

FIG. 2. Rayleigh intensity (corrected for attenuation) versus pressure for the six isotherms indicated in Fig. 1. Insert: peak intensity versus temperature for each of seventeen isotherms.

sure the width of the Rayleigh line. For this experiment a longer spacer was used in the Fabry-Perot (1.3 vs 0.3 cm) which, with a finesse of 20, gave a resolution of  $0.02 \text{ cm}^{-1}$  (600 MHz). No changes in the width of the Rayleigh line were observable as a function of pressure and temperature, indicating that the scattering either has a very narrow spectrum or is completely elastic.

The intensity versus pressure data were normalized and corrected for incident beam attenuation as discussed above. The resulting intensity-versus-pressure curves for the six isotherms indicated on Fig. 1 are shown in Fig. 2. At the highest temperature (258.7°K) the scattering is relatively weak, but as the transition line is crossed at successively lower temperatures the peak scattering becomes progressively stronger down to a temperature of about 255°K. Below this temperature the scattering becomes weaker. For temperatures below 254°K the scattering again becomes progressively stronger with decreasing temperature. This behavior is shown in the insert of Fig. 1, where the maximum intensities obtained on all seventeen isotherms studied are plotted as a function of temperature.

The peak in the plot of maximum intensity versus temperature occurs at around 255°K, which is within a degree of the temperature where Garland found the transition to change from first order to second order, and we believe that this

peak may be associated with the proposed tricritical point. The large increase in the scattering at the lowest temperatures is probably due to domain scattering. At these temperatures the transition becomes noticeably discontinuous, and the domain walls should therefore be highly strained, leading to an increase in elastic scattering.

Unfortunately, the mechanism of the Rayleigh scattering was not determined by this experiment. There are three immediately obvious possible mechanisms, any combination of which might contribute to the scattering: (1) The scattering could be from the fluctuating order parameter  $\eta$ . Because of the high symmetry, the coupling to the dielectric tensor would be quadratic,  $\Delta\epsilon \propto \Delta(\eta^2)$ , and the Landau-Ginzburg (LG) theory would be applicable. (2) Since longitudinal strains are coupled to  $\eta$ , there could be scattering from critical strain fluctuations.<sup>5</sup> (3) The scattering could be from domains, and critical effects could be observed indirectly through their effect on the domain structure.

With the explicit understanding that these uncertainties (plus the somewhat uncertain normalization and attenuation correction procedures) make any quantitative interpretation of the data highly tentative, we wish to present evidence that our data are consistent with the LG theory of critical opalescence.

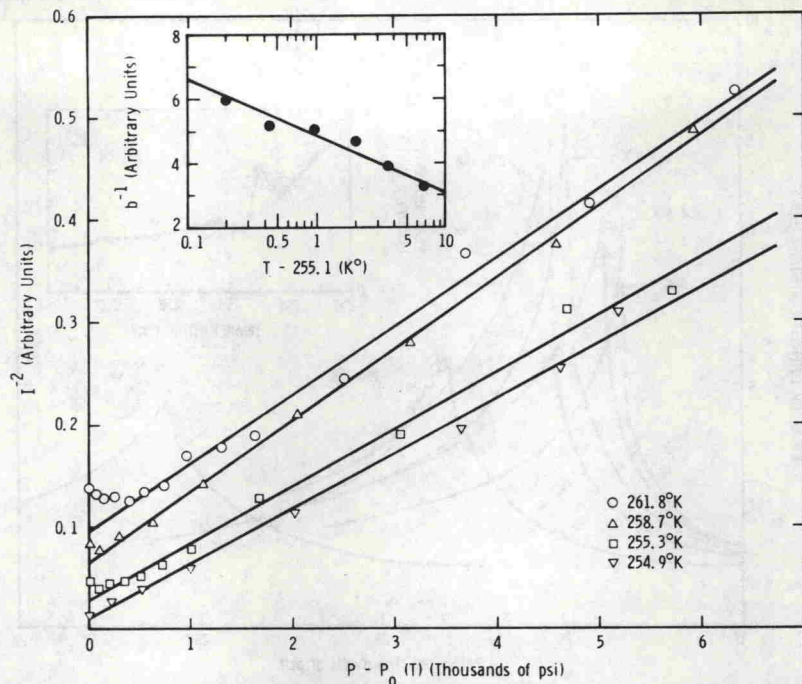


FIG. 3. Linear fits to  $I^{-2}$  vs  $p - p_0(T)$ . Insert: approximately logarithmic divergence of  $b$  for  $T > 255^\circ\text{K}$ .

LG<sup>4</sup> expand the free energy of the crystal as  $A(\eta, p, T) = A_0 + a\eta^2 + \frac{1}{2}b\eta^4 + \frac{1}{6}c\eta^6$ , where  $A_0$  is constant and  $a$ ,  $b$ , and  $c$  are functions of pressure and temperature. The coefficient  $a$  is positive in the disordered phase and negative (except near a first-order transition) in the ordered phase. The  $p$ - $T$  dependence of  $b$  is unknown, and  $c$  is usually taken to be a positive constant. If it is assumed that  $\eta$  couples quadratically to the dielectric tensor, then critical opalescence is expected in the ordered phase with intensity given by<sup>4</sup>

$$I \propto (b^2 - 2ac)^{-1/2}.$$

If  $b$  is positive at the transition, then the transition (which is continuous) occurs at  $a=0$ , and the maximum intensity is  $b^{-1}$ . If  $b$  is negative at the transition, then the transition (which is discontinuous) occurs at  $a=3b^2/8c$ , and the maximum intensity is  $2|b|^{-1}$ . At the Curie critical point,  $b$  is zero and the intensity diverges (critical opalescence).

To describe experiments done along isotherms, we can write  $a$  as<sup>6</sup>  $a = -a_0[p - p_0(T)]$ , where  $p_0(T)$  is the transition pressure at temperature  $T$  (see Fig. 1), and  $a_0$  is positive. If we make the crude assumption that  $b$  is nearly constant along isotherms, then we expect the data plotted as  $I^{-2}$  vs  $p - p_0(T)$  to fall on straight lines having intercepts of  $b^2$ . In Fig. 3 such plots are shown for

four different temperatures, along with linear least-squares fits (solid lines). All data are from the ordered phase. Except for the highest temperatures, where the curves turn up near the transition, the data are reasonably well represented by straight lines, as predicted, with  $b$  smallest for temperatures near  $255^\circ\text{K}$ . The actual divergence of  $b^{-1}$  along the transition line in the second-order region is found to be weak. The data are reasonably well represented by either  $b^{-1} \propto (T - 255.1)^r$  with  $r \approx 0.2$ , or by  $b^{-1} \propto \ln(T - 255.1)$ , for  $T$  in  $^\circ\text{K}$ . The insert to Fig. 3 shows the approximately linear behavior of  $b^{-1}$  vs  $\ln(T - 255.1)$ .

Our measurements of the pressure-temperature dependence of the total Rayleigh intensity support the conclusion that the nature of the  $\text{NH}_4\text{Cl}$  phase transition changes at a temperature of about  $255^\circ\text{K}$  and a pressure of about 20 000 psi. Although we have not determined how much of the scattering is due to fluctuation of the order parameter, the data are consistent with the LG theory of critical opalescence. Further experimental work is needed to determine the mechanism of the scattering, preferably spectroscopy of high-enough resolution to separate the spectrum of any critical scattering from domain scattering. High-magnification photography to study domain effects, and studies of the angular dependence of the scattering would also be useful.