

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}
$c(295^\circ\text{K})$	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
$(\partial \ln c/\partial p)_{T=295^\circ\text{K}}$	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 Indeed, the unpublished results of Weintraub²³ on the variation of c_{11} with temperature between 300° and 375°K indicate that c_{11} becomes linear with respect to T only above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 $T_{11} = -5.27 \times 10^{-4}$ 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 type²⁴ 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

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

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

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

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

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 NH₄Br 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 β - γ 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).