V. ULTRASONIC PROPERTIES OF SOLIDS

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A. ORDER-DISORDER LAMBDA TRANSITION IN AMMONIUM CHLORIDE AT HIGH PRESSURES

The lambda transition in NH_4Cl, which involves an ordering of the orientations of the NH_4^+ ion, has been extensively studied by the ultrasonic pulse technique. Both longitudinal and tranverse (shear) acoustic velocities have been measured over a wide range of frequencies (5-60 Mc) and temperatures (150-320°K) at 1 atm, with special emphasis on the region close to the lambda point (243°K). At a fixed frequency of 20 Mc and at five temperatures spaced between 250°K and 310°K, the pressure dependence of the velocities has now been measured between 1 atm and 12,000 atm, with emphasis on the region where the isotherms cross the lambda line. (At 310°K the lambda transition occurs at ~10,000 atm; thus our pressure work gives data on both the ordered and disordered phases at a series of temperatures.)

The results of these velocity measurements as a function of pressure are shown in Figs. V-1, V-2, and V-3. The McSkimin pulse-superposition method was used, and the values of the three independent elastic constants are known within an error of less than 0.05%. As seen in Figs. V-1 and V-2, the shear constants c_{44} and C' undergo a rapid increase when the pressure is increased near the lambda line. This variation is related to the volume changes that occur in the crystal upon ordering. Indeed, it can be shown that c_{44} and C' show very little variation with temperature or the degree of ordering if the volume is maintained constant. The anomalous variations of the shear constants with temperature, which were observed previously at constant pressure,[1] can now be shown to be due to the anomalous volume changes and not to the ordering *per se*. Since these shear constants provide a sensitive probe for the behavior of the volume upon ordering, it is interesting to note the rapidly changing character of the anomaly near the lambda point at high pressures.

Longitudinal waves are strongly coupled to the ordering process, and c_{11} values at 1 atm show an abrupt dip to a *finite* minimum at T_λ (and thus the adiabatic compressibility goes through a sharp but finite maximum).[1] Our new data in Fig. V-3 show this type of finite dip in c_{11} upon crossing the lambda line with increasing pressure. Note again the change in the behavior of the anomaly at higher pressures. For c_{11}, there is still an appreciable influence of the volume, but the entire anomaly is by no means all due to volume changes. Figure V-4 shows the variation of c_{11} with temperature at a constant pressure of 1 atm and at a constant volume of 34.15 cm^3 $mole^{-1}$. The most important difference between these two curves is the way in which the minimum value is approached from temperatures above and below. Thus, these new data, together with

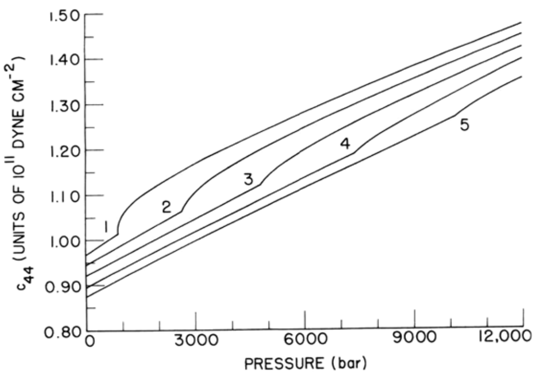

Fig. V-1. Shear elastic constant c_{44} versus pressure at (1) 250.7°, (2) 265.0°, (3) 280.0°, (4) 295.0°, and (5) 308.0°K.

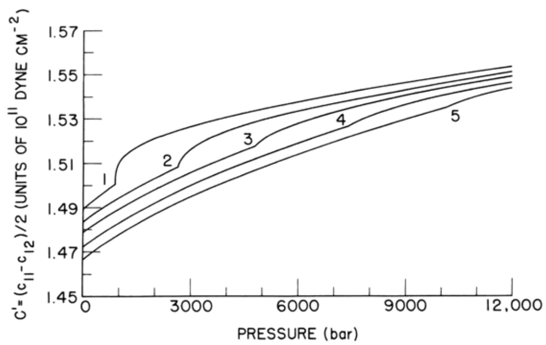

Fig. V-2. Shear elastic constant C' versus pressure at (1) 250.7°, (2) 265.0°, (3) 280.0°, (4) 295.0°, and (5) 308.0°K.

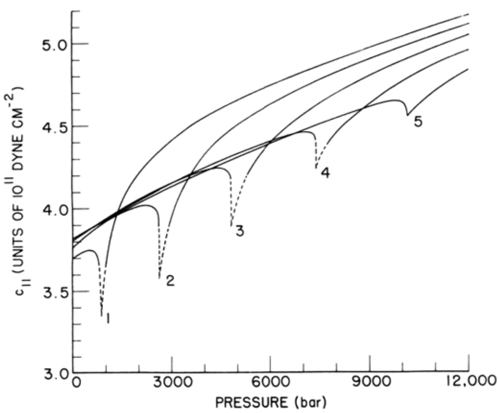

Fig. V-3. Compressional elastic constant c_{11} versus pressure at (1) 250.7°, (2) 265.0°, (3) 280.0°, (4) 295.0°, and (5) 308°K. Because of very high attenuation near the lambda line, data could not be obtained through the lambda point except at 308°K; for other temperatures the anticipated behavior is shown by the dashed lines.

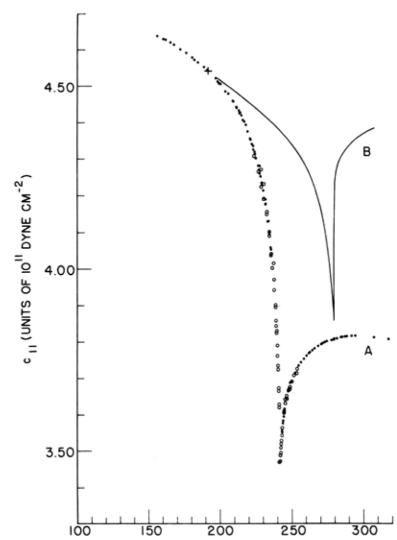

Fig. V-4. Variation of c_{11} with temperature at (a) constant pressure of 1 atm, and (b) constant volume of 34.15 cm^3 $mole^{-1}$. Solid dots represent new 1-atm measurements at 20 Mc/sec, and were obtained with the McSkimin method; open circles represent corrected data of Garland and Jones[1] at 5 and 15 Mc/sec.

our previous data, permit us to separate the effect of ordering, volume changes, and temperature changes. A detailed analysis of the effect of ordering alone (at constant volume and temperature) is in progress and will be reported elsewhere.

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References

1. C. W. Garland and J. S. Jones, J. Chem. Phys. 39, 2874 (1963).