

V. ULTRASONIC PROPERTIES OF SOLIDS

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RESEARCH OBJECTIVES

At present, the principal goal of our ultrasonic investigations is to obtain information about the equilibrium and the dynamic behavior near transition points. In particular, we have used a variety of experimental and theoretical approaches to study lambda-point transitions in crystals.

The attenuation coefficient α of longitudinal ultrasonic waves has been measured in single-crystal ammonium chloride as a function of acoustic frequency and of temperature near the lambda point. As one would expect, the temperature dependence is large, and a very sharp maximum is observed in α at the order-disorder critical temperature. These results have been analyzed in terms of a relaxation model with a highly temperature-dependent relaxation time for the ordering of NH_4^+ orientations. In the future, it is planned to extend the frequency range and the temperature stability in the immediate vicinity of $T_\lambda = 243^\circ\text{K}$.

High-pressure measurements have been made to separate the effect of volume changes from the effect of ordering on the elastic constants of NH_4Cl near its lambda transition. Using McSkimin's pulse superposition method, which is accurate to at least 1 part in 10^4 , we have measured c_{11} , c_{44} , and C' as functions of pressure at five different temperatures. It is interesting to note that the character of the transition changes slowly as one moves up along the λ -line. At high pressures, anomalous changes in elastic properties near $T_\lambda(p)$ are much smaller than at 1 atm. Details will be reported later.

Ammonium bromide is currently being studied because it also undergoes an order-disorder lambda transition near 235°K . In contrast to NH_4Cl , the ordered phase consists of antiparallel chains of NH_4^+ ions, and has a larger molal volume than the disordered phase. Velocity data that determine c_{11} and C' have been obtained down to the transition temperature but not below; data on c_{44} were measured through the transition (down to 215°K). Presumably, scattering of the ultrasonic waves because of the presence of antiphase domains makes measurements impossible below T_λ , except for pure angle shears. Pressure coefficients in the disordered phase are being measured at several temperatures, and they agree well with our NH_4Cl data. Future work at high pressures and low temperatures to observe the parallel ordered structure is contemplated.

Some theoretical work has been devoted to the so-called Pippard equations. These are phenomenological equations interrelating various thermodynamic quantities (the volume thermal expansion α , the isothermal compressibility β and the heat capacity C_p) which change very rapidly near a λ -point transition. The Pippard equation relating C_p to α has been shown to be valid for β -brass near its order-disorder transition at $\sim 735^\circ\text{K}$. As a result of this, one can predict that the static adiabatic compressibility should have a very small peak at T_λ . Failure to observe such an anomaly in elastic data obtained with 10 Mc/sec ultrasonic waves is most probably due to a long relaxation time associated with the ordering in β -brass. Another aspect of work on the Pippard equations was a generalization of the previous theory in terms of stress-strain variables. The resulting equations, which interrelate α_i , s_{ij}^T , and C_p near a λ -point, were used to

(V. ULTRASONIC PROPERTIES OF SOLIDS)

correlate and explain various data on quartz near its α - β transition. A consequence of the new equations is the prediction that $C' = (c_{11} - c_{12})/2$ should be constant near a λ point. Our previous data on the elastic constants of ammonium chloride show that C' has a very much smaller change than either c_{11} or c_{12} , but some change is observed. This is presumably due to volume effects that occur at T_λ , but it suggests that the Pippard equations are only completely valid for harmonic solids.

Finally, a calculation has been made of the change in lattice energy and compressibility for the process of ordering at constant volume in ammonium chloride. It was assumed that the NH_4^+ ion is rigid and has a fixed charge distribution. Although the calculated energy change ΔU was in reasonable agreement with the value to be inferred from the experimental critical temperature for ordering, the calculated change in the bulk modulus $\Delta(1/\beta)$ was of the wrong order of magnitude and had the wrong sign as compared with our experimental value. It definitely seems that one must use a model in which the charge distribution in the NH_4^+ changes with the $\text{NH}_4^+ - \text{Cl}^-$ distance (because of polarization).

In the future, we hope to begin new work on other types of crystals (such as ferroelectrics and ferromagnets near their Curie temperatures or antiferromagnets near the Néel temperature) and on binary-liquid systems near their critical points, and also to explore familiar liquid-gas critical points.

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