

STRUCTURE AND MAGNETIC PROPERTIES OF SOME BINARY AND TERNARY LANTHANIDE FLUORIDES

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Binary and ternary fluorides of some lanthanides (Ce, Eu(II,III), Yb) and Al were synthesized and annealed at high temperatures and deep vacuum. Their structure and composition have been studied by both X-ray analysis and chemical one. Magnetic susceptibilities of the samples were measured by the Faraday method. Some of them exhibited significant deviation in the composition from the stoichiometry. Most of the Eu(II,III) did not satisfy the Curie-Weiss equation due to electron exchange interaction.

Cerium, Europium, Ytterbium are the elements of a lanthanide series, for which the variable valence state is peculiar [1]. This feature represents a great opportunity for exhibiting various magnetic and optical properties by their compounds, particularly fluorides.

The initial binary compounds were obtained by a fluoridation of oxides of lanthanides or aluminum hydroxide by hydrofluoric acid with the subsequent dehydration and high-temperature annealing under an inert-gas atmosphere (He). Some of them (EuF₃, CeF₃, YbF₃) were melted in graphite crucibles. The specimens of the systems EuF₃-CeF₃ and YbF₃-CeF₃ were melted as well. High-temperature solid-phase synthesis of EuF₂ was performed using EuF₃ + Si mixture with components taken in a stoichiometric ratio [2]. The complex fluoride EuAlF₅ was synthesised in an analogous manner by reduction of the mixture EuF₃ + AlF₃ with silicon.

The obtained materials (as well as the refuses after evaporation) were tested using the X-ray phase and structure analysis, chemical analysis. The diffraction spectra were detected by the automated DRON-3 diffractometer in a discrete regime (step scan (0.02 - 0.05)°, counting time (4 - 8) s) using the filtered copper radiation (anode voltage 30 kV, current 20 mA, entrance slits 2, 4 mm, detector slit 0.1 mm). The angle interval (2θ) of diffraction spectra registration for the phase analysis was equal to (20 - 70)°. The diffraction spectra for crystal structure determination were registered in a whole angle range. The preliminary treatment of the diffraction spectra was carried out by full profile analysis. The centers of gravity of the peaks and their integrated intensities have been determined within the accuracy of ±(0.001÷0.005)° and ±(5÷15)% respectively. The phase analysis and structure calculations were carried out using developed earlier apparatus and software complex [3] based on the Rietveld approach principles.

The oxidation ability of Eu(II) has been used to determine its content in EuF₃ samples. In order to avoid oxidation of Eu(II) by the atmospheric oxygen during the samples' decomposition they were dissolved in a concentrated H₃PO₄ over the volumetric solution of oxidant. The compounds of V (vanadium) were used as the oxidants. The procedure of Eu(II) content

determination was as follows: a charge of (0.03÷0.05) g of the sample was mixed with 5 ml of 0.025 M solution of vanadium (V) compound and 10 ml of the concentrated H₃PO₄. Then the mixture was heated up to the charge dissolving. 5 ml of 9M H₂SO₄ was added to the hot solution and the obtained liquid was diluted by water up to ~ 50 ml. The excess of oxidant was titrated by the solution of iron (II) sulfate in phenyl-anthranilic acid (indicator). Simultaneously the check experiment was carried out.

The evaporation of the samples of EuF₃ was performed either under the action of electron beam (emission current 30 mA) or by the resistive heating from the molybdenum boats (heating current up to 120 A).

Temperature dependences of the magnetic susceptibilities (χ) were recorded on the automated magnetometer in the interval of temperature 300-800 K using relative Faraday method. Sensitivity of the setup was $5 \cdot 10^{-11}$ cm³/g, relative deviation in the determination of susceptibility $\Delta\chi / \chi$ did not exceed 1%.

Table – Composition and magnetic properties of the fluorides.

No of the specimen	Formula	Phase composition	Chemical composition, mol. %	Specific magnetic susceptibility, cm ³ /g	Effective magnetic moment per Ln-ion, μ_B
1	EuF ₃	α EuF ₃ , rh	EuF ₃ - 100	20.6	3.61 [1]
2	EuF ₃ , melted	α EuF ₃ , rh	EuF ₂ - 2.7	22.8	3.79 ³⁾
3	EuF _{3-x} (EBE) ¹⁾	α EuF ₃ , rh; EuF _{2+x} , β -c	EuF ₂ - 6.5	24.9	4.03 ³⁾
4	EuF _{3-x} (RE) ²⁾	α EuF ₃ , rh; EuF _{2+x} , β -c	EuF ₂ - 14.5	34.6	4.50 ³⁾
5	EuF _{3-x} , melted (RE)	α EuF ₃ , rh; EuF _{2+x} , t	EuF ₂ - 16.9	36.7	4.63 ³⁾
6	EuF ₂	EuF _{2+x} , α -c	EuF ₂ ~ 100	115.8	7.91 [1]
7	EuF ₃ -CeF ₃	EuF _{2+x} , α -c; β EuF ₃ , h; β CeF ₃ , h	EuF ₂ - 14.0	23.7	4.02 ³⁾
8	CeF ₃	CeF ₃ , h	CeF ₃ ~ 100	12.4	2.53; 2.39 [1]
9	EuAlF ₅	EuAlF ₅ , t	EuF ₂ - 47.4	45.5	7.81
10	YbF ₃	α YbF ₃ , rh	YbF ₃ - 100	43.5	4.59; 4.4 [1]
11	YbF ₃ -CeF ₃	α YbF ₃ , rh; CeF ₃ , h	YbF ₃ ~ 50	24.5	3.74; 3.54 ³⁾

¹⁾ EBE – refuse after electron beam-evaporation; ²⁾ RE – refuse after resistive thermal evaporation, h – hexagonal, rh. – rhombic, c – cubic and t – tetragonal structure; ³⁾ calculated.

The data of the X-ray diffraction study proved (Table) that the heat-treated source EuF₃ synthesized products (sintered sample of white colour (specimen 1) and the melted sample of white colour with the yellow tint (specimen 2)) were single-phase.

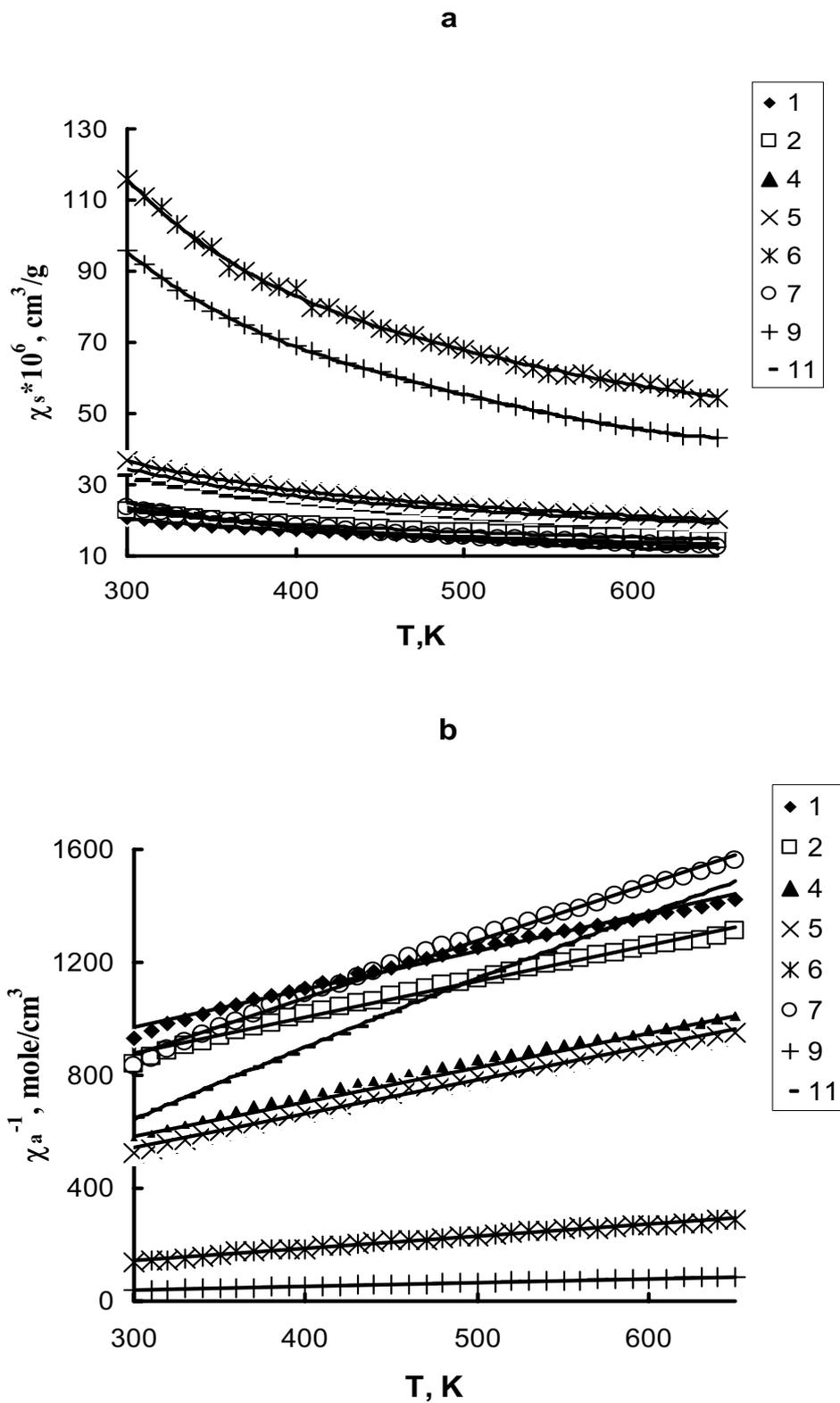


Fig. Temperature dependences of the magnetic susceptibility (a) and inverse molar magnetic susceptibility (b) of the binary and ternary fluorides (numbers of the curves correspond to the numbers of the specimens in the Table).

Their diffraction spectra were indexed in a rhombic lattice (Table), i.e. were responded to α -EuF₃. According to the X-ray phase analysis α -EuF₃ is the main phase constituent of the refuse of EuF₃ evaporation (specimens 3-5). However, these probes contain besides this phase an essential amount of EuF_{2+x} fluorite-like phase both in cubic and tetragonal forms (Table). Therewith, the content of this phase increases when the electron-beam evaporation is substituted by the resistive one.

The data of chemical analysis (Table) display the absence of Eu(II) in the sintered EuF₃ sample (specimen 1). Therewith the melted sample after evaporation (specimen 2) contains a noticeable amount of Eu(II). EuF₃ samples subjected to the high-temperature treatment during the evaporation process contain significantly higher contents of Eu(II). It should be noticed that the effect of the resistive evaporation on the EuF₃ composition is more pronounced. The difference between Eu(II) contents in the melted and sintered samples (specimen 4 and 5) just corresponds to the difference of Eu(II) content in the source samples (specimen 1 and 2).

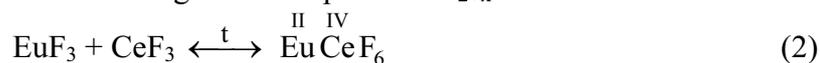
The obtained data testify an essential change in Eu valence state under severe heat treatment of EuF₃. Under the action of high temperature and vacuum the reducing of Eu(III) to Eu(II) occurs according to the equation:



Thermodynamic calculations of ΔG^0_T for this process at $T = T_{\text{melt}}(\text{EuF}_3)$ and $P = 10^{-3}$ Pa (vacuum in a working chamber) resulted in a value almost equal to zero. Temperature increasing leads to the negative ΔG^0_T values. Besides, it should be taken into account that the stabilization of Eu(II) valence state in EuF₃ structure is favorable to the reducing process. Such stabilization occurs due to the chemical interaction of the formation of mixed-valence europium compounds (Eu₂EuF₇ etc.). It is necessary to note more significant changes of Eu(II) content in the case of melted EuF₃ (specimen 6). The reason is that it contains some amount of Eu(II) ions in EuF₃ structure, i.e. is in fact the high-temperature solid solution on the base of EuF₃ rhombic modification. Evidently, the presence of EuF_{2+x} phase is a consequence of decomposition of EuF₂ – based high-temperature solid solution. Thus it was shown that during α -EuF₃ synthesis performed under different thermal conditions (sintering or melting) the atoms in its structure either orderly occupy the sites of anti-Fe₃C structure type, or fluorine is partially substituted by europium in *8f* Wyckoff positions. Heat treatment during the vacuum evaporation of α -EuF₃ leads to the formation of EuF_{2+x} phase containing Eu(II). This phase formation is a consequence of EuF₃ thermal destruction in high vacuum. EuF_{2+x} composition and its content in the samples depend on both the source material and the mode of thermal evaporation (resistive evaporation seems to be more efficient).

It follows from the table that the samples of EuF_{2+x} composition and of cubic structure resembling most closely EuF₂ were obtained by the solid-state synthesis with silicon as a reducing agent.

On the other hand, a high content of Eu(II) in the form of EuF_{2+x} phase was observed in the case of EuF₃–CeF₃ system (Tab.1). It is connected with a partial transfer of valence states Eu(III) → Eu(II) and Ce(III) → Ce(IV) due to the consequent donor-acceptor interaction to form EuCeF₆ compound which is stable only at high temperatures [4]. Some of Ce(IV) fluoride volatilizes at high temperatures remaining the cubic phase EuF_{2+x}:



At that time the system YbF₃–CeF₃ almost did not exhibit such phenomenon although high-temperature annealing in a deep vacuum results in some amount of the YbF_{2+x} phase.

As it has been shown, complex fluoride EuAlF_5 crystallizes in the tetragonal structure of the SrAlF_5 type. The characteristic feature of the crystal structure of this compound is the network made of deformed octahedral AlF_6 . Free intervals in this network are occupied by the atoms of Europium, which are surrounded by the atoms of Fluorine at the distances from 0.243 to 0.349 nm.

The data of magnetic susceptibility measurements prove the processes of reduction of Eu(III) to Eu(II) during high-temperature annealing (melting, evaporation in vacuum or right reduction both with Silicon and CeF_3). The values of χ gradually decrease with temperature for all specimens (Fig. a) in accordance with the Curie-Weiss equation:

$$\chi = \chi_0 + \frac{N \cdot \mu_{\text{eff}}^2}{3k(T - \theta_p)}, \quad (4)$$

where N is the Avogadro constant, k is the Boltzmann constant, θ_p is the paramagnetic Curie temperature, χ_0 is the temperature - independent component of susceptibility (Van-Fleck constant), μ_{eff} is the effective magnetic moment in Bohr magneton (μ_B). As the value of μ_{eff} sufficiently increases from Eu(III) to Eu(II) , increasing content of Eu(II) in the specimens 1-6 should result in significant increasing values of χ . This is actually observed (Fig., Table). Using the chemical analysis data and the well - known equation:

$$\overline{\mu_{\text{eff}}} = \sqrt{x \cdot \mu_{\text{eff}}^2(\text{Eu(II)}) + (1 - x) \mu_{\text{eff}}^2(\text{Eu(III)})}, \quad (5)$$

where x is a molar fraction of EuF_2 in the specimens, we calculated their effective magnetic moments (Table). We have also calculated the values of μ_{eff} using the above mentioned Curie-Weiss equation (neglecting the value of χ_0) in the inverse form:

$$\chi^{-1} = \frac{1}{\mu_{\text{eff}}^2} \cdot \frac{3k}{N} \cdot (T - \theta_p). \quad (6)$$

It has been established that only some of the fluorides (specimens 8-11) adequately satisfy this equation (Fig.,b). Values of μ_{eff} calculated from the functions χ^{-1} vs. T for CeF_3 and YbF_3 appeared to be close to those from scientific literature (Table). The same should be noted for EuAlF_5 proving a complete valence state stabilization of Eu(II) in this compound.

Unfortunately most of the Eu -based fluorides (specimens 1-7) did not satisfy equation (4) exhibiting strong deviation from the straight lines (Fig., b). It might be caused by the electron exchange between Eu(II) and Eu(III) in the phases containing atoms in the various valence states.

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