FIG. 9. Dependence of C' on pressure at various temperatures (see Fig. 3 legend).

determine c_{11} at pressures near the critical value except at T_5. For the other temperatures, smooth curves were rather arbitrarily drawn in the critical region. Shear waves are not attenuated; therefore the complete pressure dependence of c_{44} and C' could be studied. In measuring the velocity of shear waves we looked for hysteresis near the lambda line. No hysteresis was observed for any of the temperatures T_1, T_2, $\cdots$, T_5. We then made special runs at lower temperatures for the shear wave corresponding to c_{44}. At 245.42°K a hysteresis in pressure of about 30 bar was observed. At 248.41°K this hysteresis had disappeared. The hysteresis shown in Fig. 1 is based on these c_{44} data and the previously mentioned shear velocities at atmospheric pressure.

The application of a pressure to the crystal does not introduce any new source of errors which are not present for atmospheric-pressure measurements. However, the seal corrections are less and less accurate as the pressure increases because we do not know the characteristics of the seal under pressure. As a result, the random error in the elastic constants is of the order of ±0.05% at low pressure, but the uncertainty increases as the pressure increases. Both c_{11} and c_{44} have a fairly large pressure dependence which minimizes the importance of changes in the seal on the pressure derivative $d \ln c / dp$. Since C' varies only slowly with pressure, the error in $d \ln C' / dp$ could be much larger especially at higher pressures.

Constant-Volume Data

From the data presented above it is possible to get several new pieces of information. Combining the known temperature dependence of the length of the unit cell at atmospheric pressure, and the pressure dependence of s it was possible to compute the pressure which must be applied to the crystal to keep its volume constant. We did this for the following different values of the volume: $V_1 = 34.002$; $V_2 = 34.150$; $V_3 = 34.266$; $V_4 = 34.428$; $V_5 = 34.507$; $V_6 = 34.768$; $V_7 = 34.928$ cm³ mole⁻¹. The corresponding p–T isochores are plotted in Fig. 1, which also shows the critical pressure p as a function of temperature. With these isochores we could

evaluate the effective adiabatic elastic constants at constant volume. In Figs. 5 and 6 we have plotted the temperature dependence of c_{44} and C' at V_1, V_2, $\cdots$, V_7. The crosses correspond to the values obtained from data at T_1, T_2, $\cdots$, T_5. To avoid confusion on Fig. 4 we have plotted the temperature dependence of c_{11} only at volume V_2. These constant-volume plots are very important from a theoretical point of view because the theories of order–disorder phenomena are usually valid at constant volume and not at constant pressure.

DISCUSSION

The temperature–pressure region near the lambda line is of primary theoretical interest in the present work. Data obtained far from the transition region can be interpreted in terms of a crystal which is completely ordered or completely disordered. Observations of this kind on ammonium chloride are discussed elsewhere in connection with comparable data on the disordered phase of ammonium bromide.[22] We only point out here that, away from the lambda line, the elastic behaviors of the ordered and of the disordered crystal are essentially normal and very similar to each other. In previous papers,[6,23] the temperature dependence of the elastic constants at 1 atm near a lambda point has been discussed in terms of phenomenological Pippard

TABLE III. Smooth-curve values of the effective adiabatic elastic constants c_{11}, c_{44}, and C', in units of 10^{11} dyn cm⁻², as a function of temperature and pressure. $T_1 = 250.72°K$; $T_2 = 265.00°K$; $T_3 = 280.05°K$; $T_4 = 295.02°K$; $T_5 = 308.04°K$.

p (kbar)	T_1	T_2	T_3	T_4	T_5
			c_{11} values		
2	4.206	4.009	4.054	4.043	4.032
4	4.547	4.318	4.227	4.242	4.221
6	4.740	4.623	4.394	4.402	4.389
8	4.896	4.818	4.692	4.453	4.544
10	5.035	4.972	4.888	4.765	4.635
12	5.166	5.111	5.045	4.955	4.836
			c_{44} values		
2	1.1219	1.0335	1.0041	0.9773	0.9568
4	1.2065	1.1621	1.0867	1.0563	1.0353
6	1.2782	1.2453	1.1961	1.1353	1.1124
8	1.3457	1.3172	1.2800	1.2262	1.1869
10	1.4121	1.3852	1.3521	1.3155	1.2622
12	1.4742	1.4511	1.4238	1.3964	1.3536
			C' values		
2	1.5212	1.5032	1.4982	1.4919	1.4870
4	1.5308	1.5245	1.5127	1.5069	1.5017
6	1.5377	1.5336	1.5280	1.5189	1.5139
8	1.5438	1.5401	1.5372	1.5314	1.5249
10	1.5490	1.5461	1.5438	1.5407	1.5346
12	1.5540	1.5516	1.5495	1.5467	1.5442

[22] C. W. Garland and C. F. Yarnell, J. Chem. Phys. **44**, 1112 (1966).

[23] C. W. Garland, J. Chem. Phys. **41**, 1005 (1964).

equations. The discussion below is given in terms of the elastic behavior of an Ising model.

The two preceding papers[4,5] present an analysis of the mechanical properties of an Ising model. Paper I is concerned with an instability very close to the critical point and the resulting hysteresis which may occur in many properties. Leaving aside for the moment this important but relatively narrow range where instability may occur, it is possible to discuss the effect of ordering at constant volume on the elastic constants of an Ising model. We have carried out a general stress–strain analysis of the two-dimensional Ising lattice in Paper II and have obtained explicit formulae for the isothermal stiffnesses c_{11}, c_{44}, and $C' = (c_{11} - c_{12})/2$.

Now the order–disorder transition in ammonium chloride can be represented to a very good approximation by an Ising model of a simple-cubic ferromagnet. Although no exact solution of the three-dimensional Ising problem is yet available, the formal calculation of the elastic properties of a simple-cubic lattice will lead to results very similar to those for a square lattice. We see from Eqs. (41), (43), and (55) of Paper II that the constant-volume elastic properties of a cubic Ising lattice can be represented by

$$\frac{1}{\beta^T} \equiv c_{11}{}^T - (\tfrac{4}{3}C') = \frac{1}{\beta_{dl}{}^T} - \frac{vT}{J^2}\frac{C_I(0, \mathrm{H})}{N}\left(\frac{dJ}{dv}\right)^2$$

$$+ \frac{v}{J}\frac{U_I(0, H)}{N}\left(\frac{d^2J}{dv^2}\right), \quad (6)$$

$$C' = C_{dl}' - mG(0, H) - nU_I(0, H)/NJ, \quad (7)$$

$$c_{44} = c_{44, dl} - lU_I(0, H)/NJ, \quad (8)$$

where $C_I(0, \mathrm{H})/N$ and $U_I(0, \mathrm{H})/N$ are the configurational heat capacity per "spin" and the Ising internal energy per "spin" as a function of $H \equiv J/kT$, J is the interaction energy between nearest-neighbor $NH_4{}^+$ ions, $G(0, H)$ is the three-dimensional analog of the function defined by Eq. (38) of Paper II, and v is the unit cell volume (which replaces σ, the area per spin, used in Paper II). The isothermal character of the reciprocal compressibility $1/\beta^T$ and the compressional stiffness $c_{11}{}^T$ is denoted by a superscript T; this is not necessary for the shear constants c_{44} and C' since the isothermal and adiabatic values are identical. The subscript dl indicates a disordered-lattice contribution (see Paper I for details) which corresponds to the essentially normal variations observed at temperatures far above T_λ. The coefficients m, n, and l are temperature-independent quantities, defined by Eqs. (39), (40), and (55) of Paper II except that σ must be changed to v.

For ammonium chloride, the parameter J is positive but dJ/dv and d^2J/dv^2 are negative with $|d^2J/dv^2| \ll |dJ/dv|$. Thus, we see from Eqs. (39) and (40) of II that both m and n are positive. The sign of l is not known since $\partial^2J/\partial\theta^2$ is unknown (θ is the angle by which the equilibrium angle of the cubic unit cell is istorted), but Eq. (55) and the accompanying dis-

cussion in Paper II make it physically reasonable that l is also positive.

The three-dimensional behavior of $U_I(0, H)$ and $G(0, H)$ is not known, but it will be generally similar to that found in two dimensions. A plot of $-U_I/NJ$ and $-G$ as a function of temperature is given in Paper II for the two-dimensional case. Note that $(-U_I)$ is zero in the completely disordered lattice and positive in the ordered lattice, while $(-G)$ is zero in both the completely ordered and completely disordered state but negative in the region of the transition. Both quantities are finite and continuous at all temperatures but have an inflection point of infinite slope at T_λ. In three dimensions, one would expect a sharpening of the variation above T_λ but no drastic changes.

Thus, we can predict from Eqs. (7) and (8) the qualitative behavior of the shear constants c_{44} and C'. Both "disordered-lattice" contributions should show a slow, smooth (almost linear) increase as the temperature is decreased; this is based on the behavior of any normal ionic crystal. The term $-lU_I(0, H)/NJ$ in Eq. (8) increases from zero in the completely disordered state to a constant positive value at temperatures quite a bit below T_λ. This increase is especially rapid as the temperature is decreased through the lambda point (which depends on the volume since J is a function of V). The constant-volume c_{44} curves in Fig. 5 show excellent agreement with this prediction. Indeed, the shape of these curves is what one would expect from an internal energy curve. The elastic constant C' should have qualitatively the same behavior as c_{44}, although they are not identical because Eq. (7) contains the term $-mG(0, H)$. Figure 6 does show that the temperature variation of C' at constant volume is similar to that of c_{44} although the effect of ordering is much smaller for C' and the shape of the curve changes with volume.

In order to discuss c_{11}, let us consider the appropriate linear combination of Eqs. (6) and (7). Since the configurational heat capacity has a sharp maximum at T_λ, the term $-(vT/J^2)(C_I/N)(dJ/dv)^2$ will dominate the temperature dependence of $c_{11}{}^T$. Hence $c_{11}{}^T$ should display a very pronounced minimum at the lambda point. From ultrasonic data we obtain $c_{11}{}^S$ rather than $c_{11}{}^T$, but these are related by

$$c_{11}{}^S = c_{11}{}^T + 9\alpha^2VT/C_v(\beta^T)^2, \quad (9)$$

where α is the linear coefficient of thermal expansion. Although these isothermal and adiabatic stiffnesses differ considerably very close to T_λ, the difference between $c_{11}{}^T$ and $c_{11}{}^S$ is less than 10% when $|T - T_\lambda| \sim 1°K$ and this difference decreases as $|T - T_\lambda|$ increases. Thus the observed $c_{11}{}^S$ should agree quite closely with the predicted behavior of $c_{11}{}^T$. From Fig. 4 we see that the shape of $c_{11}{}^S$ at constant volume is strikingly related to the shape expected from the heat-capacity curve.[24]

[24] F. Simon, Ann. Physik **68**, 4 (1922); C. C. Stephenson (private communication).