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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