

PHASE TRANSITIONS IN AMMONIUM HEXAFLUOROMETALLATES (III): A CRYSTALLOGRAPHIC AND CALORIMETRIC STUDY

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Phase transitions have been characterized in several $(\text{NH}_4)_3\text{MF}_6$ hexafluorometallates (III) using X-ray diffraction and microcalorimetric techniques. For small trivalent cations ($M = \text{Al}, \text{V}, \text{Cr}, \text{Fe}, \text{Ga}$), an $\text{Fm}\bar{3}\text{m}$ cubic \rightarrow triclinic transition occurs below room temperature [as proposed by MASSA for $M = \text{Cr}$ and Fe , Habilitation, Univ. of Marburg, 1982]. For larger trivalent species, two-phase transitions have been detected, the low-temperature phases being monoclinic ($\text{P}2_1/\text{n}$) and tetragonal ($\text{P}4/\text{mnc}$) for Sc and In , respectively.

Heat capacity of ammonium hexafluorometallates have been measured in a miniaturized adiabatic calorimeter from 12 to 310 K. The entropy variation associated with the transitions (Table) may be accounted for by orientational order-disorder changes of $(\text{MF}_6)^{3-}$ units and of NH_4^+ ions occupying the octahedral sites. The variation of the transition temperature can be correlated with the cubic root of the unit-cell volume.

Table

Transition temperatures and entropy variations of $(\text{NH}_4)_3\text{MF}_6$ compounds

M^{III}	Al	Cr	Ga	V	Fe	Sc	In
T_1 (K)	193	-	-	-	-	291	318
T_2 (K)	220.8	269.6	246.1	280.4	267.0	330	352
$\Delta_{\text{tr}} S_1$ ($\text{JK}^{-1}\text{mol}^{-1}$)	4.2	-	-	-	-	2.2	2.0
$\Delta_{\text{tr}} S_2$ ($\text{JK}^{-1}\text{mol}^{-1}$)	18.5	19.4	21.3	24.9	24.8	10.6	10.3