Ultrasonic Investigation of the Lambda Transition in NH_4Br†

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The ultrasonic-attenuation coefficient α 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 ϵ 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 λ 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 λ 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 λ transition at low pressures involves an ordered tetragonal phase with "antiparallel" chains of NH_4^+ ions. Although the λ temperatures are fortuitously similar at 1 atm ($T_\lambda \simeq 242$ °K for NH_4Cl and 234.5 °K for NH_4Br), the λ 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 λ 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 τ for long-range ordering. A similar analysis 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_λ in NH_4Br. In addition to this qualitative difference, the critical exponents for the divergence of τ (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