

MAGNETIC PROPERTIES OF SOME LANTHANOID FLUOROARSENATES AND FLUOROBORATES[†]

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[†]This paper is dedicated to the memory of Dr. Karel Lutar

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Abstract

GdF(AsF₆)₂, GdF₃·2BF₃, H₃OGdF₃BF₄ and TbF(AsF₆)₂ obey Curie-Weiss law in the temperature range 4.2 K < T < 300 K with $\mu_{\text{eff}} = 7.35, 7.08, 7.51$ and 8.72 B.M. Compounds can be considered as magnetically dilute. Deviations of observed values from predicted are not major, suggesting that 4f shell is not substantially affected by the environment of the cation. EuF₃·2BF₃ doesn't obey Curie-Weiss law. Data obtained in the 150 K < T < 300 K temperature range can be fitted to linear curve giving $\mu_{\text{eff}} = 3.10$ B.M.

Introduction

Rare earth trifluorides (LnF₃) reacts with Lewis acids (e.g. AsF₅, BF₃) in anhydrous hydrogen fluoride (aHF) at room temperature. In the system LnF₃/AsF₅/aHF stable solutions of solvated rare earth cations Ln(FH)_x³⁺ and AsF₆⁻ anions were obtained. After removal of volatile components at room temperature La(AsF₆)₃, LnF(AsF₆)₂ (Ln = Ce-Nd, Sm-Er and Y) and Ln₂F₃(AsF₆)₃ with Ln = Tm, Yb and Lu were isolated.¹ All attempts to grow single crystals of compounds LnF_x(AsF₆)_{3-x} (x = 0, 1 or 1.5) failed. The stabilization of these compounds was finally achieved by using additional ligands (e.g. HF², XeF₂³, AsF₃³) and the corresponding crystal structures could be determined.

Products between LnF₃ and BF₃ are only slightly soluble in aHF. Characterization of the isolated products showed that they form two types of compounds: LnF₃·2BF₃ (Ln = La-Nd, Sm-Er) and LnF₃·nBF₃ (Ln = Ho-Lu). The composition of the last phase is still unclear (n = 1 or 1.5).⁴

When Ln_2O_3 oxides were used as starting materials in Lewis acid/aHF superacid medium new oxonium compounds of lanthanoids were isolated (e.g. $(\text{H}_3\text{O})_3\text{La}_2\text{F}(\text{AsF}_6)_8$ ^{3,5}, $(\text{H}_3\text{O})_8\text{La}_2\text{F}(\text{AsF}_6)_{13}$ ^{3,5}, $\text{H}_3\text{OGdF}_3\text{BF}_4$ ⁶).

There are no structural reports of the measured compounds. The vibrational spectra of $\text{LnF}_x(\text{AsF}_6)_{3-x}$ compounds are consistent with distorted AsF_6^- octahedra, indicating the presence of covalent contribution to the fluorine bridges between LnF_3 and AsF_5 .¹ The vibrational spectra of fluoroborates also show significant distortions of BF_4^- and evidence an appreciable covalent character of the compounds. The bonding should be thus formulated as $\text{F}_3\text{B}\cdots\text{LnF}\cdots\text{BF}_3$ with bridging fluorine atoms.⁷

This work is devoted to the investigation of the magnetic behavior of some selected lanthanoid hexafluoroarsenates and fluoroborates. In the $\text{LnF}_3/\text{AsF}_5$ systems $\text{GdF}(\text{AsF}_6)_2$ (**1**) and $\text{TbF}(\text{AsF}_6)_2$ (**2**) were investigated. Two other examples were also taken from the LnF_3/BF_3 system (e.g. $\text{GdF}_3\cdot 2\text{BF}_3$ (**3**) and $\text{EuF}_3\cdot 2\text{BF}_3$ (**4**)). Additionally, results of magnetic measurements of $\text{H}_3\text{OGdF}_3\text{BF}_4$ (**5**) are given.

Results and discussion

The temperature dependence of the inverse magnetic susceptibility of **1**, **3**, **5** under an applied field of 1.7 T and **2** under an applied field of 0.6 T are presented in Fig. 1-4. Comparison between experimental values of the effective moment μ_{eff} and the calculated ones from Ln^{3+} ions configurations is given in Table 1. In the temperature range $4.2 \text{ K} < T < 300 \text{ K}$ the reciprocal magnetic susceptibilities are linear with

Table 1: Calculated and experimental values of μ_{eff}

Compound	$\mu_{\text{eff}} = g[J(J+1)]^{1/2} / \text{B.M.}$	$\mu_{\text{eff}} (\text{experimental}) / \text{B.M.}$
$\text{GdF}(\text{AsF}_6)_2$	7.94	7.35
$\text{GdF}_3\cdot 2\text{BF}_3$	7.94	7.08
$\text{H}_3\text{OGdF}_3\text{BF}_4$	7.94	7.51
$\text{TbF}_3\cdot 2\text{BF}_3$	9.72	8.72

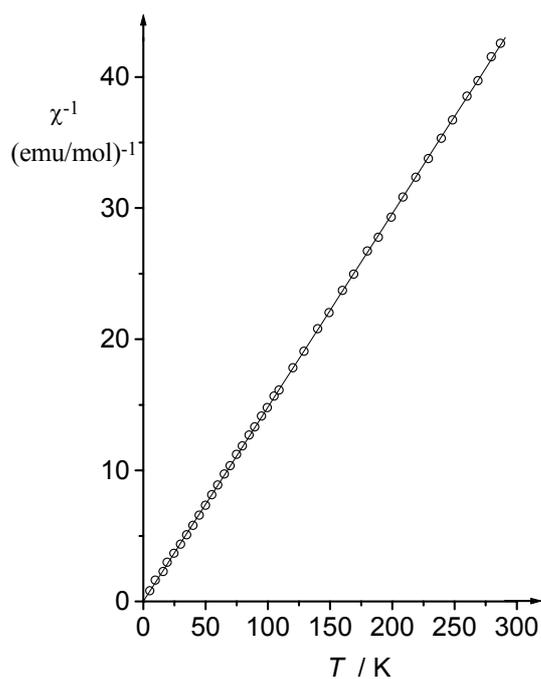


Fig. 1: Temperature dependence of the reciprocal susceptibility of $\text{GdF}(\text{AsF}_6)_2$

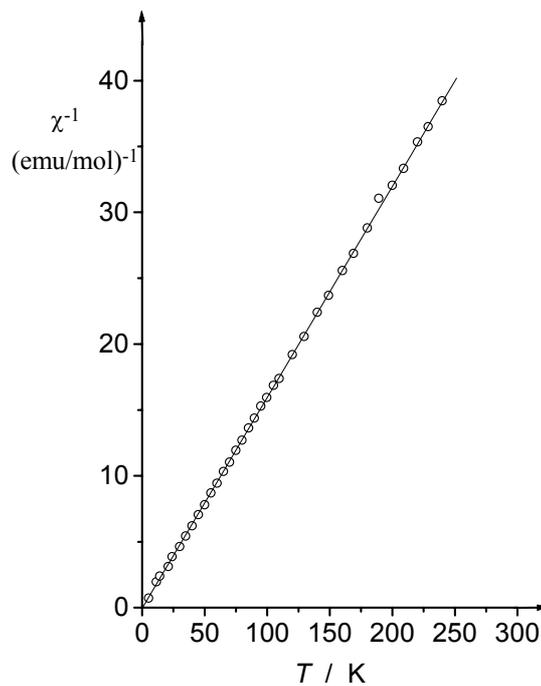
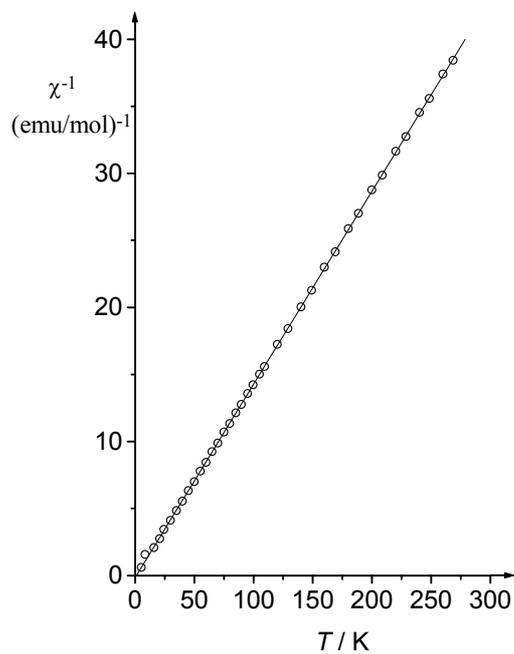


Fig. 2: Temperature dependence of the reciprocal susceptibility of $\text{GdF}_3 \cdot 2\text{BF}_3$



$\text{GdF}_3 \cdot 2\text{BF}_3$

Fig. 3: Temperature dependence of the reciprocal susceptibility of $\text{GdF}_3 \cdot 2\text{BF}_3$

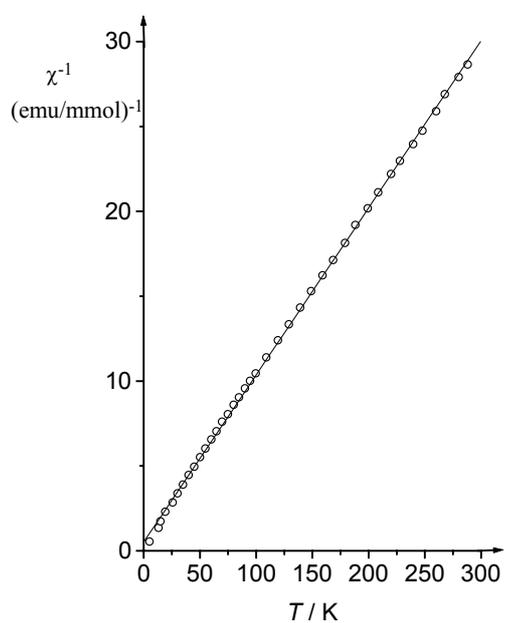


Fig. 4: Temperature dependence of the reciprocal susceptibility of $\text{GdF}_3 \cdot 2\text{BF}_3$

reciprocal susceptibility of $\text{H}_3\text{OGdF}_3\text{BF}_4$
 $\text{TbF}(\text{AsF}_6)_2$

reciprocal susceptibility of

temperature. In this temperature range measured compounds are paramagnetic and their magnetic susceptibility follow a Curie-Weiss law. Values of μ_{eff} derived from experimental results (Table 1) are close to the values calculated from the equation $\mu_{\text{eff}} = g[J(J+1)]^{1/2}$, where $g = 3/2 + [S(S+1) - L(L+1)]/[2J(J+1)]$, valid for Ln^{3+} ions. In these equations S is the spin contribution and L the orbital contribution to magnetic moment. They couple together to give a new quantum number J .

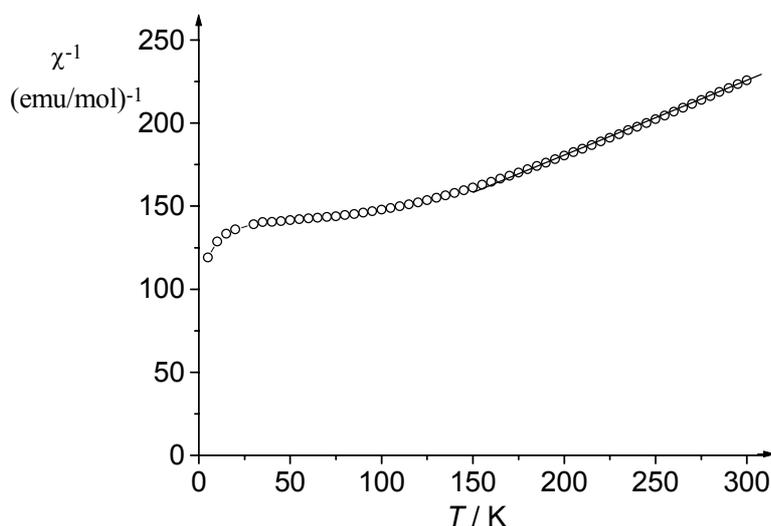


Fig. 5: Temperature dependence of the reciprocal susceptibility of $\text{EuF}_3 \cdot 2\text{BF}_3$

For the Eu^{3+} compound the Curie-Weiss law is not followed. This is due to the small energy difference between the ground state and next energy state of the Eu^{3+} ($\approx 400 \text{ cm}^{-1}$).⁸ Some electrons can be promoted by the energy of the thermal motion and partly populate the higher state. The consequence is that magnetic behavior is not solely determined by the ground state configuration as in the case of other Ln^{3+} ions with exception of Sm^{3+} . Data obtained in the $150 \text{ K} < T < 300 \text{ K}$ temperature range can be fitted to linear curve giving $\mu_{\text{eff}} = 3.10 \text{ B.M.}$ The obtained value of μ_{eff} is close to

experimental data reported in the literature for other Eu^{3+} compounds ($\mu_{\text{eff}} = 3.4\text{--}3.6$ B.M.).⁹

Conclusions

Magnetic data of **1**, **2**, **3**, **5** show that these compounds can be treated as magnetically dilute. Deviations of μ_{eff} observed values from the predicted ones are not important, suggesting that $4f$ shell is not substantially affected by the environment of the cation. Magnetic susceptibility of **4** does not follow a Curie-Weiss law. High temperature data of **4** can be fitted to a linear curve giving $\mu_{\text{eff}} = 3.10$ B.M.

Experimental

1, **2** and **3**, **4** compounds were prepared as white powders by reaction between LnF_3 and AsF_5 or BF_3 , respectively, in anhydrous hydrogen fluoride as a solvent.^{1,5,6} Oxonium compound was prepared from Ln_2O_3 and excess of BF_3 as described in the literature.⁶ The compounds were prepared pure and characterized by chemical analysis, vibrational spectroscopy^{1,6,7} and in the case of the two $\text{LnF}_3 \cdot 2\text{BF}_3$ ($\text{Ln} = \text{Gd}, \text{Eu}$) complexes also with X-ray analysis.^{6,7} Lanthanoid fluoroarsenates were nearly amorphous and X-ray photographs of poor quality were always obtained. All investigated compounds being extremely moisture-sensitive, the transfer into suitable sample containers was made in a dry-box. The residual amount of water present in the atmosphere of the dry-box never exceeded 1 ppm. Cylindrical screw-capped sample containers ($V \approx 0.5$ ml, $m \approx 0.25$ mg) were made of Kel-F (polytrifluorochloroethylene) and were additionally tightened with Teflon gaskets. Prior to their use, both the container and Kel-F packing tool were passivated with elemental fluorine. A known

quantity of compound **4** (18.73 mg) was measured on a SQUID magnetometer (SHE Corp.) and compounds **1**, **2**, **3**, **5** (20–24 mg) on MANICS DSM8 susceptometer.

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Povzetek

Magnetne lastnosti spojin $\text{GdF}(\text{AsF}_6)_2$, $\text{GdF}_3 \cdot 2\text{BF}_3$, $\text{H}_3\text{OGdF}_3\text{BF}_4$ in $\text{TbF}(\text{AsF}_6)_2$ se podrejajo Curie-Weissoveemu zakonu v temperaturnem območju $4.2 \text{ K} < T < 300 \text{ K}$ z $\mu_{\text{eff}} = 7.35, 7.08, 7.51$ oziroma 8.72 B.M. Spojine lahko obravnavamo kot magnetno razredčene. Odstopanja izmerjenih vrednosti od teoretičnih niso velika. To kaže da okolica kationa zelo malo vpliva na $4f$ -orbitale. Magnetne lastnosti spojine $\text{EuF}_3 \cdot 2\text{BF}_3$ se ne podrejajo Curie-Weissoveemu zakonu. Rezultati meritev izmerjeni v temperaturnem območju $150 \text{ K} < T < 300 \text{ K}$ se prilegajo premici z $\mu_{\text{eff}} = 3.10 \text{ B.M.}$