TABLE IV. 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 pressure at various temperatures. Calculated values of $1/\beta^S$ are also given at two temperatures.

$T=315°K$

p(kbar)	c_{11}	p(kbar)	c_{11}	p(kbar)	c_{11}
0	3.396	4	3.757	8	4.063
2	3.583	6	3.914	10	4.205

$T=295°K$

p(kbar)	c_{11}	c_{44}	C'	$1/\beta^S$
0	3.419	0.792	1.318	1.662
2	3.615	0.805	1.343	1.824
4	3.789	0.879	1.363	1.972
6	3.949	0.951	1.3815	2.107
8	4.097	1.020	1.398	2.233
10	4.236	1.091	1.4145	2.350

$T=275°K$

p(kbar)	c_{11}	c_{44}	p(kbar)	c_{11}	c_{44}
0	3.430	0.754	6	3.978	0.975
2	3.639	0.830	8	4.129	1.046
4	3.819	0.903	10	4.272	1.114

$T=255°K$

p(kbar)	c_{11}	c_{44}	C'	$1/\beta^S$
0	3.411	0.778	1.330	1.638
2	3.654	0.856	1.358	1.843
4	3.843	0.931	1.379	2.004
6	4.010	1.003	1.397	2.147
8	4.162	1.073	1.4135	2.277
10	4.302	1.140	1.4285	2.397

compressible than a single crystal. Indeed, the same kind of discrepancy between single crystal and Bridgman's polycrystalline value is also observed in ammonium chloride.[12]

Constant-Volume Data

In the temperature region above the lambda point, it is possible to combine the results presented above to obtain the variation of the elastic constants with temperature at constant volume. From the known temperature dependence of the cubic cell parameter at 1 atm and the pressure dependence of $s(p)$, one can compute the hydrostatic pressure which must be applied to the crystal at any given temperature in order to maintain its volume at a constant value. This has been done for the 17 different values of the volume: V_1 corresponds to a unit cell dimension of $a_1=3.985$ Å; V_2 through V_{12} correspond to a values which are each 0.005 Å greater than the previous value (up to $a_{12}=4.040$ Å); V_{13} through V_{17} correspond to $a_{13}=4.0425$, $a_{14}=4.045$, $a_{15}=4.0476$, $a_{16}=4.0496$, and $a_{17}=4.0517$ Å. The corresponding $p–T$ isochores are plotted in Fig. 2. With these isochores, one can easily evaluate the effective adiabatic elastic constants at constant volume. Such constants have been plotted in Figs. 3–5 for a few high-volume values as a comparison with the variation at constant pressure. Constant-volume elastic con-

stants are shown in Fig. 9 as a function of temperature for all 17 values of V.

DISCUSSION

Far from the Lambda Transition

As shown in Fig. 2, the principal region of this investigation is the disordered β phase of ammonium bromide. At pressures up to about 3000 bar the elastic constants show a nonlinear variation with pressure due to the fact that the crystal is still in the vicinity of the $\beta–\gamma$ lambda line. At higher pressures, farther from the lambda line, the variation is linear as expected for a normal solid having no transition. This is clearly illustrated by the temperature variation of the constant-volume elastic constants shown in Fig. 9. Presented in Table V is a comparison of our data on ammonium bromide with recent data on ammonium chloride[12]; these results are discussed below in the general context of the behavior which is known for alkali halide crystals. The NH$_4$Cl elastic constants have been measured in a region of the phase diagram which contains the lambda line[12]; therefore the behavior of these constants will be somewhat influenced by the proximity of the order–disorder transition. On the other hand, NH$_4$Br should be typical of a "normal" CsCl-type crystal (at least above 3000 bar).

Haussuhl[22] has found that all alkali halides of the NaCl type obey the inequality $T'<T_{11}<T_{44}$, where T_{ij} represents $(\partial \ln c_{ij}/\partial T)_p$ at atmospheric pressure and is a negative quantity. For several alkali halides of the CsCl type the inequality has been found[20] to be

$$T_{44}<T_{11}<T'. \qquad (8)$$

As shown in Table V, the slopes at 320°K of the elastic constants of ammonium bromide obey this CsCl in-
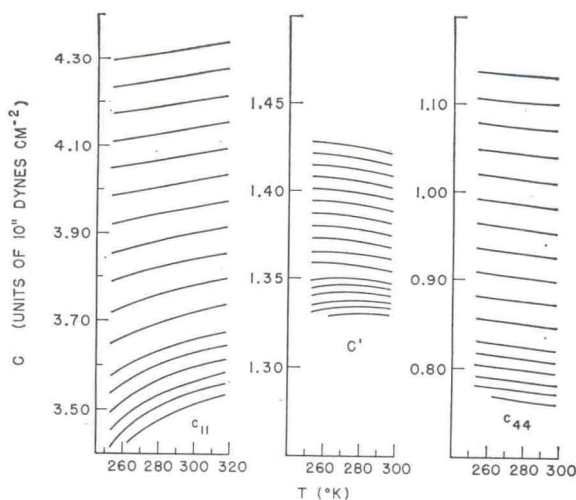

FIG. 9. Adiabatic elastic constants versus temperature at various constant volumes from V_1 to V_{17} (see text). The highest curves correspond to V_1.

[22] S. Haussuhl, Z. Physik 159, 223 (1960).

TABLE V. The adiabatic elastic constants of ammonium bromide and their temperature and pressure derivatives compared with the results of Garland and Renard (Ref. 12) for ammonium chloride. The value of $\partial \ln c_{11}/\partial T$ at 350°K was measured by Weintraub (Ref. 23); the other $\partial \ln c/\partial T$ values were determined at 320°K. The elastic constants are in units of 10^{11} dyn cm^{-2}; the temperature derivatives are in units of 10^{-4} deg^{-1}, and the pressure derivatives are in units of 10^{-12} cm^2 dyn^{-1}.

	NH$_4$Cl			NH$_4$Br		
	c_{11}	C'	c_{44}	c_{11}	C'	c_{44}
c(295°K)	3.814	1.466	0.8753	3.419	1.318	0.7285
$(\partial \ln c/\partial T)_{p-0}$	−1.5 −5.3(350°K)	−2.83	−17.1	−4.32	−2.93	−19.8
$(\partial \ln c/\partial T)_V$	4.0	−0.78	−2.66	3.60	−0.05	−5.86
$(\partial \ln c/\partial p)_{T-295°K}$	4.63	0.81	5.12	3.17	1.03	5.30

equality. At 320°K the slope of c_{11} for ammonium chloride does not seem to fit the pattern; however, if one assumes that c_{11} hasn't reached its limiting "normal" behavior (i.e., that it is still being influenced by the nearby lambda transition), the slopes for the elastic constants would obey the inequality. Indeed, the unpublished results of Weintraub[23] on the variation of c_{11} with temperature between 300° and 375°K indicate that c_{11} becomes linear with respect to T only above 335°K, where $T_{11}=-5.27\times10^{-4}$ deg^{-1}. This value would satisfy the CsCl inequality very well.

The pressure derivatives of the elastic constants, $P_{ij}=(\partial \ln c_{ij}/\partial p)_T$, will obey similar inequalities. Data as a function of pressure are available for several alkali halides of the NaCl type[24] for which the inequality is $P'>P_{11}>P_{44}$. This is reasonable since a decrease in temperature corresponds to an increase in pressure in terms of its effect on the molar volume (and thus the elastic constants). Although no data appear to be available on the pressure dependence of the elastic constants of alkali halides of the CsCl type, the expected inequality would be

$$P_{44}>P_{11}>P'. \qquad (9)$$

Both the ammonium bromide and chloride data obey this inequality over the entire range of temperatures for which pressure measurements have been made; the values of P_{ij} at 295°K, as given in Table V, are typical.

At *constant volume* the inequalities for the temperature derivatives of the alkali halides of the NaCl type which have been studied is $T'<T_{44}<T_{11}$ (constant volume). For the ammonium halides at constant volume the corresponding inequality is

$$T_{44}<T'<T_{11} \qquad \text{(constant volume)}. \qquad (10)$$

This comparison of the behavior of the ammonium halides with that of NaCl-type alkali halides imme-

diately reveals a significant difference: the slope of c_{11} versus temperature at constant volume for ammonium bromide and chloride is *positive* while it is always negative for the NaCl-type salts.[24] This behavior cannot be due to an influence of the lambda transition since for NH$_4$Br at the lowest volumes (far from the transition) anomalous temperature variations in c_{11} are absent and c_{11} varies linearly with temperature (as a normal crystal should).

Comparison of the elastic constant values in Table V shows that those of ammonium chloride are greater than the corresponding ones for the bromide. This is in general what is observed for all of the alkali halides. As the molar volume (and mass) increases, the stiffness (and thus the elastic constants) decreases. The temperature and pressure derivatives of the elastic constants of ammonium bromide are very similar to those of ammonium chloride, although the pattern is not regular enough to permit scaling. If these derivatives are taken as measures of the anharmonicity of the crystal, then ammonium chloride and ammonium bromide have quite similar anharmonicity.

Near the Lambda Transition

Our information concerning the $\beta-\gamma$ transition is limited to data obtained at 1 atm, especially on c_{44} for which measurements could be made below the lambda point.

As the temperature is lowered, c_{44} for ammonium bromide increases linearly with temperature down to the lambda point where it abruptly *decreases* and then at a lower temperature (about 40°K below the lambda point) resumes its normal increase with decreasing temperature (see Fig. 5). The temperature behavior of c_{44} for ammonium bromide is qualitatively compatible with that for ammonium chloride where there is an anomalous increase in c_{44}. This is expected since c_{44} is a sensitive function of the volume, and ammonium chloride contracts on ordering while ammonium bromide expands. A quantitative analysis of the effect of ordering at constant unit-cell dimension is complicated by the

[23] A. Weintraub, senior thesis, MIT, 1963.
[24] D. Lazarus, Phys. Rev. **76**, 545 (1949); R. A. Miller and C. S. Smith, J. Phys. Chem. Solids **25**, 1279 (1964).