Phase Transition in Hexammine Nickel Halides

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Palma-Vittorelli *et al.*[1] found a sudden broadening of the ESR absorption line of Ni^{2+} in $[Ni(NH_3)_6]X_2$ crystals (X; halogens) at low temperature. It was pointed out that this anomalous behavior is not of magnetic origin but is concerned with the motional state of ammonia. Aiello *et al.*[2] showed that over a narrow range temperature a sharp line was superposed on a broader one in the ESR spectrum of the chloride, indicating coexistence of the two phases. These works and an entropy anomaly in the analogous iodide briefly mentioned by van Kempen *et al.*[3] stimulated us to investigate the thermodynamic property of the substances. We report here a preliminary result of a heat capacity measurement on $[Ni(NH_3)_6]Cl_2$ and $[Ni(NH_3)_6]Br_2$. The specimens were crystals 0.5—1 mm in size prepared by the standard method and dried in a desiccator over calcium oxide for a year. The heat capacity measurement was performed between 12 and 300 K with an adiabatic calorimeter of nearly the same construction as that of the previous one.[4,5] the accuracy of the measurement was estimated to be better than 1% at 30 K and 0.3% at 200 K. In total 132 heat capacity data were collected for the chloride and 125 data for the bromide, some of which are shown in Fig. 1. The anomalous increase of heat capacity was found to occur with peaks at 83.17 K and 34.99 K for the chloride and the bromide, respectively. These temperatures are to be compared with 82.5 K and 35 K at which the line width transitions were observed in the ESR spectra.[1] Time required for attaining thermal equilibrium in the calorimeter was usually 5—10 min, but in the transition region of the chloride more than 45 min was required, while for the bromide roughly 20 min was sufficient even at the peak of the anomaly. In contrast to the sharp peak of the bromide the peak of the chloride is rather broad. A preliminary estimate of the entropy of transition was made by interpolating the normal heat capacity smoothly to the transition region. It was found to be 35.1 $JK^{-1}mol^{-1}$ for the chloride and 17.4 $JK^{-1}mol^{-1}$ for the bromide, with a somewhat larger ambiguity for the latter due to larger arbitrariness in the interpolation.

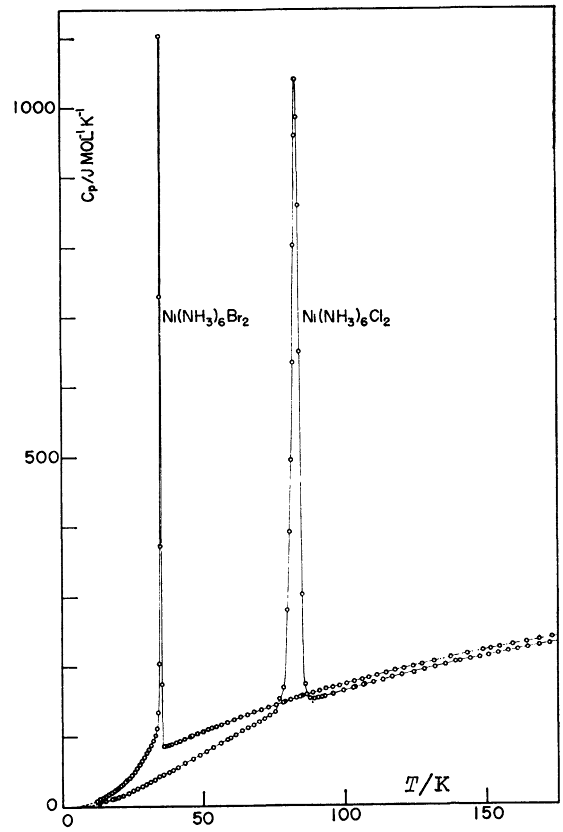

Fig. 1. Heat capacity of $[Ni(NH_3)_6]Cl_2$ and $[Ni(NH_3)_6]Br_2$.

Recently, Klaaijsen *et al.*[6] found heat capacity anomalies in several hexammine metal iodides. They inferred from the estimated entropy change that the transitions in the series of the iodides might have the same physical background. As Bates and Stevens[7] pointed out on an electrostatic model, it is possible that there are eight equivalent configurations which the single complex cation can take in the isolated state. If one of them is favorable at low temperature, the transition entropy would amount to Rln8, which is close to the estimated value for the bromide.

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