

## Specific Heat of $\text{NiCl}_2\cdot 6\text{NH}_3$ Between 0.3 and 4.2 K

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A careful specific heat measurements of nickel hexamine chloride, at liquid helium temperatures, revealed two maxima of magnetic origin in agreement with one of the works available in the literature. An inequivalency of Ni ions, resulting from a structural change at high temperatures, is considered as the new explanation of the magnetic ordering.

Uma cuidadosa repetição da medida do calor específico do cloreto de níquel hexaamoniaco, a temperaturas do hélio líquido, revelou dois picos de origem magnética, concordando com um dos resultados existentes na literatura. A existência de íons de Ni não equivalentes, produzidos por uma mudança de estrutura em altas temperaturas, é considerada como uma nova explicação da ordenação magnética.

### 1. INTRODUCTION

The crystal structure study of the nickel hexamine chloride performed by Wyckoff<sup>1</sup>, at room temperature, has shown that it has a fcc structure. It is isomorphic to a large class of metal II hexamine complexes which have been of large interest mainly on their ammonia cooperative phase transition<sup>2</sup>. This transition is attributed to a freezing of the  $\text{NH}_3$  rotation and was first observed by EPR technique. Theoretical prevision of a structural deformation at the transition temperature<sup>3</sup> was experimentally observed by Ash and coll.<sup>4</sup> in the  $\text{FeCl}_2\cdot 6\text{NH}_3$  salt by X-ray diffraction at  $T_c = 116$  K. Below this temperature the freezing of  $\text{NH}_3$  rotation effect was observed by Mössbauer effect technique<sup>4</sup>. In the  $\text{NiCl}_2\cdot 6\text{NH}_3$  compound a similar structural transformation can occur<sup>2,5</sup>. The critical temperature of this salt has been established as  $T_c = 76$  K. The structure below this temperature seems to be of the monoclinic type built

on two cubic unit cells, similar to that observed in  $\text{FeCl}_2\cdot 6\text{NH}_3$ . This structure can give a new explanation of the low temperature specific heat of  $\text{NiCl}_2\cdot 6\text{NH}_3$  remeasured in the present work.

The first measurement of specific heat of the  $\text{NiCl}_2\cdot 6\text{NH}_3$  was reported by Ukei and Kanda<sup>6</sup>, between 1.1 and 4.0 K. They found a  $\lambda$ -type peak at 1.5 K which was attributed to the ordering of the Ni spin system. Van Kempen and coll.<sup>7</sup> also reported specific heat of this compound, between 0.08 and 1.6 K. A maximum at 1.45 K was obtained in agreement with the Ukei and Kanda measurements. A second pronounced maximum at 1.02 K, not yet observed, was also obtained. Their specific heat values are about 25% greater than the Ukei and Kanda results. The difference between these two results is attributed by van Kempen and coll.<sup>7</sup> to an inhomogeneity of the sample due to ammonia lost by some part of their sample, when two transition temperatures may also occur.

Magnetic susceptibility measurements of this compound performed at high enough temperature gave antiferromagnetic Weiss temperature<sup>8,9,10</sup> of about 9 K. Powder susceptibility measurements<sup>10</sup> down to 0.3 K show abrupt slope change at the two specific heat singularities, indicating that they are of magnetic origin. Magnetic  $H$  vs  $T$  phase diagram of a powder specimen obtained by differential magnetization technique<sup>11</sup> gave a behaviour not expected for an uniaxial antiferromagnetic.

## 2. EXPERIMENTAL

The specific heat measurements were performed in an conventional adiabatic type vacuum calorimeter using the heat pulse method. Five runs were carried out with about 10 g of independently prepared samples of  $\text{NiCl}_2\cdot 6\text{NH}_3$ . No significant difference was found in the results of these runs. The salt was prepared reacting  $\text{NiCO}_3$  with  $\text{HCl}$  and adding  $\text{NH}_4\text{OH}$  in excess to the solution. Small blue octahedrally-shaped microcrystals were obtained and were dried in a dessicator containing silica-gel over an atmosphere of  $\text{NH}_3$ . The ammonia content analysis after the experiments by distillation process indicated less than 5% of ammonia loss, which ensures that the samples were not deteriorated.

### 3. RESULTS AND DISCUSSION

The representative points of the specific heat of this material are shown in Figure 1.

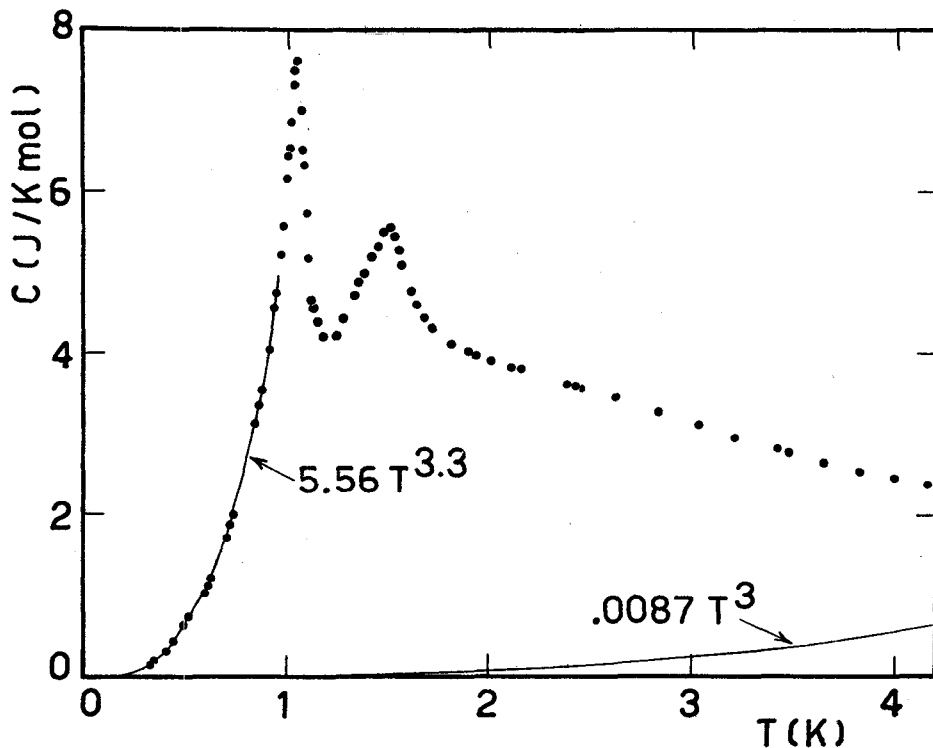


Fig.1 - The molar specific heat of  $\text{NiC}_{26}\text{NH}_3$ . The cubic law is the lattice contribution and the  $5.56 T^{3.3}$  law represents an extrapolation obtained by best fit of the experimental points.

Two reproducible singularities were found at  $T_{c1} = 1.05 \pm 0.05$  K and  $T_{c2} = 1.50 \pm 0.05$  K in nice agreement with the van Kempen and coll<sup>7</sup> result. The specific heat values also agree with their measurements in the overlapping region, between 0.3 and 1.6 K.

The experimental entropy obtained by the integration formula

$$\Delta S = \int_0^T \frac{C}{T} dT$$

is plotted in Figure 2.

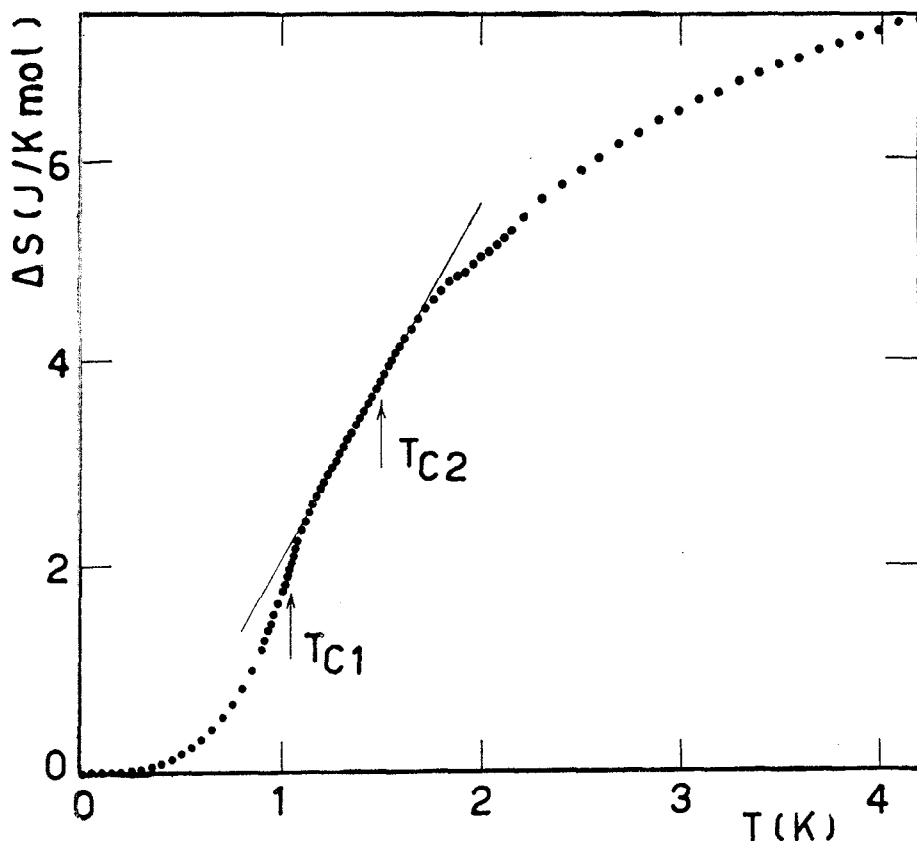


Fig.2 - The experimental molar entropy of  $\text{NiCl}_2 \cdot 6\text{NH}_3$ . The linear region is shown by a straight line.

At the low temperature side, below 0.3 K, the entropy curve was extrapolated to zero degree using the expression  $C = 5.56 T^{3.3}$  obtained by a computer best fit of the experimental data between 0.3 and 0.95 K. This extrapolated entropy amounted to 0.03 J/K mol. The entropy values at other temperatures were obtained by numerical integration. The lattice specific heat was estimated plotting  $CT^2$  vs  $T^5$  and was found to obey the law  $C = 0.0087 T^3$  J/K mol which is comparable to the lattice term of the  $\text{MnCl}_2 \cdot 6\text{NH}_3$  reported by Suga and coll.<sup>12</sup>,  $C = 0.0108 T^3$  J/K mol. The lattice contribution to the total entropy is only 2.5% at 4 K and so the graph of the Figure 2 was not corrected. Since no other degree of freedom is expected to contribute to the entropy, this graph re-

presents the magnetic entropy variation except for small amount affected at high temperature side as described above. A linear variation between  $T_{c1}$  and  $T_{c2}$  with  $\frac{dS}{dT} \approx 3.5 \text{ J/K}^2 \text{ mol}$  is observed in this curve which is very similar to one reported by Polgar and coll.<sup>13</sup> in the  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ . A  $\frac{dS}{dT} \approx 0.8 \text{ J/K}^2 \text{ mol}$  can be estimated on their data at this linear region. The lower value of  $\frac{dS}{dT}$  in this case is due to the high values of the critical temperatures  $T_{c1} = 6.309 \text{ K}$  and  $T_{c2} = 7.258 \text{ K}$ . The position of the critical temperatures on the  $\Delta S$  vs  $T$  curve are similar in both salts,  $T_{c1}$  at the maximum slope and  $T_{c2}$  at the linear region. The entropy above  $T_{c2}$  is also of the same order: 60% and 54% for  $\text{NiCl}_2 \cdot 6\text{NH}_3$  and  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$  respectively. These facts suggest that the magnetic structures of these two salts have something in common.

As at this time, no detailed magnetic structure of  $\text{NiCl}_2 \cdot 6\text{NH}_3$  is available, the specific heat results of the present work can be understood comparing the known properties of  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ . A  $H$  vs  $T$  magnetic phase diagram study by susceptibility and magnetization measurements<sup>14</sup> on  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$  revealed a complicated array of spins when a magnetic field is applied. At zero field, the spin system consists of an antiferromagnetically coupled ferromagnetic chains below  $T_{c1}$ . No detailed magnetic structure is known between  $T_{c1}$  and  $T_{c2}$  except that it is also antiferromagnetic. De Neef and de Jonge<sup>15</sup> attributed the anomaly at  $T_{c1}$  to a reorientation of the magnetic moments. An X-ray diffraction study<sup>16</sup> revealed that the room temperature monoclinic unit cell transforms to another monoclinic cell with doubled  $c$ -axis below 230 K. This new unit cell comports two inequivalent  $\text{Ni}^{++}$  ions which can order each at one critical temperature and this was suggested as a possible explanation for the double anomalies in the specific heat<sup>16</sup>. If  $\text{NiCl}_2 \cdot 6\text{NH}_3$  has the monoclinic structure at low temperature as observed in  $\text{FeCl}_2 \cdot 6\text{NH}_3$ <sup>4</sup> it comports also two inequivalent  $\text{Ni}^{++}$  ions. They may be responsible for the two peaks in the specific heat. A spin reorientation hypothesis can not also be discarded.

Many other nickel compounds with similar double peak in the specific heat have been reported. In the  $\text{Ni}(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$  (Ref.17) and  $\text{NiI}_2[(\text{NH}_2)_2\text{CS}]_6$  (Ref.18) salts the two peaks are also related to  $\text{Ni}^{++}$  ions not magnetically equivalent in the unit cell. In the hexagonal  $\text{CsCl}_3$  (Ref.19) the NMR experiments<sup>20</sup> suggested some form of spin reo-

orientation where the  $c$  component of Ni spins orders antiferromagnetically at  $T_{c2} = 4.84$  K while below  $T_{c1} = 4.40$  K the perpendicular component becomes ordered. In the  $\text{MnCl}_2 \cdot 6\text{NH}_3$ , isomorphous to  $\text{NiCl}_2 \cdot 6\text{NH}_3$ , the double peak is attributed to chemical instability of the sample in the presence of traces of water<sup>12</sup>, but there is another possibility to consider, as the room temperature fcc structure is not conserved at low temperature<sup>5</sup>. The change to monoclinic structure in this salt gives rise also to two inequivalent  $\text{Mn}^{++}$  ions. In the  $\text{NiBr}_2 \cdot 2\text{H}_2\text{O}$  salt the two specific heat peaks were also observed<sup>21</sup> but the isomorphism to  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$  has not been confirmed and the inequivalency of ions could not be verified. It seems that the double peak is associated always with the existence of inequivalent Ni ions. Experiments as neutron diffraction are necessary to give detailed information about the magnetic structure of  $\text{NiCl}_2 \cdot 6\text{NH}_3$  which should clarify the double anomalies.

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