Elastic Constants of Ammonium Bromide. II. High-Pressure Ultrasonic Investigation of the Phase Transitions*

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The abiabatic elastic constants of single-crystal ammonium bromide have been measured at 20 MHz as functions of temperature and pressure in the region from 180°–240°K and from 0–6 kbar. A new high-pressure ordered phase, denoted as O_{II}, has been discovered in this temperature range. The acoustic properties of the new O_{II} phase were investigated with emphasis on the regions of the first-order phase transition from the O_{II} phase to the ordered tetragonal phase and the lambda transition from the O_{II} phase to the disordered cubic phase. The region of the lambda transition from the ordered tetragonal phase to the disordered cubic phase was also studied. A detailed comparison is made with the behavior of ammonium chloride near its order–disorder phase transition.

INTRODUCTION

Ammonium halide crystals undergo lambda transitions of the order–disorder type involving the relative orientations of the tetrahedral NH_4^+ ions. The most detailed investigations have been devoted to NH_4Cl and NH_4Br, and it is well established that both of these crystals at room temperature 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.[1] 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. In NH_4Br, an ordered tetragonal phase is known to exist at low pressures in addition to a low-temperature ordered cubic phase.

An earlier paper[2] (to be called Paper I) has reported the results of ultrasonic velocity measurements on NH_4Br over a wide range of pressure (0–12 kbar) at temperatures between 255° and 315°K; a general review of other investigations of NH_4Br was given at that time and will not be repeated here. The high-pressure data in Paper I all pertain to the disordered phase away from any transition lines and provide a clear indication of the "normal" behavior of any CsCl-type ammonium halide free from the effects of ordering. In addition, Paper I includes some results of velocity measurements made at 1 atm near the order–disorder transition at 234.5°K; indeed, this lambda point has been the center of interest for most previous investigations of NH_4Br.

The present paper is closely related to an ultrasonic study of NH_4Cl which was made over a wide pressure–temperature region on both sides of the lambda line.[3] Special emphasis was given to the anomalous behavior in the NH_4Cl elastic constants due to the cooperative ordering process, and it was possible to interpret those results in terms of a compressible Ising model.[4] In view of the fact that no information was obtained in Paper I about high-pressure phase transitions, it was felt that new work on NH_4Br at lower temperatures would provide some interesting comparisons between cooperative phenomena in NH_4Cl and NH_4Br. This idea was confirmed by the fact that there were several puzzling aspects to the limited high-pressure data that were available on NH_4Br. Bridgman[5] found a phase change at 201°K and 1630 bar, which he assumed to be between the same two phases as that at 234.5°K and 1 bar. However, the volume change associated with this high-pressure transition was essentially discontinuous, as in a first-order change, and not the continuous rapid variation observed for NH_4Cl at 1 atm[6] and at high pressures[5] or for NH_4Br at 1 atm.[6] Furthermore, Stevenson[7] had obtained phase diagrams of several ammonium halides, but his high-pressure transition line for NH_4Br did not correlate well with the supposedly corresponding lambda line in NH_4Cl.

Therefore, we have made velocity measurements on both longitudinal and transverse accoustic waves in single-crystal ammonium bromide at pressures from 0 to 6 kbar and at temperatures between 180° and 240°K. These results are presented in terms of the variation of the three adiabatic elastic constants c_{11}, c_{44}, and $C' = (c_{11} - c_{12})/2$, which can all be obtained directly from experimental ultrasonic velocities (see Paper I for the relations between c_{ij} and the velocities). Third-order

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elastic constants are not used, and for pressures above 1 atm the quantities c_{11}, c_{44}, and C' are "effective" elastic constants.[8]

To provide a framework for the subsequent presentation of quantitative data, the most important qualitative result of our work will be stated immediately: A new high-pressure ordered phase (to be denoted as O_{II}) has been discovered. The NH₄Br phase diagram, as largely determined by the present work, is shown in Fig. 1. Extensive measurements were made with both shear and longitudinal waves in the new high-pressure ordered phase O_{II} and in the disordered cubic phase D as well as along the new lambda line between these phases. Domain formation takes place in the ordered tetragonal phase O_T, and the resulting attenuation makes velocity measurements difficult. Various attempts were made to align the tetragonal axes and obtain a single-domain crystal, but these were unsuccessful. Pressure measurements were made, however, in this phase for the "average" c_{44} shear constant which results from a random orientation of the tetragonal axes of the domains along the directions of the three equivalent axes in the disordered cubic phase.[2] A few measurements were also made in the low-temperature ordered phase O_I. This was very difficult since single crystals crack upon undergoing the first-order phase change from O_{II} to O_I. The O_I phase definitely has a CsCl-type cubic structure,[9] and the ordering almost certainly corresponds to the parallel orientation of all NH₄⁺ ions which is observed in the low-temperature phases of NH₄Cl and ND₄Br.[1] Although there are many simi-

larities in the acoustic behavior along the D–O_{II} lambda line and along the lambda line in NH₄Cl, it can be proved acoustically that the O_{II} phase is *not* analogous to the parallel-ordered cubic phase of NH₄Cl. Suggestions for possible O_{II} structures are given in the Discussion.

EXPERIMENTAL DETAILS

Ultrasonic velocity measurements were made by a pulse-superposition method at a frequency of 20 MHz. Since the experimental procedures were very similar to those used previously,[2,3] only a few changes in detail will be described here.

A new high-pressure cell, made from A-286 stainless steel and suitable for use at low temperatures, was obtained from the Harwood Engineering Company. Petroleum ether was used as the hydraulic pressure fluid, and the pressure cell was immersed in a large, sealed thermostat bath of petroleum ether. Down to about −40°C, this bath was cooled with a commercial Freon refrigerating unit; below that temperature, cold nitrogen gas (obtained by boiling liquid nitrogen) was circulated through the cooling coils. A proportional temperature controller, Bailey Instrument Model 87-8, was used to maintain any given temperature to within ±0.05°K. Pressures, as determined with a calibrated manganin resistance gauge, could be maintained constant to within ±3 bar. With this modified apparatus, it was possible to operate from 0 to 6 kbar over the temperature range from ∼180° to ∼260°K.

Almost all of the data were obtained with the pressure system described above since petroleum ether could be pressurized to 6 kbar at 180°K without freezing. However, the lubricating properties of petroleum ether are very poor, and its extended use as the hydraulic fluid led to serious leaks in the sliding seals of the pressure intensifier. Therefore, a system utilizing argon as the pressure-transmitting fluid was installed in place of the original liquid hydraulic system. The data obtained using this gas system (all in the 0–3-kbar range) were in complete agreement with the earlier data.

Dow Resin 276-V9 was used for bonding the quartz transducers to the NH₄Br crystals in almost all cases. This bonding material worked very well for transmitting both transverse and longitudinal waves at pressures up to 6 kbar and temperatures down to 180°K when the sample was immersed in petroleum ether. McSkimin[10] has made impedance measurements for this resin, so the seal correction due to the phase shift at the transducer-bond end of the sample could be calculated. When gas was used as the high-pressure fluid, seals made with Dow Resin 276-V9 broke quite often upon applying pressure. Therefore, Dow 200 fluid with a viscosity of 1000 centistoke was substituted for
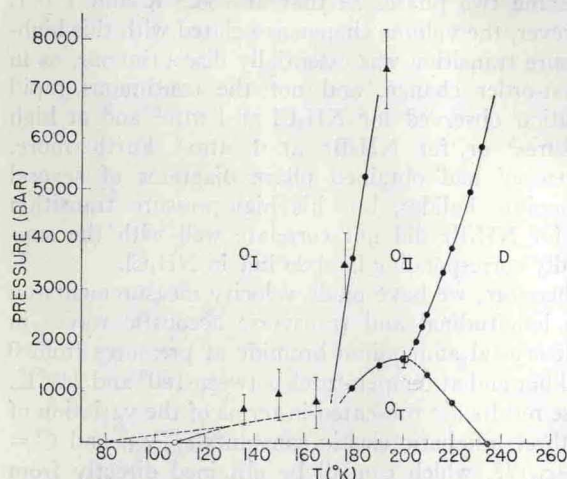

FIG. 1. Phase diagram for NH₄Br. Solid circles represent the present data, the open square point is from Bridgman (Ref. 5), the triangles are from Stevenson (Ref. 7), and the open circles at one atmosphere are from Stephenson and Adams (Ref. 14). The phases shown are the disordered cubic (D), ordered tetragonal (O_T), the new ordered phase (O_{II}), and the low-temperature ordered phase (O_I), which is thought to be the parallel-ordered CsCl-type cubic form.

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