

The low-lying quasi-phonon branch of the spectrum also plays an important role for the longitudinal nuclear relaxation time  $T_1$ . We calculate the direct relaxation rate,

$$1/T_1 \cong \frac{3\pi(6\pi^2)^{2/3}\hbar A^4 S^6 G^2}{2M a^2 (k_B \Theta)^4 (\hbar \gamma H_A)^2} (T/\Theta), \quad (4)$$

where  $A$  is the hyperfine coupling constant. In  $\text{MnF}_2$ , where  $A \cong 10^{-18}$  erg, a relaxation rate proportional to  $T$  has been observed<sup>3</sup> and agrees in order of magnitude with (4) when the parameters above are used. Thus the nuclear relaxation and magnetization data find a consistent explanation. The Raman relaxation rate has a  $T^7$  temperature dependence and agrees again with the observations<sup>2</sup> in  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  where  $G \cong 10^{-13}$  erg. The expression for the Raman relaxation rate is

$$1/T_1 \cong \frac{27\pi^3(6\pi^2)^{1/3} A^2 S^6 G^4}{16\hbar(\gamma H_A)^4 M^2 a^4 (k_B \Theta)^3} (T/\Theta)^7 P_6, \quad (5)$$

where  $A$  is the strength of the dipolar coupling and  $P_6$  is given by

$$P_6 = \int_0^{x_{\max}} \frac{x^6 e^x}{(e^x - 1)^2} dx; \quad x_{\max} = \hbar \nu k_{\max} / k_B T. \quad (6)$$

Thus by the use of the magnon-phonon interaction we are able to explain several experiments. We require, however, somewhat larger coupling constants than have been reported in more symmetrical crystals.

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## RELATION BETWEEN THERMAL CONDUCTIVITY DEFECT IN SODIUM CHLORIDE AND ACOUSTIC RELAXATION EFFECTS AT LOW TEMPERATURES

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Recently an anomalously large reduction in thermal conductivity at low temperatures has been measured<sup>1</sup> for NaCl single crystals grown by the Harshaw process. No such reduction occurs for crystals grown free from atmospheric contamination, and evidence is presented that the reduction in thermal conductivity is associated with an impurity ion in the crystal in which oxygen is one of the components. The thermal conductivity varies nearly as the square of the temperature from 1°K to 20°K. Evidence is presented that the mean free path satisfies an equation of the type

$$\lambda = (3.3 \times 10^{-5} \omega/V)^{-1} \text{ cm}, \quad (1)$$

where  $V$  is the average sound velocity in the De-

bye sense and  $\omega = 2\pi$  times the frequency of the phonon. Several mechanisms for this effect were considered but no conclusive evidence was found for any of them.

One possibility was that a relaxation process might be involved. Recently a mechanical relaxation effect has been measured at low temperatures which is associated with the same set of impurity ions, and it is the purpose of this note to show that these relaxations are in agreement with the loss in thermal conductivity.

The crystals were obtained from Harshaw and from Isomet and were provided with oriented, parallel, flat faces.  $X$ -cut and  $AC$ -cut quartz plates were bonded to the specimens with 4-methyl-1-pentene. The temperature was controlled by

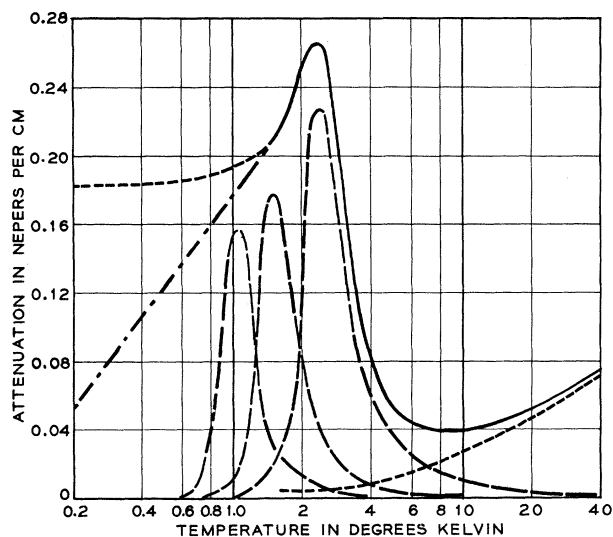


FIG. 1. Attenuation in Harshaw sodium chloride crystal for 57-Mc/sec shear wave along  $[110]$  with polarization direction  $[1\bar{1}0]$ . Short-dash line shows assumed background loss (due mostly to dislocations). Long-dash lines show three relaxation mechanisms.

means of a liquid helium bath and an electric heater, and was determined from vapor pressure and carbon resistor readings. The attenuation was measured with a pulse-echo method. The relative velocity was determined using pulse overlap and a phase-comparison technique.

Figure 1, shows the attenuation in nepers per cm along the  $[110]$  direction for a 57-Mc/sec shear wave with its polarization in the  $[1\bar{1}0]$  direction. A large increase is seen below 5°K. No such increase was found for Isomet crystals, which are grown in a vacuum, as contrasted with Harshaw crystals, which are grown in air. It is, therefore, concluded that the observed relaxation effect is caused by a gaseous impurity introduced from air into the melt.<sup>2</sup> Similar conclusions on thermal conductivity were found by

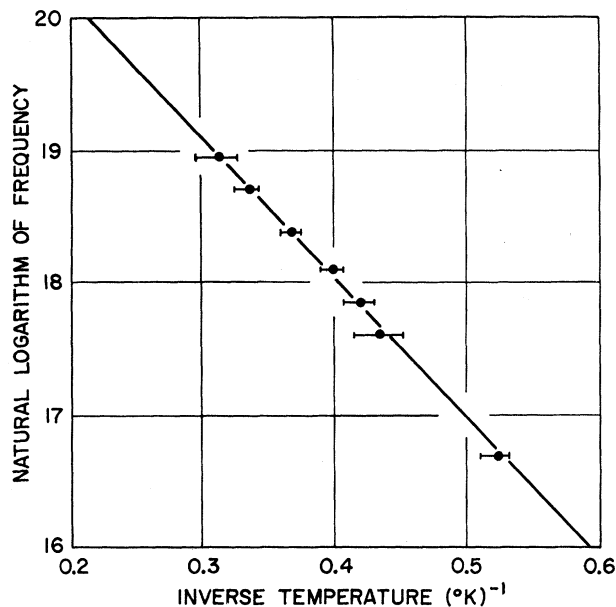


FIG. 2. Temperature shift of attenuation peak with frequency.  $\ln f = \ln f_0 - E/kT$ .

Klein.<sup>1</sup> Table I gives the number of  $\{110\}$  planes in which shear stresses are set up by the types of waves employed in this investigation and indicates the corresponding presence or absence of a peak. The correlation is excellent. Incidentally, the  $\{110\}$  planes are also the slip planes for dislocations. But in view of the small activation energy, a Bordoni relaxation effect can be discounted.

The temperature shift of the peak as a function of the frequency was measured over the range from 18 to 173 Mc/sec using shear waves polarized along  $[1\bar{1}0]$  and propagating along the  $[110]$  direction. The result, plotted in Fig. 2, satisfies the Arrhenius relation,

$$f = f_0 \exp(-E/RT), \quad (2)$$

which is typical of a relaxation process.  $f$  is the

Table I. Wave types, shear stress, and attenuation in Harshaw NaCl.

Wave mode	Direction of propagation	Direction of polarization	Number of $\{110\}$ planes with shear stress	Attenuation peak
Longitudinal	$[100]$	...	4	Yes
Transverse	$[100]$	in $(100)$	0	No
Longitudinal	$[110]$	...	4	Yes
Transverse	$[110]$	$[1\bar{1}0]$	6	Yes
Transverse	$[110]$	$[001]$	0	No

measuring frequency and  $T$  the peak temperature. The constants  $f_0$  and the activation energy  $E$  are graphically determined to be

$$f_0 = 5 \times 10^{9 \pm 0.2} \text{ cps}, \quad E = 21 \pm 2.3 \text{ cal/mole.} \quad (3)$$

For the same shear wave, the dispersion of the sound velocity was measured at 57 Mc/sec in a Harshaw crystal as a function of the temperature. The curve obtained is typical of a broad relaxation process (at 1.5°K the value of  $V/V_0$  is 0.9986, where  $V$  is the measured velocity and  $V_0$  is the velocity at the broad flat maximum which stretches from 15 to 25°K).<sup>3</sup>

A similar attenuation curve was found for KCl at 56 Mc/sec with one maximum occurring at 5°K and a rise occurring down to 1.5°K. Unfortunately no thermal conductivity data are available for this crystal. The attenuation peaks of both crystals show some evidence of a fine structure and the width of the peaks and of the dispersion region indicate the existence of a distribution of activation energies, rather than a single one. As shown by the highest temperature long-dash relaxation curve of Fig. 1, a single relaxation agrees with the measurement above the peak temperature if we assume a background loss—mostly due to dislocations—as shown by the short-dashed line. However, at low temperatures, the indicated attenuation requires a distribution of relaxation frequencies. While the distribution may be a continuous one, a good approximation for a slowly varying attenuation is obtained by a series of relaxation energies which vary by a small ratio or increment.<sup>4</sup> The attempt frequency of  $5 \times 10^9$  cps indicates a low probability of occurrence for the effect. A relation of the form

$$f_i = 10^{12} e^{(\Delta S_i/R)} e^{-H_i/RT} \quad (4)$$

is assumed for the relaxation frequency of each process. The value of  $10^{12}$  cps is a commonly observed value for relaxation processes. For the highest energy value,  $\Delta S$  has to be negative and equal to 10.6 cal/mole. The lower the activation energy  $H_i$ , the lower the disorder so that  $\Delta S_i$  is assumed proportional to  $H_i$ . Then Eq. (4) becomes

$$f_i = 10^{12} e^{-0.252H_i} e^{-H_i/RT} \quad (5)$$

The internal friction of a series of relaxation processes, and the shear modulus change associated with them, can be written in the form

$$Q^{-1} = \sum \frac{A_i (f/f_i)}{1 + (f/f_i)^2}; \quad \frac{\Delta\mu}{\mu} = \sum \frac{A_i}{1 + (f/f_i)^2}, \quad (6)$$

where  $A_i$  is a series of constants required to fit the shape of the attenuation curve which is related to the internal friction curve by the equation

$$\alpha = \frac{Q^{-1}\omega}{2V} = \frac{\pi f}{V} \sum \frac{A_i (f/f_i)}{1 + (f/f_i)^2}. \quad (7)$$

By assuming activation energy values varying by ratios of 1.23,<sup>4</sup> a series of constants  $A_i$  were obtained for fitting the attenuation curve of Fig. 1 above 0.1°K. These constants were tested on the available data up to higher frequencies and reproduced the measured data with good precision. The three top relaxation mechanisms are shown by the long-dash curves of Fig. 1.

Thermal conduction occurs by means of quantized longitudinal and shear waves in the crystal of much higher frequency and these can interact with the relaxation mechanisms found by the ultrasonic measurements. Since these phonons come from all directions, on the average they will have a much smaller component of shearing strain in the {110} planes than do the waves whose attenuation is shown by Fig. 1. A calculation indicates that the factor is  $\frac{1}{3}$  for shear phonons which carry most of the energy. While a complete calculation would require an integration of the distribution of frequencies occurring at each temperature, a fairly good indication is obtained by taking the dominant frequency of the distribution given by

$$hf \doteq kT \text{ or } f \doteq 2 \times 10^{10} T, \quad (8)$$

where  $h$  is Planck's constant and  $k$  is Boltzmann's constant. Hence, one can calculate the average distance required to cause the phonon intensity to be reduced to  $1/e$  of its original value—which is one definition of the mean free path—by calculating from Eq. (7) the distance required to produce an attenuation of one neper at the frequency corresponding to the temperature  $T$  in Eq. (9). Using the measured values of  $\alpha_i$  shown by the short-dashed curve of Fig. 1, and multiplying by the directivity factor  $\frac{1}{3}$ , the mean free path is shown by the solid line labelled 1 of Fig. 3. The shape of the attenuation curve at low temperatures is not very critical and the solid line of Fig. 3 labelled 2 indicates the result of a calculation for an attenuation which goes from zero at 0.1°K to the measured value at 1.4°K along the dot-dash line of Fig. 1. Either curve gives good agreement with the thermally measured value shown by the dashed line of Fig. 3, since there is no assurance that the same number of impurities occurs in each sample. The slope of the solid lines varies nearly

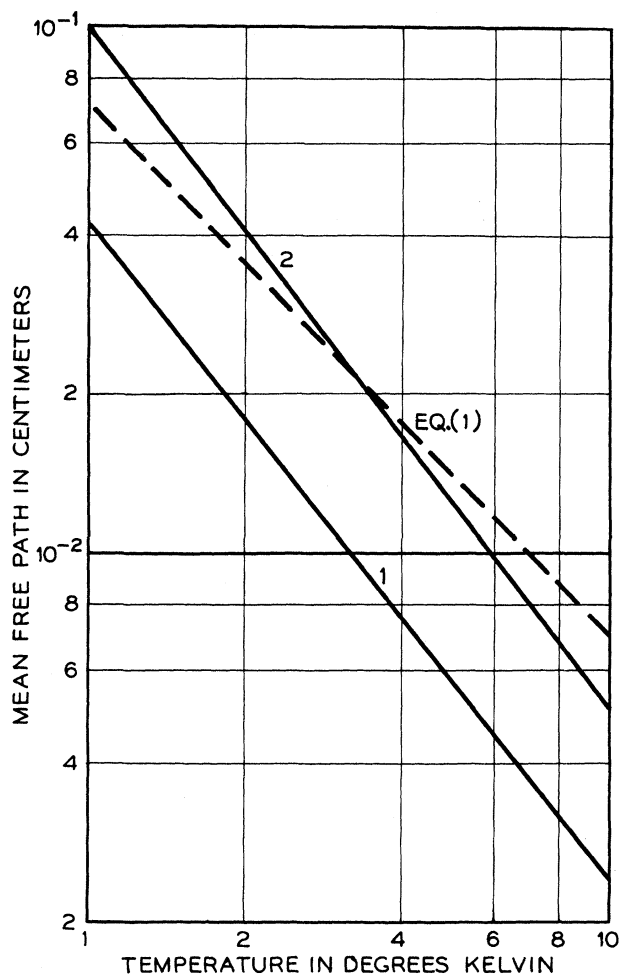


FIG. 3. Mean free path of thermal phonons. Solid line 1 calculated from dashed attenuation curve in Fig. 1. Solid line 2 calculated from dot-dash curve in Fig. 1. Dashed line represents Eq. (1).

as  $T^{-1.25}$  which is actually in better agreement with the measurements<sup>1</sup> than the assumed slope of  $T^{-1}$ .

Thermal resistance caused by a relaxation effect appears to be a new process not covered by any of the ordinary mechanisms.<sup>5</sup> It appears that the change in the equilibrium states associated with the acoustic relaxation effect, produces considerable attenuation for thermal waves and a corresponding short mean free path. Since the cross section of the scattering mechanism can be obtained from the mean free path and the density of scatterers,<sup>1</sup> it appears that the scattering cross section for relaxation processes of this type is much larger than the size of the impurity. The very low activation energy range suggests a spectrum of normal modes of low-energy separation such as might occur for a tunneling process.

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<sup>3</sup>In Isomet crystals the sound velocity below 25°K is constant to within 1 part in 10<sup>5</sup>.

<sup>4</sup>See Warren P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Company, Princeton, New Jersey, 1958), Chap. X, p. 300.

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