===================== **MAGNETISM** =====================

Synthesis, Crystal Structure, and Magnetic Properties of the $Li_8FeSm_{22}O_{38}$ Single Crystal

**A. M. Vorotynov, G. A. Petrakovskii, D. A. Velikanov,
L. V. Udod*, and M. S. Molokeev**

*Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences,
Akademgorodok 50–38, Krasnoyarsk, 660036 Russia*
* e-mail: luba@iph.krasn.ru
Received January 30, 2012

Abstract—New single crystals of $Li_8FeSm_{22}O_{38}$ have been grown by spontaneous crystallization from a solution in melt. The structure of these crystals has been determined: it corresponds to the space group $Im\bar{3}m$. Investigations of the magnetic susceptibility in the ranges of temperatures 2–24 K and fields up to 50 kOe have revealed a magnetic transition near 3 K. The temperature behavior of the magnetic susceptibility of the two-level system has been simulated. The results of the simulation agree with the experimental data. The resonance properties of $Li_8FeSm_{22}O_{38}$ have been studied in the temperature range 100–300 K.

1. INTRODUCTION

Oxide crystals of $3d$ and $4f$ elements are of interest from the viewpoint of the variety of physical properties, in particular, magnetic ones. Indeed, among such compounds, there are high-temperature superconductors, multiferroics, ferrites, and materials with a giant magnetoresistance. The variety of magnetic properties of these compounds is caused by the difference in the electronic structures of $3d$ and $4f$ elements, which leads to formation of different types of magnetic order. Therefore, the synthesis and study of new compounds are urgent problems (especially the synthesis of crystals and the study of their magnetic properties). In the present work, we synthesized $Li_8FeSm_{22}O_{38}$ single crystals and studied their crystal structure and magnetic properties.

2. SYNTHESIS OF CRYSTALS AND THE CRYSTAL STRUCTURE

The crystals were grown by spontaneous crystallization from a solution in melt. Single crystals having the form of $4 \times 3 \times 1$ mm plates and black color were removed from a crucible by melting in a weak nitric acid solution.

The X-ray diffraction experiment was performed on a SMART APEXII single-crystal diffractometer using the monochromatized MoK_α-radiation with $\lambda = 0.7106$ Å at room temperature. The orientation matrix and the unit cell parameters are determined and refined for all 7729 reflections. The unit cell corresponds to the cubic crystal system, the space group is $Im\bar{3}m$, the lattice constant is $a = 11.9078(5)$ Å, and

$Z = 2$. A detailed description of the synthesis conditions and the crystal structure is given in [1].

The model of the structure was sought with the SHELXS program [2] by direct methods. As a result, the coordinates of all atoms were found. The obtained structure was refined by the least-squares method with the SHELXL-97 program [3]. The structure is disordered, and the positions O3 and O4 are positions of disordered oxygen atoms. The structure is shown in Fig. 1.

The $Li_8FeSm_{22}O_{38}$ crystal has a three-dimensional framework structure. It consists of two independent octahedra $(Sm/Fe)O_6$, a trigonal prism LiO_6, and two types of polyhedra with the Sm ion at the center: SmO_9 is a three-capped trigonal prism (the Sm_4 ion at the center), and SmO_8 is a square antiprism (the Sm_3 ion at the center), in which two vertices are disordered with respect to two positions with the occupancy of each position of 0.5 (O_3 and O_4 atoms). The octahedra $(Sm1/Fe1)/O_6$ have a common face with a trigonal prism $LiO6$, whose opposite face is common with the octahedron $(Sm2/Fe2)O_6$. The opposite face of the octahedron $(Sm2/Fe2)O_6$ is also common with the other symmetry-equivalent polyhedron LiO_6. Thus, a chain of polyhedra connected by faces along four threefold axes in the form $...-(Sm1/Fe1)O_6-LiO_6-(Sm2/Fe2)O_6-LiO_6-(Sm1/Fe1)O_6...$ is realized, so the octahedra $(Sm1/Fe1)O_6$ and $(Sm2/Fe2)O_6$ have no common vertices but are connected through Li ions (Fig. 2). The notation Sm/Fe in Figs. 1 and 2 indicates that these positions are occupied by samarium or iron ions in the following ratios: $Sm1/Fe1 = 0.58/0.42$ and
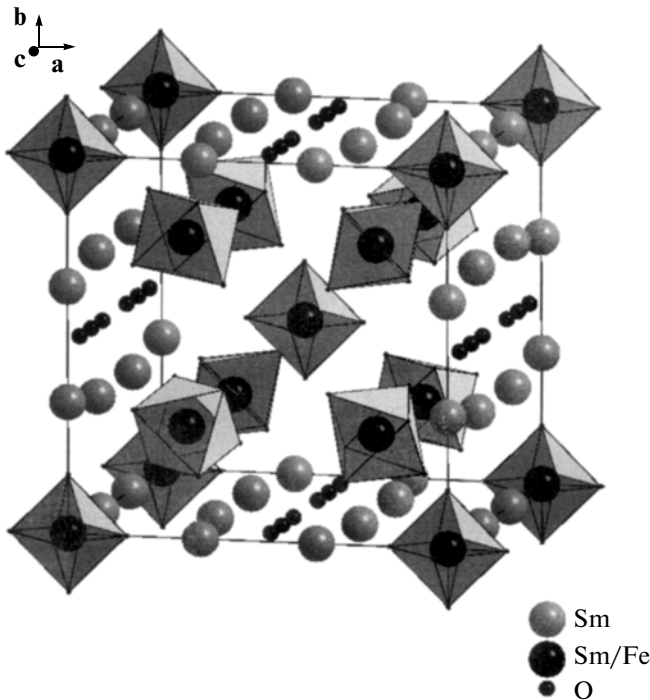
Fig. 1. Structure of $Li_8FeSm_{22}O_{38}$ (not all atoms are shown).

$Sm2/Fe2 = 0.84/0.16$. $Sm1/Fe1$ ions are found at the sites of the crystal lattice with the coordinates $(0, 0, 0)$, and $Sm2/Fe2$ ions have the coordinates $(1/4, 1/4, 1/4)$ (Figs. 1 and 2). In this case, the octahedron $(Sm1/Fe1)O_6$ has six common faces with the prisms LiO_6 and $(Sm2/Fe2)O_6$ has only two ones.
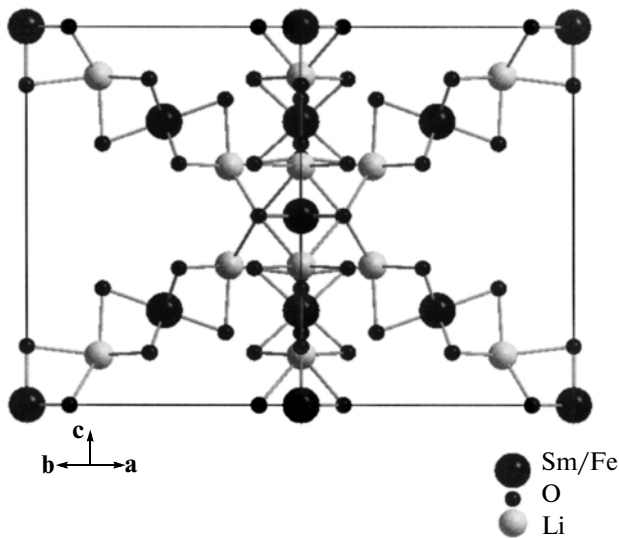
3. MAGNETIC AND RESONANCE PROPERTIES. RESULTS AND DISCUSSION

The magnetic susceptibility of the crystal was measured on an MPMS device in the range of temperatures 2–24 K and on a SQUID magnetometer in a field of 5 kOe. It has been established that the magnetic transition temperature is about 3 K. The temperature dependences of the inverse magnetic susceptibility of $Li_8FeSm_{22}O_{38}$ measured in fields of 100 Oe (curve *1*) and 50 kOe (curve *2*) are shown in Fig. 3. We see in curve *1* two sections obeying the Curie–Weiss law with the parameters $\theta = -150$ K and $\mu_{eff} = 13.09 \mu_B$ at 200 K $\leq T \leq$ 300 K and, $\theta = -8$ K and $\mu_{eff} = 9.97 \mu_B$ at 70 K $\leq T \leq$ 200 K. Curve *2* has only one high-temperature section obeying the Curie–Weiss law with the parameters $\theta = -150$ K and $\mu_{eff} = 13.09 \mu_B$ at 200 K $\leq T \leq$ 300 K. The asymptotic Curie temperature is negative in all cases, which evidences the domination of negative exchange interactions in the crystal.

The presence of two sections with different parameters of the Curie–Weiss law may be an indirect evidence of a significant change in the population of the energy levels of the ground and excited states of Fe^{2+} and Sm^{3+} ions with a variation in temperature. As a rule, these levels are separated by several hundreds of inverse centimeters [4]. Application of a sufficiently strong (~50 kOe) external magnetic field reduces the distances between the energy levels of the ground and excited states by about 30 K, which, apparently, leads to disappearance of the low-temperature section governed by the Curie–Weiss law.
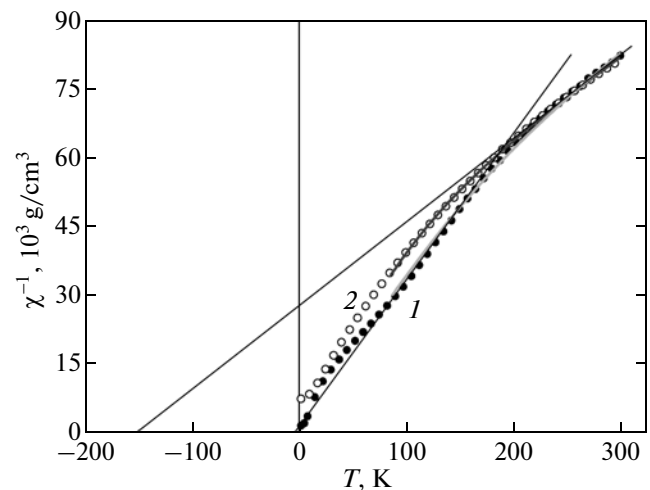

Fig. 2. A view of chains $Sm1/Fe1–Li–Sm2/Fe2–Li–Sm1/Fe1$ in the $Li_8FeSm_{22}O_{38}$ compound. The $(Sm1/Fe1)O_6$ octahedra are located in the lattice sites. Not all atoms are shown.

Fig. 3. Temperature dependences of the inverse magnetic susceptibility of $Li_8FeSm_{22}O_{38}$ measured in magnetic fields of (*1*) 100 Oe and (*2*) 50 kOe. The straight lines show the approximations of the linear sections, and the solid curves correspond to fitting (see text).
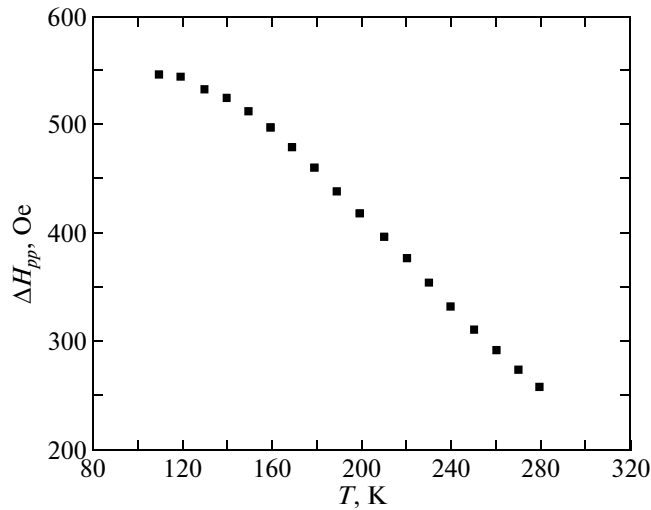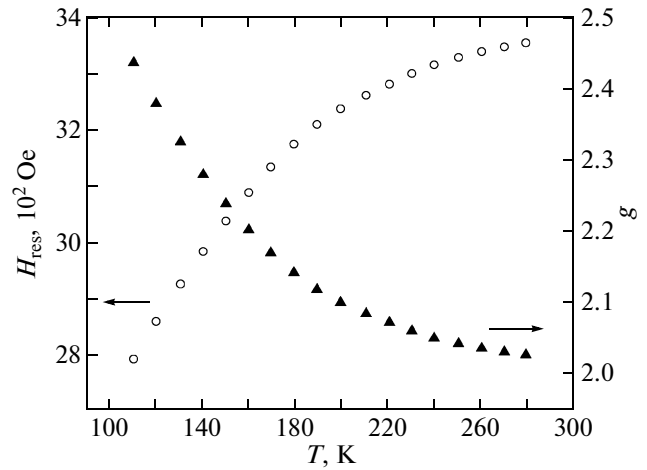
Fig. 4. Temperature dependence of the magnetic resonance line width in $Li_8FeSm_{22}O_{38}$. The field is parallel to one of the crystal axes.

Fig. 5. Temperature dependences of the resonance field and g-factor of the magnetic resonance in $Li_8FeSm_{22}O_{38}$. The field is parallel to one of the crystal axes.

In order to verify this assumption, we simulated the temperature behavior of the magnetic susceptibility of a two-level system. This model can be a rough approximation of the real situation in a $Li_8FeSm_{22}O_{38}$ crystal. The main distinction is that the compound under study has two magnetic ions of different sorts, which, in addition, are in different ligand environments. This situation presumes that the system has a set of excited levels. Nevertheless, we assume that our model, despite the above-made assumptions, must correctly reflect the typical features of the temperature behavior of the magnetic susceptibility. Thus, the magnetic susceptibility of $Li_8FeSm_{22}O_{38}$ in this model can be represented as

$$\chi = \frac{N_0 \mu_a^z}{3k\left[1 + e^{\left(-\frac{\Delta}{T}\right)}\right]} \frac{1}{(r + 8 \text{ K})}$$

$$+ \frac{N_0 \mu_b^z}{3k\left[1 + e^{\left(\frac{\Delta}{T}\right)}\right]} \frac{1}{(T + 150 \text{ K})};$$

Values of the fitting parameters

Number of the curve in Fig. 1.	Δ, K	μ_a, μ_B	μ_b, μ_B
1	401 ± 1	9.97 ± 1.00	16.43 ± 1.00
2	257 ± 3	9.09 ± 1.00	17.4 ± 1.00

where the first and second terms correspond to the low- and high-temperature sections of the dependence described by the Curie–Weiss law, N_0 is the Avogadro number; μ_i is the effective magnetic moment; Δ is the energy gap between the ground, N_a, and excited, N_b, levels; and k is the Boltzmann constant. The fitting parameters in this model are the effective magnetic moments of the ground and excited states and the quantity Δ.

The curves obtained as a result of fitting are shown in Fig. 3. The values of the fitting parameters for the experimental data in the fields of 100 Oe and 50 kOe are presented in the table.

It is readily seen that the values of the effective magnetic moments obtained in the fitting are in a sufficiently good agreement with the experimental data ($\mu_{eff} = 13.09$ μ_B and 9.97 μ_B). The field dependence of Δ also qualitatively agrees with the proposed model. Fitting by the least-squares method of the high-temperature section yields the following values of the g-factors: $g = 2.58$ for the Fe^{2+} ion (for $S = 2$) and $g = 0.84$ for the Sm^{3+} ion (for $S = 5/2$), which is typical for these ions [5].

The resonance properties of $Li_8FeSm_{22}O_{38}$ were studied in the temperature range 100–300 K with a Bruker Elexsys E580 device operating in the X-band. In the entire temperature interval, a single line of the Lorentz form was observed. No angular dependence of the resonance field and the line width has been found. The temperature dependences of the line width ΔH_{pp} and the resonance field H_{res} are shown in Figs. 4 and 5.

4. CONCLUSIONS

Single crystals of $Li_8FeSm_{22}O_{38}$ have been grown. Their crystal structure has been studied for the first time. The unit cell corresponds to the cubic crystal system, the space group is $Im\bar{3}m$, the lattice constant is $a = 11.9078(5)$ Å, and $Z = 2$. It has been established that the ligand environment of magnetic ions changes from the regular octahedron $(Sm/Fe)O_6$ to two types of polyhedra with the Sm ion at the center: SmO_9 is a three-capped trigonal prism (with the Sm4 ion at the center), and SmO_8 is a square antiprism (with the Sm3 ion at the center). We also observed a large variety of angles and lengths of exchange bonds between magnetic ions. In our opinion, this situation can lead to peculiarities of the magnetic properties of $Li_8FeSm_{22}O_{38}$, such as the presence of lowly-lying excited energy levels and frustration of exchange interactions. This circumstance can also explain the sufficiently low Néel temperature and the temperature behavior of the g-factor. A model is proposed that describes the temperature and field dependences of the magnetic susceptibility.

In order to determine the type of magnetic structure in the magnetically ordered phase and to perform a detailed study of magnetic peculiarities, additional studies are planned.

REFERENCES

1. M. S. Molokeev, G. A. Petrakovskii, A. M. Vorotynov, D. A. Velikanov, and L. V. Udod, Crystallogr. Rep. (2012) (in press).
2. G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallorg **46**, 467 (1990).
3. G. M. Sheldrick, *SHELXL-97: A Computer Program for Refinement of Crystal Structures* (University of Göttingen, Göttingen, Germany, 1997).
4. W. Low, *Paramagnetic Resonance in Solids* (Academic, New York, 1960; Inostrannaya Literatura, Moscow, 1962).
5. S. A. Al'tshuler and B. M. Kozyrev, *Electron Paramagnetic Resonance* (Academic, New York, 1964; Nauka, Moscow, 1972).

Translated by E. Chernokozhin