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# INVESTIGATION OF HEAT CAPACITY OF SOME AMMONIUM FLUOROMETALLATES HAVING DIFFERENT STRUCTURAL TYPES

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## ABSTRACT

A triple heat bridge method with an error not exceeding 3 % was used to measure heat capacities of $(NH_4)_3MF_6$ (M = Al, Ga, In, Fe) and $NH_4MF_3$ (M = Cr, Mn, Co, Cu, Zn, Cd) compounds. On the basis of the heat capacity data we evaluated phase transitions enthalpy of $(NH_4)_3MF_6$(M = Al, Ga, In, Fe) and $NH_4MF_3$(M = Mn, Cu, Cd) compounds.

## INTRODUCTION

It is known that many complex fluorides belonging to cryolite ($A_3BF_6$) and perovskite ($ABF_3$) structural types are characterized by phase transitions of different nature. The availability of such transitions was found also in a number of complex ammonium fluorides. But information on thermodynamic properties (in particular numerical data on heat capacity) is often missing in the literature.

## RESULTS AND DISCUSSION

The aim of this paper was to determine experimentally heat capacities of $(NH_4)_3MF_6$ (M = Al, Ga, In, Fe) and $NH_4MF_3$ (M = Cr, Mn, Co, Cu, Zn, Cd) compounds by means of a triple heat bridge method /I/ with an error not exceeding 3 %.

All the compounds were synthesized according to /2/ by interaction of corresponding metal bromides with ammonium fluoride in "absolute" methanol. X-ray and chemical analyses methods showed that the obtained individual compounds had a purity close to 100%.

The heat capacity measurements were conducted in the atmosphere of dried argon on compacted polycrystalline samples at heating rate equal to 2 deg/min.

Experimental results of the heat capacity measurements are shown in Fig.I and Fig.2. The figures show that within the investigated temperature range for $(NH_4)_3MF_6$(M = Al, Ga, In, Fe) and $NH_4MF_3$(M = Mn, Cd, Cu) compounds we found heat capacity anomalies with maxima at the temperatures given in Table I. Here we also provide the compounds heat capacity values in their maximum

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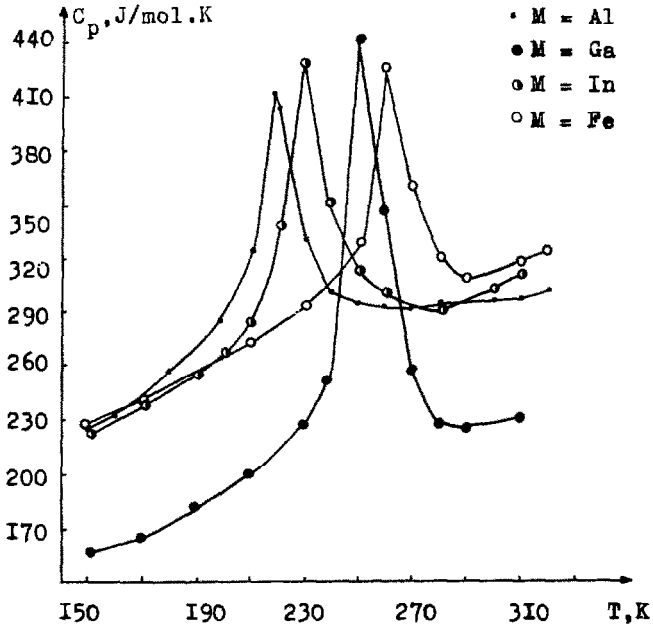


Fig.I. Heat capacity of the $(NH_4)_3MeF_6$ compounds .

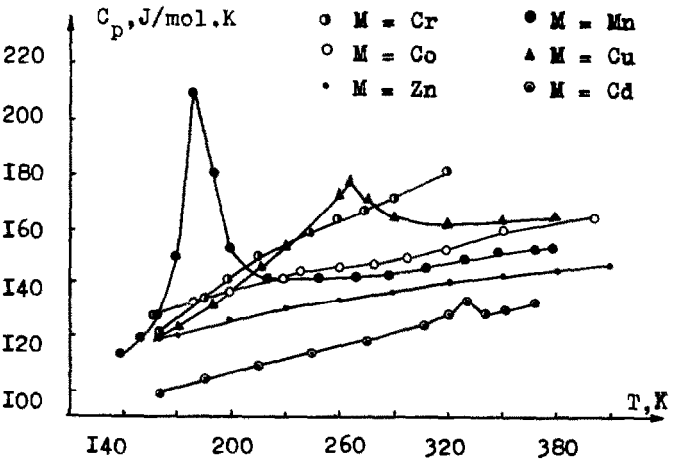


Fig.2. Heat capacity of the $NH_4MF_3$ compounds.

points.

Table I.

| Compound | $T_{max}$,K | $C_{p\ max}$,J/mol.K |
|---|---|---|
| $(NH_4)_3AlF_6$ | 218 ± 2 | 410.3 ± 12.3 |
| $(NH_4)_3GaF_6$ | 251 ± 2 | 449.2 ± 13.5 |
| $(NH_4)_3InF_6$ | 230 ± 2 | 430.6 ± 12.9 |
| $(NH_4)_3FeF_6$ | 261 ± 2 | 440.4 ± 13.2 |
| $NH_4MnF_3$ | 180 ± 2 | 218.8 ± 6.6 |
| $NH_4CuF_3$ | 267 ± 2 | 175.1 ± 5.3 |
| $NH_4CdF_3$ | 330 ± 2 | 132.8 ± 4.0 |

A good coincidence $T_{max}$ with the known temperatures of polymorphic phase transitions for the compounds with M = Al, Ga, Fe, Mn /3-5/ as well as a reversible character of all fixed anomalies allow to refer them to the processes of polymorphic transitions.

In our opinion heat capacity anomalies found in $(NH_4)_3InF_6$, $NH_4CuF_3$ and $NH_4CdF_3$ compounds may be due to earlier unknown phase transitions of these compounds, but detailed determination of their nature requires special investigations.

By integrating $C_p(T)$ dependence in the region of the anomalies we evaluated phase transitions enthalpies of $(NH_4)_3MF_6$(M = Al, Ga, In, Fe) and $NH_4MF_3$(M = Mn, Cu, Cd) compounds.

Table 2.

| Compound | $\Delta H_{trans.}$,kJ/mol | Compound | $\Delta H_{trans.}$,kJ/mol |
|---|---|---|---|
| $(NH_4)_3AlF_6$ | 2.1 | $NH_4MnF_3$ | 1.8 |
| $(NH_4)_3GaF_6$ | 4.5 | $NH_4CuF_3$ | 1.3 |
| $(NH_4)_3InF_6$ | 4.0 | $NH_4CdF_3$ | 0.1 |
| $(NH_4)_3FeF_6$ | 2.1 | | |

An accurate calculation of $\Delta H_{trans.}$ is impossible because of the fact that from the heat capacity data it is difficult to determine accurately temperatures of the beginning and the end of the transition.

Table 3 gives heat capacity values of all investigated compounds at standard conditions.

Table 3.

| Compound | $C_{p\ 298}^{o}$, J/mol.K | Compound | $C_{p\ 298}^{o}$, J/mol.K |
|---|---|---|---|
| $(NH_4)_3AlF_6$ | 299.4 ± 9.0 | $NH_4MnF_3$ | I44.0 ± 4.3 |
| $(NH_4)_3GaF_6$ | 226.4 ± 6.8 | $NH_4CoF_3$ | I48.3 ± 4.5 |
| $(NH_4)_3InF_6$ | 297.7 ± 8.9 | $NH_4CuF_3$ | I62.8 ± 4.9 |
| $(NH_4)_3FeF_6$ | 3II.4 ± 9.3 | $NH_4ZnF_3$ | I37.3 ± 4.I |
| $NH_4CrF_3$ | I73.8 ± 5.2 | $NH_4CdF_3$ | I23.7 ± 3.7 |

Comparison of experimental values $C_{p\ 298}^{o}$ with the ones calculated on the additive scheme:

$$C_{p\ 298}^{o}\ (NH_4)_xMF_y = xC_{p\ 298}^{o}\ (NH_4F) + C_{p\ 298}^{o}\ (MF_{y-x})$$

using known literature data on $NH_4F$ and corresponding simple metal fluorides heat capacity shows that for $(NH_4)_3MF_6$(M = Al, Fe) and $NH_4MF_3$(M = Cr, Mn, Cu, Zn) compounds one can observe positive deviation from the additivity (for M = Ga, In and Cd such calculations were not conducted, since data on $GaF_3$, $InF_3$ and $CdF_2$ heat capacity are missing). Such a positive deviation may be due to peculiarities of intramolecular motion of $NH_4^+$ ion in complex fluorometallates. In /6/ it is shown that for ammonium fluoride, unlike complex $(NH_4)_3MF_6$ fluorides, rotation of $NH_4^+$ group is difficult due to existence of strong hydrogen bonds.

Lack of enough reliable experimental data does not allow to make a final conclusion whether the positive heat capacity deviation from the additive value is a general property of all complex ammonium fluorometallates.

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