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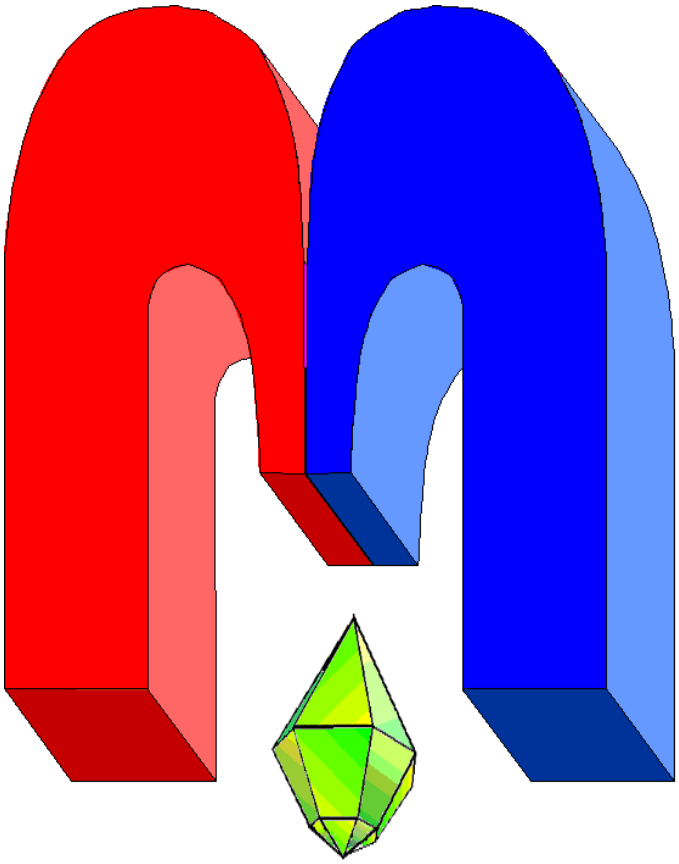

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Studies of magnetization of lithium-rare earth tetra-fluoride single crystals†

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Temperature and magnetic field dependences of the magnetization of $LiHoF_4$ and $LiDyF_4$ single crystals were measured with a dc-SQUID magnetometer and by the inductance method with the magnetic field applied along and perpendicular to the *c*-axis. The results of measurements are compared with the results of simulations.

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Keywords: crystal field parameters, magnetization, magnetostriction, magnetoelastic interactions

1. Introduction

Double lithium-rare earth fluorides $LiRF_4$, as well as dilute compounds $LiR_{1-x}Y_xF_4$ (R = Tb, Dy, Ho, Er), which crystallize in the tetragonal scheelite structure attract a lot of interest as model objects in physics of dipolar magnets and spin glasses [1, 2]. The unit cell of $LiRF_4$ contains two magnetically equivalent lanthanide R^{3+} ions at sites with the S_4 point symmetry. Magnetic dipole-dipole interactions play the dominant role in spontaneous low-temperature ordering of magnetic moments of R^{3+} ions in these compounds. $LiTbF_4$ and $LiHoF_4$ are dipolar Ising-like ferromagnets with magnetic moments of the Tb^{3+} and Ho^{3+} ions along the crystallographic *c*-axis and Curie temperatures $T_c = 2.885$ K and 1.53 K, respectively [1]. $LiDyF_4$ and $LiErF_4$ are antiferromagnets of easy-plane type with magnetic moments of the Dy^{3+} and Er^{3+} ions normal to the crystal symmetry axis, and transition temperatures $T_N = 0.62$ K and 0.38 K, respectively [1]. Quantum phase transitions driven by transverse magnetic fields were observed in $LiHoF_4$ at temperatures below T_c [3]. It was shown recently that $LiRF_4$ single crystals can serve as new and improved Faraday rotators in the ultraviolet-visible wavelength region [4].

Spectral, magnetic and magnetoelastic properties of $LiRF_4$ crystals were widely studied earlier [5-9]. In particular, $LiErF_4$ and the isostructural $LiTmF_4$ exhibit a giant forced magnetostriction at liquid helium temperatures [10, 11]. However, a due attention for the interaction between the rare earth ions and dynamic and static deformations of the crystal lattice was not paid for. The main goal of the present study was to elucidate the role of magnetoelastic interactions in formation of the magnetization and the energy level structure of R^{3+} ions in $LiRF_4$ crystals in the external magnetic fields.

2. Experimental details and the results of measurements

Single crystals of $LiDyF_4$ and $LiHoF_4$ were grown by Bridgeman-Stockbarger method. The samples were oriented by means of X-ray diffractometer. The samples used for magnetization measurements were shaped by polishing as spheres to acquire a definite demagnetizing factor. To prevent rotation of

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the sample in the strong magnetic field, it was fixed in Stycast 1266 epoxy (the accuracy of orientation was ±3). The temperature dependences of the magnetization of single crystals in the temperature range of 2-300 K and the dependences of the magnetization on the magnetic field in the interval 0-5 T applied along and perpendicular to the *c*-axis were measured with a dc-SQUID magnetometer MPSM-2 (Quantum Design). As an example, the measured field dependences of the $LiHoF_4$ magnetization at different temperatures, as well as the results of simulations described below, are presented in figure 1.

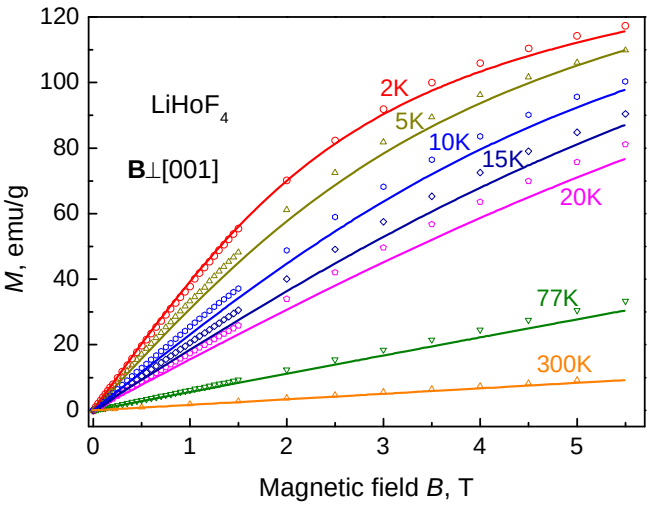

Figure 1. Magnetic field dependences of the $LiHoF_4$ magnetization. Solid lines correspond to the results of calculations, symbols correspond to experimental data.

Angular dependences of the magnetization in the basis plane of $LiDyF_4$ and $LiHoF_4$ were measured by the inductance method with the magnetic field B (up to 2 T) applied perpendicular to the *c*-axis at the temperature 4.2 K. The inductance of the coil with the sample was measured on a forward and backward field sweeps by LCR-meter E7-14 using the inductance bridge circuit balanced at zero field on the 1 kHz frequency.

The background from the empty coil was measured independently and subtracted from the total signal. The sample was glued inside the capsule and could be rotated inside the coil with the accuracy of ±5. Magnetization curves $M(B)$ were extracted from the experimental data by integrating the field scans of the derivatives dM/dB (in arbitrary units) at various sample orientations. The obtained curves were calibrated using magnetization data for $LiDyF_4$ and $LiHoF_4$ single crystals measured with a dc-SQUID [12].

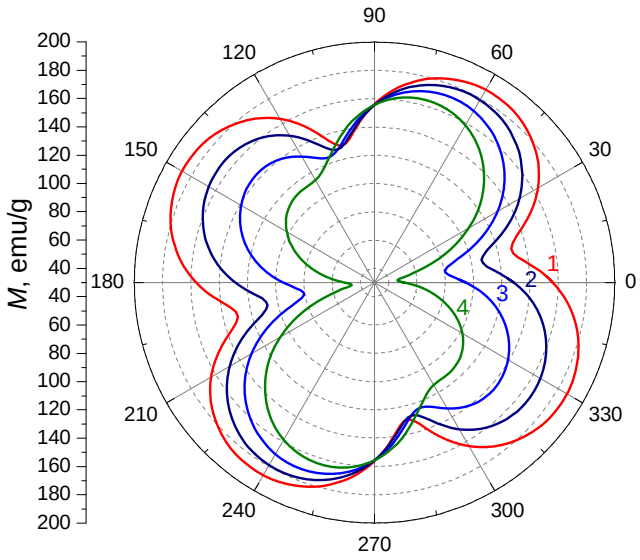

Figure 2. Calculated angular dependences of the magnetization of $LiDyF_4$ single crystal at $T = 4.2$ K in different planes containing the external magnetic field ($B = 2$ T): (1, red line) $\theta = 0$, $\alpha = 0$; (2, dark blue line) $\theta = 5$, $\alpha = 30$; (3, blue line) $\theta = 5$, $\alpha = 45$; (4, green line) $\theta = 5$, $\alpha = 60$.

At the first step, we studied theoretically the behavior of the magnetization in the external magnetic field rotating around an arbitrary axis (the orientation of the rotation axis was defined by the angle θ relative the crystallographic *c*-axis and the angle α between the projection of the rotation axis on the crystal *ab*-plane and the *a*-axis). The results of calculations for the $LiDyF_4$ single crystal are presented in figure 2. The measured angular dependences of the magnetization in the basis plane of $LiDyF_4$ and $LiHoF_4$ are compared with the results of calculations in figures 3 and 4, respectively. The experimental and theoretical results agree satisfactorily.

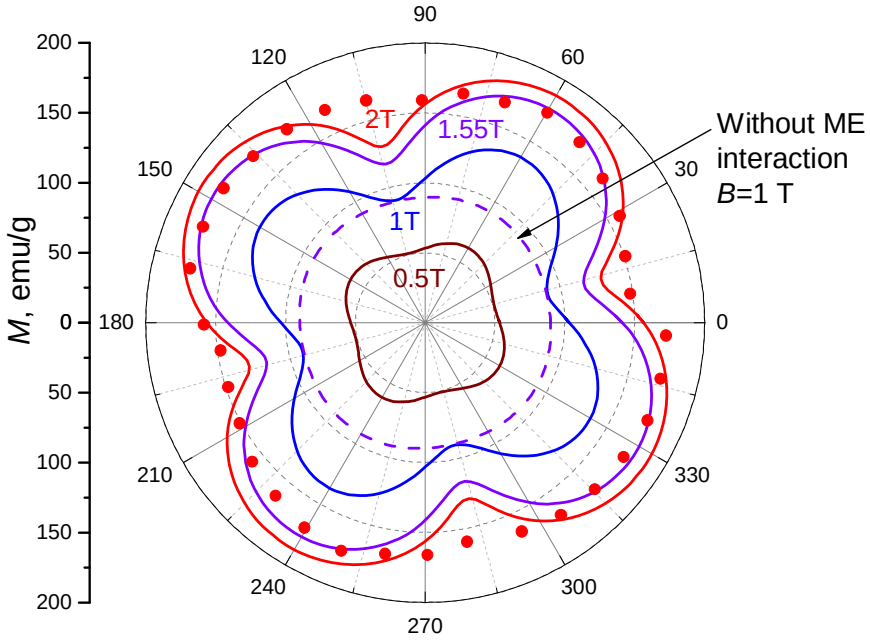

Figure 3. Angular dependences of the magnetization in the basis plane of $LiDyF_4$ single crystal at $T = 4.2$ K. Solid lines correspond to the results of calculations, symbols correspond to experimental data. The dashed curve corresponds to zero magnetoelastic coupling.

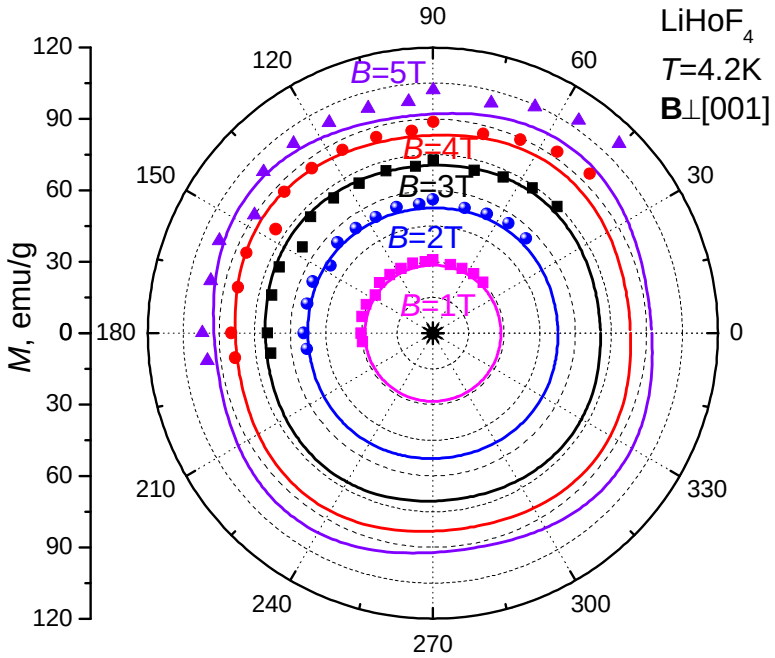

Figure 4. Angular dependences of the magnetization in the basis plane of $LiHoF_4$ single crystal at $T = 4.2$ K. Solid lines correspond to the results of calculations, symbols correspond to experimental data. The dashed curves correspond to zero magnetoelastic coupling.

3. Discussion

In the presence of an applied magnetic field **B**, we write the Hamiltonian of a single R^{3+} ion in the following form

$$H = H_0 + H_{cf} + \sum_{\alpha\beta} V'_{\alpha\beta}\, e_{\alpha\beta} + \sum_{\alpha,s} V''_{\alpha}(s)\, w_{\alpha}(s) + \sum_{j} [\mu_{\rm B}(\mathbf{B} + \hat{\mathbf{Q}}\mathbf{M})(\mathbf{l}_j + 2\mathbf{s}_j) - \sum_{pkp'k'} \lambda_{pp'}^{kk'} \langle O_p^k \rangle O_{p'}^{k'}]. \quad (1)$$

Here, the first term is the free ion energy, the second term is the crystal field Hamiltonian

$$H_{cf} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_4^{-4} O_4^{-4} + B_6^0 O_6^0 + B_6^4 O_6^4 + B_6^{-4} O_6^{-4} \quad (2)$$

determined in the crystallographic system of coordinates by the set of seven crystal field parameters B_p^k (O_p^k are the Stevens operators). The third and fourth terms correspond to linear interactions of rare-earth ions with the homogeneous macro- and microdeformations, respectively, where $\hat{\mathbf{e}}$ is the deformation tensor, and $\mathbf{w}(s)$ is the vector of the s-sublattice displacement.

The electronic operators $\hat{\mathbf{V}}'$ and $\mathbf{V}''(s)$ in the Hamiltonian (1) can be presented, similar to the crystal field energy, through the linear combinations of Stevens operators with the parameters which have been calculated earlier in the framework of the exchange charge model (see [13, 14, 15]).

The fifth term in (1) is the electronic Zeeman energy where $\mu_{\rm B}$ is the Bohr magneton, $\mathbf{l}_j$ and $\mathbf{s}_j$ are operators of electronic orbital and spin moments, and the sum is taken over 4*f* electrons, **M** is the equilibrium magnetization, the tensor $\hat{\mathbf{Q}}$ defines magnetic dipole-dipole interactions between the rare-earth ions. The last term corresponds to the energy of interaction between paramagnetic ions via the phonon field, parameters $\lambda_{pp'}^{kk'}$ were calculated by making use of the characteristics of the lattice dynamics of the $LiRF_4$ crystal lattices.

The crystal free energy (per unit cell) is

$$F = \frac{v_0}{2}(\hat{\mathbf{e}}\hat{\mathbf{C}}'\hat{\mathbf{e}} + 2\hat{\mathbf{e}}\hat{\mathbf{b}}\mathbf{w} + \mathbf{w}\hat{\mathbf{a}}\mathbf{w}) + \sum_{pkp'k'} \lambda_{pp'}^{kk'} \langle O_p^k \rangle \langle O_{p'}^{k'} \rangle + v_0 \mathbf{M}\hat{\mathbf{Q}}\mathbf{M} - 2k_{\rm B}T \ln \mathrm{Tr} \exp(-H / k_{\rm B}T), \quad (3)$$

where v_0 is the volume of the unit cell containing two rare-earth ions, $k_{\rm B}$ is the Boltzman constant, $\hat{\mathbf{a}}$ is the dynamic matrix of the lattice at the Brillouin zone centre, the tensor $\hat{\mathbf{b}}$ determines interaction between macro- and microdeformations, $\hat{\mathbf{C}}' = \hat{\mathbf{C}} - \hat{\mathbf{b}}\hat{\mathbf{a}}^{-1}\hat{\mathbf{b}}$ where $\hat{\mathbf{C}}$ is the tensor of elastic constants. From the equilibrium conditions

$$\partial F / \partial \langle O_p^k \rangle = \partial F / \partial e_{\alpha\beta} = \partial F / \partial w_{\alpha}(s) = \partial F / \partial M_{\alpha} = 0 \quad (4)$$

we obtain self-consistent equations for the magnetization vector and the deformation tensor components. This system of equations was solved by making use of the method of consecutive approximations at fixed values of the temperature and the external magnetic field.

In particular, we obtain the lattice macro-deformation induced by the external magnetic field:

$$\hat{\mathbf{e}}(\mathbf{B}) = -\frac{n}{v_0}\hat{\mathbf{S}}[\langle \hat{\mathbf{V}} \rangle_B - \langle \hat{\mathbf{V}} \rangle_0], \quad (5)$$

and the sublattice displacements, which define the internal magnetostriction:

$$\mathbf{w}(\mathbf{B}) = -\frac{n}{v_0}\hat{\mathbf{a}}^{-1}[\langle \mathbf{V}'' \rangle_B - \langle \mathbf{V}'' \rangle_0]. \quad (6)$$

Here $\hat{\mathbf{S}}$ is the compliance tensor of the lattice, and angular brackets $\langle ... \rangle_B$, $\langle ... \rangle_0$ indicate thermal

averages for $B \neq 0$ and $B = 0$, respectively. Operators $\hat{\mathbf{V}}$ in the expression (5) are equal to operators $\hat{\mathbf{V}}'$ renormalized due to linear coupling of macro- and micro-deformations: $\hat{\mathbf{V}} = \hat{\mathbf{V}}' - \hat{\mathbf{b}}\hat{\mathbf{a}}^{-1}\mathbf{V}''$. Calculations of the magnetic properties were carried out considering the matrix of the Hamiltonian (1) in the subspace of the lower 146 states of the $4f^9$ configuration of the Dy^{3+} ion and in the total space of 1001 states of the $4f^{10}$ configuration of the Ho^{3+} ion.

The procedure involved the following steps: first, the matrix of the Hamiltonian (1) with $\mathbf{M} = 0$, $\hat{\mathbf{e}} = 0$, $\mathbf{w} = 0$ is diagonalized, and the macro- and micro-deformations ($\hat{\mathbf{e}}(\mathbf{B})$ and $\mathbf{w}(\mathbf{B})$), and the magnetization $\mathbf{M}$ are calculated. At the next step, the obtained values of $\mathbf{M}$, $\hat{\mathbf{e}}$, $\mathbf{w}$ are substituted into the Hamiltonian and the calculations are repeated. Considering the expansion of the free energy in power series in deformation parameters up to second order, we receive corrections to the elastic constants depending on the magnetic field and temperature. At the last step, the obtained values of $\mathbf{M}$, $\hat{\mathbf{e}}$, $\mathbf{w}$ and $\hat{\mathbf{C}}(\mathbf{B})$ are substituted into the Hamiltonian and the values of $\mathbf{M}$ are calculated. The results of calculations are presented in figures 1-4.

4. Conclusion

The measured temperature, field and angular dependences of the magnetization in $LiDyF_4$ and $LiHoF_4$ single crystals are compared with the results of simulations. The simulated temperature, magnetic field and anglular dependences of the magnetization are in good agreement with the experimental results. It follows from calculations that magnetoelastic interactions in double lithium-rare earth fluorides contribute essentially to the magnetization in external magnetic fields at liquid helium temperatures. A strong anisotropy of the magnetization in the basis *ab*-plane in $LiDyF_4$ single crystals is caused by the magnetoelastic interaction, and the corresponding contribution is induced by the magnetostriction. The detailed study of the magnetostriction in $LiDyF_4$ and $LiHoF_4$ single crystals will be presented in our next work.

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