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Paramagnetic Susceptibility of Nonstoichiometric Fluorides with the Fluorite-Type Structure

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Magnetic properties of single crystals of nonstoichiometric fluorides $M_{1-x}R_xF_{2+x}$ (M=Ca, Sr, Ba; R=Ce, Pr, Nd, Gd, Ho, Er, Tm, Yb; with $0.05 \leq x \leq 0.28$) with the fluorite-type structure have been studied for the first time. The magnetic susceptibility was measured using a Faraday balance in the 15–300 K temperature range. The samples are paramagnetic following the Curie–Weiss law. The values of paramagnetic Curie temperatures and effective magnetic moments of rare-earth ions have been found. Deviations of the temperature dependence of magnetic susceptibility from the Curie–Weiss law are observed for some nonstoichiometric fluorides at temperatures ranging from 60 to 85 K. Possible reasons for these deviations are discussed. Measurements of magnetic susceptibility provide an effective technique for a rapid and accurate determination of the concentration of rare-earth ions in nonstoichiometric fluorides.

Introduction

The ability of crystalline matrices CaF_2, SrF_2, BaF_2 to dissolve large quantities of trifluorides of rare earth elements (up to 50 mole% (*1–3*) enables control of their physico chemical characteristics over a wide range. This is the reason why in recent years single crystalline $M_{1-x}R_xF_{2+x}$ solid solutions with the fluorite-type structure have been studied intensely using various experimental techniques of solid-state physics and chemistry, electrochemistry, and structural analysis (*4*). Multicomponent nonstoichiometric fluorides, which comprise the $M_{1-x}R_xF_{2+x}$ phases, are used as laser and optical materials, superionic conductors, scintillators, etc.

Of special theoretical interest is study of the physical–chemical properties of crystals with grossly perturbed stoichiometry (dozens of mole% of a rare-earth trifluoride) that are found in the fluorite structural type of fluorides. The necessity to compensate for abundant positive charge of rare-earth ions by a negative charge of additional interstitial fluorine ions gives rise to impurity disorder (appearance of structural-defects). The results of studies using such techniques as electric conductivity (*5*), NMR (*6*), EPR (*7*),

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X-ray and neutron diffraction (*8*), and dielectric and thermostimulated spectroscopy (*9*), characterize mainly the disorder of the anionic (fluorine) sublattice in fluorite crystals. The experimental data on defects in the cationic sublattice of grossly nonstoichiometric crystals are scarce. They are reduced to spectroscopy data on inhomogeneous broadening of absorption spectra and luminescence of ions of rare-earth elements due to energy inequivalence of various activator ions (short range) (*10*). To elucidate the state of cationic sublattice, to be more exact, its "rare earth component" we have carried out a magneto-chemical study of grossly nonstoichiometric $M_{1-x}R_xF_{2+x}$ crystals. This communication reports the results of our measurements of magnetic susceptibility of concentrated solid solutions with the fluorite-type structure.

Experimental

Single crystals of nonstoichiometric fluorides were grown from melt by the Stockberger technique; experimental details are given in (*11*). The samples were grown in fluorizing atmosphere created by pyrolysis of tetrafluoroethylene creating a decreased oxygen content in samples. Growth rates were 3–10 mm/hr. In some samples a 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 dependences of unit cell parameters. In case this technique was not quite accurate, we used the X-ray fluorescence technique. Sometimes the difference between the initial RF_3 content in sample and melt was quite great. Table I lists the chemical compositions for most of the samples.

The magnetic susceptibility was measured by the Faraday technique in the temperature range 15–300 K (magnetic balance, Air Products, USA). A plastic bag containing the sample was attached to a quartz thread 1 m long and 0.1 mm thick, and placed into a cryostat (helium atmosphere, pressure 200 mbar). Since, the interaction of a magnetic field with magnetic moments of ions results an increase (for a paramagnetic crystal) of the effective sample weight, the magnetic susceptibility per unit mass is

$$\chi_{\text{mass}} = f \cdot \frac{\Delta p_s - m_b \cdot \Delta p_b}{m_s} \tag{1}$$

where f is the calibration multiplier and m_s, m_b, and Δp_s, Δp_b are mass and weight increments of the sample (s index) and the plastic bag (b index), respectively. The calibration factor f was found from measurements of dependence $\chi = \chi(T)$ for the standard $HgCo(NCS)_4$ (*12*).

The molar magnetic susceptibility of crystals was obtained by multiplication of χ_{mass} by the molar weight M:

$$\chi_m = \chi_{\text{mass}} \cdot M. \tag{2}$$

Results and Discussion

We studied magnetic properties of the fluorite-type nonstoichiometric $M_{1-x}R_xF_{2+x}$ phases: (i) where x the rare earth content is varied in $Ba_{1-x}Gd_xF_{2+x}$ ($x = 0.05, 0.1, 0.2$) crystals; (ii) where, at constant x, the type of rare earth is varied for either $Ba_{0.9}R_{0.1}F_{2.1}$ (R = Ce, Pr, Gd, Ho, Er, Tm, Yb) or $Ca_{0.9}Gd_{0.1}F_{2.1}$; (iii) a sample with a large deviation from the stoichiometric composition, $Sr_{0.72}Nd_{0.28}F_{2.28}$. The temperature dependencies of the magnetic susceptibility for some samples are shown in Figs. 1 and 2. All the nonstoichiometric fluorides studied are paramagnetic and follow the Curie–Weiss law

$$\chi_m = \frac{C_m}{T - \theta}, \tag{3}$$

where C_m is the Curie constant and θ is the paramagnetic Curie temperature. The resultant magnetic moment of an incomplete 4*f*-

TABLE I

EFFECTIVE MAGNETIC MOMENTS OF RARE EARTH IONS AND PARAMAGNETIC CURIE TEMPERATURES FOR SINGLE CRYSTALLINE FLUORITE-TYPE $M_{1-x}R_xF_{2+x}$ SOLID SOLUTIONS

	$M_{1-x}R_xF_{2+x}$			ΔT^a	ΔT_l^b	μ_{eff} (μ_B)			θ	$\chi_{300} \times 10^2$
M	R	x nom.	x meas.	(K)	(K)	Exp. from x nom.	Exp. from x meas.	Cal.	(K)	$\frac{\text{cm}^3}{\text{mol}}$
Ba	Gd	0.05	—	15–300	—	7.74 ± 0.01	—	7.94	−1.4 ± 0.4	2.51
Ba	Gd	0.10	0.101	15–300	—	7.74 ± 0.01	7.66	7.94	−2.1 ± 0.4	2.53
Ba	Gd	0.20	—	20–300	—	7.71 ± 0.01	—	7.94	−2.2 ± 0.5	2.50
Ba	Ce	0.10	—	15–300	15–60	2.35 ± 0.01	—	2.54	23.2 ± 1.5	0.21
Ba	Pr	0.10	0.106	15–295	—	3.33 ± 0.02	3.14	3.58	15.2 ± 2.1	0.43
Ba	Ho	0.10	0.084	15–260	—	10.42 ± 0.03	11.41	10.60	6.7 ± 1.0	4.21
Ba	Er	0.10	0.084	15–300	—	9.29 ± 0.04	10.12	9.59	−4.4 ± 1.6	3.72
Ba	Tm	0.10	0.095	15–300	—	7.12 ± 0.04	7.49	7.57	8.4 ± 2.3	2.11
Ba	Yb	0.10	0.096	15–300	15–45	4.26 ± 0.01	4.47	4.54	34.1 ± 0.7	0.70
Ca	Gd	0.10	—	15–300	—	7.62 ± 0.02	—	7.94	−6.5 ± 0.8	2.49
Sr	Nd	0.28	—	15–300	15–85	3.53 ± 0.01	—	3.62	56.2 ± 1.7	0.44

[a] ΔT, measured temperature range.

[b] ΔT_l, temperature range, where deviation of $\chi = \chi(T)$ dependence from the Curie–Weiss law is observed.

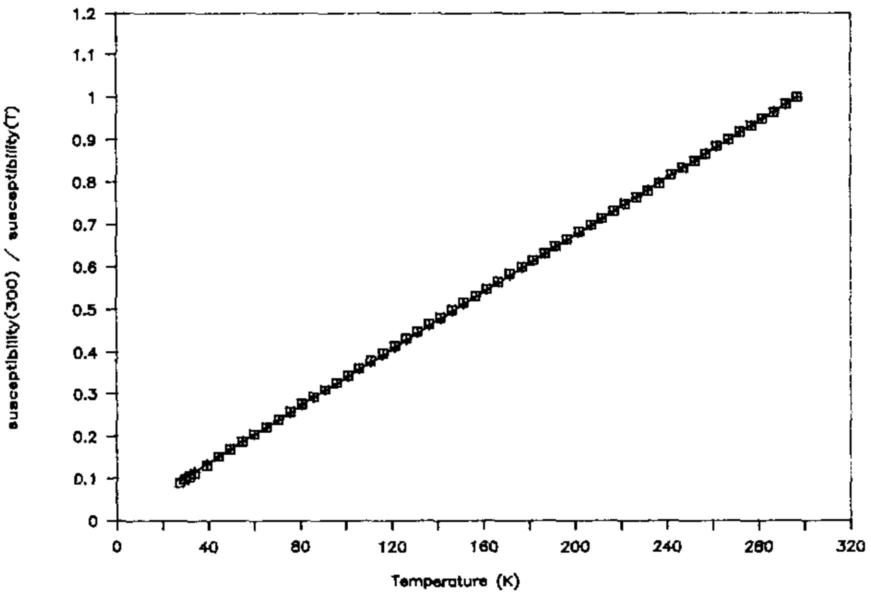

FIG. 1. Temperature dependence of inverse magnetic susceptibility for single crystalline nonstoichiometric $Ba_{0.9}Gd_{0.1}F_{2.1}$ fluorides. The value χ_{300} is presented in Table I. (□) Experimental values, (+) theoretical values.

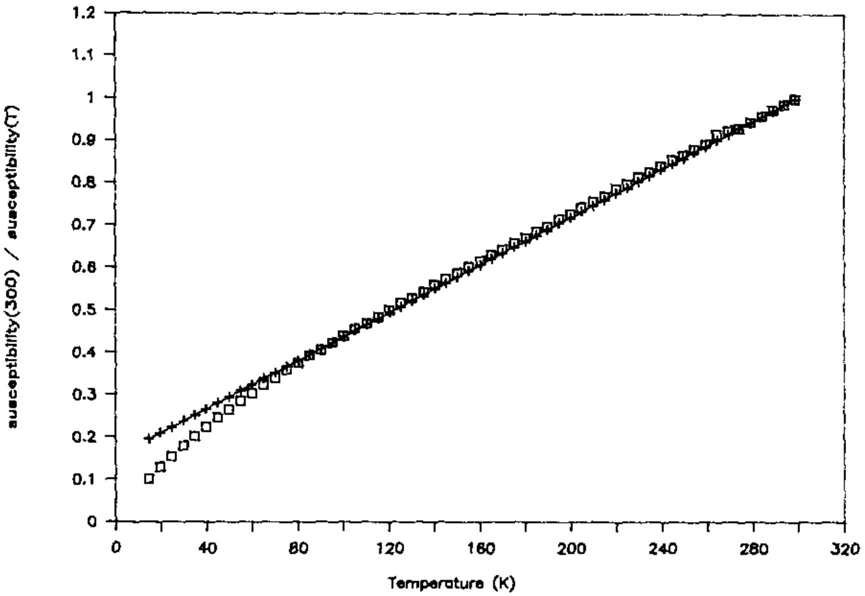

FIG. 2. Temperature dependence of inverse magnetic susceptibility for single crystalline nonstoichimetric $Sr_{0.72}Nd_{0.28}F_{2.28}$ fluorides. The value χ_{300} is presented in the Table I. (□) Experimental values, (+) theoretical values.

layer of the electron shell of rare earth ions is responsible for paramagnetism in nonstoichiometric fluorides (the electron configuration of the outermost electron shell of rare-earth ions has form . . . $4f^{0-14}5s^2 5p^6$). The Curie constant is

$$C_m = \frac{\mu_{\text{exp}}^2 \cdot N_A \cdot x}{3 \cdot k_B}, \tag{4}$$

where μ_{exp} is the effective magnetic moment calculated per rare-earth ion, expressed in Bohr magnetons $\mu_B = 9.27 \times 10^{-21}$ erg/G, x is the mole fraction of rare-earth ions in the sample, N_A is the Avogadro number, and k_B is the Boltzmann constant. The values of μ_{eff}, θ, and χ_{300} (at 300K), calculated according to (3) and (4), are presented in Table I. Table I also lists the theoretical values of the magnetic moments of rare earth ions, which are calculated from *(13)*

$$\mu_{\text{cal}} = \left[\frac{3}{2} + \frac{1}{2} \cdot \frac{S(S+1) - L(L+1)}{J(J+1)}\right] \cdot [J(J+1)]^{1/2} \mu_B + \alpha_F, \tag{5}$$

where S, L, J are the quantum numbers for the fundamental state of a rare earth multiplet and α_F is the Van Vleck term.

As shown in Fig. 3, the experimental values of magnetic moment of rare earth ions in the cubic fluorides studied nearly coincide with the theoretical values μ_{cal}, $(\mu_{\text{cal}} - \mu_{\text{exp}})/\mu_{\text{exp}} = 2$–$7\%$. For the nonstoichiometric $Ba_{1-x}Gd_xF_{2+x}$ $(0.05 \leq x \leq 0.2)$ phase based on the BaF_2 matrix the value of $\mu_{\text{eff}} = 7.7$ μ_B are independent of gadolinium trifluorite content, and they agree well with $\mu_{\text{eff}} = 7.6$ μ_B for the nonstoichiometric $Ca_{0.9}Gd_{0.1}F_{2.1}$ phase based on the CaF_2 matrix. This indicates the possibility of using the values of magnetic moments μ_{exp} (μ_{cal} can be used in the rough approximation) for the determina-

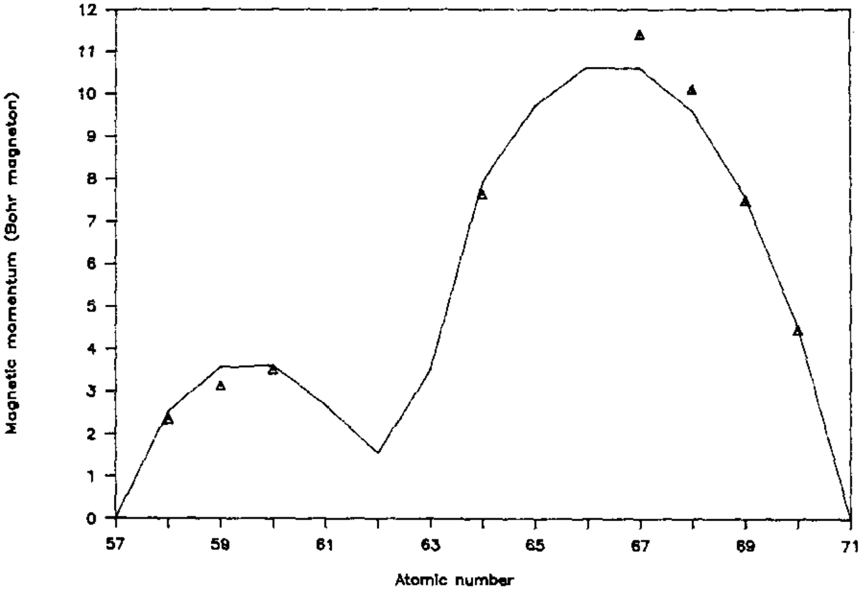

FIG. 3. Magnetic moments of nonstoichiometric fluorides of rare earth elements.

tion of the real rare earth ion content in the nonstoichiometric fluorides.

The temperature dependencies of the magnetic susceptibility for some nonstoichiometric fluorides are described by Eq. (3) only within the temperature range from 300K to a lower temperature T_1 between 40 and 85 K that depends on the sample. Below T_1 deviations of $\chi = \chi(T)$ dependencies from the Curie–Weiss law are observed. Note that the value of T_1 increases when the rare-earth ion content in the fluorite matrix increase. Admittedly, if the behavior of $\chi(T)$ in the paramagnetic region is described by the Curie–Weiss law, the magnetic interaction between magnetic carriers cannot be ignored (in our case, rare earth ions). One of the possible reasons of the deviations can be the manifestation of ferromagnetic ($\theta > 0$) and antiferromagnetic ($\theta < 0$) interaction between the rare-earth ions. This follows from the fact that for solid solutions containing gadolinium ions in the fluorite matrices, the absolute values $|\theta|$ increase with a decrease of a lattice parameter, i.e., a reduction of cation to cation distances.

Two different regimes of magnetic susceptibility behavior for the samples containing Ce^{3+}, Nd^{3+}, and Yb^{3+} may be distinguished in Fig. 2. In the regime where the temperature exceeds 60 K (Ce^{3+}), 45 K (Yb^{3+}), and 85 K (Nd^{3+}) a Curie–Weiss law is obeyed with an effective magnetic moment corresponding to Ce^{3+}, Nd^{3+}, and Yb^{3+}. The high values for the Curie temperature are indicative of strong antiferromagnetic interactions.

Below 60 K (Ce^{3+}), 45 K (Yb^{3+}), and 85 K (Nd^{3+}) a deviation of the high-temperature Curie–Weiss behavior is observed which indicates the development of short-range magnetic order or spin clusters among the Ce^{3+}, Yb^{3+}, and Nd^{3+} (respectively) species.

It should be noted that the results of investigations using such techniques as EXAFS (*14*), NMR (*6*), structure analysis (*8, 15*), thermocurrent (*9*), and dielectric spectroscopy (*5, 16*) are also in favor of incomplete disorder of R^{3+} ions in the fluorite matrix. In (*7*) optical techniques were used to detect the EPR spectra of clusters from paramagnetic Er^{3+}, Tm^{3+}, Yb^{3+} ions in very diluted solid solutions based on CaF_2, SrF_2, and BaF_2. It was shown that these clusters, apparently, are similar in their structure with the Y_6F_{37} clusters found in the superstructural fluorite phases with high rare earth element contents (*17*). According to (*13*), the cryomagnetic (below 70 K) anomalies of the temperature dependence $\chi(T)$ can be due to the influence of inhomogeneous electric fields created by the neighboring ions. These fields give rise to the splitting of the multiplet levels that we believe explains the θ correction in the Curie law at high temperatures, while at low temperatures there are significant deviations $\chi = \chi(T)$ from the Curie–Weiss law. Apparently the resulting magneto-nonordered state can be described as a cluster spin glass; a nonmagnetic fluorite matrix with randomly distributed magnetic clusters (tetrahedral and octahedral regions related coherently with the matrix (*8, 14, 15*). Features of the transition to the spin-glass state were found in a weakly doped $CaF_2 : Er^{3+}$ crystal (*18*). A possibility of the transition to the spin-glass state in such systems was proved theoretically in (*19*). However, further magnetic studies of nonstoichiometric fluorides at temperatures below 15 K are required to make final conclusions about the nature of low-temperature deviations $\chi = \chi(T)$ from Curie–Weiss law.

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