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Low-temperature ultrasonic relaxation and resonance in RbCl:OH

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The ultrasonic attenuation and velocity in RbCl crystals containing OH^- ions was measured as a function of polarization, temperature, frequency, and OH^--ion concentration. A relaxation peak and velocity dispersion was observed near 6 K for 10-MHz C_{11}- and C'-mode waves [with $C' \equiv (C_{11} - C_{12})/2$]. Below the relaxation peak temperature an anomalous attenuation increase and velocity decrease was observed and interpreted as a resonance phenomenon.

I. INTRODUCTION

Hydroxyl ions in alkali halide crystals are known as tunneling systems and are attracting continuous interest because their low-temperature behavior can be similar to that of glasses. Many investigations of tunneling systems in the alkali halide crystals have been reported.[1] Among a variety of available experimental techniques, ultrasonic measurements are one of the most suitable methods for the study of the dynamical response of the system. The ultrasonic method has been successfully applied to glassy materials,[2] and two kinds of phenomena, namely, resonance and relaxation interaction of the sound with two-level systems (TLS) have been observed. However, there still remains questions about the microscopic origin of the TLS in glasses. Substitutional OH^- ions in alkali halide crystals are rather well-defined systems and could be a model for the study of the fundamental properties of tunneling systems. Some ultrasonic studies on alkali halides containing OH^- ions have been reported[3-6] but they are mainly concerned with elastic constant changes (diaelastic effect) and attempts to separate resonance effects from relaxation effects were not made.

The purpose of the present paper is to study the interactions between the OH^- ions and MHz sound systematically be means of ultrasonic attenuation and velocity measurements. Rubidium chloride crystals containing OH^- ions are chosen as the specimen material for the present study for the following reasons. First, the relaxation time observed by electric-field-induced optical dichroism measurements[7] is close to the frequency of MHz sound, and a relaxation peak in the decrement has been observed in preliminary studies.[8] Second, the reported tunnel splitting energy Δ is rather small ($\sim$7 mK) (Refs. 9 and 10) and resonance absorption may be possible. Thus effects due to both resonance and relaxation are expected simultaneously.

II. EXPERIMENTAL METHOD

Single-crystal boules of RbCl containing OH^- ions were grown by F. E. Rosenberger at the University of Utah. The crystals were cut into cubes larger than 1 cm^3 with [100] and [110] faces. The crystal orientation was adjusted within an accuracy of $\frac{1}{10}$ degree by an x-ray method, and the faces were polished parallel and flat by using an α-alumina powder (1.0 μm). The concentration of OH^- ions in the specimens was determined by ultraviolet absorption using a Cary 14 spectrophotometer.

For the generation and the detection of the ultrasound, a 10-MHz quartz transducer was used. The difference of thermal contractions between RbCl and quartz is very large, namely, the linear contractions in RbCl and in quartz for cooling from 300 to 4.2 K are 0.77% and 0.2%, respectively. To avoid bonding damage, the transducer was bonded on a specimen surface using natural gas, which freezes around 65 K. Simultaneous measurements of velocity and attenuation were made using a pulse superposition method.[11,12] In this method, the fractional change of the elastic constant C or sound velocity v is related to the frequency of the synthesizer, f, as

$$\frac{\Delta C}{C} = \frac{2\,\Delta v}{v} - \frac{3\,\Delta l}{l} = \frac{2\,\Delta f}{f} - \frac{\Delta l}{l} \tag{1}$$

where $\Delta l/l$ corresponds to the change of the specimen length. The accuracy of the velocity change measurement was better than 10^{-6}. The ultrasonic attenuation α was determined from the ratio of the pulse heights of two selected echoes. The loss angle (δ/π), where δ is the decrement, can be related to the attenuation as

$$\frac{\delta}{\pi} = \frac{\alpha(\mathrm{dB}/\mu\mathrm{sec})}{8.686 f(\mathrm{MHz})} . \tag{2}$$

A ^{3}He pumping cryostat was used for cooling the specimen down to 0.6 K. Germanium and platinum resistance thermometers were used for both temperature measurement and control. Two carbon resistor thermometers were also placed on the top and the bottom of the specimen to monitor the temperature gradient in the specimen.

III. EXPERIMENTAL RESULTS

A. C_{11} measurements

A longitudinal wave propagating along $\langle 100 \rangle$ directions is characterized by the elastic constant C_{11}. The temperature dependence of the decrement and velocity change for the C_{11} wave in a sample containing 15-ppm OH^- ions is shown in Fig. 1. A constant background

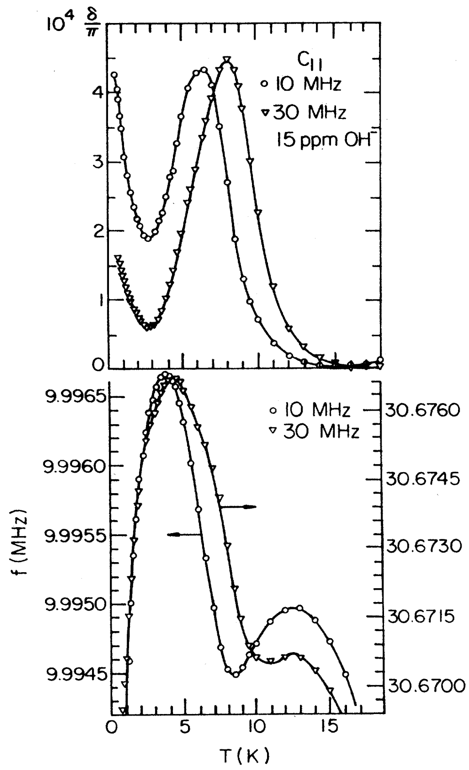

FIG. 1. C_{11} mode loss angle and velocity changes for a 15-ppm speciemn at 10 and 30 MHz.

was subtracted from the data. It is seen that the absorption has a peak near 6.5 K at 10 MHz and near 8 K at 30 MHz and the velocities show dispersions at these temperatures. The frequency dependence of the peak temperature and the velocity dispersion clearly shows features of relaxation phenomena. However, contrary to a simple relaxation, the attenuation increases with decreasing temperature below 3 K and the velocity decreases with decreasing temperature below ~4 K. The decrease of the velocity above 16 K can be attributed to the temperature dependence of the elastic constant of the host crystal.[13]

Figure 2 shows the results for a specimen with 57 ppm OH^- ions. The qualitative features are similar to those for the 15-ppm specimen, but the low-temperature increase of the attenuation is more pronounced. It is to be noted that the absolute values of the high-temperature decrease of the velocities do not change with defect concentration, but the low-temperature behavior is steeper. The data for the 57-ppm OH^- specimen are replotted against $1/T$ in Fig. 3. It can be seen that both the increase of the decrement and the decrease of the velocity at lower temperatures is approximately linear in $1/T$.

The 10-MHz results for specimens containing 3.7 and 1.5-ppm OH^- ions are shown in Fig. 4. The relaxation absorption peaks, which are now smaller as expected for lower OH^- concentration, occur near 7 K. The corresponding velocity dispersions are seen as small depressions in the neighborhood of 8 K. The high-temperature velocity drop begins at lower temperatures than for the 15- and 57-ppm specimens because the relaxation velocity changes are diminished. The low-temperature velocity decrease is also present but the corresponding increase in absorption does not appear. The lack of a low-temperature absorption seems to be associated with the trapping of the OH^- ions by Ca^{2+} impurities. Fritz *et al.*[14] have reported that Ca^{2+} impurities have a strong

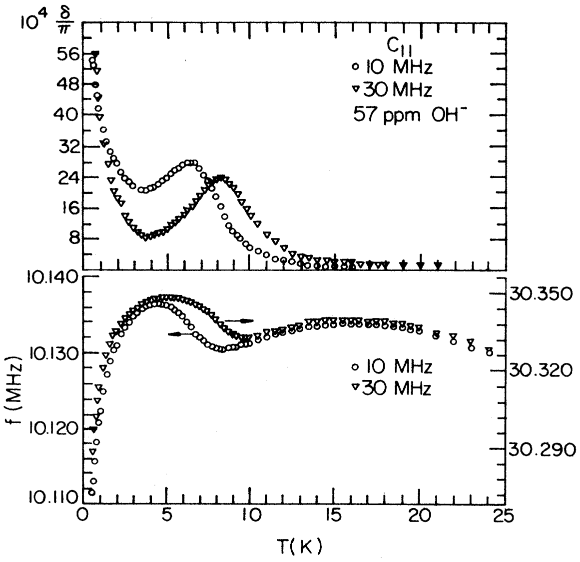

FIG. 2. C_{11} mode loss angle and velocity change for a 57-ppm specimen at 10 and 30 MHz.

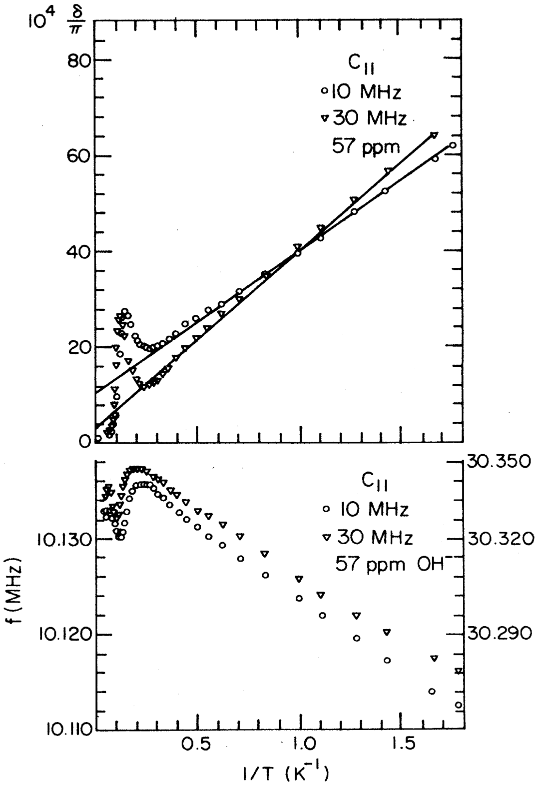

FIG. 3. C_{11} mode loss angle and velocity changes for a 57-ppm specimen at 10 and 30 MHz vs inverse temperature.

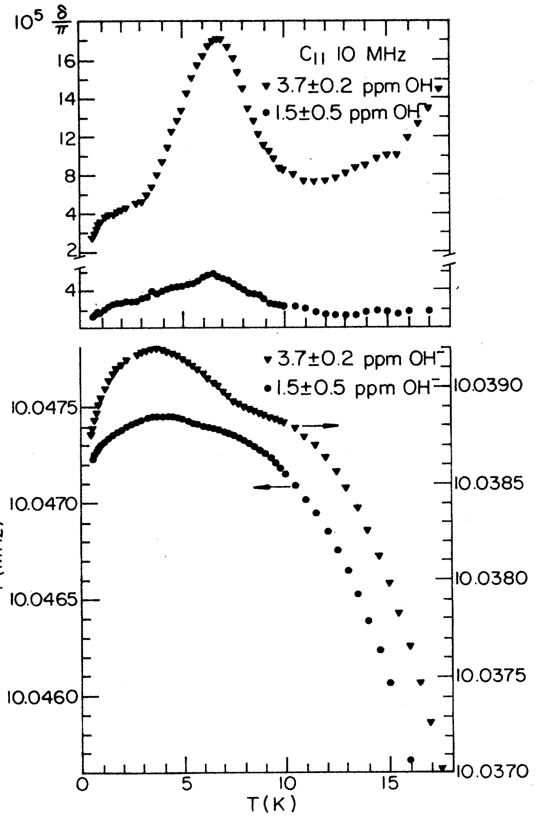

FIG. 4. C_{11} mode loss angle and velocity changes for a 1.5- and a 3.7-ppm specimen at 10 MHz.

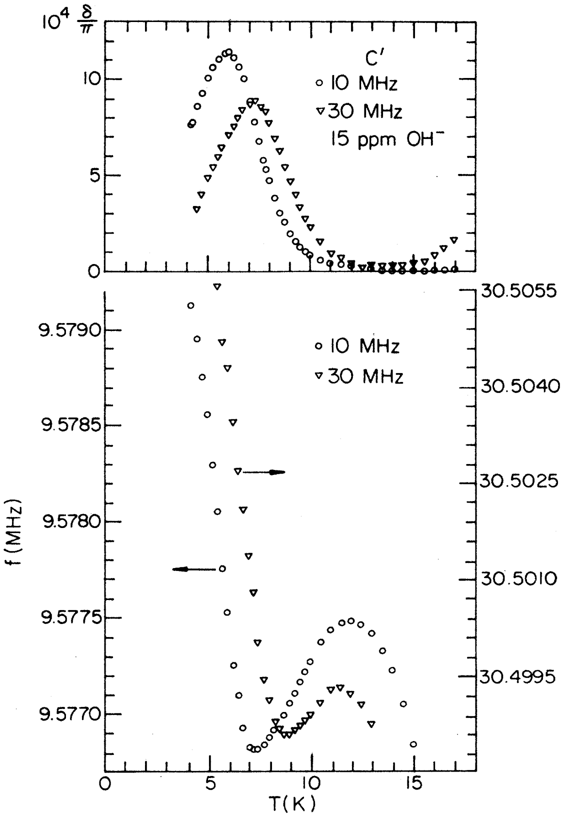

FIG. 5. C' mode loss angle and velocity changes for a 15-ppm specimen at 10 and 30 Mhz.

affinity toward OH⁻ ions to form reaction products. By using an optical-absorption analysis, 3.0±0.5 ppm of Ca^{2+} was detected in the present specimen. Therefore, an appreciable fraction of the OH⁻ ions may be tied up with the Ca^{2+} ions in low-concentration specimens.

B. C' measurements

Transverse waves propagating along ⟨110⟩ directions with the polarization vector along $\langle 1\bar{1}0 \rangle$ directions measure the elastic constant $C' \equiv (C_{11}-C_{12})/2$. According to group theoretical considerations, both the C_{11} and C' modes belong to the same irreducible representation under O_h point-group symmetry, i.e., they yield the same symmetry information about the defect system.

The C' measurements were made using a cryostat that could not be cooled below 4.2 K and no low-temperature data were obtained below this temperature. The results for the 15-ppm OH⁻ specimens are shown in Fig. 5. A relaxation peak similar to that found for the C_{11}-mode measurement is seen, but the magnitude of the peak is about twice as large as that for the C_{11} mode and the peak temperature is shifted by about $\frac{3}{4}$ degree to a lower temperature.

C. C_{44} measurement

The existence of C_{11} and C' relaxation peaks only rule out the possibility of ⟨111⟩ type defects, but leaves open the possibility of ⟨100⟩ or ⟨110⟩ type defects. To distinguish between the two possibilities, a C_{44} measurement is required. It can be realized by measuring a transverse wave propagating along ⟨100⟩ directions with polarization in any direction perpendicular to the propagation direction.

The results for the C_{44} mode for the 15-ppm OH⁻ specimen are shown in Fig. 6. Neither the relaxation absorption nor the velocity dispersion that occurred in the C_{11} and C' modes was observed. This shows that OH⁻ ions in RbCl are ⟨100⟩ defects in agreement with the result by Kapphan and Lüty.[15] However, there was a gradual increase in attenuation and a decrease in velocity as the temperature was decreased.

D. Amplitude dependence

The observed increase of the decrement in the C_{11} and C' measurements below the relaxation peak ($T<3$ K) cannot be explained as a part of the relaxation. From the standard Debye relaxation formula, the ratio of the decrement and the fractional velocity change $\Delta v/v$ is proportional to the relaxation time τ_1. In the present case, both decrement and velocity changes are proportional to $1/T$ (see Fig. 3), so that τ_1 would be independent of temperature. A temperature-independent relaxation time[16] can be expected when the tunnel splitting is greater than 3 K, but the reported tunnel splitting ($\sim$7 mK) (Refs. 9

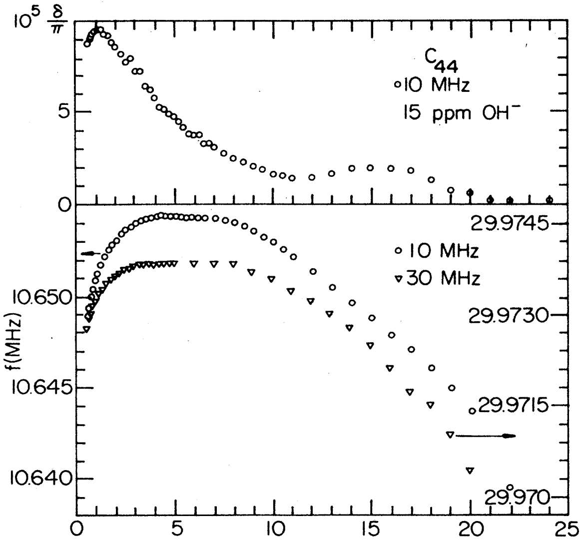

FIG. 6. C_{44} loss angle at 10 MHz and velocity changes at 10 and 30 MHz for a 15-ppm specimen.

and 10) is too small for this. As a different possibility we may consider the decrement increase to correspond to the high-temperature tail of another relaxation peak, in which case the phenomena should shift to higher temperatures for higher frequency measurements. However, the experimental results do not show this shift (see Figs. 1 and 2). Therefore, the low-temperature increase of the decrement is not likely to be a relaxation phenomena, and as a next step we proceed to examine the possibility of a resonance process. One of the characteristic features of a resonance process is a saturation of attenuation at high levels of input power.[2,17,18]

Measurements of the amplitude dependence of the attenuation were attempted at 10 MHz for a RbCl crystal containing 12-ppm OH⁻ ions. The temperature of the specimen was measured at the upper and lower surfaces to correct for the heating effect caused by the ultrasonic power. An effective temperature $T_{\rm eff}$ defined by

$$\frac{1}{T_{\rm eff}}=\frac{1}{T_2-T_1}\int_{T_1}^{T_2}\frac{dT}{T} \qquad (3)$$

was used after considering the inverse temperature dependence. In Eq. (3), T_1 and T_2 are, respectively, the temperatures measured at the top and the bottom of the specimen. The largest temperature difference (T_1-T_2) in the measurements was about 0.1 K.

No evidence for an amplitude dependence was found for an increase in power level of 10 dB, but for a 20 dB increase, a small decrease in decrement was observed below 1 K, of the order of 10% at 0.65 K. While this provides some evidence for a resonance, it is not strong enough by itself to establish resonance as the source of the low-temperature attenuation. We proceed, therefore, to examine other aspects of the low-temperature loss.

E. Frequency dependence of the low-temperature absorption

The results shown in Fig. 3 suggest that the low-temperature absorption or loss angle may be expressed as

$$\delta/\pi=\Delta^0_{da}(n_0,\omega)/T+A(n_0,\omega)\ , \qquad (4)$$

where A and Δ^0_{da} are functions of the angular sound frequency ω and OH⁻-ion concentration n_0. An attempt was made to obtain the frequency dependence of the low-temperature decrement over a wider frequency range.

Since the attenuation increases with concentration and frequency, a high concentration specimen would generate an attenuation at high frequencies too high for accurate measurements. Therefore a 9-ppm specimen was chosen for the purpose.

The C_{11} decrement as a function of inverse temperature is shown in Fig. 7. The decrement values at 16 K have been subtracted as an assumed constant background, to provide a direct comparison. The results were fitted to Eq. (4) and the two constants A and Δ^0_{da} were determined. The results for different concentrations already shown in Figs. 1 and 2 were fitted in the same way. The values of A and Δ^0_{da} are summarized in Table I. The values Δ^0_{da} decrease as the frequency increases for the 9- and the 15-ppm specimens, whereas they increase with frequency for the 57-ppm specimen. If the frequency (f) dependence of $\Delta^0_{da}(n_0,\omega)$ is expressed as

$$\Delta^0_{da}(n_0,\omega)=k(n_0)f^n \qquad (5)$$

then the values n determined from the data in Table I for the three specimens are −0.42 (9 ppm), −0.47 (15 ppm), and + 0.36 (57 ppm). The negative values for the inter-

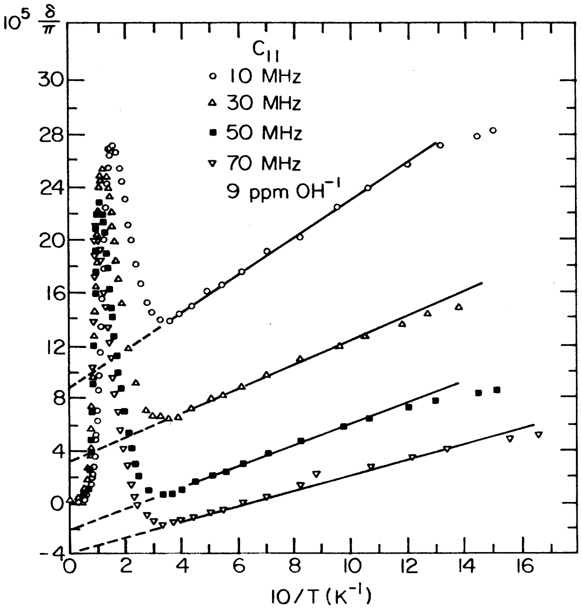

FIG. 7. Frequency dependence of the C_{11} mode absorption vs inverse temperature for a 9-ppm specimen.

TABLE I. Values of the intercepts and slope of the low-temperature absorption in an inverse temperature plot.

	$A(n_0,\omega)$	$\Delta^0_{da}(n_0,\omega)$ (K^{-1})
9 ppm		
10 MHz	$(8.3\pm0.4)\times10^{-5}$	$(1.40\pm0.2)\times10^{-4}$
30 MHz	$(3.2\pm0.2)\times10^{-5}$	$(9.0\pm0.3)\times10^{-5}$
50 MHz	$(-2.2\pm0.1)\times10^{-5}$	$(7.9\pm0.3)\times10^{-5}$
70 MHz	$(-4.0\pm0.2)\times10^{-5}$	$(5.9\pm0.2)\times10^{-5}$
15 ppm		
10.0 MHz	$(7.7\pm0.5)\times10^{-5}$	$(2.34\pm0.2)\times10^{-4}$
30.7 MHz	$(1.6\pm0.15)\times10^{-5}$	$(1.38\pm0.2)\times10^{-4}$
57 ppm		
10.1 MHz	$(9.2\pm0.4)\times10^{-4}$	$(2.68\pm0.3)\times10^{-3}$
30.3 HMz	$(3.1\pm0.3)\times10^{-4}$	$(3.96\pm0.4)\times10^{-3}$

cept $A(n_0,\omega)$ at 50 and 70 MHz for the 9-ppm specimen are unphysical. These results may be due to improper choices of the background.

If the low-temperature increase was the high-temperature side of a lower temperature relaxation peak, then one would expect $n=1$.

IV. ANALYSIS AND DISCUSSION

A. Theoretical basis—resonance and relaxation

The ultrasonic response of RbCl:OH at the lowest temperatures (<4 K) cannot be explained as a relaxation process. On the other hand, the experimental results suggest that the qualitative features of the mechanical response has a close similarity to that of tunneling systems such as the TLS in glass, substitutional impurities in alkali halides, and trapped hydrogen in niobium.[19] It is known that the elastic constant of alkali halide crystals containing tunneling impurities decreases at low temperatures. The effect is due to the change of the energy of the quantum state produced by the measuring sound wave strain, namely, the polarization or elastic dipole moment changes adiabatically following the external strain without dipole reorientation. It can be characterized as a diaelastic effect and corresponds to the low-frequency limit of a resonance interaction. The observed velocity change at lower temperature, which is seen to be proportional to $1/T$ in Fig. 7 for the 9-ppm specimen, seems to be this diaelastic effect.

Another mechanism of interaction between the sound wave and the tunneling system is the relaxation process. When the energy of the quantum states changes in response to an external strain, the population of the dipoles at each energy level changes toward a new thermal equilibrium distribution through phonon induced transitions. The relaxation effect accompanies the absorption and emission of the thermal phonons, and the characteristic time required for the system to attain a new equilibrium is called the relaxation time τ_1.

Both the resonance and the relaxation processes can be treated analytically for the two-level tunneling model. The eigenenergy for the system under static (internal) starting ε can be expressed as

$$E_{\pm}=\pm[\Delta^2+(\alpha\varepsilon)^2]^{1/2}\ . \tag{6}$$

Here, Δ is the tunneling energy and α is a coupling constant between the dipole and strain. The elastic dipole tensor $\delta\lambda$ ($=\lambda_1-\lambda_2$) is related to α by $v_0\,\delta\lambda=\alpha/c$, where v_0 is a volume occupied by one dipole and c is an elastic constant. The fractional change of the elastic constant for the resonance and relaxation process can be expressed as

$$\begin{aligned}\left[\frac{\Delta c}{c}\right]_{\mathrm{res}} &= -\frac{n_0\alpha^2}{c}\frac{\Delta^2}{\Delta^2+(\alpha\varepsilon)^2}\tanh\left[\frac{[\Delta^2+(\alpha\varepsilon)^2]^{1/2}}{kT}\right]\\ &\quad\times\frac{1}{\hbar}\left[\frac{(\omega_0-\omega)\tau_2^2}{1+(\omega_0-\omega)^2\tau_2^2}+\frac{(\omega_0+\omega)\tau_2^2}{1+(\omega_0+\omega)^2\tau_2^2}\right],\\ \left[\frac{\Delta c}{c}\right]_{\mathrm{rel}} &= -\frac{n_0\alpha^2}{c}\frac{(\alpha\varepsilon)^2}{\Delta^2+(\alpha\varepsilon)^2}\frac{1}{kT}\\ &\quad\times\mathrm{sech}^2\left[\frac{[\Delta^2+(\alpha\varepsilon)^2]^{1/2}}{kT}\right]\frac{1}{1+(\omega\tau_1)^2}\ .\end{aligned} \tag{7}$$

Here, n_0 is the number of dipoles in unit concentration, $\omega_0=2[\Delta^2+(\alpha\varepsilon)^2]^{1/2}$ is the resonance frequency, τ_2 is the lifetime for the resonance process, and τ_1 is the relaxation time. The loss angle can be obtained from the imaginary part of the elastic constant as

$$\begin{aligned}\left[\frac{\delta}{\pi}\right]_{\mathrm{res}} &= \frac{n_0\alpha^2}{c}\frac{\Delta^2}{\Delta^2+(\alpha\varepsilon)^2}\tanh\left[\frac{[\Delta^2+(\alpha\varepsilon)^2]^{1/2}}{kT}\right]\\ &\quad\times\frac{1}{\hbar}\left[\frac{\tau_2}{1+(\omega_0-\omega)^2\tau_2^2}-\frac{\tau_2}{1+(\omega_0+\omega)^2\tau_2^2}\right],\\ \left[\frac{\delta}{\pi}\right]_{\mathrm{rel}} &= \frac{n_0\alpha^2}{c}\frac{(\alpha\varepsilon)^2}{\Delta^2+(\alpha\varepsilon)^2}\frac{1}{kT}\\ &\quad\times\mathrm{sech}^2\left[\frac{[\Delta^2+(\alpha\varepsilon)^2]^{1/2}}{kT}\right]\frac{\omega\tau_1}{1+(\omega\tau_1)^2}\ .\end{aligned} \tag{8}$$

Equations (7) and (8) have been obtained by using simple time-dependent perturbation theories, which was also applied extensively to a six-level system, and the details of the calculation are given in a separate paper. The form of Eqs. (7) and (8) was first given by Jäckle.[18] It was also derived by Jäckle *et al.*[20] by analogy with the dynamics for a spin-$\frac{1}{2}$ system. Also Pirc and Gosar[21] treated the same problem using a Green's-function method. The form given above showing the explicit strain dependence is useful for analysis of ultrasonic measurements and was given earlier for $\omega\ll\omega_0$ by Granato, Hultman, and Huang.[22]

If the conditions $[\Delta^2+(\alpha\varepsilon)^2]^{1/2}\ll kT$, $\hbar\omega\ll[\Delta^2+(\alpha\varepsilon)^2]^{1/2}$, and $\omega_0\tau_2\gg1$ are satisfied, the elastic constant change is described by

$$\begin{aligned}\frac{\Delta c}{c} &= -\frac{n_0\alpha^2}{c}\frac{\Delta^2}{\Delta^2+(\alpha\varepsilon)^2}\frac{1}{kT} \\ &\quad -\frac{n_0\alpha^2}{c}\frac{(\alpha\varepsilon)^2}{\Delta^2+(\alpha\varepsilon)^2}\frac{1}{kT}\frac{1}{1+(\omega\tau_1)^2} \\ &\equiv -\frac{\Delta_d^0}{T}-\frac{\Delta_p^0}{T}\frac{1}{1+(\omega\tau_1)^2}\ . \end{aligned} \tag{9}$$

Here, Δ_d^0 and Δ_p^0 are the normalized resonance modulus strength and the normalized relaxation strength, respectively. These conditions are expected for low-concentration RbCl:OH systems under the present experimental conditions of $T>0.6$ K and $f=10-30$ MHz, because the reported tunnel splitting is about 7 mk and the stress interaction energy $\alpha\varepsilon$ is expected to be the same order of magnitude as Δ. It can be seen from Eq. (9) that the sum of Δ_d^0 and Δ_p^0 is constant for $\omega_0\tau_2 \gg 1$ and Δ_p^0 increases with the strain ε. The temperature dependence of the resonance decrement turns out to be proportional to $1/T$ from Eq. (8) under the same experimental conditions, in accord with the experimental results for the lower-temperature decrement given by Eq. (4).

B. Ultrasonic attenuation

As shown in Sec. III, the low-temperature increase of the attenuation has a $1/T$ temperature dependence and depends on the internal strain or defect concentration. This result strongly suggests the phenomena are due to a resonant interaction between the OH defects and the sound wave. We proceed then to analyze the data by assuming the measured loss angle consists of two components, resonance and relaxation processes,

$$\left[\frac{\delta}{\pi}\right]_{\text{mea}}=\left[\frac{\delta}{\pi}\right]_{\text{res}}+\left[\frac{\delta}{\pi}\right]_{\text{rel}}\ . \tag{10}$$

The measured low-temperature decrement is expressed by a temperature-independent term $A(n_0,\omega)$ and a term inversely proportional to temperature T [Eq. (4)]. The above discussion suggests that these two terms correspond to the relaxation and resonance decrement, respectively. The temperature-independent relaxation decrement can be understood as follows. Under the condition of $kT \gg [\Delta^2+(\alpha\varepsilon)^2]^{1/2}$, the loss angle due to the relaxation process can be written from Eqs. (8) and (10):

$$\left[\frac{\delta}{\pi}\right]_{\text{rel}}=\frac{\Delta_p^0}{T}\frac{(\omega\tau_1)}{1+(\omega\tau_1)^2}\ . \tag{11}$$

At temperatures far below from the relaxation peak, $\omega\tau_1$ is much larger than unity and the loss angle can be expressed as $(\delta/\pi)_{\text{rel}} \simeq \Delta_p^0/\omega\tau_1 T$. The relaxation rate τ_1^{-1} of the tunneling system is determined by a one-phonon process at low temperatures and is proportional to temperature as will be discussed later. Then the loss angle $(\delta/\pi)_{\text{rel}}$ turns out to be independent of temperature and inversely proportional to the sound frequency. The experimentally determined $A(n_0,\omega)$ values, which correspond to $(\delta/\pi)_{\text{rel}}$, have been given in Table I. It is seen that the $A(n_0,\omega)$ values for 10 and 30 MHz approximately satisfy the expected frequency dependence. As already mentioned, the negative $A(n_0,\omega)$ values for higher frequencies (50- and 70-MHz data on 9-ppm specimen) are unreasonable, and are probably due to an overestimation of the background. In the measurement on a very low OH^--concentration specimen (1.5 ppm), a strong increase of the attenuation above 12 K was observed which we suppose is due to dislocations. As the concentration of the OH^- defects is increased, the dislocations are pinned down by the defects and this effect is suppressed. It is noted that the inverse frequency dependence expected of $A(n_0,\omega)$ is well satisfied in the 57-ppm specimen.

On the basis of the above discussion, the attenuation data can be decomposed into resonance and relaxation parts as shown schematically in Fig. 8. The relaxation part is expressed by Eq. (11), but the temperature dependence of the relaxation time τ_1 is not known. For the numerical analysis for the relaxation time, the resonance part has to be subtracted from the decrement data. In the theory of magnetic spin resonance, τ_2 is characterized as the transverse relaxation time due to the direct spin-spin interactions. In the present case, the lifetime of the tunneling system for low concentrations should be determined by interactions with the thermal phonons and related to the relaxation time τ_1 as $\tau_2=2\tau_1$.[21] Then the condition $\omega\tau_2 \gg 1$ is satisfied for low concentrations at temperatures well below the relaxation peak, and we approximate the resonance absorption as

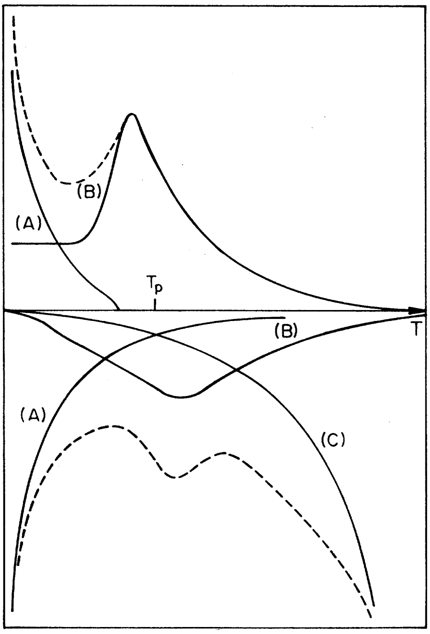

FIG. 8. Schematic decomposition of the different contributions to the measured absorption and velocity changes. Curve *A* and *B* in the upper diagram represent, respectively, the resonance and relaxation absorption effects. Curve *A*, *B*, and *C* in the lower diagram represent, respectively, the resonance, relaxation, and lattice modulus effects.

$$\left[\frac{\delta}{\pi}\right]_{\text{res}} = \begin{cases} \Delta_{da}^0/T, & T \le T_p - 2\text{ K} \\ 0, & T > (T_p - 2\text{ K}) \end{cases} . \qquad (12)$$

Here, T_p is the peak temperature and the values for Δ_d^0 are already given in Table I. The cutoff temperature $(T_p - 2\text{ K})$ is rather arbitrary but the results of the analysis are not very sensitive to the choice made for the cutoff temperature.

Figure 9 shows the derived relaxation decrement obtained by subtracting the resonance part from the measured decrement $(\delta/\pi)_{\text{mea}}$. The results were fitted to Eq. (11) and the temperature dependence of the relaxation time was determined as shown in Fig. 10, and derived values for Δ_p^0 are summarized in Table II. There are three noteworthy features in the derived τ_1. First, τ_1 shows no apparent frequency dependence over the entire temperature range. Second, τ_1 is inversely proportional to temperature below 3 K. This is consistent with the theoretical prediction for relaxation by a one-phonon assisted tunneling process.[16,23] Third, τ_1 follows a much stronger temperature dependence above 4 K, roughly being T^{-4} in the 4 to 10 K range and T^{-5} in the 10 to 15 K range. The switchover from T^{-1} to T^{-4} s especially obvious. The temperature dependence of τ_1 can be expressed as

$$\tau_1 = \begin{cases} 6.63\times10^{-7}/T^{(1\pm0.1)} & \text{for } T < 3\text{ K} \\ 1.86\times10^{-5}/T^{(4\pm0.1)} & \text{for } 4\text{ K} \le T \le 10\text{ K}. \end{cases}$$

The first two results strongly support the assumption we adopted for the analyses: the decomposition of the decrement into two parts and the $1/T$ relaxation strength. A T^{-4} dependence of τ_1 for OH^- ions in alkali halide was predicted by Dick *et al.*[24] and a numerical calculation by Sander and Shore also showed a similar (T^{-5}) temperature dependence.[25] The stronger temperature dependence at the high-temperature region can be attributed to the multiphonon processes. Sander and Shore interpret

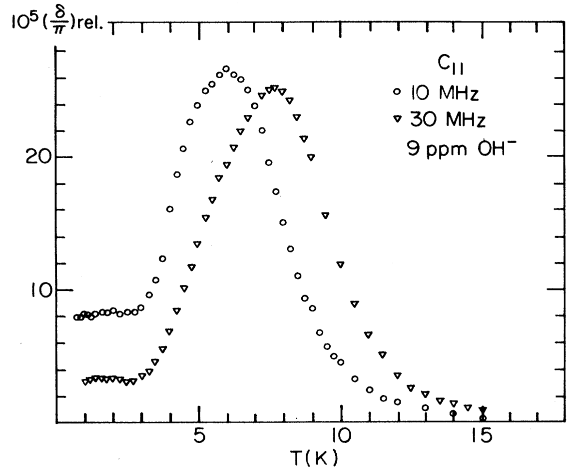

FIG. 9. Derived 10- and 30-MHz C_{11} mode relaxation absorption for a 9-ppm specimen vs temperature. The low-temperature resonance attenuation has been subtracted from the total attenuation.

TABLE II. Results derived from experimental data.

OH^- conc.	Δ_d^0 (K)	Δ_p^0 (K) (velocity)	Δ_p^0 (K) (absorption)	T_p (K)	γ (K^{-4})
		C_{11} mode			
1.5 ppm					
10 MHz	1.38×10^{-5}	1.77×10^{-5}	4.59×10^{-4}	7.0	5.12×10^{-9}
3.7 ppm					
10 MHz	4.08×10^{-5}	1.91×10^{-3}	1.93×10^{-3}	7.0	4.78×10^{-9}
15 ppm					
10 MHz	7.30×10^{-4}	5.36×10^{-3}	5.75×10^{-3}	6.75	4.96×10^{-9}
30 MHz	6.40×10^{-4}	4.80×10^{-3}	7.34×10^{-3}	8.25	4.66×10^{-9}
57 ppm					
10 MHz	3.26×10^{-3}	1.53×10^{-2}	2.02×10^{-2}	6.75	4.32×10^{-9}
30 MHz	3.38×10^{-3}	1.59×10^{-2}	1.89×10^{-2}	8.25	4.50×10^{-9}
9 ppm					
10 MHz				3.39×10^{-3}	6.75
30 MHz				4.00×10^{-3}	8.25
		C' mode			
15 ppm					
10 MHz	$(9.5\pm1.0)\times10^{-4}$		$(1.26\pm.01)\times10^{-2}$	6.25	1.16×10^{-8}
30 MHz	$(7.8\pm1.0)\times10^{-4}$		$(1.23\pm.01)\times10^{-2}$	7.5	1.44×10^{-8}
		C_{44} mode			
15 ppm					
10 MHz					1.19×10^{-9}

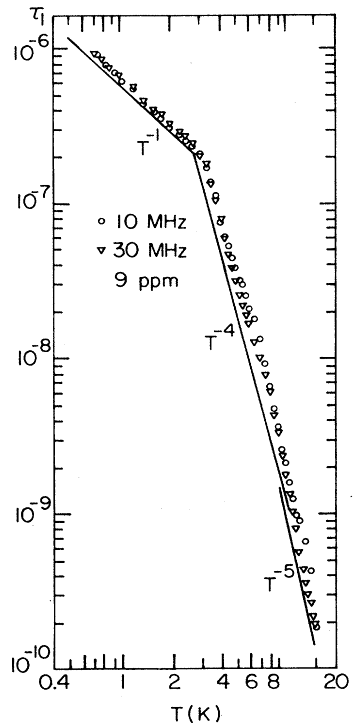

FIG. 10. Derived relaxation time τ_1 as a function of temperature for RbCl with 9-ppm OH^-.

the abrupt change in temperature dependence as resulting from an exact cancellation of a two-phonon process with a renormalization of the tunneling gap due to interaction of the tunneling system with the phonon bath. The relaxation time shown in Fig. 10 is about 17 times smaller than that Kapphan *et al.* have determined by an electric-field-induced optical dichroism measurement[7] and about 3 times larger than that given by Hess and De-Conde from measurements of the power and temperature dependence of dielectric absorption in RbCl:OH.[10] The elastic dipole moment $v_0\,\delta\lambda$ and coupling α determined from the relaxation strength Δ_p^0 are 8.3×10^{-24} cm^3 and 0.79 eV.

Finally, it can be concluded that the anomalous increase of the decrement below 3 K is a different phenomenon from the relaxation process and can reasonably be considered to be a resonance absorption. Similar anomalous absorptions have been observed in a number of defect systems. It has been observed for the Jahn-Teller ion Ni^{3+} in Al_2O_3 for 100- and 260-MHz sound waves below 4 K by Sturge *et al.*[26] A similar low-temperature absorption of both C'- and C_{11}-mode sound wave (10–60 MHz) was found in the KCl:OH system below 4 K by Brugger *et al.*[4] Recently, it has also been seen below 5 K in radiation damage studies on Al-Zn with 10- and 30-MHz C'-mode sound waves by Hultman *et al.*[27]

C. Velocity

The experimentally measured frequency change $\Delta f(T)/f$ can be expressed as

$$\frac{2\Delta f(T)}{f}=\Theta_{\text{OH}}-\gamma^4 T+A\ . \tag{13}$$

Here, Θ_{OH} is the modulus change due to the OH^- dipoles and the second term in Eq. (13) describes the combined effects of thermal expansion and the elastic constant change by thermal phonons, which is empirically known to be proportional to the fourth power of the temperature. The last term A is a constant background. According to the discussion in Sec. IV A, Θ_{OH} can be decomposed into two terms corresponding to resonance and relaxation effects, respectively, as shown by Eq. (9). It is noted that the normalized resonance modulus strength Δ_d^0 is different from the Δ_{da}^0 for the resonance absorption. This will be discussed further in a subsequent paper.

The experimental data of $\Delta f(T)/f$ were fitted to Eq. (9) by a least-squares method and the values determined for Δ_d^0 and Δ_p^0 are collected in Table II. The values for the relaxation strength Δ_p^0 obtained from velocity data are in satisfactory agreement with those obtained from the *absorption* data except for the lowest concentration specimen, which may be affected by uncertainty in the background. It is also seen that the values of Δ_d^0 and Δ_p^0 obtained from the velocity data are relatively frequency independent and $\Delta_d^0<\Delta_p^0$ as expected from the tunneling model.

The data for the C' mode were also analyzed by the same method and the values found for the constants are shown in Table II. Since Δ_p^0 is proportional to the modulus change $\Delta C/C$, then

$$\frac{\Delta C_{11}}{\Delta C'}=\frac{\Delta_p^0(C_{11})C_{11}}{\Delta_p^0(C')C'}\ . \tag{14}$$

For the 10-MHz results, this ratio is 1.07 and reasonably close to the expected value $\frac{4}{3}$ obtained by using the relation, $3C_{11}=3B+4C'$ and supposing that $\Delta B=0$. For the resonance modulus Δ_d^0, the ratio is 1.8 but there is no reason to expect this relation to hold for the diaelastic effect.

V. SUMMARY

The ultrasonic response (attenuation and velocity) for RbCl:OH has been measured as a function of temperature, frequency polarization, and concentration. There is a relaxation peak near 6 K at 10 MHz, but also an unusual behavior at temperatures below the peak which cannot be explained as a relaxation effect. On the other hand, a resonance effect is expected and the response has qualitative features expected for a resonance. A more quantitative discussion is given in a subsequent paper in which there is first a discussion of effects expected for resonance in a six-level system. The temperature dependence of the relaxation rate is found to be linear below 3 K as expected for a one-phonon process between tunneling states with an abrupt increase above 3 K to a multiphonon process, providing evidence of a renormalization of the tunneling gap as predicted by Sander and Shore.

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