

Temperature and Pressure Dependence of the Elastic Constants of Ammonium Bromide*

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(Received 6 October 1965)

The adiabatic elastic constants of single-crystal ammonium bromide have been measured as functions of temperature and pressure by a pulse-superposition technique. The values at 1 atm and 300°K are: $c_{11} = 3.414$, $C' = (c_{11} - c_{12})/2 = 1.316$, and $c_{44} = 0.722$, in units of 10^{11} dyn cm^{-2} . Measurements of c_{11} and C' were not made below the lambda transition at 234.5°K because of a sudden increase in attenuation; c_{44} was not attenuated in this manner and was measured from 105° to 320°K. The elastic constants were measured as functions of pressure between 0 and 12 kbar at constant temperatures which ranged from 255° to 315°K. In this region, which is far from the lambda line, disordered ammonium bromide behaves like a normal CsCl-type crystal.

INTRODUCTION

A LAMBDA transition at 234.5°K in crystalline ammonium bromide was first discovered from heat-capacity measurements.¹ This transition is now established as an order-disorder transition involving the relative orientations of adjacent ammonium ions. However, there are important differences between the ordering process in NH_4Br and that in NH_4Cl , which undergoes a cooperative order-disorder transition at about the same temperature (242.8°K). X-ray,² neutron-diffraction,³ Raman,⁴ and infrared⁵ investigations show that above their critical temperatures both NH_4Br and NH_4Cl have a CsCl-type cubic structure with the tetrahedral ammonium ions oriented at random with respect to the two equivalent positions in the cubic cell (hydrogen atoms pointing toward nearest-neighbor halide ions). Hettich⁶ observed that ammonium bromide does not become piezoelectric below the lambda point but does exhibit double refraction. This result and the low-temperature Raman spectrum led Menzies and Mills⁴ to suggest that the ammonium ions in two adjacent unit cells were antiparallel (have opposite orientations relative to the crystallographic axes). Low-temperature x-ray studies⁷ have shown that the crystal

structure of NH_4Br becomes tetragonal below the transition, and the neutron-diffraction work³ establishes the location of the hydrogen atoms and confirms that this phase is ordered. The tetragonal unit cell, as shown in Fig. 1, contains two molecules of ammonium bromide.

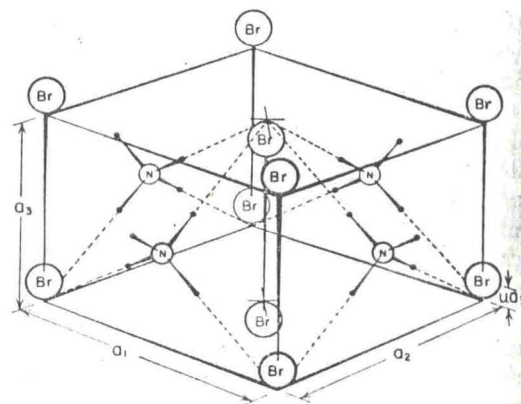


FIG. 1. Unit cell for γ -phase (ordered tetragonal) ammonium bromide. [From E. L. Wagner and D. F. Hornig, *J. Chem. Phys.* **18**, 305 (1950).]

The ammonium ions are antiparallel ordered in the a_1 - a_2 plane and parallel ordered along the a_3 or tetragonal axis. The antiparallel ordering of ammonium ions is stabilized by the bromide ions which are displaced along the tetragonal axis alternately in positive and negative directions with respect to the a_1 - a_2 plane by ua_3 where $u=0.02$. The tetragonal distortion is very slight, amounting to an extension of the a_3 axis by only 0.3% relative to the a_1 and a_2 axes.⁷ In contrast, the low-temperature ordered phase in ammonium chloride is cubic (CsCl type), and all the ammonium ions are parallel (have same relative orientation with respect to crystallographic axes).

The thermal expansion data also show a marked difference between NH_4Br and NH_4Cl . In NH_4Cl , the lattice undergoes an anomalous contraction⁸ when

* Y. Sakamoto, *J. Sci. Hiroshima Univ.* **A18**, 95 (1954).

* This work was supported in part by the Joint Services Electronics Program under Contract DA 36-039-AMC-03200 (E), and in part by the Advanced Research Projects Agency.

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¹ F. Simon, C. V. Simson, and M. Ruhemann, *Z. Physik.* **129**, 344 (1927); A. G. Cole, Ph.D. thesis, MIT, 1952.

² F. Simon and C. V. Simson, *Naturwiss.* **14**, 880 (1926); G. Bartlett and I. Langmuir, *J. Am. Chem. Soc.* **43**, 84 (1921).

³ H. A. Levy and S. W. Peterson, *Phys. Rev.* **83**, 1270 (1951); **86**, 766 (1952); *J. Am. Chem. Soc.* **75**, 1536 (1952).

⁴ A. C. Menzies and H. R. Mills, *Proc. Roy. Soc. (London)* **A148**, 407 (1935); R. S. Krishnan, *Proc. Indian Acad. Sci.* **26A**, 432 (1947); **27A**, 321 (1948).

⁵ E. L. Wagner and D. F. Hornig, *J. Chem. Phys.* **18**, 296 (1950); *J. Chem. Phys.* **18**, 305 (1950).

⁶ A. Hettich and A. Schleede, *Z. Physik* **50**, 249 (1928); A. Hettich, *Z. Physik. Chem.* **A168**, 353 (1934).

⁷ J. A. A. Ketelaar, *Nature* **134**, 250 (1934); J. Weigle and H. Saini, *Helv. Phys. Acta* **9**, 515 (1936); V. Hovi, K. Heiskanen, and M. Varteva, *Ann. Acad. Sci. Fenn. Ser. A. VI*, No. 144, 1-12 (1964).