

Temperature Dependence of the Infrared Reflection Spectrum of Sodium Chloride

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(Received October 5, 1959)

Experimental studies of the reflection spectrum of NaCl from 300°K to 985°K were carried out in the region of the fundamental lattice absorption. This reflection spectrum was analyzed using a simple dispersion formula. The damping constant deduced in this manner varied approximately with the square of the temperature. The relation of these results to various theories of lattice absorption in solids is discussed.

I. INTRODUCTION

THE shape of the strong lattice absorption band in the alkali halides can be used to obtain information about the interionic potential and lattice vibrations. Such studies on the transmission and reflection spectra of alkali halides in the region of the fundamental lattice vibration frequency have been reported by Czerny, Barnes, and others.¹⁻³ However, in order to verify some theoretical points to be discussed later, it is desirable to measure the spectrum as a function of temperature. An investigation of the reflection spectrum of LiF as a function of temperature has been reported by Heilmann.⁴ It is of interest to study other halides besides LiF as this material is somewhat unique in the behavior of its elastic constants.⁵

II. EXPERIMENTAL

These studies were carried out using a Perkin-Elmer Model 12 spectrometer modified for grating operation as suggested by Lord and McCubbin.⁶ Michigan gratings of 320 and 556.85 lines/inch were employed. The entire system was enclosed in a plexiglass housing in which air was recirculated through a molecular sieve desiccant.

Samples of NaCl single crystals were placed in an oven located at an external focus in an optical arrangement for measuring the reflectivity. The average angle of incidence was 10°. The reference aluminum mirror was assumed to reflect 98% of the incident radiation. The temperature was measured with an iron-constantan

thermocouple placed in a hole drilled in the specimen. The temperature was kept constant to $\pm 5^\circ\text{C}$.

III. MEASUREMENTS

The data are shown in Fig. 1. The room temperature data are characterized by a major absorption peak near 190 cm^{-1} , one prominent sideband at 263 cm^{-1} , and a shoulder at 235 cm^{-1} . This last shoulder was reported as a definite band by Mitsuishi, *et al.*² who examined it with higher resolution. It is not yet established quantitatively whether this additional fine structure is due to anharmonicity, second-order electric moments, or consideration of proper boundary conditions as proposed by Rosenstock.⁷ As the temperature is increased, the intensity of the main band decreases. In addition, the reflection spectrum shifts somewhat to longer wavelengths as the lattice expands.

IV. REFLECTION ANALYSIS

The absorption was estimated in the following manner. Reflection spectra were calculated using the Drude dispersion formula⁸

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 - (\omega/\omega_0)^2 + i(\gamma/\omega_0)(\omega/\omega_0)}, \quad (1)$$

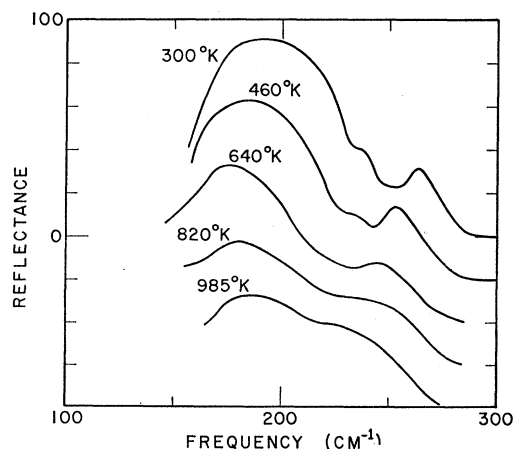


FIG. 1. Reflection spectra of NaCl as a function of temperature.

¹ M. Czerny, *Z. Physik* **65**, 600 (1930); R. B. Barnes and M. Czerny, *Z. Physik* **72**, 447 (1931); R. B. Barnes, *Z. Physik* **75**, 723 (1932); C. H. Cartwright and M. Czerny, *Z. Physik* **85**, 269 (1933); A. Mentzel, *Z. Physik* **88**, 178 (1934); C. H. Cartwright and M. Czerny, *Z. Physik* **90**, 457 (1934); C. H. Cartwright, *Z. Physik* **90**, 480 (1934); H. W. Hohls, *Ann. Physik* **29**, 433 (1937); B. Koch, *Ann. Physik* **33**, 335 (1938); T. K. McCubbin, Jr., and W. M. Sinton, *J. Opt. Soc. Am.* **40**, 537 (1950); M. Klier and L. Genzel, *Z. Physik* **144**, 25 (1956); S. Califano and M. Czerny, *Z. Physik* **150**, 1 (1958); M. Klier, *Z. Physik* **150**, 49 (1958); R. W. H. Stevenson and P. T. Nettle, *Nature* **182**, 471 (1958); D. J. Montgomery and R. H. Misho, *Nature* **183**, 103 (1959); M. Gottlieb and J. R. Nelson, *Bull. Am. Phys. Soc.* **4**, 36 (1959).

² Mitsuishi, Yoshinaga, and Fujita, *J. Phys. Soc. Japan* **14**, 110 (1959).

³ Genzel, Happ, and Weber, *Z. Physik* **154**, 13 (1959).

⁴ G. Heilmann, *Z. Physik* **152**, 368 (1958).

⁵ H. B. Huntington, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958), Vol. 7, p. 281.

⁶ R. C. Lord and T. K. McCubbin, Jr., *J. Opt. Soc. Am.* **47**, 689 (1957).

⁷ H. B. Rosenstock, *J. Phys. Chem. Solids* **4**, 201 (1958).

⁸ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), p. 121.

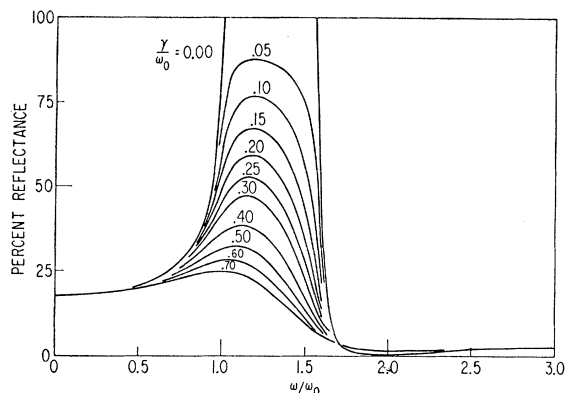


FIG. 2. Reflection spectra for a damped oscillator described by Eq. (1) with $\epsilon_0=5.90$ and $\epsilon_\infty=2.34$. These are the values for NaCl at room temperature.

where γ/ω_0 represents a damping term and ϵ_∞ and ϵ_0 are the high- and low-frequency dielectric constants, respectively. Here $\epsilon(\omega)$ defines a complex dielectric constant

$$\sqrt{\epsilon(\omega)} = n - ik, \quad (2)$$

where n is the index of refraction and k the extinction coefficient. By expressing Eq. (1) in terms of its real and imaginary parts, it is shown that

$$n^2 - k^2 = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)[1 - (\omega/\omega_0)^2]}{[1 - (\omega/\omega_0)^2]^2 + (\omega/\omega_0)^2(\gamma/\omega_0)^2}, \quad (3)$$

$$2nk = \frac{(\epsilon_0 - \epsilon_\infty)(\gamma/\omega_0)(\omega/\omega_0)}{[1 - (\omega/\omega_0)^2]^2 + (\omega/\omega_0)^2(\gamma/\omega_0)^2}. \quad (4)$$

Knowing n and k , the reflectance R is given by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \quad (5)$$

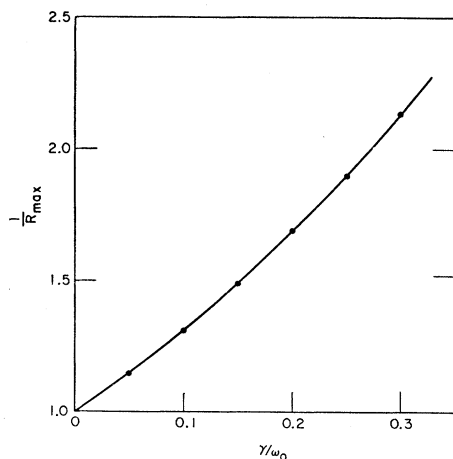


FIG. 3. Inverse of peak reflectivity $1/R_{\max}$ as a function of damping constant γ/ω_0 for system described by Eq. (1).

The results of calculating R as a function of γ/ω_0 are shown in Fig. 2.⁹

The inverse of the peak reflectivity was then plotted as a function of the damping constant as shown in Fig. 3. It can be seen from Fig. 3 that the inverse of the peak reflectivity is approximately linear with the damping constant, as has been suggested previously.¹⁰

Consequently, the damping constant can be estimated merely from a knowledge of the peak reflectivity. The validity of this procedure was checked by estimating the damping constant of LiF using the reflection spectra of Heilmann.⁴ The values obtained using the present method gave good agreement with those given by Heilmann who determined the optical constants from measurements at two different angles of incidence. The present method is advantageous in the far infrared where it is more difficult to obtain the data needed for analysis by other methods.^{4,11}

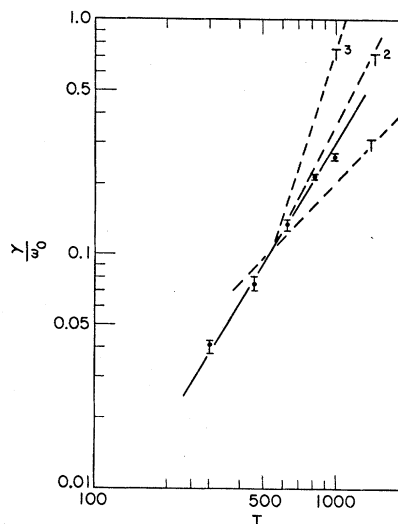


FIG. 4. Damping constant of NaCl as a function of absolute temperature T . The limits of error correspond to $\pm 1\%$ in the reflectivity. The values of ϵ_0 and ϵ_∞ were assumed to be the room temperature values.

The observed reflection spectrum of NaCl can be represented to a fair approximation by the dispersion formula given in Eq. (1) as can be seen by a comparison of Fig. 1 and Fig. 2. The structure on the high-frequency side of the band is not taken into account in this simple treatment. However, the absorption corresponding to this structure will be small in comparison with the

⁹ The dielectric constant of NaCl is taken from *Dielectric Materials and Applications*, edited by A. R. Von Hippel (Technology Press, Cambridge, and John Wiley and Sons, Inc., New York, 1954), p. 302. The index of refraction of NaCl can be used to calculate ϵ_∞ making use of the relation $\epsilon_\infty = n^2$. The value at one micron was taken from *American Institute of Physics Handbook* (McGraw-Hill Book Company, New York, 1957), Chap. 6, p. 23.

¹⁰ C. Haas and J. A. A. Ketelaar, *Phys. Rev.* **103**, 564 (1956); F. Abeles and J.-P. Mathieu, *Ann. Phys.* **3**, 5 (1958); Spitzer, Kleinman, and Walsh, *Phys. Rev.* **113**, 127 (1959).

¹¹ T. S. Robinson, *Proc. Phys. Soc. (London)* **B659**, 910 (1952).

integrated absorption of the main band.³ The damping constant of the main band can be estimated from the peak value of the reflectivity using the method just discussed. This is shown as a function of temperature in Fig. 4 and Table I. It can be seen that the damping constant varies approximately as T^2 .

V. DISCUSSION

In the harmonic approximation when cyclic boundary conditions are employed, it can be shown that a very simple spectrum consisting of a single line at the dispersion frequency ω_0 will result. The occurrence of a complex spectrum consisting of several bands of finite width indicates the inadequacy of this simple theory. Among the suggestions which have been proposed to explain this are the following: (1) use of free boundary conditions instead of cyclic boundary conditions; (2) mechanical anharmonicity; and (3) electrical anharmonicity.

The effect on the lattice absorption spectrum of using free boundary conditions was pointed out by Rosenstock⁷ who showed that in first order the main dispersion line would be broadened and that subsidiary

dependent damping constants which are not, in general, directly related to the damping constant mentioned in the experimental analysis of the previous section. In classical treatments, Blackman¹³ and Neuberger¹⁵ found these damping constants to be linear functions of the temperature in the high-temperature limit where kT is much greater than $\hbar\omega_0$. On the other hand, in a quantum-mechanical treatment, Born and Huang¹² showed that the damping constants would vary as T^3 in this limit. This does not necessarily mean that the damping constant mentioned in the experimental analysis as a convenient parameter to describe the absorption should also vary in the same manner as it is defined differently. In fact, in a one-dimensional calculation of the absorption of a diatomic lattice along the lines indicated by Born and Huang, Maradudin and Wallis¹⁴ found that the absorption, or more exactly nk , near the line center would vary somewhat less than $1/T^3$, while on the wings far away from ω_0 the absorption would vary as T^3 . This is rough agreement with experiment where nk at the frequency ω_0 can be obtained in terms of γ/ω_0 from Eq. (4) giving

$$(nk)_{\omega_0} = (\epsilon_0 - \epsilon_\infty)/2(\gamma/\omega_0).$$

Since γ/ω_0 was found to vary approximately as T^2 , $(nk)_{\omega_0}$ will vary as $1/T^2$. It is interesting to note that a similar dependence was found for LiF by Heilmann.⁴ These experiments are subject to the limitation that kT can only be made four times as large as $\hbar\omega_0$ for NaCl and only two times as large for LiF due to proximity to the melting point.

The possibility that the structure might be at least partly associated with the presence of second-order electric moments was suggested by Lax and Burstein.¹⁶ Such an explanation is needed to account for lattice absorption in diamond-type crystals where no permanent moment exists. In addition, such terms may influence the absorption in polar crystals such as MgO, ZnS, and polar semiconductors where anharmonic effects are believed to be small from other considerations. At the present time it is not known whether these moments contribute to the absorption in the alkali halides where anharmonic effects are believed to be large.

In conclusion, it appears that the temperature dependence of the lattice absorption of sodium chloride presented here is consistent with that predicted for a model assuming anharmonic forces.

ACKNOWLEDGMENTS

The author benefitted greatly from discussions with R. F. Wallis, A. A. Maradudin, and E. Burstein under whose stimulation this work was initiated.

¹⁶ M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955).

TABLE I. Damping constant of NaCl as a function of temperature.

T	R_{\max} percent	γ/ω_0
300	89	0.04
460	81	0.075
640	70	0.135
820	57	0.21
985	52	0.26

maxima would appear. The intensity of such additional effects has not yet been calculated and it is not yet certain whether they will be observable.

It is generally believed that most of the features of the lattice absorption spectrum can be accounted for using a crystal potential with anharmonic terms. Various investigations¹²⁻¹⁵ of the effect of anharmonicity on the lattice vibration spectrum have been carried out. These indicate that additional structure and broadening of the main line will occur. Some estimates of the temperature dependence of the spectrum have been carried out. In these formulations the absorption can be expressed in terms of several frequency and temperature

¹² See reference 8, Chapter VII for discussion.

¹³ M. Born and M. Blackman, Z. Physik **82**, 551 (1933); M. Blackman, Z. Physik **86**, 421 (1933); Trans. Roy. Soc. (London) **A236**, 103 (1936); Barnes, Brattain, and Seitz, Phys. Rev. **48**, 582 (1935).

¹⁴ A. A. Maradudin and R. F. Wallis, Bull. Am. Phys. Soc. **4**, 143 (1959), and private communication.

¹⁵ J. Neuberger, ARCRC-TR-353, Physics Department, New York University, 1957 (unpublished).