MAGNETIC SUSCEPTIBILITY MEASUREMENTS OF RARE EARTH NON-STOICHIOMETRIC FLUORIDES

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INTRODUCTION

In recent years there has been a large interest in studying single crystalline solid solutions $M_{1-x}R_xF_{2+y}$ using different experimental techniques of solid state physics and chemistry, electrochemistry and structural analysis [1]. The reason lies in the crystalline matrices having a high capacity to dissolve great quantities of rare earth trifluorides (up to 50% mol [2-4]).

Multicomponent non-stoichiometric fluorides that comprise the $M_{1-x}R_xF_{2+y}$ phases are used as laser and optical materials, superionic conductors, scintillators, etc. [5].

These crystals have been studied using electric conductivity technique [6], NMR [7], EPR [8], X-ray and neutron diffraction [9], and dielectric and thermostimulated spectroscopy [10] that characterize mainly the disorder of the anionic sublattice in fluorite type structure and formation of different types of clusters of structural defects. In such clusters rare earth ions are combined with interstitial F-ions and anionic vacancies.

In order to know better the behaviour of the rare earth ions in non-stoichiometric fluorides, we have carried out a magnetochemical study of these crystals. This article reports the results of our measurements of magnetic susceptibility of rare earth in non-stoichiometric and some stoichiometric fluorides in which there are no clusters of defects in the anionic sublattice.

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Experimental procedures

Synthesis

Single crystals of non-stoichiometric fluorides were grown from melt by Stockbargter technique, experimental details are given in [11]. The samples were grown in fluorizing atmosphere created by products of tetrafluoroethylene pyrolysis enabling a decrease of oxygen content in samples. Growth rates were 3-10 mm/h. In some samples constitution melt overcooling gave rise to a cellular substructure due to loss of stability of the flat crystallization front. The chemical analysis of the samples was refined from concentration dependence of unit cell parameters by X-ray powder analysis. The samples with other structure types were obtained by long heating at 700-800°C and rapid quenching.

Experimental techniques

We have measured the magnetic susceptibility using a Faraday balance, and the temperature range has fluctuated between 20 K and 300 K. The sample is inside a plastic bag that hangs on one of the arms of the scales with a quartz thread almost one meter long. The sample remains in a place in which when it interacts with the non-uniform field created by an electromagnet, the scales detect a weight increase of the sample. The weight measurements have been done with the sample inside a helium atmosphere at 200 mbarr. Previously-made calibration allows calculating the magnetic susceptibility of a mass unit from the weight increase:

$$\chi_{mass} = f \cdot \frac{\Delta p_s - \Delta p_b \cdot m_b}{m_s} + |\chi_{dia}|$$

where “f” is the calibration factor that depends on the intensity of the current that circulates through the electromagnet that produces the magnetic field, calculated from measurements made with the pattern HgCo(NCS)$_4$ [12], “m$_s$” is the mass of the sample, “m$_b$” is the mass of the bag that contains the sample, “$\Delta p_s$” is the weight increase detected by the scales, “$\Delta p_b$” is the weight increase of the bag per mass unit, previously measured and $\chi_{dia}$ is the diamagnetic correction.

The magnetic susceptibility per mole is the product of the molecular mass of the sample (by rare earth ion) M by the magnetic susceptibility per mass unit.

We have measured the magnetic susceptibility every 5 K between 20 K and 300 K.

RESULTS AND DISCUSSION

We have studied the magnetic properties of rare earth non-stoichiometric fluorides, with different concentrations of rare earth ions and different crystal structures:

1. Crystals of fluorite cubic phases $\text{Ba}_{1-x} \text{R}_x \text{F}_{2+x}$ with $\text{R} = \text{La}(x=0.31), \text{Nd}(x=0.1), \text{Sm}(x=0.1, 0.2) \text{and Gd}(x=0.1)$.

2. Crystals of fluorite cubic phases $\text{Ca}_{1-x} \text{R}_x \text{F}_{2+x}$ with $\text{R} = \text{Gd}(x=0.01)$ and $\text{Er}(x=0.1)$.

3. Crystals of fluorite cubic phases $\text{Sr}_{1-x} \text{R}_x \text{F}_{2+x}$ with $\text{R} = \text{La}(x=0.31), \text{Pr}(x=0.27), \text{Nd}(x=0.165) \text{and Gd}(x=0.15)$.

4. Crystals of fluorite ordered (trigonal) phases $\text{Ba}_{1-x} \text{R}_x \text{F}_{2+x}$ with $\text{Sm}(x=0.4)$ and $\text{Yb}(x=0.4)$.

5. Rare earth sodium fluorides with different structures and compositions: cubic fluorite crystals $\text{Na}_{0.4} \text{R}_{0.6} \text{F}_{2.2}$ (with $\text{R} = \text{Ho, Er, Tm, Yb}$), $\text{Na}_{2.35} \text{Dy}_{0.65} \text{F}_{2.3}$; ordered (fluorite structure derived) phase $\text{Na}_7 \text{Tm}_{13} \text{F}_{46}$ and $\text{Na}_{1.5} \text{Dy}_{1.5} \text{F}_6$ with gagarinite ($\text{NaCaYf}_{6}$) structure type.

All the fluorides, except those containing $\text{Sm}^{3+}$ which will be separately discussed, follow the Curie-Weiss law:

$$\chi_{\text{mol}} = \frac{C}{T - \theta}$$ (2)

where $C$ is the Curie constant and $\theta$ is the Curie temperature.

The 4f electrons of the rare earth ions are responsible for the magnetic behavior of the studied substances.

The electronic configuration of the rare earth ions is $(\text{Xe}) 4f^{n-14} 5s^2 5p^6$. The crystal field interaction with 4f-electrons of each rare earth ion is very small, as a consequence of the screening via outer electrons.

From theoretical calculations [13] we know that the Curie constant is:

$$C = \frac{\mu_{\text{eff}}^2 \cdot N_A \cdot x}{3 \cdot k_B}$$ (3)

where \( N_A = 6.02 \cdot 10^{23} \text{ mol}^{-1} \) is the Avogadro number, \( x \) is the mole fraction of \( R^{+3} \) ions in fluorides, \( k_B = 1.38 \cdot 10^{-16} \text{ erg/K} \) is the Boltzmann constant, \( \mu_{\text{eff}} \) is the effective magnetic moment, given by the expression:

\[
\mu_{\text{eff}} = \left[ \frac{3}{2} + \frac{1}{2} \cdot \frac{S(S+1)-L(L+1)}{J(J+1)} \right] \cdot [J(J+1)]^{1/2} \mu_B
\]

where \( \mu_B = 9.27 \cdot 10^{-21} \text{ erg/G} \) and \( S, L, J \) are the quantum numbers of the fundamental-state of the rare earth ion.

From the experimental data and using equation (1) we can obtain the values of \( \chi = \chi(T) \) and, therefore, in case we notice a behaviour according to the Curie-Weiss law, like the one in figure 1, we can obtain the experimental values for the magnetic moment, \( \mu_{\text{eff}} \) and the Curie temperature, using the expressions (2) and (3). We can see in Table 1 the results coming out of the experimental data compared with the values theoretically calculated, using expression (4), for the magnetic moments.

For most of the calculated samples we can observe a behaviour following the Curie-Weiss law, also, the magnetic moments found experimenta-

Fig. 1. Temperature dependence of the relative inverse magnetic susceptibility for samples with Curie-Weiss behavior. The list of these samples and the \( \chi_{300} \) values are presented in Table II.
- Experimental values.
- Fitted line using the Curie-Weiss law.
Table 1. Effective magnetic moments of rare earth ions, Curie temperature and Curie constant for non-stoichiometric \(M_{1-x}R_xF_{2+x}\), \(Na_{2.5-x}R_{2.5+x}F_{2+2x}\) and some stoichiometric binary compounds.

<table>
<thead>
<tr>
<th>(M_{1-x}R_xF_{2+x})</th>
<th>Magnetic moments ((\mu_B))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M)</td>
<td>(R)</td>
</tr>
<tr>
<td>Ba La</td>
<td>0.310</td>
</tr>
<tr>
<td>Ba Nd</td>
<td>0.095</td>
</tr>
<tr>
<td>Ba Sm</td>
<td>0.1</td>
</tr>
<tr>
<td>Ba Sm</td>
<td>0.2</td>
</tr>
<tr>
<td>Ba Sm</td>
<td>0.4</td>
</tr>
<tr>
<td>Ba Gd</td>
<td>0.091</td>
</tr>
<tr>
<td>Ba Yb</td>
<td>0.4</td>
</tr>
<tr>
<td>Ca Gd</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca Er</td>
<td>0.1</td>
</tr>
<tr>
<td>Sr La</td>
<td>0.31</td>
</tr>
<tr>
<td>Sr Pr</td>
<td>0.27</td>
</tr>
<tr>
<td>Sr Nd</td>
<td>0.165</td>
</tr>
<tr>
<td>Sr Gd</td>
<td>0.15</td>
</tr>
</tbody>
</table>

- Experimental magnetic moments calculated at 300 K.

llly coincide rather well with those theoretically calculated. The relative difference:

\[
E = \frac{\left| \mu_{\text{cal}} - \mu_{\text{exp}} \right|}{\mu_{\text{exp}}}
\]

between the calculated and experimental magnetic moments is about 1-6% as shown in figure 2.

A separate discussion is required in the case of non-stoichiometric samarium fluorides. As it is shown in figure 4, these compounds follow the Curie-Weiss law only in a narrow temperature range. It is not possible to fit the curve to a straight line at any temperature range. This anomalous behaviour had already been predicted by Van Vleck [14]. The reason why \(Sm^{3+}\) is widely deflected from the Curie behaviour is that the spacing between its energy levels is comparable to \(k_B T\). Therefore, according to [15], we write the complete expression for the susceptibility.

Fig. 2. Magnetic moments of rare earth ions. The value of samarium magnetic moment is at 300K.

- Experimental values are presented in Table I.
- Experimental values from [16].

\[
\chi = \frac{\sum_{J=|L-S|}^{J=|L+S|} N \left[ \frac{g^2 \mu_B^2}{3} \frac{J(J+1)}{k_B T} \right] + \alpha(J) \cdot (2J+1) \cdot e^{\frac{-E(J)}{k_B T}}}{\sum_{J=|L-S|}^{J=|L+S|} (2J+1) \cdot e^{\frac{-E(J)}{k_B T}}} \tag{5}
\]

where \(\alpha(J)\) is the term given by Van Vleck.

\[
\alpha(J) = \frac{\left[(S+L+1)^2 - J^2\right] \cdot \left[J^2 - (S-L)^2\right]}{J}
\]

The term \(\alpha(J)\) is usually negligible since the frequency intervals \(v_{J-1,J}, v_{J+1,J}\) are smaller than \(k_B T\), but with samarium they are comparable, and the Van Vleck's term becomes noticeable.

In this way we can predict a different behaviour as compared to that of the Curie-Weiss law: the effective magnetic moment \(\mu_{\text{eff}}\):

Fig. 3. Temperature dependence of the relative inverse magnetic susceptibility for samples with deviation from the Curie-Weiss law. The list of these samples and the $\chi_{300}$ values are presented in Table 2.

- Experimental values.
- Fitted line in the temperature range where the Curie-Weiss law is observed.

$$\mu_{\text{eff}} = \sqrt{\frac{3 \cdot k_B \cdot \chi \cdot T}{N \cdot \mu_B^2}}$$  

will not be constant but will depend on the temperature, and this does not happen when $\alpha$ (J) is negligible, since $\chi T \approx C$ Curie constant.

Comparing the theoretical values obtained from equations (5) and (6), assigning a constant screening $\sigma = 34$, with the experimental values obtained from our measurements, we see that the agreement is quite good at temperatures above 80K, as it is shown in figure 5. Therefore, in order to interpret the samarium susceptibility data, it is necessary to add the second order Zeeman terms. We can interpret the deviation between the theoretical values and experimental values of the magnetic susceptibility and magnetic moments in the temperature range under 80K as the inclination to the magnetic order at low temperatures and the formation of small clusters. We suggest carrying out more measurements at temperatures under 20K to investigate some transition appears.
Fig. 4. Temperature dependence of the relative inverse magnetic susceptibility of samarium samples. The $\chi_{300}$ values are presented in Table 2.

Fig. 5. Temperature dependence of the effective magnetic moment in samarium ions.
- Experimental values for $\text{Ba}_2\text{Sm}_{0.1}\text{F}_{2.1}$ sample.
- Experimental values for $\text{Ba}_4\text{Sm}_{0.2}\text{F}_{2.2}$ sample.
- Experimental values for $\text{Ba}_4\text{Sm}_{0.4}\text{F}_{2.4}$ sample.
- Theoretical values.
Table 2. Susceptibility at 20K and 300K and temperature range deviation of the Curie-Weiss law for $M_{1-x}R_xF_{2+x}, Na_{2.5-x}R_{0.5+x}F_{2+2x}$ and some stoichiometric binary compounds.

<table>
<thead>
<tr>
<th>M</th>
<th>R</th>
<th>x</th>
<th>Deviations</th>
<th>$\chi(20)$ emu/mol</th>
<th>$\chi(300)$ emu/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>La</td>
<td>0.31</td>
<td>Diamag</td>
<td>-2.24 e-4</td>
<td>-1.13 e-4</td>
</tr>
<tr>
<td>Ba</td>
<td>Nd</td>
<td>0.1</td>
<td>20 - 70</td>
<td>3.29 e-2</td>
<td>3.77 e-3</td>
</tr>
<tr>
<td>Ba</td>
<td>Sm</td>
<td>0.1</td>
<td>20 - 180</td>
<td>2.40 e-3</td>
<td>1.08 e-3</td>
</tr>
<tr>
<td>Ba</td>
<td>Sm</td>
<td>0.2</td>
<td>20 - 180</td>
<td>3.23 e-3</td>
<td>1.32 e-3</td>
</tr>
<tr>
<td>Ba</td>
<td>Sm</td>
<td>0.4</td>
<td>20 - 180</td>
<td>3.06 e-3</td>
<td>1.02 e-3</td>
</tr>
<tr>
<td>Ba</td>
<td>Gd</td>
<td>0.1</td>
<td>-</td>
<td>5.30 e-1</td>
<td>2.52 e-2</td>
</tr>
<tr>
<td>Ba</td>
<td>Yb</td>
<td>0.4</td>
<td>20 - 60</td>
<td>6.61 e-2</td>
<td>8.18 e-3</td>
</tr>
<tr>
<td>Ca</td>
<td>Gd</td>
<td>0.01</td>
<td>-</td>
<td>4.04 e-1</td>
<td>2.39 e-2</td>
</tr>
<tr>
<td>Sr</td>
<td>La</td>
<td>0.31</td>
<td>Diamag.</td>
<td>-2.63 e-5</td>
<td>-1.12 e-5</td>
</tr>
<tr>
<td>Sr</td>
<td>Pr</td>
<td>0.27</td>
<td>-</td>
<td>3.20 e-2</td>
<td>4.82 e-3</td>
</tr>
<tr>
<td>Sr</td>
<td>Nd</td>
<td>0.165</td>
<td>20 - 70</td>
<td>3.22 e-2</td>
<td>5.05 e-3</td>
</tr>
<tr>
<td>Sr</td>
<td>Gd</td>
<td>0.15</td>
<td>-</td>
<td>4.15 e-1</td>
<td>2.81 e-2</td>
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<tr>
<td>Na$_{0.35}$</td>
<td>Dy$_{0.65}$</td>
<td>F$_{2.3}$</td>
<td>-</td>
<td>5.97 e-1</td>
<td>4.82 e-2</td>
</tr>
<tr>
<td>Na$_{1.5}$</td>
<td>Dy$_{1.5}$</td>
<td>F$_{6}$</td>
<td>-</td>
<td>5.87 e-1</td>
<td>4.90 e-2</td>
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<tr>
<td>Na$_{5.4}$</td>
<td>Ho$_{0.6}$</td>
<td>F$_{2.2}$</td>
<td>-</td>
<td>4.97 e-1</td>
<td>4.64 e-2</td>
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<tr>
<td>Na$_{5.4}$</td>
<td>Er$_{0.6}$</td>
<td>F$_{2.2}$</td>
<td>-</td>
<td>3.87 e-1</td>
<td>3.94 e-2</td>
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<tr>
<td>Na$_{5.4}$</td>
<td>Tm$_{0.6}$</td>
<td>F$_{2.2}$</td>
<td>-</td>
<td>2.01 e-1</td>
<td>2.36 e-2</td>
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<tr>
<td>Na$_{5.4}$</td>
<td>Yb$_{0.6}$</td>
<td>F$_{2.2}$</td>
<td>-</td>
<td>2.20 e-1</td>
<td>2.29 e-2</td>
</tr>
</tbody>
</table>

$\chi(20)$ emu/mol $\chi(300)$ emu/mol

$^\circ$ Cubic (fluorite-type) phase.
$^+$ Trigonal (fluorite-derived) phase.
$^*$ Gagarinite-type phase.
$^\cdot$ Fluorite-derived (ordered) phase.

When we compare the measurements done with the same ion inside different matrices, we do not clearly observe different values for both the susceptibility and the magnetic moments of the rare earth ions in the studied temperature range.

The magnetic moment of Gd$^{3+}$ in Ba$_{0.5}$Gd$_{0.1}$F$_{2.1}$ and in Ca$_{0.059}$Gd$_{0.01}$F$_{2.01}$ is 7.60 $\mu_B$, and 8.17 in Sr$_{0.85}$Gd$_{0.15}$F$_{2.15}$; its theoretical value is 7.94. The magnetic moment value of Nd$^{3+}$ is 3.98 in Ba$_{0.9}$Nd$_{0.1}$F$_{2.1}$ and 3.59 in Sr$_{0.835}$Nd$_{0.165}$F$_{2.165}$; its theoretical value is 3.62.

The obtained magnetic moment values are independent of the crystal phase in agreement with the fact that there is a negligible magnetic coupling between the rare earth cations and the matrix.

Because of the good agreement between the magnetic moments found experimentally and those theoretically calculated, our method can be used to determine the rare earth concentration in different fluoride samples.
CONCLUSIONS

There are some samples for which deviations from the Curie-Weiss law for temperatures are observed under 60 K, as is shown in figure 3. In Table 2 there is a list of substances and the range of temperatures where there is a deflection from the behaviour predicted by of the Curie-Weiss law. This anomalous behaviour at low temperatures can be due to the influence of the inhomogeneity of the crystalline field that surrounds each ion. A more profound study of the anomalous behaviour of these compounds is needed in a wider temperature range, between 4 K and 80 K, to be able to draw any definite conclusion.

ABSTRACT

For the first time we have studied the magnetic properties of single crystals of rare earth non-stoichiometric $M_{1+x}R_xF_{2+y}$ ($M = Ca, Sr, Ba$ and $R = La, Pr, Nd, Sm, Gd, Dy, Er, Yb$) and $Na_{0.5-x}R_{0.5+x}F_{2+2y}$ ($R = Dy, Ho, Er, Tm$) fluorides with the fluorite-type structure, of noncubic $Na_{1.5}Dy_{1.5}F_6$ fluoride with the gagarinite-type structure and of $Na_2Tm_{13}F_{46}$ fluorite with derivated (ordered) fluorite-type structure. The magnetic susceptibility ($\chi$) has been measured with a Faraday balance in the temperature range between 20 K and 300 K. We have observed that these crystals are paramagnetic, since they follow the Curie-Weiss law. There are changes in the behavior of $\chi (T)$ curve under 80 K for some samples. We have carried out a special study of compounds with $Sm^{3+}$ ions, due to the temperature dependence of their magnetic moment. The magnetic susceptibility measurements allow one to determine quickly and accurately the rare earth ions concentration in non-stoichiometric fluorides.
REFERENCES