II. PHYSICAL CHEMISTRY

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A. THE ELASTIC CONSTANTS OF AMMONIUM CHLORIDE NEAR THE LAMBDA TRANSITION

The three independent adiabatic elastic constants of single-crystal ammonium chloride have been measured as functions of sound frequency from 5 mc to 55 mc and as functions of temperature from 160°K to 300°K by an ultrasonic pulse technique.[1] Special attention was given to the temperature region around 243°K; at this critical temperature ammonium chloride undergoes an order-disorder transition[2] involving the relative orientations of the tetrahedral ammonium ions in a CsCl-type cubic lattice.

The quantity measured in the ultrasonic pulse-echo technique is the time required for an elastic wave, excited by a quartz transducer, to traverse the sample, be reflected, and return to the transducer. This delay time in combination with the known dimensions of the sample, corrected for thermal expansion effects, gives the velocity of sound in the crystal. The three independent elastic constants of a cubic crystal can be determined from the following equations[3]:

(a) For a longitudinal wave propagating in the [100] direction,

$$c_{11} = \rho U_{\ell}^2.$$

(b) For a transverse wave propagating in the [100] direction,

$$c_{44} = \rho U_t^2.$$

(c) For a transverse wave propagating in the [110] direction with particle motion perpendicular to the [100] axis,

$$\tfrac{1}{2}(c_{11}-c_{12}) = \rho U_{t'}^2.$$

Here, ρ is the mass density, and U is the velocity of sound.

The results of these measurements are shown in Figs. II-1, II-2, and II-3, in which are shown the variations of c_{11}, c_{44}, and $(c_{11}-c_{12})/2$ with temperature at various frequencies. The longitudinal-wave data show a large variation in c_{11} near T_c and, also, a definite frequency dependence of c_{11} between 243°K and 285°K. Both sets of transverse-wave data show smaller changes near T_c and exhibit no systematic frequency dependence.

Figure II-4 shows the variation of c_{12} as calculated from the data given in Figs. II-1 and II-3. It is clear that the behavior of c_{12} is very similar to that of c_{11}, as one might expect on the basis of a very simplified model proposed by Dzialoshinskii and Lifshitz[4] to explain the elastic constants of $NaNO_3$.

The fact that c_{44} has different frequency and temperature dependencies in the

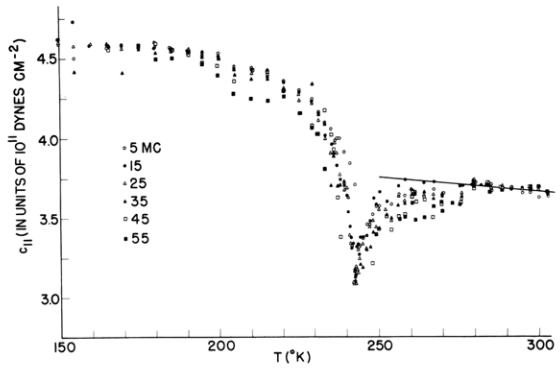

Fig. II-1. c_{11} vs T at various frequencies.

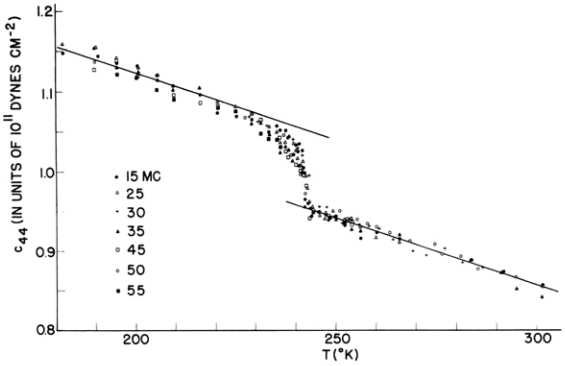

Fig. II-2. c_{44} vs T at various frequencies.

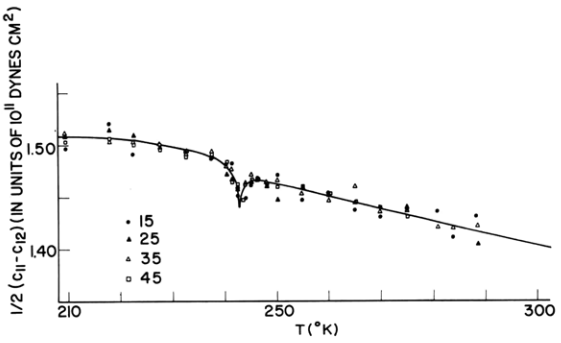

Fig. II-3. $\frac{1}{2}(c_{11}-c_{12})$ vs T at various frequencies.

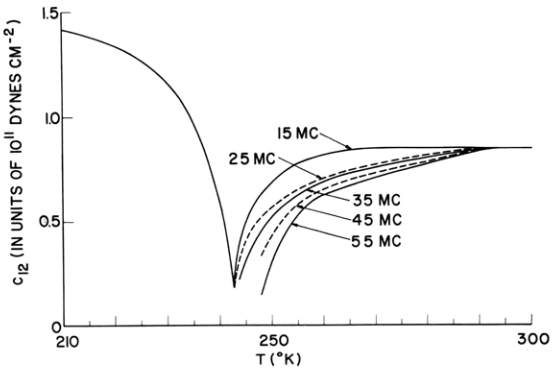

Fig. II-4. c_{12} vs T at various frequencies, calculated from smooth curves through the data shown in Figs. II-1 and II-3.

transition region than c_{11} and c_{12} is related to the fact that c_{11} and c_{12} are involved in a coupling between mechanical and thermal parameters, whereas c_{44} is not, as can be seen by considering the generalized stiffness matrix.[5]

The absorption of sound by the sample was also measured for the waves directly related to c_{11} and c_{44}. For the shear wave, no noteworthy absorption peaks were observed in the temperature range 135°K to 300°K between 5 mc and 55 mc. For the longitudinal wave, absorption peaks were observed at the transition temperature and also in the vicinity of 160°K. These low-temperature absorption peaks are caused by a relaxation effect in which ammonium ions cross a barrier between two unequal potential-energy minima; the temperatures at which maximum attenuation occurred for various frequencies are in good agreement with those predicted from nuclear magnetic resonance experiments.[6]

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References

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