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ULTRASONIC ATTENUATION NEAR THE LAMBDA TRANSITION IN NH_4Cl AT HIGH PRESSURES*

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Abstract—The attenuation coefficient α of longitudinal ultrasonic waves propagating in the [100] direction of NH_4Cl has been measured as a function of both temperature and pressure in the vicinity of the lambda line. For seven different temperatures between 241–270°K measurements were carried out at 10, 20 and 30 MHz as the pressure was varied from 1 to 3500 bar. Lines of constant attenuation lie parallel to the lambda line in the ordered phase; however, such lines of constant attenuation in the disordered phase converge toward the lambda line as the pressure is increased. In both phases, isobaric values of α vary like $|T-T_\lambda(p)|^{-1}$ near the lambda line, where $T_\lambda(p)$ is the transition temperature at pressure p.

1. INTRODUCTION

THE LAMBDA transition in ammonium chloride is well established as an order-disorder transition involving the relative orientations of the NH_4^+ ions in a CsCl-type cubic structure [1]. In the ordered phase all the NH_4^+ ions are oriented 'parallel' to each other, while in the disordered phase they are randomly distributed with respect to two equivalent orientations. Thus the ordering in NH_4Cl is directly analogous to spin ordering in a simple-cubic ferromagnet.

Both the ultrasonic velocity and attenuation are 'anomalous' near this transition, although the only quantitative high-pressure work has been concerned with velocity measurements. Garland and Renard[2] used the pulse-superposition method to determine both longitudinal and shear velocities at 20 MHz over a wide range of temperature and pressure. Shear waves exhibited a distinct step-like velocity anomaly but gave no indication of unusual attenuation. These shear data thus provide an accurate indication of the pressure dependence of the transition temperature. In contrast, longitudinal waves showed a very sharp velocity minimum and were strongly attenuated near the lambda transition. All the velocity anomalies become less pronounced as the lambda line is crossed at higher and higher pressures.

There have been three investigations of the attenuation of [100] longitudinal waves at one atmosphere[3–5]. The most detailed of these is by Garland and Yarnell[4] and indicates the presence of first-order instability and hysteresis very close to T_λ. The present work involves a study of the longitudinal acoustic attentuation as a function of pressure up to 3·5 kbar at various constant temperatures between 235–280°K. This will allow us to define the temperature and pressure dependence in both the ordered and disordered phases.

2. EXPERIMENTAL PROCEDURE

The ultrasonic equipment used in most of this work was essentially identical to that used by Garland and Yarnell[4]. Toward the end, runs at 270·2 and 281·8°K were made using new ultrasonic equipment manufactured by Matec. A Model 120 master synchronizer was used to trigger a Tektronix 546A oscilloscope and to alternately trigger (at one-half

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the oscilloscope repetition rate) a Model 6000 pulsed generator/receiver and a Model 666 pulse comparator. The pulse comparator operates at 60 MHz for use with the superheterodyne receiver, which eliminates the time-consuming tuning involved for variable frequency units. The sample echoes and the comparison pulse are displayed alternately on the screen, but persistence of vision causes the two traces to appear simultaneously. The comparison pulse is superimposed directly on the echo to be measured and its amplitude is adjusted by the use of a calibrated attenuator.

The pressure equipment and constant-temperature bath were the same as those described by Garland and Young[6], except that Univis J-43 oil was substituted for petroleum ether as the bath fluid above 265°K. Argon gas was used as the pressure fluid. The pressure could be held constant to within ±3 bar during a measurement, and the temperature was held constant to within ±0·05°K during an entire run.

The ammonium chloride single crystals, which were grown by Schumaker[7], had sample lengths L at 25°C of 1·1615 cm (I), 0·8286 cm (II) and 0·8465 cm (III). Parallel faces were flycut on crystal II with a high-speed milling machine. Natural faces were used for crystals I and III. The orientation of each specimen was checked by a back-reflection X-ray method, and the normal was found to be within 0·5 deg of the [100] axis in all cases. Chrome-gold plated X-cut quartz transducers were bonded to the samples with a phthallic anhydride–glycerin polymer[2], and measurements were made at 10, 20 and 30 MHz.

In making a run, the bath was brought to the desired temperature and the system was allowed to equilibrate for at least one hour. After the attenuation was measured at atmospheric pressure, the system was pressurized to about 3·5 kbar and allowed to equilibrate for another 15–20 min. Then a series of attenuation measurements was made as argon was vented from the cell. Well away from the transition line, a period of ten minutes was allowed for equilibration after each change in pressure. Close to the transition line, a period of twenty to thirty minutes was required. At the end of a pressure run, the one-atmosphere balance point of the manganin resistance bridge was remeasured and used to correct the readings for any drift from the original zero setting.

The echo pattern for all runs below 250°K deteriorated when the pressure had dropped to about 500 bar. Although about half the runs in the range 250·6–260·6°K also showed this deterioration, the runs at 265·6 and 270·2°K showed a good echo pattern at all pressures. Fortunately, the signal always reformed into a good echo pattern when the cell was re-pressurized, indicating difficulties with the bond rather than the sample. However, after prolonged use, crystals I and III developed small cleavage cracks (parallel to the direction of propagation and 1 to 2 mm deep) on the face bonded to the transducer. Reflections from these cracks distorted the echo display, and the crystals could no longer be used.

3. RESULTS AND DISCUSSION

Background attenuation

Separation of the anomalous attenuation associated with the order-disorder transition from the uninteresting but appreciable 'background' attenuation represent the principal difficulty in evaluating our data. The background attenuation is due to a combination of pressure-independent contributions (such as beam spread and scattering losses) and pressure-dependent losses. Both types of loss are appreciable in our case, but the dominant contribution arises from changes in the impedance match at the gas-sample interface. As the gas is compressed, its acoustic impedance increases and more ultrasonic energy is transmitted into the gas. This causes a considerable attenuation per echo at high pressures. In principle one could calculate the background attenuation, but in practice it is necessary to carry out an

emprical determination. In doing this, we have assumed that the observed attenuation per echo, α_{total}, is a sum of background and intrinsic cooperative contributions. Once α_{back} is known, the desired attenuation coefficient α (in neper cm^{-1}) is obtained by simply dividing $(\alpha_{\text{total}} - \alpha_{\text{back}})$ by 8·69 $(2L)$.

Total attenuation values obtained at 30 MHz as a function of pressure on a fused-silica test sample at 250 and 260°K showed very little change with temperature, which strongly suggests that the background attenuation is independent of temperature over a moderate range. All the 20 MHz runs were made on crystal I using transducers with an $\frac{1}{8}$ in. active spot, and these data at various temperatures were combined to construct a temperature-independent background as a function of pressure. Almost all the 30 MHz runs were made on crystal II, also using $\frac{1}{8}$ in. transducers, and the same analysis was made for these data. This analysis consisted of plotting α_{total} vs. $|T - T_\lambda|^{-1}$ at several constant pressures, where Γ_λ at each pressure is determined from the phase diagram of Renard and Garland[8]. This method of handling the data produces almost linear plots which can be easily extrapolated to zero (infinite ΔT) to yield the background attenuation. For Garland and Yarnell's 1-atm data[4], where there is little or no background attenuation, such plots are close to linear over a wide temperature range. It appears that a comparable behavior persists at high pressures even though the fraction of the total attenuation due to the background loss is increasing.

Another method of determining the background attenuation is to carry out isotherm runs which do not cross the lambda line in the range 0–3·5 kbar. This was done at 236·4°K on crystal I, and the results at pressures above 1 kbar (sufficiently far away from the lambda line) were in good agreement with those obtained with the first method. A series of runs were made at 10 and 30 MHz on crystal III using $\frac{1}{4}$ in. transducers. Data obtained at 240·5°K were used to establish a high-pressure ($p > 1{\cdot}5$ kbar) background curve for a 255·6°K run, and 281·8°K data provided a complete background curve for a 270·2°K run. It was observed that the pressure variation of the background attenuation was the same in the ordered and in the disordered phase.

Critical attenuation

One-atmosphere data has shown that the critical attenuation α is quadratic in frequency over the range 5–60 MHz except perhaps at temperatures very close to Γ_λ[3, 4]. Our present attenuation data at 10–30 MHz are proportional to ω^2 at all temperatures and pressures. Typical isotherms of ω^2/α vs. pressure are shown in Figs. 1 and 2. The arrow

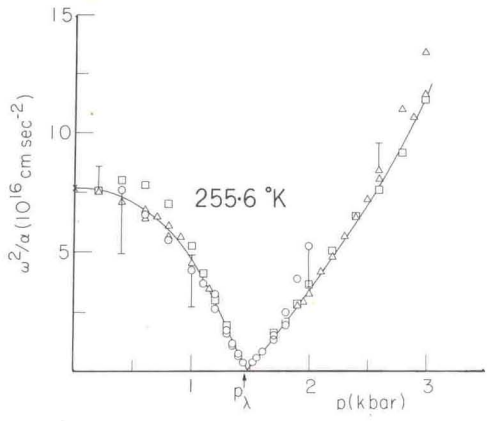

Fig. 1. Variation of ω^2/α with pressure at 255·6°K (see text): ○ 10 MHz. □ 20 MHz. △ 30 MHz.

labelled p_λ on each plot indicates the critical pressure at that temperature as determined from shear velocity data[2]. Garland and Yarnell's ω^2/α values[4] are indicated by the crosses on the vertical axis, and the smooth curves were drawn so as to tie into these values. Smooth-curve ω^2/α values along all seven isotherms are listed in Table 1. These results are subject to both experimental errors in α_{total}, which are largely random in nature, and to systematic errors related to the choice of α_{back}. These two contributions to the

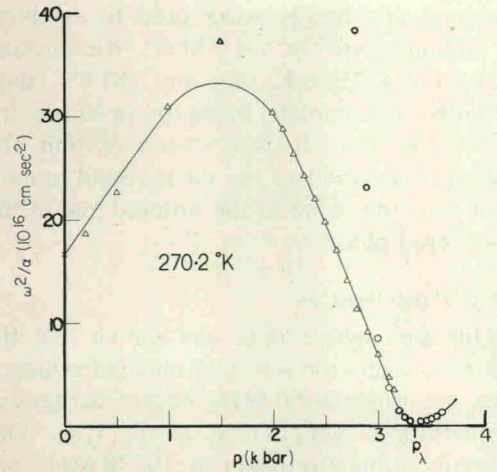

Fig. 2. Variation of ω^2/α with pressure at 270·2°K: ○ 10 MHz, △ 30 MHz.

uncertainty are comparable near the transition but uncertainties due to α_{back} are dominant away from the transition region.

A somewhat non-exponential variation in the echo amplitudes is the limiting factor in the accuracy of our α_{total} values. However, the character of the echo pattern did not change during a pressure run, and ±5 per cent represents our estimate of the random error in measuring α_{total}. The effect of fluctuations or errors in the temperature and pressure varies considerably. Near the lambda line, where α is a sensitive function of p and T, this can cause ±4 per cent errors in α. In the essentially normal region away from the lambda line, this will cause only a 0·7 per cent uncertainty in α. An estimate of the systematic error in α due to the choice of α_{back} was obtained for the 255·6°K run by drawing an alternate background for each frequency. The vertical error bars shown in Fig. 1 illustrate the effect of this change on a few representative data points. Near the transition pressure, the α values change by about 10 per cent at 10 MHz and 5 per cent at 20 and 30 MHz. Far from the transition, the change

Table 1. *Smooth-curve values of* ω^2/α, *in units of* 10^{16} cm sec^{-2}, *as a function of pressure at various constant temperatures*

p (kbar)	241·0	246·5	250·6	255·6	260·6	265·6	270·2°K
0·001	0·80		4·95	7·70	10·40	13·60	16·7
0·2	1·55		4·55	7·60	10·90	14·50	19·5
0·4	2·45		3·80	7·30	11·00	15·00	22·4
0·6	3·55	1·35	2·55	6·75	10·85	15·25	25·2
0·8	4·75	2·25	0·95	5·90	10·50	15·35	27·9
1·0	6·00	3·25	0·75	4·70	9·85	15·15	30·5
1·2	7·35	4·30	1·75	2·90	9·00	14·70	32·3
1·4	8·80	5·45	2·85	0·80	7·75	14·00	33·0
1·6	10·30	6·65	4·25	0·85	6·00	12·85	32·9
1·8	11·80	7·90	6·05	2·10	3·70	11·20	32·0
2·0	13·35	9·15	8·15	3·40	1·00	9·20	30·1
2·2	14·90	10·45	10·45	4·75	0·80	6·90	26·4
2·4	16·50	11·75	12·80	6·15	2·50	4·45	21·9
2·6				7·70	4·15	1·90	17·0
2·7						0·60	
2·8				9·45	5·80		11·9
2·9						0·40	
3·0				11·45	7·45	1·15	6·60
3·2						2·75	1·50
3·3							0·35
3·4							0·40
3·5							0·80
3·6							1·35

is about 35 per cent at 10 MHz and 10 per cent at 20 and 30 MHz. It is felt that the original choices of background were definitely preferable, which is supported by the agreement among ω^2/α values at different frequencies. However, alternate background curves cannot be completely ruled out as limiting possibilities.

Figure 3 shows the NH_4Cl phase diagram

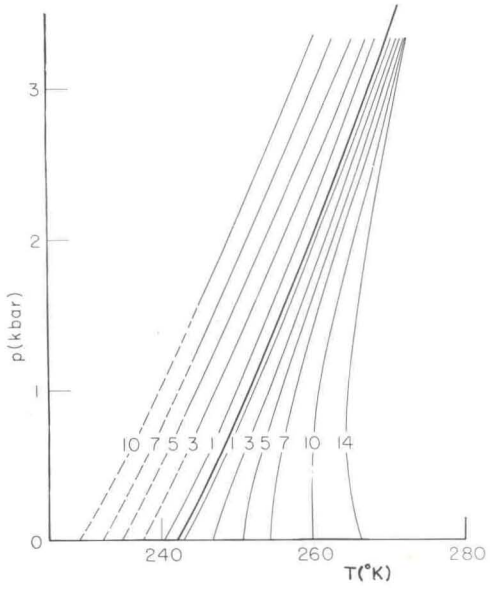

Fig. 3. Topology of the α-p-T surface. The heavy line is the lambda line as reported in Ref. [2] and the light contour lines represent the loci of constant values of ω^2/α (in units of 10^{16} cm sec^{-2}). The dashed portions of these lines indicate a region of greater experimental uncertainty; however, the 1-atm values are well known at low temperatures from Ref. [4].

with lines of constant ω^2/α added. In the low-temperature ordered phase these lines of constant attenuation lie nearly parallel to the lambda line. In the disordered phase, constant-attenuation lines are closely spaced at 3 kbar and spread apart considerably at lower pressures. This difference in behavior between the two phases is emphasized by the attenuation isobars shown in Fig. 4. These isobars were constructed from the smooth-curve values in Table 1. Although there was some scatter in the available points, no

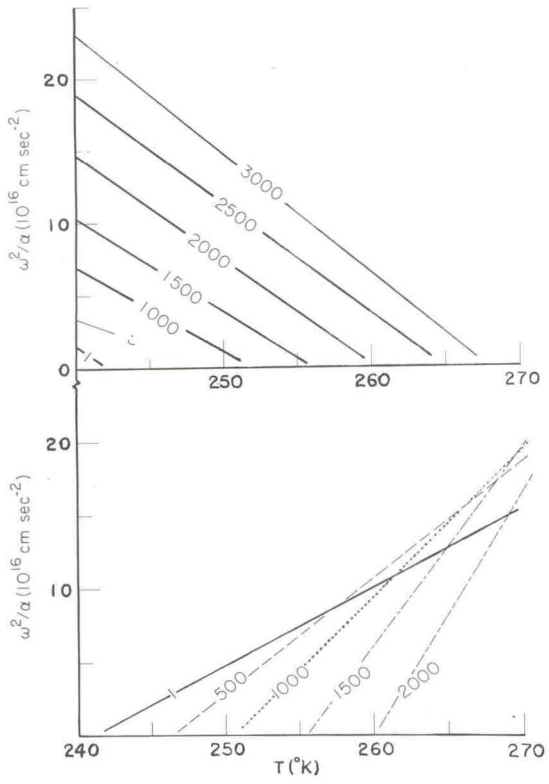

Fig. 4. Isobaric variation of ω^2/α with temperature. Pressure values indicated on each line are in bar.

systematic curvature could be seen and the best straight lines were drawn (giving greater weight to those points close to the transition temperature). Lines corresponding to directly measured one-atmosphere data[4] have been added to this figure for comparison with our high pressure results. The isobars in the ordered phase are roughly parallel and have slopes approximately equal to the one-atmosphere value of $7{\cdot}2 \times 10^{15}$ cm sec^{-2} deg^{-1}. Isobars in the disordered phase have slopes which are a strong function of pressure ranging from $5{\cdot}1 \times 10^{15}$ cm sec^{-2} deg^{-1} at 1 atm to $16{\cdot}4 \times 10^{15}$ at 2000 bar. Figures 3 and 4 both indicate a corresponding-states behavior for the ordered phase but not for the disordered phase. However, the variation $\alpha \sim \omega^2|T - T_\lambda(p)|^{-1}$ seems to hold at all pressures up to 3 kbar in both phases.

A brief review of Landau theory for the critical relaxation of long-range ordering near an order-disorder transition has been given previously in connection with the 1-atm attenuation measurements on NH_4Cl [3, 4]. Recently, there has been a rapid development of fluctuation theories which predict that $\alpha \sim \omega^2|T-T_c|^{-\theta}$ but do not yet agree on the critical exponent θ [9]. No theoretical work has yet been done on the isothermal variation of α as a function of $|p-p_c|$.

In the future we hope to extend these measurements with special emphasis on the immediate vicinity of the lambda line. One can already notice a distinct difference in the sharpness of the attenuation peak as p_λ increases (see Figs. 1 and 2). It would be of interest to follow this behavior up to higher pressures.

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