value,⁷ 9×10^{-4} , obtained with $10^{12} \Omega\text{-cm}$ material. The value $\gamma_3/\nu_3 = 0.6$ was used to calculate the loss tangent.

The significance of the γ_3/ν_3 curve of Fig. 3 is not understood at the present time. While the specific shape of this curve is sensitive to the choice of dispersion parameters for the ν_1 and ν_2 resonances, the general features of the curve are preserved. One of the interesting features of the curve is the rapid decrease with increasing frequency of γ_3/ν_3 in certain spectral regions, i.e., 190–180, 395–365, and 800–770 cm^{-1} . These “cut-offs” in γ_3 appear to be related. If the frequency of the low-frequency cutoff is called A , $A = 190\text{--}180 \text{ cm}^{-1}$; then $\nu_2 + A = 389\text{--}379 \text{ cm}^{-1}$ which agrees with the observed frequency for the second cutoff, 395–365 cm^{-1} . Also, $\nu_1 + A = 740\text{--}730 \text{ cm}^{-1}$, which is close to the frequency of the third cutoff region, 800–770 cm^{-1} . These considerations suggest the following mechanism: The γ_3 in the low-frequency range is controlled by the decay of phonons of the ν_3 branch of the vibrational spectrum

by a two-phonon process into a pair of phonons, probably acoustic, such that the total phonon wave vector is zero. When the photon frequency exceeds the maximum value for the sum of the acoustic frequencies, the γ_3 becomes small. However, when the photon frequency exceeds that of another normal mode, for example ν_2 , then γ_3 again becomes large since decay becomes possible via a three-phonon process, ν_2 plus the two acoustical frequencies. This process is illustrated qualitatively in Fig. 4. The transverse optical branches, ν_1 , ν_2 , and ν_3 shown in Fig. 4, are determined by the present data at $q=0$ only. These data give no information on the acoustical branches, two of which are indicated schematically in Fig. 4. There are difficulties, however, with the process described above. One would expect γ_3 to be smaller for $\nu_2 < \nu < \nu_2 + A$ and $\nu_1 < \nu < \nu_1 + A$ than for $\nu < A$ since the former regions correspond to a 3-phonon decay while the latter corresponds to a 2-phonon process. As seen in Fig. 3, there is no indication of this effect. Also it might be expected that γ_3 would peak at fre-

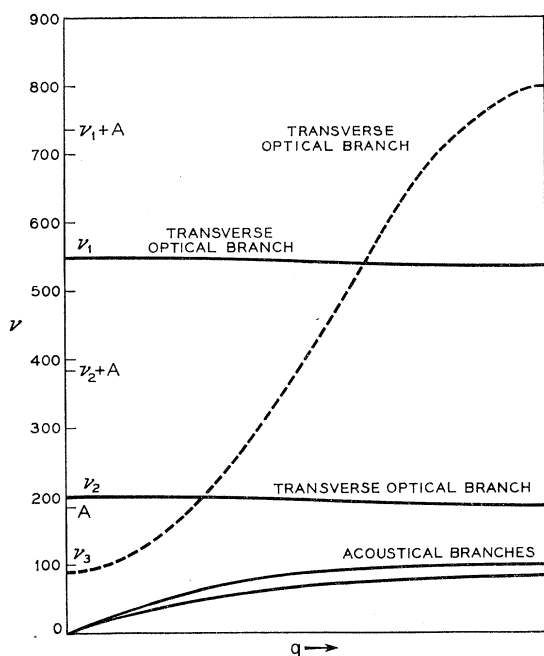


FIG. 4. Phonon spectrum which explains in a qualitative manner some features of the observed frequency dependence of γ_3/ν_3 .

quencies slightly less than the cutoff values since this corresponds to regions where the density of states for the acoustic modes would be at a maximum. Again no evidence for this effect is observed in Fig. 3.

In obtaining Fig. 3, it was assumed that γ_3 may be frequency dependent but that the classical dispersion expressions still apply. This represents the simplest extension of the analysis as it was applied to a number of other materials.¹⁰ Dispersion theories which include effects of cubic¹¹⁻¹³ and quartic¹⁴ anharmonic terms in the lattice potential have been described recently by several investigators. These theories differ in some respects from the much earlier theory of Born and Huang¹⁵ which Wallis and Maradudin¹³ show has several weaknesses. All of these theories lead to a frequency-dependent damping constant. The most attractive theory is that developed by Jepsen and Wallis¹⁴ who demonstrate that quartic anharmonic terms in the lattice potential are required to explain the observed temperature dependence of the damping constant for NaCl.¹⁶ However, it is not possible to compare the present data on $\gamma(\nu)$ with this theory, or the other recent theories¹¹⁻¹³ which assume only cubic anharmonic terms in the lattice potential, since the theoretical expressions have only been evaluated for a linear diatomic chain. Experimental data similar to those presented in this paper, e.g., Figs. 2 and 3, should be most valuable for comparing with an appropriate theory when one is developed.

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¹² A. A. Maradudin and R. F. Wallis, Phys. Rev. **123**, 777 (1961).

¹³ R. F. Wallis and A. A. Maradudin, Phys. Rev. **125**, 1277 (1962).

¹⁴ D. W. Jepsen and R. F. Wallis, Phys. Rev. **125**, 1496 (1962).

¹⁵ M. Born and K. Huang, *Dynamic Theory of Crystal Lattices* (Oxford University Press, New York, 1959).

¹⁶ M. Hass, Phys. Rev. **117**, 1497 (1960).