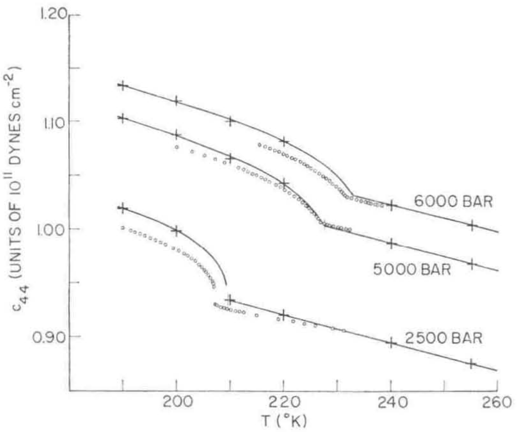

FIG. 6. Variation of c_{44} with temperature: Detail of transition from disordered cubic to O_{II} phase. Crosses represent points take from the smoothed curves in Fig. 3. The circles indicate data points taken on cooling runs during which the pressure varied slightly (see text).

at 1 atm and room temperature and these properties might be different at low temperatures and high pressures. A significant phase shift may also occur at the free end of the sample as the pressure fluid is cooled and compressed.

The $n=0$ condition[3] for c_{11} was independently determined for our crystal, and the present c_{11} value at 240°K and 1 atm differs by 0.05% from the value reported in Paper I, which is well within the experimental error. For C' it was decided to use the values reported in Paper I to get the correct n. In this case the difference between the two C' measurements at 240°K and 1 atm was 0.18%, whereas a change by ± 1 in n would give C' values differing by $\pm 2\%$. The determination of the correct n value is not as easy for c_{44} as for the other two constants. Thus it was felt to be necessary to make another independent check on the previous values. With data on two crystals with different path lengths, the correct n was unambiguously determined, and the present c_{44} value at 240°K and 1 atm was found to differ by 0.25% from the value reported in Paper I. Thus the present data tie in very well indeed with those reported previously.

Constant-Pressure c_{44} Data

Several isobaric plots of c_{44} versus temperature are shown in Fig. 6, where the crosses represent points read from smooth curves of c_{44} as a function of pressure at various constant temperatures. Values of c_{44} at 255°K were taken from Paper I; values at 240°K and below are from the present work. Associated with each curve is a series of open circles. These circles are directly determined data points taken in the closed pressure cell with the temperature slowly varying. Because the system was closed, the pressure naturally decreased as the cell was cooled. However, the pressure variation is small (about a 400 bar difference between lowest and highest temperature for a given run), and the circles provide a direct indication of the behavior of c_{44} through the lambda transition from disordered cubic to O_{II} as a function of temperature at several almost constant pressures. The lambda point, indicated on each curve by a light vertical line, was determined from the phase diagram given in Fig. 1.

Figure 7 is similar to Fig. 6, with the solid curves representing the temperature dependence of c_{44} at constant pressures of 1300 and 1 bar. At both these pressures the crystal undergoes a lambda transition from disordered cubic to O_T. The curve at 1 bar is taken from Paper I as is the point at 255°K and 1300 bar. The crosses are taken from smooth curves of c_{44} as a function of pressure at various temperatures, and the solid circles are data points taken on a cooling run with the pressure cell closed (again, the pressure changed slightly with the temperature).

As can be seen from Figs. 6 and 7, c_{44} at constant pressure varies in the normally expected way with temperature in the disordered cubic phase. Indeed, when all the data from Paper I and the present investigation are combined, it becomes clear that c_{44} varies in a very regular way with both p and T throughout the entire disordered phase. Over the range 220°–320°K and 0–8000 bar, one can represent c_{44} *in the disordered phase* by

$$c_{44}(p,T)=c_{44}(1\text{ bar},\,295^\circ\text{K})+3.85(p-1)$$
$$-2.5\times10^{-11}(p-1)^2-1.31\times10^{8}(T-295),\quad (3)$$

where c_{44} (1 bar, 295°K) $=0.728\times10^{11}$ dyn cm^{-2} and p is also expressed in dyn cm^{-2} units. The only region for which Eq. (3) is not quite valid is close to the

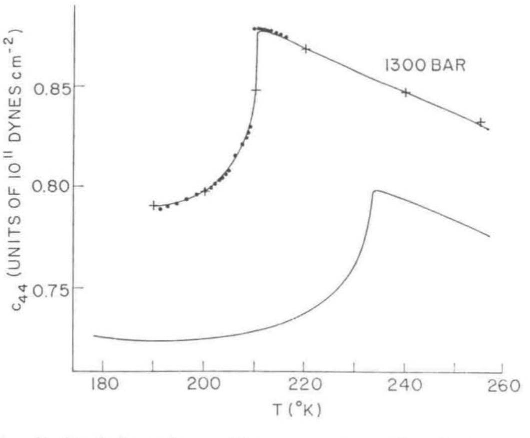

FIG. 7. Variation of c_{44} with temperature: Detail of transition from disordered cubic to O_T phase. The symbols on the upper curve have the same significance as in Fig. 6. The lower curve, taken from Paper I for comparison, represents the directly observed variation at 1 bar.

D–O_T lambda line. There is a very small anomalous variation in c_{44} at temperatures just above this transition line; for example, c_{44} observed at 235°K and 1 bar is 0.005×10^{11} smaller than the value calculated with Eq. (3).

Constant-Volume Data

It is possible to combine the results presented above and those from Paper I to obtain the variation of the effective adiabatic elastic constants with temperature at constant volume. From Fig. 2, one can determine the hydrostatic pressure which must be applied to the crystal at any given temperature in order to maintain its volume at a specified constant value. The value of the constant-volume elastic constant is then obtained by interpolation from the smoothed isothermal plots of c_{ij} as a function of pressure (Figs. 3–5 of this paper together with Figs. 6–8 of Paper I).

Such constant-volume plots of c_{44} and c_{11} in the vicinity of the D–O_{II} lambda line are shown in Figs. 8 and 9. The variation of c_{44} has been evaluated at six values of the volume: $V_1=38.12$ cm^3 mole^{-1} corresponds to a cubic lattice parameter $a_1=3.985$ Å, and volumes V_2–V_6 correspond to successive increases of 0.005 Å in the lattice parameter; thus a_6 equals 4.010 Å and $V_6=38.84$ cm^3 mole^{-1}. From Fig. 8 it is evident that the anomalous behavior of the constant-volume c_{44} is essentially the same for every volume. This is in contrast to the isobaric variations shown in Fig. 6, where the anomalous effect diminishes in magnitude and abruptness with increasing pressure. Note also that the anomalous changes in c_{44} at constant volume are opposite in sign to those observed at constant pressure. The variation of c_{11} is only given at a single volume (V_5) in Fig. 9. Unfortunately, there were not sufficient data points near the lambda temperature at other volumes to make a significant comparison between the shape of this V_5 curve and any other.

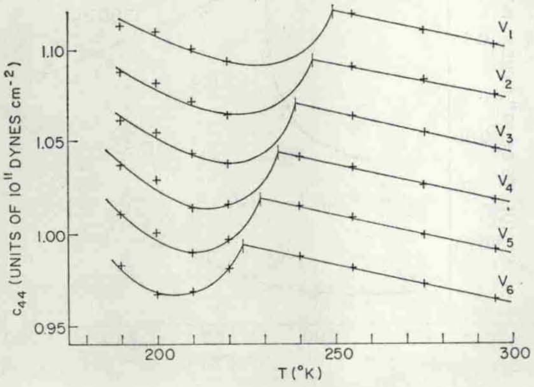

FIG. 8. Variation of c_{44} with temperature at various constant volumes: Region of lambda transition from disordered cubic to O_{II} phase. Crosses represent points taken from smooth-curve plots of c_{44} and V (see text).

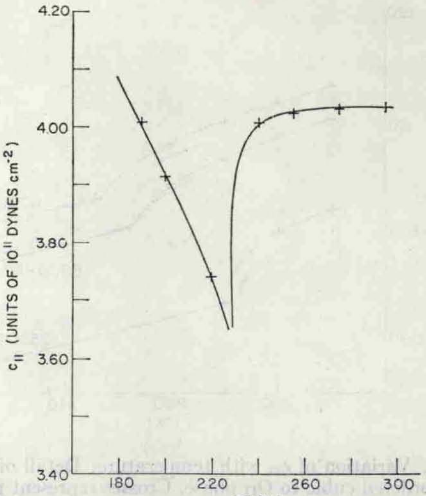

FIG. 9. Variation of c_{11} with temperature at constant volume. Points are shown for $V_5(a=4.005$ Å$)$, at which volume the D–O_{II} lambda temperature is 229°K.

DISCUSSION

Behavior far from Any Phase Transition

The temperature and pressure dependence of the elastic constants of ammonium bromide in the disordered cubic phase far from any phase transitions were discussed in Paper I. Our new data in the disordered phase agree very well with those results and will not be discussed further here. It is now possible, however, to compare the "normal" behavior (meaning behavior unaffected by phase transitions) of the disordered phase with that of the O_{II} phase and, to a limited extent, with that of the O_I phase. Significant comparison with the O_T phase is not possible due to the presence of domains and the small p–T range of that phase.

Over-all, the pressure variations of all three elastic constants are very similar in the O_{II} and D phases. As indicated by Eq. (3), $(\partial c_{ij}/\partial p)_T$ values vary somewhat with pressure but little with temperature. Thus, comparison will be made at a given molar volume (i.e., lattice parameter) although the temperatures at which the respective values are evaluated will, of course, differ. For $(\partial c_{11}/\partial p)_T$, one finds 6.9 for the disordered phase at 255°K, 9.3 kbar (3.985 Å) and 7.0 for the O_{II} phase at 190°K, 5.4 kbar (3.985 Å). For $(\partial c_{44}/\partial p)_T$, the corresponding values are 3.3 for the D phase and 3.1_5 for the O_{II} phase. For the other shear constant, $(\partial C'/\partial p)_T=0.75$ for the D phase at 255°K, 8.5 kbar (3.990 Å) and 0.73 for the O_{II} phase at 220°K, 5.5 kbar (3.990 Å). Also the inequality $P_{44}>P_{11}>P'$, where $P_{ij}=(\partial \ln c_{ij}/\partial p)_T$, holds for the O_{II} phase as it does in the disordered phase. This is what would be expected for a CsCl-type structure[2] and indicates that there is