

Rayleigh Scattering Studies of NH_4Cl at High Pressures*

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(Received 29 November 1971)

The integrated Rayleigh intensity of NH_4Cl in the region of the order-disorder transition line has been studied as a function of pressure and temperature. Increased scattering is observed near the tricritical point recently detected by Garland. Although the presence of domain scattering makes unambiguous interpretation of the data difficult, these data are consistent with the Landau-Ginzburg theory of critical opalescence.

Ammonium chloride undergoes an order-disorder phase transition involving an orientational ordering of NH_4^+ tetrahedra within a cubic lattice, and much experimental work has been done on this system in an effort to elucidate the detailed nature of the transition. Recent experiments^{1,2} have indicated that certain characteristics of the transition are different at high pressures than they are at atmospheric pressure. For example, Weiner and Garland² have measured changes in the length, l , of single crystals of NH_4Cl as a function of pressure along a number of isotherms and found that l exhibits a discontinuous jump at the transition line for temperatures below about 256°K, but is a continuous function of pressure for higher temperatures. (For these tempera-

tures the transition occurs at pressures greater than ~1500 bars.) Thus, their experiment indicates the existence of a tricritical point, where the line of first-order transitions (in the p - T plane) changes into a line of second-order transitions.

The possible existence of tricritical points (or Curie critical points) is included in Landau's phenomenological theory of phase transitions.³ Ginzburg⁴ has used this theory to predict the possible existence of critical opalescence associated with Curie critical points, but this effects has never been definitely observed in any crystal. In order to test the Landau-Ginzburg theory, we have studied the Rayleigh scattering intensity of NH_4Cl as a function of pressure for temperatures

between 252 and 264°K.

The sample used in this experiment was a single crystal, approximately $3 \times 5 \times 7$ mm³ in size, which was grown by slow evaporation from an aqueous solution containing about 20% by weight of urea as a habit modifier. The crystal was carefully polished with Linde A and methanol on Pellon paper and mounted in a black Bakelite holder, which served both to mask stray light from the sample and to hold the sample in the high-pressure, three-window optical cell. The cell itself was mounted inside a thermally insulated brass can, which was cooled by a Forma constant temperature bath (0.01°K) and circulator. Three windows through the can and insulation allowed a 90° light-scattering geometry to be utilized. A thermocouple and potentiometer were made to measure the temperature at the outside of the pressure cell to precision of $\pm 0.05^\circ\text{K}$ and an accuracy of $\pm 0.2^\circ\text{K}$. Pressure was generated with a hand pump and was measured to a precision of ± 10 psi and an accuracy of 1% with a Harwood Manganin gauge and a homemade Carey-Foster bridge circuit. Octoil S was used for the pressurizing fluid.

Light from a Spectra Physics 125 HeNe laser (6328 Å, 30 mW) was focused into the sample, and the light scattered at 90° was collected, filtered to eliminate Raman lines, and passed through a Fabry-Perot interferometer which was tuned to the Rayleigh line. The wave vectors of the incident and scattered light were directed along cubic axes of the crystal. As no width was ever observed to the Rayleigh line (see below),

it is assumed that the signal from the interferometer was proportional to the integrated Rayleigh intensity. The intensity of the beam transmitted through the crystal was recorded along with the Rayleigh intensity. This was necessary because the incident beam is so strongly attenuated near the transition (as much as 70% for the lowest temperature used), that the measured scattered intensity must be corrected in order to reflect the actual cross section.

The total Rayleigh intensity was measured as a function of pressure along seventeen different isotherms, six of which are indicated by the vertical lines crossing the transition line on the phase diagram of Fig. 1. The pressures used typically ranged from 5000 psi above the transition to 5000 psi below. The most serious experimental difficulty encountered was large day-to-day variations in the scattered intensity, due mainly to the beam and crystal shifting relative to each other. Fortunately, the shape of the curve of intensity versus pressure for a given temperature was reproducible from day to day; thus the appropriate correction factor was found to be multiplicative. The data were multiplicatively normalized to have unit intensity at a pressure 5000 psi below the transition line, which is well into the disordered phase, where normal behavior is expected. Separate measurements have indicated that this quantity, $I(p_0(T) - 5000)$, may actually decrease slightly with increasing temperature.

After the scans of intensity versus pressure were completed, an attempt was made to mea-

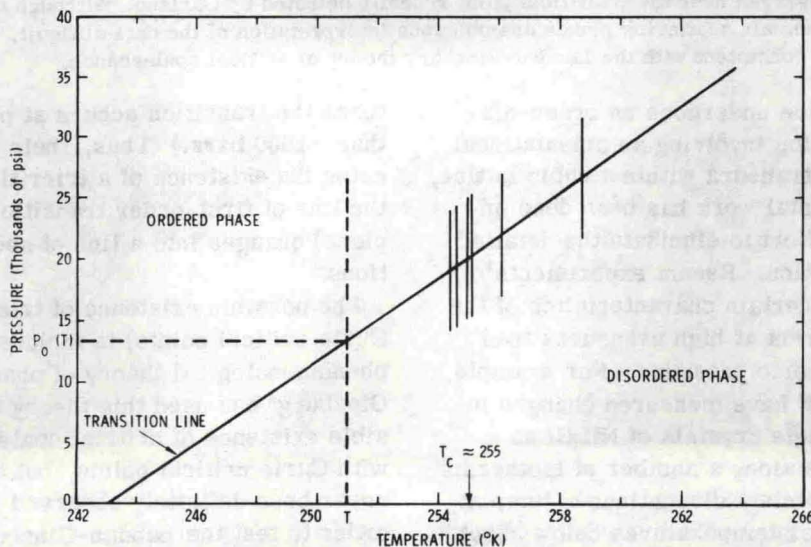


FIG. 1. Partial phase diagram of NH_4Cl showing the order-disorder transition line and six isotherms used in the experiment.