# Ultrasonic Investigation of the Lambda Transition in NH₄Br†

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The ultrasonic-attenuation coefficient $\alpha$ has been measured in the disordered phase of $NH_4Br$ at 10, 30, and 50 MHz as a function of temperature for the [100] longitudinal wave and the [110] transverse wave associated with the $c'$ shear. By combining these data with available ultrasonic- and hypersonic-velocity data it is possible to determine the dynamical behavior near the order-disorder transition if one assumes a single-relaxation model. The critical relaxation time for the longitudinal wave is well represented by $1/\tau$ (in units of $10^8$ sec$^{-1}$) $= 1.8 + 1780\epsilon^{1.0}$, where $\epsilon$ is the reduced temperature $(T - T_\lambda)/T_\lambda$. The transverse relaxation time is quite similar. The critical attenuations themselves can be approximately represented by a power law of the form $\alpha_c = S\omega^2\epsilon^{-l}$, where $l \simeq 1.35$. It was found possible to obtain an essentially single domain $NH_4Br$ crystal in the tetragonal ordered phase by cooling the crystal slowly with a small temperature gradient along one of its axes. Longitudinal and shear velocities were measured in the ordered phase as a function of temperature from 120 °K to $T_\lambda \simeq 234.5$ °K. Critical attenuation measured at 10 MHz for the longitudinal wave was well described by a power law with the exponent $l = 0.75$.

## I. INTRODUCTION

Both $NH_4Cl$ and $NH_4Br$ crystals undergo order-disorder transitions of the $\lambda$ type involving the relative orientations of the tetrahedral $NH_4^+$ ions. At room temperature, both crystals have a disordered CsCl-type cubic structure with the $NH_4^+$ ions distributed at random with respect to two equivalent orientations in the cubic cell. However, there are major differences between the types of ordering observed in the chloride and in the bromide. In the case of $NH_4Cl$, there is a single $\lambda$ line marking the transition between the disordered cubic phase and a "parallel" ordered cubic phase. The phase diagram for $NH_4Br$ is much more complicated,[1] and the $\lambda$ transition at low pressures involves an ordered tetragonal phase with "antiparallel" chains of $NH_4^+$ ions. Although the $\lambda$ temperatures are fortuitously similar at 1 atm ($T_\lambda \simeq 242$ °K for $NH_4Cl$ and 234.5 °K for $NH_4Br$), the $\lambda$ lines have slopes of opposite sign. Recent theoretical works[2] indicate that there are two competing interactions between neighboring ammonium ions—a direct octopole-octopole interaction and an indirect interaction via the polarizable halide ion. This octopole-dipole term appears to be dominant in $NH_4Br$ and explains the "antiferromagnetic" ordering in that case.

Thus it is of interest to compare the dynamical behavior of $NH_4Br$ near its $\lambda$ transition with the analogous behavior recently reported for $NH_4Cl$.[3] Acoustic attenuation and dispersion measurements in $NH_4Cl$ have been carried out at 1 atm and at high pressures, and these data have been analyzed in terms of a single-relaxation formalism to evaluate the critical variation of the relaxation time $\tau$ for long-range ordering. A similar analy-

sis will be presented here for the acoustic behavior of $NH_4Br$ in its disordered phase at 1 atm. Unlike the case of $NH_4Cl$, where only longitudinal waves exhibit dispersion and critical attenuation, the $c'$ shear wave propagating in the [110] direction and polarized perpendicular to [001] is also strongly attenuated near $T_\lambda$ in $NH_4Br$. In addition to this qualitative difference, the critical exponents for the divergence of $\tau$ (as obtained from data on [100] longitudinal waves) are quite different in the two crystals.

Ultrasonic-velocity measurements in $NH_4Br$ have been made previously over a wide range of temperatures and pressures.[1,4] Thus the low-frequency limiting values of all three independent elastic constants $c_{11}$, $c_{44}$, and $c' = (c_{11} - c_{12})/2$ are well known in the disordered phase. The velocity and attenuation of hypersonic acoustic waves have been determined at room temperature as a function of frequency from Brillouin scattering measurements; in addition, the velocity of the [110] longitudinal wave has been measured as a function of temperature at ~ 16 GHz.[5] On the basis of these data it is possible to estimate the temperature dependence of the velocity dispersion for the $c_{11}$ and $c'$ waves. In this paper we report the ultrasonic attenuation of $c_{11}$ and $c'$ waves in disordered $NH_4Br$ as a function of temperature and frequency at 1 atm. By assuming a single-relaxation model, we are then able to determine the critical behavior of the relaxation time for $T > T_\lambda$.

Previous ultrasonic investigations of $NH_4Br$ have been largely confined to the disordered phase. When a single crystal undergoes the transition from the cubic disordered phase to the tetragonal ordered phase, many ordered domains are formed with their tetragonal axes oriented randomly along the

original cubic axes. Such a multidomain crystal
scatters sound very strongly, and the echo pat-
tern disappears for longitudinal waves and the $c'$
shear wave. In the present investigation, it was
found possible to obtain an essentially single-
domain ordered crystal. Thus we were able to
measure the velocities of both longitudinal and
shear waves and the anomalous attenuation of the
longitudinal wave as a function of temperature in
the ordered phase.

## II. EXPERIMENTAL PROCEDURES

The ultrasonic techniques used in this investiga-
tion were very similar to those used previously to
study ammonium chloride. Attenuation measure-
ments were carried out with a single-transducer,
pulse-echo method using Matec ultrasonic equip-
ment.[6] Velocity measurements were made at 10
MHz with a pulse-superposition method.[7]

A Lauda refrigerating circulator and dry-ice
heat exchanger were used for measurements in the
disordered phase. Liquid nitrogen and a variable-
pressure transfer gas were used for measurements
in the ordered phase. In both cases, regulation of
the temperature of a copper sample holder was
achieved with a Bayley model-250 proportional
temperature controller. The resulting tempera-
ture stability, as measured with a calibrated Rose-
mount platinum resistance thermometer, was
$\pm 5$ m $^\circ$K.

The NH$_4$Br single crystals used in this experi-
ment were from the same batch as those studied in
an earlier high-pressure investigation.[1] They
were at least 99.9% pure, were free from visible
defects, and had well-developed (100) faces which
were parallel to within $\pm 0.0001$ cm. Some pre-
liminary measurements in the [100] direction were
made using a slightly imperfect crystal with a
length $L = 0.7066$ cm. Final measurements in that
direction were made on a larger and more perfect
crystal, denoted as crystal I. With the exception
of attenuation values in the ordered phase, data
obtained on these two crystals agreed well with
each other. Crystal $Ia$ was used as grown for
longitudinal attenuation measurements in the dis-
ordered phase; the length of this crystal in the
[100] direction was $0.8928 \pm 0.0001$ cm at 20 $^\circ$C.
Subsequently, one face of this crystal was water
damaged and a new face was flycut parallel to the
undamaged (100) face; the new length was 0.8179
$\pm 0.0005$ cm at 20 $^\circ$C. This crystal, designated as
crystal $Ib$, was then used for measurements in the
ordered phase. Crystal II was flycut to obtain a
pair of (110) faces; the parallelity of these faces
was within $\pm 0.0003$ cm and the length along the
[110] direction was 0.7562 cm at 20 $^\circ$C. It should
be noted that NH$_4$Br crystals are soft and hygro-

scopic and must be handled with considerable care.

The transition temperature $T_\lambda$ for each crystal
was determined by measuring the shear velocity
corresponding to the elastic constant $c_{44}$. This
shear wave is not attenuated near $T_\lambda$ and can even
be propagated in a polydomain ordered crystal.
Furthermore, this shear velocity undergoes a
very rapid variation at the transition. Indeed, the
temperature coefficient $(\partial c_{44}/\partial T)_p$ changes abrupt-
ly from a small negative value in the disordered
phase to a very large positive value, and the transi-
tion point is easily established. The $\lambda$ tempera-
ture was found to be $(234.3 \pm 0.1)$ $^\circ$K in crystal I
and $(234.8 \pm 0.1)$ $^\circ$K in crystal II. These values
agree reasonably with the value 234.5 $^\circ$K cited by
Garland and Yarnell.[4]

Dow resin 276-V9 was used to bond the $\frac{1}{4}$-in. -
diam quartz transducers to the NH$_4$Br crystals.
However, this bond broke when the sample was
cooled below 160 $^\circ$K, and the less viscous Dow-
Corning 200 silicone fluids were used for mea-
surements in the ordered phase.

It was found possible to obtain an effectively
"single-domain" NH$_4$Br crystal in the tetragonal
ordered phase by cooling the crystal slowly
through the transition after a temperature gra-
dient has been established along one of the [100]
axes. This gradient was obtained by placing a
small heating element in good thermal contact
with the face opposite from the transducer (which
is itself in good thermal contact with the copper
sample holder). The optimal gradient, as mea-
sured with a gold-chromel difference thermo-
couple, was 4 to 5 $^\circ$K cm$^{-1}$. The gradient heat-
er was turned on and the sample holder was
maintained at $\sim 237$ $^\circ$K for several hours to al-
low the system to achieve a steady-state tem-
perature distribution. The sample holder was
then cooled slowly to about 210 $^\circ$K. The rate
of cooling was not crucial, but a constant rate
of 4 $^\circ$K h$^{-1}$ seemed to give the best results. The
criterion for deciding whether a single domain
had been formed was the ability to propagate
longitudinal waves and obtain a good exponen-
tial echo pattern with at least five echoes at
$\sim 200$ $^\circ$K. Ultrasonic pulses were not propagated
in the sample during the cooling process, and
the gradient heater was turned off before the
echo pattern was inspected. Although there is
no direct evidence about the tetragonal domain
structure formed below $T_\lambda$, the observed ultra-
sonic behavior is consistent with a single dom-
inant domain and we shall consider the ordered
tetragonal phase to be a single-domain crystal.
After the gradient is turned off, there is no
indication of any change in the domain struc-
ture with time or with temperature variations
(as long as the temperature is kept below $T_\lambda$).

## III. RESULTS

### A. Attenuation in the Disordered Cubic Phase

*Longitudinal waves.* The attenuation $\alpha$ of longitudinal waves propagating in the [100] direction ($c_{11}$ wave) has been measured as a function of temperature at 10, 30, and 50 MHz. Plots of the observed $\alpha$ values versus $f^2$ at various constant temperatures between 236 and 255 °K gave a family of straight lines with a common intercept $\alpha_0 = 0.3 \pm 0.1$ dB cm$^{-1}$. Thus the total attenuation consists of a large critical attenuation $\alpha_c$ related to the order-disorder transition and a small background attenuation $\alpha_0$ which is independent of frequency and temperature. This background attenuation is caused by various effects such as beam spreading due to the finite size of the transducer, scattering from imperfections in the sample, and energy losses in the bond between the transducer and the sample.

The behavior of the critical attenuation $\alpha_c = \alpha_{obs} - \alpha_0$ is shown in Fig. 1, where $\log \alpha_c$ is plotted against $\log(T - T_\lambda)$. The straight lines shown in this figure represent the best fit to the data with a power-law of the form

$$\alpha_c (\text{Np cm}^{-1}) = S\omega^2 \epsilon^{-l}, \qquad (1)$$

where $\omega = 2\pi f$ and $\epsilon$ is the reduced temperature $|T - T_\lambda|/T_\lambda$. The values of the parameters are $S = (1.4 \pm 0.3) \times 10^{-19}$ sec$^2$ cm$^{-1}$ and $l = 1.35 \pm 0.05$. In fact, the data show a definite systematic deviation from a simple power law. Smooth-curve values of $\alpha_c/\omega^2$ as obtained from the slopes of $\alpha_{obs}$-vs-$f^2$ plots are given in Table I and will be used in further analysis of these data.
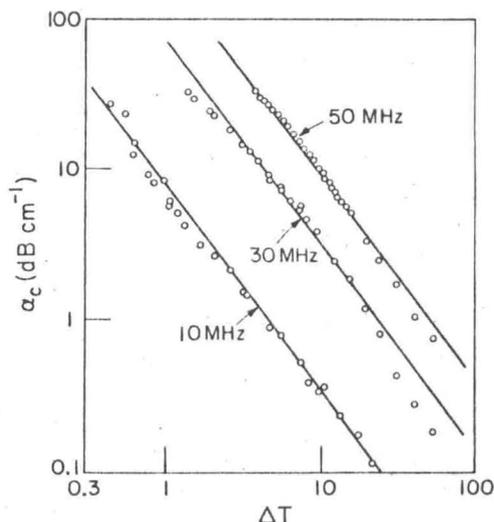


FIG. 1. Log-log plots of $\alpha_c$ vs $\Delta T$ (in °K) for [100] longitudinal waves in the disordered cubic phase of NH$_4$Br. The lines represent a simple power-law fit to the data using Eq. (1).

TABLE I. Smooth-curve values of $\alpha_c/\omega^2$ (in units of $10^{-18}$ Np sec$^2$ cm$^{-1}$) at different values of $\Delta T = T - T_\lambda$.

| $c_{11}$ wave | | $c'$ wave | | $c_{long}$ wave | |
| --- | --- | --- | --- | --- | --- |
| $\Delta T$ (°K) | $\alpha_c/\omega^2$ | $\Delta T$ (°K) | $\alpha_c/\omega^2$ | $\Delta T$ (°K) | $\alpha_c/\omega^2$ |
| 1.5 | 96.5 | 0.8 | 77.4 | −1.57 | 530 |
| 2.0 | 74.3 | 1.0 | 65.2 | −1.89 | 471 |
| 2.5 | 60.2 | 1.2 | 59.8 | −2.44 | 389 |
| 3.0 | 48.5 | 1.5 | 47.2 | −3.06 | 332 |
| 3.5 | 40.9 | 1.8 | 40.4 | −4.21 | 238 |
| 4.0 | 35.6 | 2.0 | 35.7 | −5.99 | 191 |
| 4.5 | 30.8 | 2.5 | 28.3 | −7.45 | 170 |
| 5.5 | 24.6 | 3.0 | 23.2 | −9.46 | 145 |
| 6.5 | 20.2 | 3.5 | 18.4 | −11.27 | 133 |
| 7.5 | 16.7 | 4.0 | 14.6 | −12.84 | 117 |
| 8.5 | 14.0 | 4.5 | 12.3 | −15.09 | 99 |
| 10.5 | 10.3 | 5.0 | 10.5 | −17.74 | 92 |
| 12.5 | 7.82 | 5.5 | 9.34 | −20.18 | 79 |
| 13.5 | 6.90 | 6.0 | 8.09 | −22.98 | 67 |
| 15.5 | 5.64 | 6.5 | 7.21 | −24.98 | 66 |
| 17.5 | 4.65 | 7.0 | 6.42 | −28.15 | 59 |
| 20.5 | 3.60 | 7.5 | 5.84 | −32.51 | 51 |
| | | 8.0 | 5.28 | −36.56 | 50 |
| | | 9.0 | 4.23 | −42.07 | 46 |
| | | 10.0 | 3.50 | −52.21 | 40 |
| | | 12.0 | 2.63 | −63.29 | 36 |

The most important factor limiting the accuracy of the attenuation is a slight nonexponential character in the echo pattern. The average deviation in the $\alpha_{obs}$ values obtained from adjacent pairs of echoes was ~ 10% in regions of small or moderate attenuation. Since the character of the echo pattern remained essentially the same throughout a run, changes in $\alpha_{obs}$ with temperature could be determined with somewhat higher accuracy. The scatter in the data indicates that 5% would be a reasonable estimate of the random error.

The attenuation of longitudinal waves propagating in the [110] direction was measured only at 10 MHz since good echo patterns could not be obtained at higher frequencies. The (110) faces of crystal II had deteriorated during an extensive set of earlier measurements on the $c'$ shear wave, and recutting this crystal did not improve the parallelity of the faces or reduce the distortion in the high-frequency echo pattern. The critical attenuation for this wave could be shown to agree with that for the $c_{11}$ wave at 10 MHz if the background attenuation $\alpha_0$ was assumed to have the rather large value of 1.8 dB cm$^{-1}$ in the [110] direction. However, these limited data did not permit us to make any conclusive determination of the dependence of $\alpha_c/\omega^2$ on the direction of propagation of longitudinal waves in NH$_4$Br. Attenuation measurements on NH$_4$Cl have shown that $\alpha_c$ values in the disordered phase of that crystal are essentially the same for longitudinal waves propagating in the [100] and [110] directions,[8]

and it is likely that the values in these two directions are very similar, if not identical, in $NH_4Br$ also.

*Transverse waves.* There is no appreciable attenuation for ultrasonic shear waves corresponding to the elastic constant $c_{44}$. However, the transverse wave propagating in the [110] direction and polarized perpendicular to the [001] direction ($c'$ wave) does exhibit critical attenuation. Initially it was difficult to obtain a satisfactory echo pattern at high frequencies, but proper impedance matching and improvement of the parallelity of the (110) faces by repeated flycutting of crystal II resulted in a reasonably good exponential pattern of more than 15 echoes at room temperature. Because the attenuation of this $c'$ wave was smaller than that of the $c_{11}$ wave, it was possible to carry out 30 and 50 MHz measurements closer to $T_\lambda$ than before. Plots of $\alpha$ vs $f^2$ were linear at all temperatures, but the intercept was not independent of temperature as in the case of the $c_{11}$ wave. The background attenuation $\alpha_0$ had an essentially constant value of 1.3 dB cm$^{-1}$ in the range $4.5 < \Delta T < 12.5$ °K but increased steadily on approaching the transition (for example, $\alpha_0 = 2.1$ at $\Delta T = 2.37$ °K and 4.8 at $\Delta T = 0.80$ °K). Smooth-curve values of $\alpha_c/\omega^2$ as obtained from the slopes of these $\alpha_{obs}$-vs-$f^2$ plots are given in Table I. It is possible to approximate these transverse $\alpha_c/\omega^2$ values with the power law given in Eq. (1), but since a log-log plot of $\alpha_c/\omega^2$ vs $\epsilon$ shows distinct curvature, one is not able to determine an unambiguous value for the exponent $l$. Values of $l$ between 1.35 and 1.5 are compatible with the data: for $l = 1.35$, one finds $S = 0.6 \times 10^{-19}$ sec$^2$ cm$^{-1}$; for $l = 1.5$, the corresponding $S = 0.3 \times 10^{-19}$ sec$^2$ cm$^{-1}$.

### B. Attenuation in the Tetragonal Ordered Phase

Since no measurements were made below $T_\lambda$ on crystal II, we observed only the longitudinal attenuation corresponding to that measured for the $c_{11}$ wave in the disordered phase. It is not known for certain that the ordered crystal consisted of a single domain. Even if it did, the tetragonal axis could have been oriented either parallel or perpendicular to the direction of sound propagation (see Sec. III C). Since the longitudinal attenuation and velocity measurements were made in the same run, without heating the crystal above $T_\lambda$, the $\alpha$ values reported here and the $c_{1ong}$ values reported in Sec. III C definitely correspond to the same configuration of the ordered crystal.

The longitudinal attenuation in the tetragonal phase was only measured at 10 MHz since echoes could not be obtained at higher frequencies between 200 °K and the transition. The data reported here were obtained from an echo pattern which was as

exponential as those in the disordered phase. Far from the transition, five echoes were measured and the average deviation of the attenuation values obtained from different echo pairs was less than 10%. (Two preliminary runs on the somewhat imperfect crystal with path length $2L = 1.4132$ cm gave much larger $\alpha$ values and more scatter in the data as a function of temperature. This suggests the necessity of having a very good single crystal in order to achieve a single domain in the tetragonal phase.)

A simple power-law dependence of $\alpha_c = \alpha_{obs} - \alpha_0$ on $\Delta T$ could be obtained when $\alpha_0$ was assigned any constant value between 0.3 and 0.7 dB cm$^{-1}$. In view of the fact that $\alpha_0$ was 0.3 dB cm$^{-1}$ in the disordered phase, a value of 0.5 dB cm$^{-1}$ was assumed to be a reasonable choice for the ordered phase since some additional background attenuation would be expected owing to imperfections in the domain structure. The $\alpha_c$ values shown in Fig. 2 and the $\alpha_c/\omega^2$ values given in Table I were calculated using this choice of $\alpha_0$. As indicated by Fig. 2, the 10-MHz longitudinal attenuation can be well represented by Eq. (1) with $S = (130 \pm 30) \times 10^{-19}$ sec$^2$ cm$^{-1}$ and $l = 0.75 \pm 0.05$.

### C. Velocity Measurements

The ultrasonic velocity $u$ in the tetragonal ordered phase has been measured at 10 MHz by bonding a transducer to one of the (100) faces of a disordered cubic crystal and cooling the crystal slowly with a temperature gradient applied parallel to the direction of sound propagation (see Sec. II). When a good echo pattern was observed be-
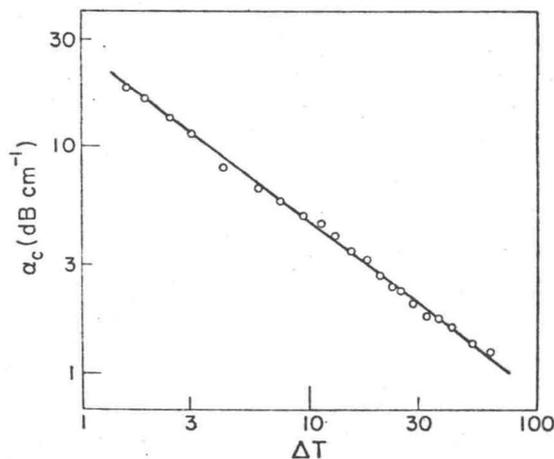


FIG. 2. Log-log plot of $\alpha_c$ vs $\Delta T$ (in °K) for a 10 MHz longitudinal wave in the tetragonal ordered phase of $NH_4Br$. These $\alpha_c$ values were obtained using $\alpha_0 = 0.5$ dB cm$^{-1}$. The line represents a power-law fit to the data using Eq. (1).

low $T_\lambda$ for longitudinal waves, it was assumed that the crystal consisted of a single tetragonal domain. However, there could have been multidomain regions near the surface or a few large domains with their tetragonal axes perpendicular to each other. The velocity measurements cited below strongly support the view that the crystal was effectively a single domain along the acoustic path, but the data are not definitive. Even if the crystal does become a single domain, the orientation of the tetragonal axis is not known and could be different each time the crystal is cooled below $T_\lambda$.[9] Depending on the orientation of the tetragonal axis, different thermal-expansion correction factors are needed to calculate the elastic stiffness $c = \rho u^2$ as a function of temperature. There are two possible cases: (a) The tetragonal axis is parallel to the direction of propagation of the sound wave:

$$\rho u^2 = \frac{\rho^0 (2L^0)^2}{\delta^2} \frac{(a_1^0/a_1)^2}{(a_3^0/a_3)} . \qquad (2)$$

(b) The tetragonal axis is perpendicular to the direction of propagation of the sound wave:

$$\rho u^2 = \frac{\rho^0 (2L^0)^2}{\delta^2} \frac{a_3^0}{a_3} . \qquad (3)$$

In Eqs. (2) and (3), $\delta$ is the round-trip transit time for the acoustic pulse, $\rho$ is the mass density, $2L$ is the round-trip path length in the crystal, $a_1$ is the lattice parameter of one of the two equivalent axes, and $a_3$ is that of the tetragonal axis. The superscript zero denotes the values at a convenient reference temperature, which is 20 °C. The values $\rho^0 = 2.4336$ g cm$^{-3}$ and $a_1^0 = a_3^0 = 4.0580$ Å were taken from Garland and Yarnell.[4] The values of $a_1$ and $a_3$ as functions of temperature were taken from Bonilla, Garland, and Schumaker,[10] since their values fall between those obtained in two independent measurements by Hovi and co-workers.[11]

The elastic constants obtained from shear-wave measurements are shown in Fig. 3, and those obtained from longitudinal waves in Fig. 4. Smooth-curve values are given in Table II. In the case of shear waves, two independent sets of measurements on the same crystal were carried out under exactly the same conditions except that the $Y$-cut quartz transducer (and thus the direction of polarization) was rotated by 90°. The elastic constants calculated from these two sets of data were in excellent agreement if it were assumed that the tetragonal axis was parallel to the propagation direction for the first run and perpendicular to it for the second run. If either Eq. (2) or (3) were used for both sets of data, the resulting $\rho u^2$ values showed a systematic difference of about 0.8%. Thus the shear elastic constant measured in this experiment is almost certainly $c_{44}$. As can
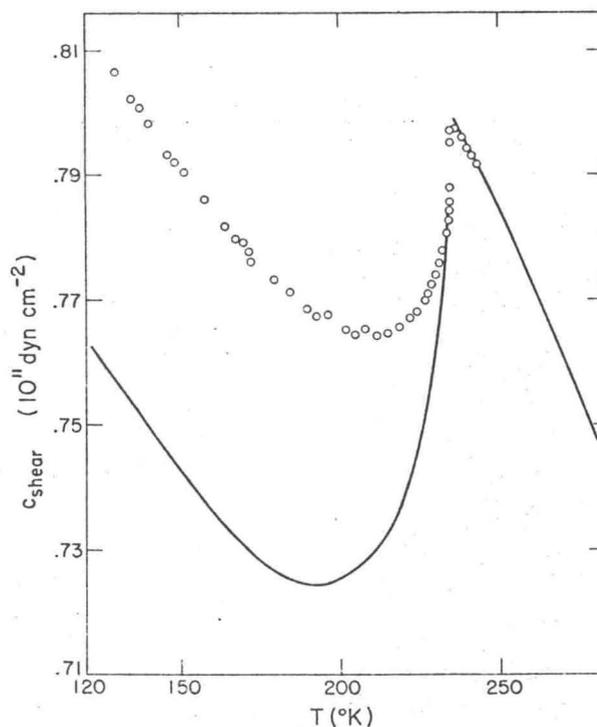


FIG. 3. Temperature dependence of $c_{shear}$ as determined from a "single-domain" crystal in the tetragonal ordered phase. It is probable, but not certain, that these data represent $c_{44}$ values in the ordered phase (see text). The solid line represents the well-characterized variation of $c_{44}$ in the disordered cubic phase above $T_\lambda$ and the average shear stiffness $\bar{c}$ reported previously from measurements on multidomain ordered crystals (Ref. 4).

be seen from Fig. 3, the variation of $c_{shear}$ is very rapid just below $T_\lambda$. Indeed, the value changes from 0.783 at 234 °K to 0.797 at 234.5 °K. It is possible that there is a discontinuous jump in the shear stiffness and hysteresis in the transition temperature, as is seen in $NH_4Cl$ at 1 atm.[7] However, such effects must be very small if they do occur. We estimate that $\Delta c = 0.032 \times 10^{11}$ dyn cm$^{-2}$ and $\Delta T = 40$ m °K are upper limits on the possible discontinuity and hysteresis.

In the case of longitudinal waves, measurements were made on two different crystals but the orientations must have been fortuitously the same since the $\rho u^2$ values agree on using either Eq. (2) or (3). Thus we do not know which longitudinal elastic constant has been measured in this experiment. It was arbitrarily assumed that the tetragonal axis was parallel to the propagation direction,[9] and Eq. (2) was used in calculating the $c_{long}$ values in Fig. 4 and Table II. If Eq. (3) had been used instead, the resulting values of $c_{long}$ would all be lower by roughly 0.8%.

The scatter in the data indicates that the random errors in the elastic constants are about 0.1%.
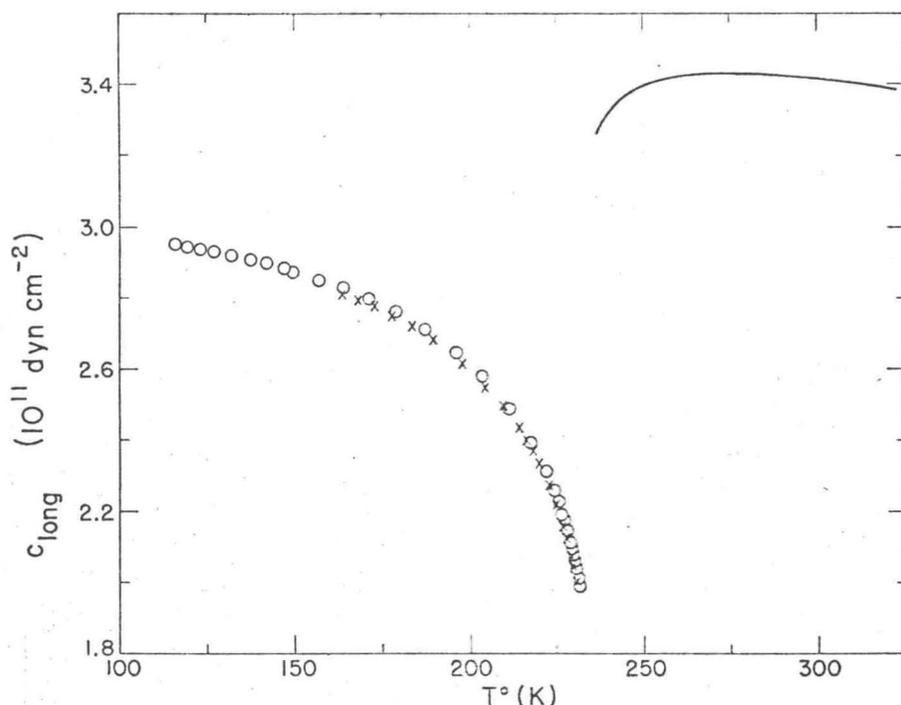
FIG. 4. Temperature dependence of $c_{long}$ as determined from a single-domain crystal in the tetragonal ordered phase. The solid line shows the smooth-curve variation of $c_{11}$ in the disordered phase (Ref. 4). The circles indicate data obtained on crystal I$b$, and the crosses denote data obtained on the crystal with path length $2L = 1.4132$ cm.

Possible systematic errors arise not only from the ambiguity in the orientation of the tetragonal axis but also from the choice of the $n = 0$ condition[7] for the pulse-superposition method. For shear waves, where the echo pattern could be followed through the transition region, the choice of $n = 0$ was made by matching the present $c_{44}$ values above $T_\lambda$ with those reported previously.[4] For longitudinal waves, it was necessary to establish the choice of $n = 0$ independently in the ordered phase. As a check on this choice, $c_{long}$ was measured on two crystals of different lengths, and Fig. 4 shows that the results are in good agreement.

### IV. DISCUSSION

There are no elastic constant data in the tetragonal phase with which to compare our present results except for the average shear stiffness $\bar{c}$ obtained from measurements on multidomain crystals.[4] As shown in Fig. 3, the temperature variation of $\bar{c}$ is qualitatively similar but quantitatively very different than the $c_{shear}$ variation determined in a single-domain crystal. It was thought previously that $\bar{c}$ represented the average $(2c_{44} + c_{66})/3$, which would result from a random orientation of the tetragonal axes of the domains along the directions of the three equivalent axes of the disordered cubic crystal. This now seems questionable. If the assignment of $c_{shear}$ as $c_{44}$ is correct, then $c_{66}$ would have rather low values (a minimum value of $0.637 \times 10^{11}$ dyn cm$^{-2}$ at $\sim 190\,°$K and $0.658 \times 10^{11}$ at $130\,°$K). Such a large tetragonal

"splitting" between $c_{44}$ and $c_{66}$ seems unlikely. Another possible explanation for the low $\bar{c}$ values could be that the effective acoustic pathlength is larger in the multidomain crystal owing to reflections of the wave at domain boundaries. It should also be noted that the minimum in $c_{shear}$ occurs at $\sim 210\,°$K, whereas the minimum in $\bar{c}$ is at $\sim 190\,°$K. A minimum value near $210\,°$K is more reasonable in view of the lattice-parameter variation.[10] It is known that the shear stiffness $c_{44}$ is a sensitive function of volume in the case of NH$_4$Cl.[12] By analogy, the rapid decrease in $c_{shear}$ for NH$_4$Br

TABLE II. Smooth-curve values of the elastic constants $c_{long}$ and $c_{shear}$ (in units of $10^{11}$ dyn cm$^{-2}$) for a single-domain crystal of NH$_4$Br in the tetragonal phase. The number of significant figures does not indicate the absolute accuracy.

| $T$ (°K) | $c_{long}$ | $c_{shear}$ | $T$ (°K) | $c_{long}$ | $c_{shear}$ |
|---|---|---|---|---|---|
| 120 | 2.941 | ··· | 200 | 2.605 | 0.7654 |
| 130 | 2.920 | 0.8056 | 205 | 2.555 | 0.7648 |
| 140 | 2.898 | 0.7981 | 210 | 2.498 | 0.7643 |
| 150 | 2.870 | 0.7910 | 215 | 2.429 | 0.7645 |
| 155 | 2.854 | 0.7876 | 220 | 2.342 | 0.7660 |
| 160 | 2.838 | 0.7842 | 225 | 2.225 | 0.7689 |
| 165 | 2.813 | 0.7810 | 229 | 2.092 | 0.7730 |
| 170 | 2.790 | 0.7779 | 230 | 2.048 | 0.7742 |
| 175 | 2.767 | 0.7751 | 231 | 1.998 | 0.7758 |
| 180 | 2.745 | 0.7726 | 231.5 | 1.980 | 0.7768 |
| 185 | 2.718 | 0.7703 | 232 | ··· | 0.7775 |
| 190 | 2.685 | 0.7683 | 233 | ··· | 0.7796 |
| 195 | 2.648 | 0.7665 | 234 | ··· | 0.7825 |

just below $T_\lambda$ would be expected because of the anomalous expansion which takes place on ordering. The fact that $NH_4Br$ expands on cooling into the tetragonal ordered phase whereas $NH_4Cl$ undergoes an anomalous contraction on transforming into its cubic ordered phase presumably explains the observation that $c_{1_{ong}}$ far below $T_\lambda$ is *smaller* than $c_{11}$ in the disordered phase for $NH_4Br$ (see Fig. 4), while the opposite is true for $NH_4Cl$. [7]

Our attenuation data can be compared with the recently reported results of Velichkina and co-workers, [13] who measured the [100] longitudinal attenuation at 5, 15, and 25 MHz in the range $5 \geq T - T_\lambda \geq -6\,°K$. Their method involves measuring the *relative* change with temperature in the height of a single pulse transmitted through a thin crystal. This is advantageous when the attenuation is very high but not too accurate in regions of low to moderate attenuation. (Indeed, a systematic correction of ~ 4.5 dB cm$^{-1}$ must be made to all their data owing to an unfortunate choice of the reference point from which changes in attenuation were measured.) The values of $\alpha_c/\omega^2$ estimated from their data are larger than those given in Table I by a roughly constant factor of about 1.5. The reason for such a multiplicative difference is unclear. It should be pointed out that their attenuation data in the multidomain ordered phase appear, rather surprisingly, to be more reliable than those in the disordered phase; $\alpha_c$ varies with frequency in a somewhat erratic way above $T_\lambda$ but shows a good quadratic dependence below. Incidentally, the presence of multiple domains in a crystal cooled below $T_\lambda$ in the absence of a thermal gradient was demonstrated by the depolarization of linearly polarized light. [13]

Velichkina *et al.* have interpreted their ordered-phase attenuation in terms of the Landau-Khalatnikov model involving a critical relaxation time $\tau = 2.2 \times 10^{-9}/(T_\lambda - T)$. This does not seem compatible with the quadratic frequency dependence of their data or with the fact that both their $\alpha_c/\omega^2$ values and the values in Table I vary like $(\Delta T)^{-0.75}$. If one ignores the multiplicative factor of ~ 1.5 between our results and theirs and considers only the ratio of $\alpha_c$ in the ordered phase to that in the disordered phase, the critical attenuation in the tetragonal ordered phase would not seem to depend on the domain structure. Yet our experience indicates that two crystals which show the same attenuation in the disordered phase can give quite different $\alpha_c$ values in the ordered phase, depending on the perfection of the crystal and the manner of cooling. Thus the interpretation of $\alpha_c$ in the ordered phase is puzzling.

Although the critical attenuation in the disordered phase can be approximately fit by a simple power law (see Fig. 1), the $\chi^2$ value is rather large (5.9)

and the data show systematic deviations from Eq. (1). These deviations are seen to become even larger for the 25-MHz data of Velichkina *et al.* when $\Delta T < 1\,°K$. Thus it is of interest to analyze the data in terms of a relaxation model. Whether a single-relaxation model is adequate to describe the low-frequency dynamical behavior of the order-disorder transition in $NH_4Br$ is unclear. According to theoretical predictions for magnetic[14] and fluid[15] systems, a spectrum of relaxation times would be expected. However, none of the current theories seem to be directly pertinent to the analysis of $NH_4Br$. Moreover, the extensive hypersonic attenuation and dispersion data at room temperature show that, at least for temperatures far from $T_\lambda$, $NH_4Br$ is well described by a single-relaxation model. In any event, the assumption of such a model leads to an empirical analysis of the ultrasonic attenuation data in which attractively simple behavior of both the relaxation strength and the relaxation time is obtained.

Since the critical attenuation data exhibit an $f^2$ frequency dependence, we shall adopt the low-frequency form of the single-relaxation expression:

$$\alpha_c = C\omega^2 \tau_{S,x},\quad\quad\quad\quad (4)$$

where $\alpha_c$ is the amplitude attenuation (in Np cm$^{-1}$), $\tau_{S,x}$ is the adiabatic relaxation time at constant strain, and the appropriate relaxation strength $C$ is defined by

$$C = \frac{u^2(\infty) - u^2(0)}{2u(\omega)u^2(0)} \approx \frac{c^\infty - c^0}{2u(0)c^0}.\quad\quad (5)$$

The analysis is based on using hypersonic-velocity data to estimate the high-frequency limiting stiffness $c^\infty$ and ultrasonic data for the low-frequency limiting values $u(0)$ and $c^0 = \rho u^2(0)$. The resulting value of $C$ at a given temperature is then combined with the corresponding experimental value of $\alpha_c/\omega^2$ to yield $\tau_{S,x}$. One could, of course, also analyze the data in terms of the adiabatic relaxation time at constant stress $\tau_{S,X}$. However, these two times are simply related to each other by $\tau_{S,x}/\tau_{S,X} = c^\infty/c^0$, and the behavior of $\tau_{S,X}$ does not differ in any significant way from that of $\tau_{S,x}$.

The temperature variations of $c_{11}^0$ and $c'^0$ are well known from ultrasonic measurements at 20 MHz. [4] Values of $c_{11}^\infty$ and $c'^\infty$ are known at 24 °C from an analysis of Brillouin scattering data at angles corresponding to frequencies between 6.5 and 24 GHz. [5] In order to estimate $c'^\infty$ values near the transition, we have *assumed* a linear temperature dependence with a slope equal to the value of $d(c'^0)/dT$ at room temperature (see Fig. 5). This is a plausible but essentially arbitrary assumption. Fortunately, $c_{11}^\infty$ near the transition can be estimated with much greater certainty. The hypersonic velocity of the [110] longitudinal wave is known as
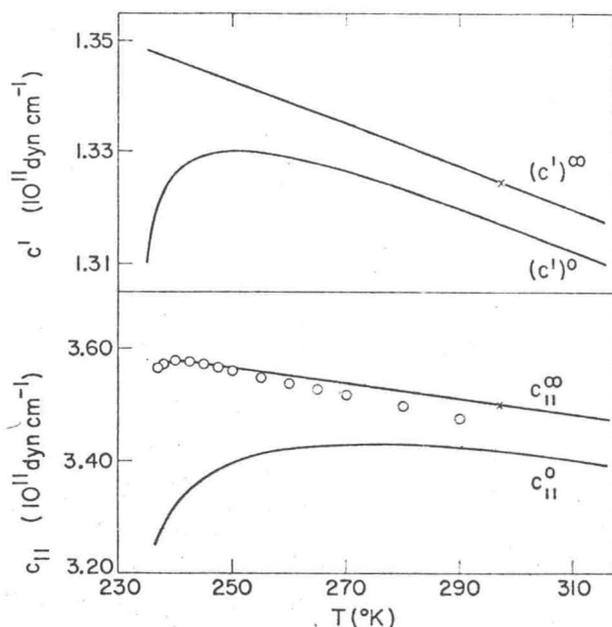
FIG. 5. Variation of the limiting values of $c_{11}$ and $c'$. The smooth curves for $c_{11}^0$ and $c'^0$ are taken from Ref. 4. The crosses are infinite-frequency elastic constants reported in Ref. 5; see text for a discussion of the choice of the $c_{11}^\infty$ and $c'^\infty$ smooth curves. Note that the vertical scale for $c'$ is 10 times larger than that for $c_{11}$.

a function of temperature at ~ 16 GHz,[5] and the elastic stiffness corresponding to this wave is $c_L = c_{11} - c' + c_{44}$. The open circles shown in Fig. 5 represent $c_{11}$ values calculated from $c_{11} = c_L(16 \text{ GHz}) + c'^\infty - c_{44}^\infty$. (Since there is no dis-

persion for the [100] shear wave, $c_{44}^\infty$ can be replaced by the known $c_{44}^0$.) Near the transition these $c_{11}$ values should correspond to $c_{11}^\infty$ since the relaxation times becomes very long. The $c_{11}^\infty$ values between 242.5 and 297 °K were obtained by linear interpolation (see Fig. 5). Uncertainties in $c_{11}^\infty$ due to ambiguities in the $c'^\infty$ values are less than 1%, which would correspond to less than a 10% possible systematic error in the relaxation strength for the $c_{11}$ wave.

The values of the relaxation strength $C$ calculated at various temperatures from the smooth-curve values of $c^\infty$ and $c^0$ are shown in Fig. 6, where $1/C$ is plotted versus $\Delta T = T - T_\lambda$. The relaxation strength for the $c_{11}$ wave in NH$_4$Cl at 1 atm is also shown for comparison. This empirical plot indicates that $1/C$ varies linearly with $\Delta T$ for the [100] longitudinal wave in both NH$_4$Cl and NH$_4$Br. Indeed, this linear variation extends out to $\Delta T = 50$ for NH$_4$Cl.[3] The inverse relaxation strength for the longitudinal wave can be represented in the form

$$C^{-1}(\epsilon) = C^{-1}(0) + b\epsilon^m , \qquad (6)$$

where $\epsilon$ is the reduced temperature and $m$ is an empirical exponent equal to 1 at 1 atm. The parameters $C^{-1}(0)$ and $b$ are, respectively, 6.4 and 120 (in units of $10^6$ cm sec$^{-1}$) for NH$_4$Br; the



FIG. 6. Inverse relaxation strengths as a function of $\Delta T = T - T_\lambda$ (in °K). The results for NH$_4$Cl are taken from Ref. 3.
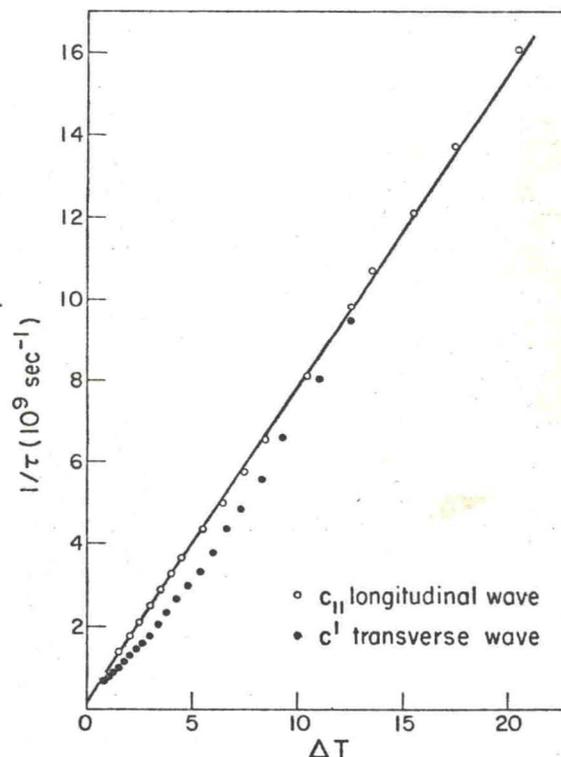


FIG. 7. Inverse relaxation times for the [100] longitudinal wave and the [110] transverse wave as a function of $\Delta T$ (in °K).

corresponding values are 5.8 and 67.7 for $NH_4Cl$.[3] In the case of the $c'$ wave, the relaxation strength is less well established and it does not seem justifiable to attempt an analytical representation.

The relaxation times obtained from Eq. (4) by using the experimental $\alpha_c/\omega^2$ data in Table I and the above choices of $C$ values are shown in Fig. 7, where $1/\tau$ is plotted versus $\Delta T$. This figure indicates that the longitudinal relaxation times can be well represented by

$$1/\tau = 1/\tau(0) + a\epsilon^n, \tag{7}$$

where the subscript $S, x$ has been dropped for convenience. The parameters $1/\tau(0)$ and $a$ corresponding to the line in Fig. 7 are 1.8 and 1780 (in units of $10^8$ $sec^{-1}$) and the exponent $n = 1$. However, the limiting value of $\tau$ at $T_\lambda$ should not be considered as well established, since a reasonably good fit can also be achieved with $1/\tau(0) = 0$ and $a = 1830$. The transverse relaxation times are quite similar in magnitude to the longitudinal $\tau$ values but appear to vary in a systematically different manner. Indeed, the best fit to these $1/\tau$ values gives an exponent $n = 1.25$. A decision as to whether such differences are real or not will require reliable values of $c'^\infty$ as a function of temperature.

It is important to note that the fit to the attenuation using Eq. (4) with experimental $C$ values and the form for $\tau$ given in Eq. (7) is much better throughout the entire temperature range than the fit with Eq. (1). The $\chi^2$ value is quite good (0.9) and there are no systematic deviations. Even if a single relaxation formalism is not valid, the analysis we have carried out for low-frequency attenuation data is an appropriate way to treat the slowly varying strength $C$ and obtain the exponent $n$ for the critical relaxation frequency. That is, we can reinterpret Eq. (4) as the low-frequency form of a more general relaxation theory involving a spectrum of relaxation times. If the sound wave is coupled to the order-parameter fluctuations via a dependence of the $NH_4^+$-ion interactions on the lattice parameter (volume magnetostrictive coupling in the analogous magnetic case), the major contributions to $\alpha$ at small $\omega$ should come from fluctuations with $k \approx \kappa$, where $\kappa$ is the inverse correlation length.[14] In this case, our $1/\tau \propto \Omega_\kappa$,

which is the characteristic frequency for order-parameter fluctuations with wave vector $\kappa$. Since the ammonium halides are formally quite similar to magnetic systems in their ordering, we will briefly state a few theoretical results for antiferromagnets. For an isotropic Heisenberg antiferromagnet[16] $n$ would equal $\theta\nu$, where $\theta = \frac{3}{2}$ and $\nu$ is the exponent for the inverse correlation length $(\kappa = \kappa_0 \epsilon^\nu)$. Thus, the conventional choice of $\nu = \frac{2}{3}$ would be consistent with our value of $n = 1$. However, the Hamiltonian for $NH_4Br$ is complicated owing to the presence of two competing interactions,[2] and it does not seem that one should expect agreement with theories based on an isotropic Heisenberg model. The behavior of the critical spin relaxation rate for an anisotropic Heisenberg antiferromagnetic seems to be best described by "conventional" (van Hove-type) theory,[17,18] according to which $1/\tau$ should vary like the inverse susceptibility. Thus the exponent $n$ should equal $\gamma$, which on the basis of scaling relations is given by $\gamma = (2 - \eta)\nu$. The usual choice of $\eta \simeq 0$ and $\nu \simeq \frac{2}{3}$ gives $\gamma \simeq \frac{4}{3}$, in poor agreement with $n$. In much previous acoustic work, the variation of the relaxation strength was unknown and ignored, which led to the assumption that the exponent $l$ in Eq. (1) was the same as $n$. In this view, the value $l = 1.35$ would appear to be consistent with $\gamma \simeq \frac{4}{3}$, but we consider this to be a fortuitous agreement. Indeed, if the conventional magnetic theory is appropriate to $NH_4Br$, the value of $n$ would be consistent with the classical (Landau) exponents $\eta = 0$, $\nu = \frac{1}{2}$, $\gamma = 1$. Further progress requires a better understanding of the effective Hamiltonian for $NH_4Br$ and greater development of the dynamical theories of critical phenomena.

As a final point, let us compare the dynamical aspects of the acoustic behavior of $NH_4Br$ with those of $NH_4Cl$. Although the behavior of the maximum dispersion (i.e., the longitudinal relaxation strength $C$) is very similar in the disordered phase of $NH_4Cl$ and $NH_4Br$, the variation in the relaxation time is strikingly different. For $NH_4Cl$ at 1 atm $1/\tau = 414 \times 10^8$ $\epsilon^{0.6}$ $sec^{-1}$ up to $\Delta T = +50$ °K.[3] Furthermore, there is no dispersion or critical attenuation associated with the $c'$ wave in $NH_4Cl$. Thus the dynamical critical behavior in these two isomorphous crystals differs considerably.

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