V. ULTRASONIC PROPERTIES OF SOLIDS*

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RESEARCH OBJECTIVES AND SUMMARY OF RESEARCH

The principal goal of our ultrasonic investigations is to obtain information about the equilibrium and the dynamic behavior near phase transitions. In particular, we have emphasized both theoretical and experimental work on order-disorder lambda-type transitions in solids.

During the past year, a detailed investigation of ammonium chloride single crystals was completed. Very precise ultrasonic velocities were measured as functions of pressure from 0 to 12 kbar at temperatures of 250-315°K, and as functions of temperature from ~100 to 320°K at 1 atm. Ultrasonic attenuation data were also obtained on NH_4Cl near its λ point at ~243°K (see detailed report below).

The mechanical properties of a compressible Ising model have been investigated, and explicit expressions for the effect of ordering on the elastic constants of a cubic crystal have been derived. These theoretical predictions are in excellent agreement with the behavior of the constant-volume elastic constants of NH_4Cl. (Such constant-volume stiffnesses differ significantly from those at constant pressure, especially near the λ point.) In effect, a new approach to the study of order-disorder phenomena has been developed and exploited in a favorable case. Close to the critical temperature for ordering in NH_4Cl, we have also observed a distinct hysteresis (~0.9°K at 1 atm) and strong indications of a first-order transition. Quite general theoretical conditions have been established which predict the mechanical instability of an Ising model near its critical point. Thus, we conclude that NH_4Cl (and many other order-disorder crystals) may not undergo a pure lambda-type transition.

An investigation of NH_4Br is now complete in the disordered phase, and this work is being extended into the interesting region 100-250°K, and 0-6 kbar where several lambda transitions occur. New ultrasonic work is now beginning on two other systems – quartz near its α-β "lambda" transition at 847°K, and xenon near its liquid-vapor critical point. In the case of the quartz transition, a cooperative change in the lattice network structure is involved, and there is reason to believe that this lambda transition may show a first-order character. In both of these new systems, attenuation measurements are planned to provide an insight into the dynamical relaxation behavior near critical points.

RESEARCH REPORT: Ultrasonic Attenuation in Ammonium Chloride

The importance of a detailed investigation of the ultrasonic attenuation coefficient α very close to the order-disorder transition in NH_4Cl has been made clear by recent

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velocity measurements, which show hysteresis and strongly suggest that the crystal becomes unstable just before the "lambda point" is reached. Therefore, the attenuation of longitudinal waves propagating along the [100] direction has been carefully investigated at 10 Mc/sec, with special emphasis on the region 239.5-244.5°K. The results are shown

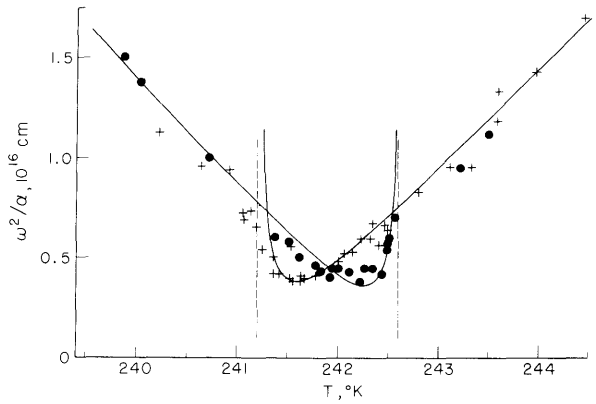

Fig. V-1. Plot of ω^2/α versus T near the order-disorder transition in NH_4Cl. Crosses indicate data obtained on cooling runs; solid points were obtained on warming runs.

in Fig. V-1. Again, hysteresis is observed. It is true that not all of the data points correspond to measurements on a crystal in complete thermodynamic equilibrium; it has not been our purpose to try to achieve the stable equilibrium state but rather to make meaningful measurements on the crystal in a metastable state.

The data in Fig. V-1 are consistent with the usual relaxation expression

$$\alpha = C\omega^2\tau/(1+\omega^2\tau^2) \tag{1}$$

with a relaxation time for long-range ordering given by $\tau = A/\Delta T$, as first suggested by Landau and Khalatnikov if we define ΔT by

$$\left.\begin{aligned} \Delta T^+ &= T - 241.2 \qquad \text{above transition} \\ \Delta T^- &= 242.6 - T \qquad \text{below transition} \end{aligned}\right\} \tag{2}$$

The lines in the figure are based on Eqs. 1 and 2 with $C \approx 3.4 \times 10^{-8}$ and $A \approx 5.6 \times 10^{-9}$ in cgs units. Thus we see that NH_4Cl above the transition (disordered phase with higher molar volume) approaches a lambda point at 241.2°K on cooling, while NH_4Cl below the transition (ordered phase with lower molar volume) approaches a different lambda point at 242.6°K upon warming. These values differ because the interaction between NH_4^+ is a function of volume. And indeed, the crystal is metastable near its lambda points (see

point taken on "cooling" after waiting one hour at 241.5°K), in agreement with our Ising model theory.

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