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 $SrTiO_3$ is not completely ionic. One possible interpretation is that the TiO_3 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 TiO_3 octahedron (Last), does not "notice" the rearrangement of the TiO_3 complex. The masses involved in this vibration and the total charge of the TiO_3 octahedron as seen by the strontium ion are not altered.

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Far Infrared Dielectric Dispersion in KTaO₃

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The room-temperature reflectivity of single-crystal $KTaO_3$ 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 TiO_6-octahedra structure. In the case of the three crystals for which experimental data have been obtained, namely, $BaTiO_3$,[2] $SrTiO_3$,[1,2] and TiO_2,[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 believed[2] to be primarily associated with TiO_6-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 $KTaO_3$. This material is in some ways quite similar to the titanates. Like $SrTiO_3$, it is cubic and paraelectric at room temperature.[5] The ferroelectric Curie point is reported[5]

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[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).

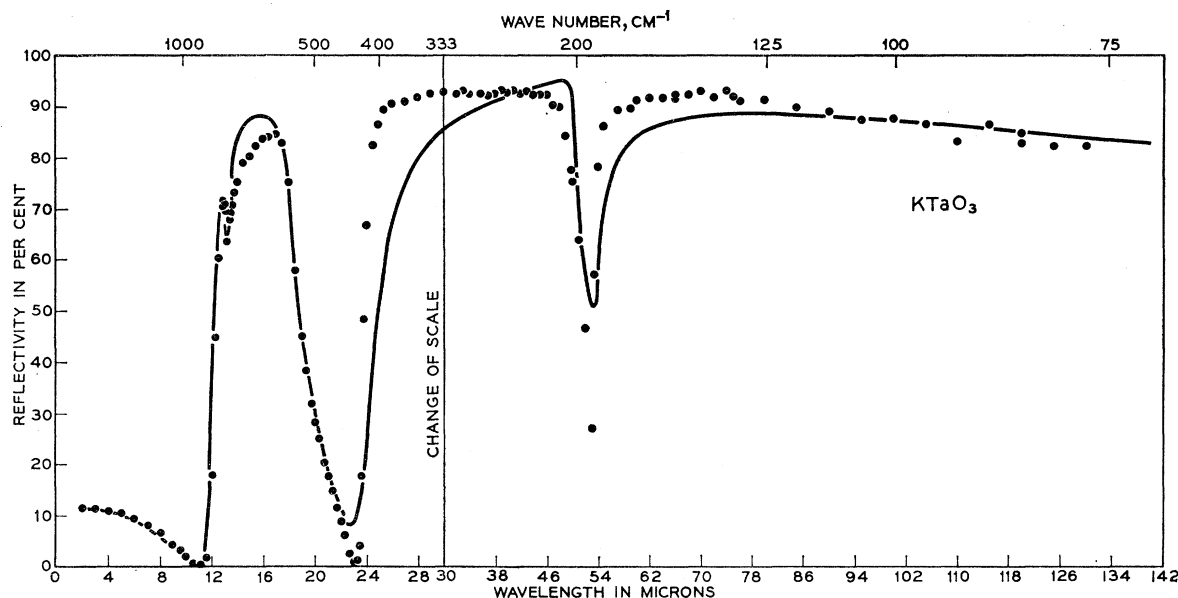[5] J. K. Hulm, B. T. Matthias, and E. A. Long, Phys. Rev. 79, 885 (1950).

FIG. 1. Reflectivity of KTaO₃. 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 4.5[6] 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

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 Ω-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 measurements[2] 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]

[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).

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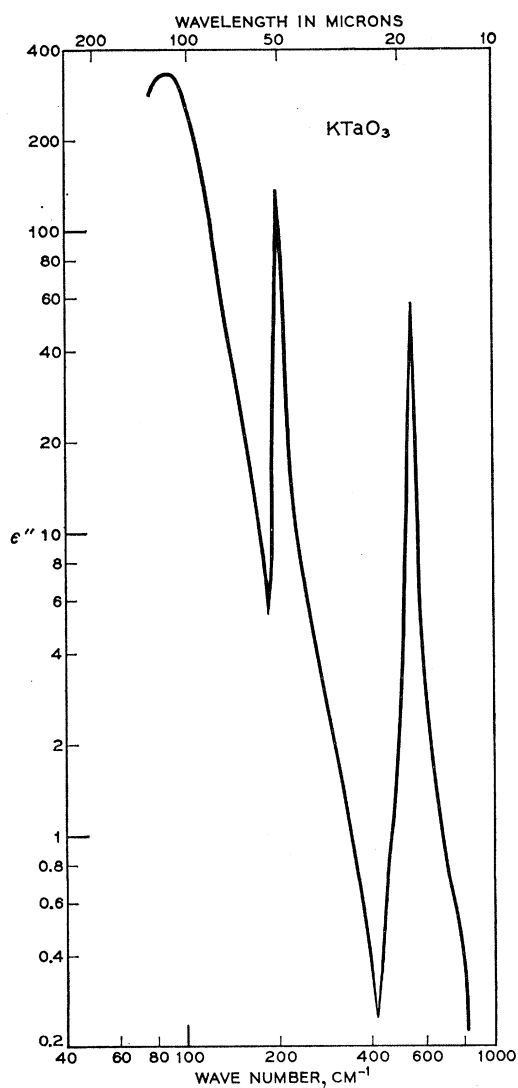
TABLE I. Dispersion parameters calculated from the K-K analysis.[a]

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 13.20μ 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

FIG. 2. Imaginary part of the dielectric constant of KTaO$_3$ calculated from the experimental data given in Fig. 1.

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	13.20μ	18.2μ	50.3μ	117.5μ
$4\pi\rho_j$	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.

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

[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 KTaO₃ 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 strength[3] and accounts for $\sim$95% of the low-frequency dielectric constant, $\epsilon_0 = \epsilon_\infty + \sum_j 4\pi\rho_j = 221$. This value of ϵ_0 is equal to that obtained from other measurements[7] 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 measured[6] 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 $\nu_c = 758$ cm⁻¹ and $\nu_1 + \nu_2 = 748$ 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 KTaO₃ are assumed to be the same as those proposed earlier[2] 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 KTaO₃ and SrTiO₃. According to this model, the resonance at $\nu_2 = 199$ cm⁻¹ involves a cation-type vibration with respect to the TaO₆ octahedra. The ν_1 and ν_3 resonances are described as modes which involve TaO₆ bending and TaO₆ stretching, respectively. A comparison of the ν_2 frequencies of 178 cm⁻¹ for SrTiO₃[2] and 199 cm⁻¹ for KTaO₃ shows that
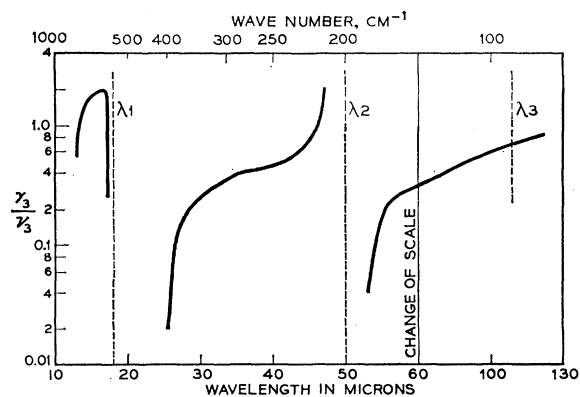

FIG. 3. The damping constant γ_3/ν_3 for the low-frequency resonance as a function of frequency. The solid curve gives the values of γ_3/ν_3 required to fit the experimental reflectivity data. Other than for γ_3/ν_3, the dispersion parameters used in the calculation are given in Table II.

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 TiO₆ and TaO₆ octahedra vibrate as a unit. A similar comparison of the ν_2 frequency of 183 cm⁻¹ for BaTiO₃[2] with that for SrTiO₃ 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} Ω-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 "cutoffs" in γ_3 appear to be related. If the frequency of the low-frequency cutoff is called A, $A = 190$–180 cm⁻¹; then $\nu_2 + A = 389$–379 cm⁻¹ which agrees with the observed frequency for the second cutoff, 395–365 cm⁻¹. Also, $\nu_1 + A = 740$–730 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, proba-
bly 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 be-
comes small. However, when the photon frequency ex-
ceeds that of another normal mode, for example ν_2,
then γ_3 again becomes large since decay becomes possi-
ble via a three-phonon process, ν_2 plus the two acousti-
cal 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 sche-
matically 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 $\nu_1<\nu<{}_1\nu+A$ than for $\nu<A$
since the former regions correspond to a 3-phonon de-
cay while the latter corresponds to a 2-phonon process.
As seen in Fig. 3, there is no indication of this effect.
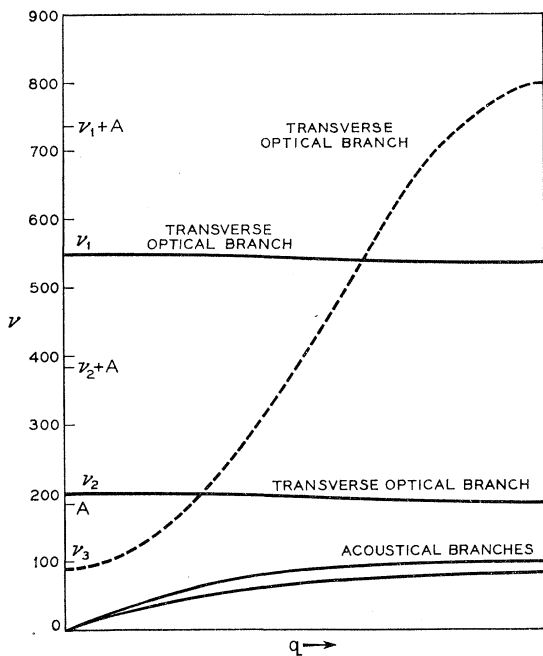Also it might be expected that γ_3 would peak at fre-

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 ex-
tension of the analysis as it was applied to a number of
other materials.[10] Dispersion theories which include
effects of cubic[11–13] and quartic[14] anharmonic terms in
the lattice potential have been described recently by
several investigators. These theories differ in some re-
spects from the much earlier theory of Born and Huang[15]
which Wallis and Maradudin[13] show has several weak-
nesses. All of these theories lead to a frequency-
dependent damping constant. The most attractive
theory is that developed by Jepsen and Wallis[14] 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 pres-
ent data on $\gamma(\nu)$ with this theory, or the other recent
theories[11–13] which assume only cubic anharmonic terms
in the lattice potential, since the theoretical expres-
sions 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.

ACKNOWLEDGMENTS

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

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