Magnetostriction in ionic rare earth paramagnets

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The deformation of $LiErF_4$ tetragonal single crystals in the direction of an external magnetic field up to 30 kOe is investigated experimentally at helium temperatures as a function of the orientation of the field with respect to the crystallographic axes. The results of measurements of the anisotropy and of the temperature and field dependences of the parastriction are interpreted on the basis of a theory in which internal strain effects are taken into account and which is based on an analysis of the dynamics of the crystal lattice, of the energy spectrum of the rare earth ions, and of the electron–phonon interaction in the exchange-charge model.

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At low temperatures, a magnetic field of 10–100 kOe induces in paramagnetic rare-earth compounds a deformation (parastriction) that is comparable in magnitude with the magnetostriction in magnetically ordered crystals and may reach enormous values $\sim 10^{-3}$ (Refs. 1–3). In the paramagnetic phase, the mechanism of the induced magnetostriction has primarily a single-ion character. The magnetization-induced redistribution of the electron density of the unfilled $4f$ shell of the rare-earth ion changes the magnitudes of the interionic forces, and the ions of the crystal lattice move to new equilibrium positions. The structure of the lattice changes as a result of the combined effect of the Zeeman and electron–phonon interactions.

Systematic investigations of parastriction in rare-earth paramagnets are useful mainly for obtaining information on the characteristics of electron–phonon interactions. Investigations of magnetostriction are necessary also for a proper interpretation of magnetoacoustic measurements.

In this work, we present results of experimental and theoretical investigations of longitudinal magnetostriction in $LiErF_4$ crystals. Measurements of the temperature and field dependences of the parastriction allowed us to separate the contributions of the induced and the intrinsic magnetic moments of the rare-earth ions to the lattice deformation. As a result of the theoretical analysis of the experimental data, we obtained estimates of the electron–phonon interaction parameters and of the dynamic spin Hamiltonian of the Er^{3+} ions. A calculation based on consideration of the structure of the energy spectrum of the rare-earth ions and of the dynamics of the crystal lattice demonstrated the essential role of internal strain (displacements and electric polarization of the sublattices) in producing the macroscopic parastriction.[4]

§1. EXPERIMENTAL INVESTIGATION OF PARASTRICTION IN THE CRYSTAL $LiErF_4$. DEPENDENCE OF THE PARASTRICTION ON TEMPERATURE AND MAGNETIC FIELD

The static longitudinal magnetostriction was measured in the temperature range 1.6–4.2 °K as a function of the external magnetic field up to 30 kOe. The measurements were performed by the capacitance-bridge method by Sokolov.[5] The crystal was placed in a helium cryostat in the center of a superconducting solenoid and was connected to the measuring device by means of a quartz rod. The signals induced by the striction change of the sample length with increasing magnetic field were directly registered with an X–Y recorder; a voltage proportional to the current through the solenoid was applied to the X input. The sign of the striction was determined and the sensitivity of the apparatus was calibrated by means of control measurements of the magnetostriction of polycrystalline nickel. To make the measurement results independent of the displacement of the sample under the action of the torque due to the interaction of the anisotropic magnetic moment of the Er^{3+} ions with the magnetic field, the sample was secured with vacuum grease or silicone oil.

The tetragonal crystal lattice of $LiErF_4$ has a scheelite structure (space group C_{4h}^6) (Refs. 6, 7). The experiments were performed on five cylindrical samples of diameter 5–6 mm and length 6–10 mm, with finely polished flat end surfaces. The axes of the samples were oriented by x-ray diffraction with an accuracy not worse than 3° along the nonequivalent crystallographic directions [001, 100, 401, 110, 210] in a Cartesian coordinate system with axes along the edges of the unit cell.

The basic experimental results are presented on Figs. 1–3. In all the measurements, the parastriction had a negative sign; its average value ($\sim 10^{-4}$) in fields of ~30 kOe was comparable with values obtained for rare-earth polycrystalline germanate and gallate garnets.[1] As seen from Fig. 1, the parastriction in $LiErF_4$ has strong anisotropy: upon rotation of the magnetic field in the {010} plane, the effect changes by more than an order of magnitude, reaching a minimum in the [001] direction.

The relative change in the dimensions of the sample on a magnetic field in a direction given by the unit vector $\mathbf{n}$ is equal to

$$\Delta l/l = n_\alpha n_\beta e_{\alpha\beta} \qquad (1)$$

(here and elsewhere, summation over repeated Greek indices is implied). Here, $e_{\alpha\beta}$ are the components of the external-field induced strain tensor. Use of the symmetry properties of the lattice substantially simplifies the consideration of the magnetostriction. The unit cell of $LiErF_4$ contains two magnetically equivalent

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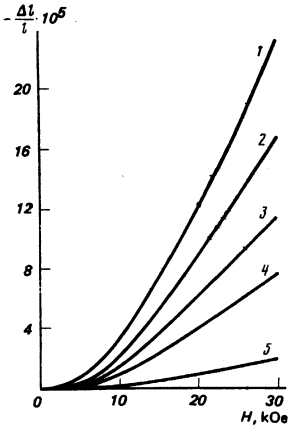

FIG. 1. Magnetic field dependence of the magnetostriction in the $LiErF_4$ crystal at $T=4.2$ °K along different directions: 1) [100], 2) [210], 3) [401], 4) [110], 5) [001].

erbium ions at lattice points with point symmetry S_4. We resolve the strain tensor in terms of the irreducible representations of the group S_4:

$$e(\Gamma_1^1)=e_{zz},\quad e(\Gamma_2^1)=e_{xx}-e_{yy},\quad e_1(\Gamma_3)=e_{xz},$$
$$e(\Gamma_1^2)=1/2(e_{xx}+e_{yy}),\quad e(\Gamma_2^2)=e_{xy},\quad e_2(\Gamma_3)=e_{yz}.$$

Then, in accordance with Eq. (1), we obtain for our samples

$$\begin{aligned}
&[001]:\ \Delta l/l=e(\Gamma_1^1);\\
&[100]:\ \Delta l/l=e(\Gamma_1^2)+0{,}5e(\Gamma_2^1);\\
&[110]:\ \Delta l/l=e(\Gamma_1^2)+e(\Gamma_2^2);\\
&[210]:\ \Delta l/l=e(\Gamma_1^2)+0{,}3e(\Gamma_2^1)+0{,}8e(\Gamma_2^2);\\
&[401]:\ \Delta l/l=0{,}21e(\Gamma_1^1)+0{,}79e(\Gamma_1^2)+0{,}39e(\Gamma_2^1)+0{,}82e_1(\Gamma_3).
\end{aligned}\qquad (2)$$

Thus, the anisotropy in the parastriction is a consequence of the onset of deformations of different symmetry as functions of the orientation of the magnetic field, and the experiment indicates that the striction is a maximum when a rhombic deformation $e(\Gamma_2^1)$ is induced.

The deformation of the lattice decreases the free energy, changing the magnetic moments of the rare earth ions, and accordingly their energy of interaction with the magnetic field. The Hamiltonian of the rare-earth ion may be represented as

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_Z+\mathcal{H}_d, \qquad (3)$$

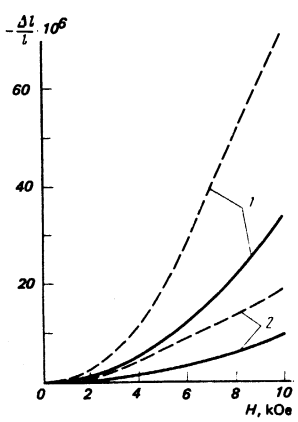

FIG. 2. Magnetostriction in $LiErF_4$ at temperatures 4.2 °K (solid lines) and 1.6 °K (dashed lines) along the directions: 1) [100], 2) [110].

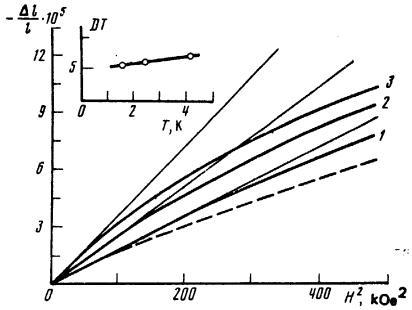

FIG. 3. Magnetostriction in $LiErF_4$ along the [401] direction at temperatures: 1) 4.2 °K; 2) 2.5 °K; 3) 1.6 °K. The straight lines are the tangents to the experimental curves at the origin, the dashed line is the graph of the function $\Delta l/l=-[0.468H+20.4\,\mathrm{th}(0.245H/T)]H\cdot 10^{-7}$ (H in kOe, T in °K) at $T=4.2$ °K. In the inset: the temperature dependence of the parameter $-10^7 Td(\Delta l/l)/d(H^2)$ as $H\to 0$.

where $\mathcal{H}_0$ is the energy of the ion in the crystal field, $\mathcal{H}_Z=g_J\mu_B\mathbf{H}\cdot\mathbf{J}$ is the Zeeman energy, and

$$\mathcal{H}_d=\sum_{nm}\Big[B^m_{n\alpha\beta}e_{\alpha\beta}+\sum_k B_{n\alpha}{}^m(k)w_\alpha(k)\Big]O_n{}^m$$
$$=\sum_{nm}\sum_{ijl}[B_{ni}{}^m(\Gamma_j^l)e_i(\Gamma_j^l)+B_{ni}{}^{m'}(\Gamma_j^l)w_i(\Gamma_j^l)]O_n{}^m \qquad (4)$$

is the change in energy of the ion in the crystal field upon deformation of the lattice. In the general case (when the point groups at the lattice points do not contain the inversion operation) the deformation is accompanied by displacements $\mathbf{w}(k)$ and electric polarization of the sublattices (for simplicity, we consider here the ions to be unpolarizable). $O_n{}^m$ are the tensor operators defined in accordance with Ref. (8). The second way of writing this, in terms of linear combinations of displacements of the sublattices and of strain tensor components that transform according to the irreducible representations of the symmetry group of the rare-earth ion (j, l, i are respectively the type, the number, and the row of the representation), is more convenient for actual calculations.

From the conditions that the free energy of an elastically strained paramagnet be minimum and that there be no internal stresses, it follows that

$$e_{\alpha\beta}=-\frac{1}{v_0}S_{\alpha\beta\gamma\delta}\sum_{nm}\sum\bar{B}^m_{n\gamma\delta}(\langle O_n{}^m\rangle-\langle O_n{}^m\rangle_0), \qquad (5)$$

where $S_{\alpha\beta\gamma\delta}$ is the elastic-compliance tensor; Σ is the sum over the non-interacting[1)] paramagnetic ions in the unit cell with volume v_0; $\langle O_n{}^m\rangle$ and $\langle O_n{}^m\rangle_0$ is the canonical average of the operators $O_n{}^m$ respectively for $\mathbf{H}\neq 0$ and $\mathbf{H}=0$; $\bar{B}^m_{n\gamma\delta}$ are the effective electron–phonon coupling constants, the terms of which are the renormalized characteristics of the interaction of the rare-earth ions with the sublattice displacements:

$$\bar{B}^m_{n\alpha\beta}=B^m_{n\alpha\beta}-\sum_{kk'}b_{\alpha\beta,\gamma}(k)a^{-1}_{\gamma\delta}(kk')B_{n\delta}{}^m(k'). \qquad (6)$$

Here, $b_{\alpha\beta,\gamma}(k)$ are the components of the force acting on the kth ion of the sublattice under macroscopic deformation:

$$b_{\alpha\beta,\gamma}(k)=\sum_{k'L'}\Phi_{\gamma\delta}\begin{pmatrix}L & L'\\ k & k'\end{pmatrix}\Big(X_\alpha\begin{pmatrix}L'\\ k'\end{pmatrix}-X_\alpha\begin{pmatrix}L\\ k\end{pmatrix}\Big); \qquad (7)$$

TABLE I. Spectral characteristics (energy E in cm^{-1} and g factors) of Stark sublevels of the ground-state term $^4I_{15/2}$ of the Er^{3+} ion in $LiErF_4$.

N	$\Gamma(S_4)$	Calculation			Experiment (Refs. 10, 11, 12)		
		E	$g_\parallel$	$g_\perp$	E	$g_\parallel$	$g_\perp$
1	Γ_{78}	0	3.78	7.99	0	3.7±0.2	8.7±0.2
2	Γ_{56}	16.5	8.12	4.70	18.2	9.1±0.2	4.6±0.2
3	Γ_{78}	22.5	0.79	7.86	23.3	0.11 *	–
4	Γ_{56}	57.3	1.91	2.68	60.0	2.38 *	–
5	Γ_{56}	246	6.93	0.73	252 *	–	–
6	Γ_{56}	289	11.3	2.90	291 *	–	–
7	Γ_{78}	317	9.28	2.94	320 *	–	–
8	Γ_{78}	344	11.09	3.08	347 *	–	–

*Data for the crystal $LiYF_4$:Er (Ref. 12).

Note. The g factors are calculated without taking into account interactions between rare-earth ions.

$\Phi_{\alpha\beta}$ are the force constants of the lattice, X_α are the coordinates of an ion with mass $m(k)$ in the cell L; the quantities

$$a_{\alpha\beta}(kk') = \sum_{L'} \Phi_{\alpha\beta} \begin{pmatrix} L & L' \\ k & k' \end{pmatrix}$$

agree within the factor $[m(k)m(k')]^{-1/2}$ with the elements of the dynamic matrix of the lattice in the center of the Brillouin zone.

In Eq. (5), the temperature and magnetic field dependences are hidden in the canonical averages; these dependences can be separated in explicit form if $\mu_B H \ll \Delta$ and $kT \ll \Delta$, where Δ is the difference between the energies of the first excited and the ground-state Stark sublevels of the rare-earth ions ($\Delta = 18.2$ cm^{-1} in $LiErF_4$; see Table I). In this case, we may consider as populated only the ground state of the rare-earth ion in the crystal field, and we may regard the Zeeman energy $\mathcal{H}_Z$ as a perturbation along with $\mathcal{H}_d$. As a consequence of the additivity of the effects due to splitting and shift of the ground-state doublet of the rare-earth ion in a magnetic field, the components of the strain tensor take the form

$$e_{\alpha\beta} = -v_0^{-1} S_{\alpha\beta\gamma\delta} (B_{\gamma\delta(s)} + B_{\gamma\delta(i)}), \tag{8}$$

where the parameters $B_{\alpha\beta(s)}$ and $B_{\alpha\beta(i)}$ correspond to the change in the intrinsic and induced magnetic moments of the rare-earth ions following the lattice deformation:

$$B_{\alpha\beta(s)} = -\frac{1}{2} \sum \frac{\mu_B}{gH} H_\gamma H_\delta g_{\sigma\sigma} G_{\sigma\gamma\alpha\beta} \operatorname{th} \frac{g\mu_B H}{2kT}, \tag{9}$$

$$B_{\alpha\beta(i)} = (g_J \mu_B)^2 H_\gamma H_\delta \sum_{nm} \sum \bar{B}^m_{n\alpha\beta} [J_\gamma J_\delta O_n^m] \tag{10}$$

In Eq. (9), $g_{\alpha\beta}$ is the g tensor and $G_{\alpha\beta\gamma\delta}$ are the dimensionless spin–phonon interaction constants in the spin Hamiltonian of the ground-state Kramers doublet

$$\mathcal{H}_S = \mu_B S_\alpha H_\beta (g_{\alpha\beta} + G_{\alpha\beta\gamma\delta} e_{\gamma\delta})$$

[$G_{\alpha\beta\gamma\delta}$ are linear functions of the electron–phonon interaction parameters $\bar{B}^m_{n\gamma\delta}$ (see Sec. 2 below),

$$g\mu_B H = \mu_B (g_{\alpha\beta} g_{\alpha\gamma} H_\beta H_\gamma)^{1/2}$$

is the splitting of the doublet in the magnetic field; the quantity $[J_\gamma J_\delta O_n^m]$ in Eq. (10) has the structure of a correction to the energy of the ground state in third-order perturbation theory; this structure is linear in each of the perturbation terms ($J_\gamma + J_\delta + O_n^m$) (Ref. 2).

TABLE II. Characteristics of the field dependence of the parastriction in $LiTRF_4$ crystals.

Orientation of the magnetic field	D (in units of 10^{-7} kOe^{-2})			
	$T=4.2$ K		$T=1.6$ K	
	Experiment	Calculation	Experiment	Calculation
$LiErF_4$				
001	0.22	0.34	–	1.1
100	3.8	3.2	7.2	9.5
110	0.9	0.76	2.1	4.1
210	2.3	4.2	–	13.0
401	1.6	3.2	3.5	8.8
$LiTmF_4$				
100	8.0	6.0	–	–
110	3.3	2.6	–	–

Our measurements showed that in the weak-field region ($H < 10$ kOe) the longitudinal parastriction has a quadratic magnetic field dependence: $\Delta l/l = -DH^2$ (see Figs. 1 and 2; the coefficients D for different orientations of the field are given in Table II); this fact becomes obvious when $\Delta l/l$ is plotted (see Fig. 3) and is in complete agreement with theoretical results. From Eqs. (1), (8)–(10) we obtain

$$\frac{\Delta l}{l} = AH^2 + CH \operatorname{th} \frac{g\mu_B H}{2kT}, \tag{11}$$

where A and C are functions of the direction cosines of the vectors H and l. When $g\mu_B H \ll kT$, in accord with Eq. (11), the coefficient D introduced above is a linear function of $1/T$.

On Fig. 3, the slopes of the lines passing through the origin give the values of D at three measurement temperatures. As is evident from the plot of the temperature dependence of DT (inset in Fig. 3), the experimental points lie on a straight line whose intercept on the y-axis determines C, and whose slope is equal to A in Eq. (11) (the calculated g factor in this case is equal to 7.27). The expression (11) with the parameters A and C found from the $DT(T)$ plot satisfactorily describes the experimental parastriction curves. The deviation is larger in the weak-field region, when effects of higher order in the magnetic field begin to appear due to significant mixing of wave functions of different Stark sublevels of the rare-earth ion; the corresponding plot is shown dashed in Fig. 3. The weak-field measurement results make it possible to estimate the behavior of the magnetostriction in the saturation region (when $g\mu_B H \gtrsim kT$); the difference between the deformation calculated on the basis of Eq. (11) and that measured at 4.2 °K in a field ≤ 30 kOe is not more than 15%. We note that the role of the induced magnetic moment (Van Vleck paramagnetism) in producing the magnetostriction increases with increasing field; accordingly, in strong fields the temperature dependence of the parastriction is weaker.

§2. CALCULATION OF PARASTRICTION IN $LiErF_4$ AND DISCUSSION OF RESULTS

As was shown above, the measured temperature and field dependences of the deformation of an $LiErF_4$ crystal agree satisfactorily with the assumption that the single-particle parastriction mechanism plays the predominant role; but a question remains concerning the quantitative estimate of the effect within the framework

of the microscopic theory. In order to calculate the parastriction, we must first find the crystal field parameters (in the Hamiltonian $\mathcal{H}_0=\sum_{nm}B_n^mO_n^m$) and the electron–phonon interaction parameters. We solved this problem within the framework of the exchange charge model,[13] in which the characteristics of the crystal field (and of the electron–phonon interaction) are represented as

$$B_n^m=B_{nq}^m+B_{nD}^m+B_{nS}^m, \tag{12}$$

where B_{nq}^m and B_{nD}^m are the parameters of the electrostatic fields of the point charges and of the dipole moments of the ions, B_{nS}^m are the parameters of the exchange-charge field due to overlap of the wave functions of the $4f$ electrons of the rare-earth ion with the wave functions of the ligands.

In the static $LiErF_4$ lattice, only the fluorine ions are polarized; the dipole moments $D(F_k^-)$ were found from a self-consistent system of equations with values of the electric fields and dipole lattice sums calculated by the Ewald method, and with an isotropic polarizability of the fluorine ions $\alpha(F^-)=0.972$ Å^3 (Ref. 13). In particular, for an ion with coordinates (x, y, z) $(x=0.282;\ y=0.164;\ z=0.0813$ are the structural lattice constants[6,7]), $D_x=-0.1389\ e$Å, $D_y=-0.0698\ e$Å, $D_z=-0.0222\ e$Å; the dipole moments of the remaining ions can be obtained by lattice symmetry operations.

Using the same characteristics of the electronic radial wave functions of the Er^{3+} and F^- ions as in the earlier analysis of the Stark structure of the spectra of Er^{3+} ions in crystals with a fluorite structure,[13] and knowing the overlap parameter $G=7.6$, we obtained a satisfactory description of the spectral characteristics of the Er^{3+} ions in the $LiErF_4$ lattice. The crystal field parameters calculated in the crysallographic coordinate system are compared in Table III with the empirical parameters transformed by a rotation of the coordinate system about the z axis through an angle selected on the basis of the relation between the calculated B_n^4 and B_n^{-4}. The calculation of the parastriction was carried out with the eigenfunctions of the Hamiltonian $\mathcal{H}_0$ and with the empirical parameters from Table III, diagonalized in the space of the functions of the ground-state term $^4I_{15/2}$ of the Er^{3+} ion. The calculated g factors and energies of the Stark-sublevels are compared with the results of investigations of the optical spectrum and EPR of the $LiErF_4$ crystal and the isostructural diluted paramagnet $LiYF_4:Er$ in Table I.

TABLE III. Crystal field parameters (B_n^m) and electron–phonon coupling parameters for Er^{3+} ions in the $LiErF_4$ crystal (in cm^{-1}).

n	m	B_n^m Calculation	B_n^m Experiment (Ref. 4)	$\bar{B}_n^m(\Gamma_1^1)$	$\bar{B}_n^m(\Gamma_1^2)$
2	0	177	190	900	−1671
4	0	−85	−80	174	518
6	0	−2.7	−2.3	83	−37
4	4	−699	−771	2400	2464
4	−4	−604	−667	1636	1031
6	4	−333	−363	761	1508
6	−4	−253	−222	203	1665

n	m	$\bar{B}_n^m(\Gamma_2^1)$	$\bar{B}_n^m(\Gamma_2^2)$	n	m	$\bar{B}_{n1}^m(\Gamma_3)$	n	m	$\bar{B}_{n1}^m(\Gamma_3)$
2	2	2377	3577	2	1	−1303	2	−1	−2213
2	−2	1590	−977	4	1	−1644	4	−1	1572
4	2	−215	−654	6	1	−970	6	−1	795
4	−2	2712	−33	4	3	23350	4	−3	17090
6	2	280	−702	6	3	2102	6	−3	−1647
6	−2	−494	−456	6	5	−7221	6	−5	315
6	6	−631	−1013						
6	−6	−875	−1650						

Since the exchange-charge model gave a satisfactory description of the spectrum of Er^{3+} ions, we also used it to calculate the electron–phonon interaction parameters in the Hamiltonian $\mathcal{H}_{el}$ [see Eq. (4)]. In the general case, the number of independent displacements of the sublattices $w_\alpha(k)$ is equal to $3(r-1)$, where r is the number of ions in the cell. The unit cell of $LiErF_4$ contains an inversion point, and since upon deformation of the lattice the displacements of sublattices coupled by the inversion operation are equal in magnitude and opposite in sign, the effective constants of the coupling with the macroscopic deformation $\bar{B}_{ni}^m(\Gamma_j^l)$ contain the renormalized characteristics of the interaction of erbium ions only with the normal lattice coordinates which are active in the Raman spectrum and transform according to the even irreducible representations of the C_{4h} symmetry group of the center of the Brillouin zone. In the normal-coordinate basis, using the compatibility relation of the irreducible representations of the groups C_{4h} and S_4 ($A_g-\Gamma_1$, $B_g-\Gamma_2$, $E_g-\Gamma_3$), Eq. (6) can be written in the form

$$\bar{B}_{ni}^m(\Gamma_j^l)=B_{ni}^m(\Gamma_j^l)-\sum_{l'}\frac{b_i(\Gamma_j^l\Gamma_j^{l'})B_{ni}^{m'}(\Gamma_j^{l'})}{\omega^2(\Gamma_j^{l'})}, \tag{13}$$

where $\omega(\Gamma_j^l)$ are the Raman-active vibrational frequencies of the lattice. In order to calculate the effective electron–phonon interaction constants, we considered the dynamics of the $LiErF_4$ lattice within the rigid-ion model with paired Coulomb and non-Courlomb interactions.

With the effective charges of the ions as integral multiples of $0.9e$, and as a result of a slight correction to the theoretical estimates[15,16] of the potentials of the Li^+-F^-, $Er^{3+}-F^-$, and F^--F^- bonds, we obtained vibrational frequencies $\omega(A_g)=123,\ 283,\ 434$; $\omega(B_g)=119,\ 211,\ 318,\ 399,\ 467$; $\omega(E_g)=120,\ 177,\ 343,\ 392,\ 466$ (in cm^{-1}), which are close to the Raman-scattering measurement results in the isostructural crystals $LiTmF_4$ and $LiYbF_4$.[17] Having thus verified the characteristics of the interionic interaction, we calculated the electron–phonon interaction parameters in accordance with Eq. (13). Since neglect of electric polarization of the ions leads to an overestimate of the sublattice displacements, we introduced an empirical factor 0.55 (the only fit parameter used in the direct calculation of the parastriction) into the parameters of the electrostatic interaction of the rare-earth ion with the sublattice displacements. The values of $\bar{B}_{ni}^m(\Gamma_j^l)$ obtained as a result are given in Table III.

The deformation of $LiErF_4$ lattices of different symmetry types is described by the following expressions [see Eqs. (5), (8)]:

$$\begin{aligned}
e(\Gamma_1^1)&=-(S_{33}B(\Gamma_1^1)+S_{13}B(\Gamma_1^2)),\\
e(\Gamma_1^2)&=-(1/2(S_{11}+S_{12})B(\Gamma_1^2)+S_{13}B(\Gamma_1^1)),\\
e(\Gamma_2^1)&=-(2(S_{11}-S_{12})B(\Gamma_2^1)+S_{16}B(\Gamma_2^2)),\\
e(\Gamma_2^2)&=-(S_{16}B(\Gamma_2^1)+1/4S_{66}B(\Gamma_2^2));\\
e_i(\Gamma_3)&=-1/4S_{44}B_i(\Gamma_3).
\end{aligned} \tag{14}$$

When parastriction is considered, the effective spin Hamiltonian of the ground-state doublet of the Er^{3+} ions may be written in the form

$$\mathcal{H}_S=\mu_B\Big[g_\parallel(HS)_1{}^1+g_\perp(HS)_1{}^2+G_{44}S_z(H_xe_{xz}+H_ye_{yz})$$
$$+G_{44}'H_z(e_{xz}S_x+e_{yz}S_y)+G_{44}''H_z(e_{yz}S_x-e_{xz}S_y)+\sum_{ijl}(HS)_j{}^iG(\Gamma_j{}^i\Gamma_l{}^l)e(\Gamma_j{}^l)\Big], \quad (15)$$

where $(HS)_j^i$ are bilinear forms constructed from the components of **H** and **S** and transforming according to the irreducible representations Γ_j of the group S_4:

$$(HS)_1{}^1=H_xS_x, \quad (HS)_1{}^2=H_xS_x+H_yS_y,$$
$$(HS)_2{}^1=H_xS_x-H_yS_y, \quad (HS)_2{}^2=H_xS_y+H_yS_x.$$

In the weak-field region, the parastriction characteristics $B(\Gamma_j^2)$ in Eq. (14) as functions of **H** and T are determined by Eqs. (9) and (10). Taking into account the labeling introduced in Eq. (15) for the spin–phonon interaction constants at arbitrary magnetic-field orientations given by the angles θ and φ (polar axis along the symmetry axis of the lattice, the angle φ in the {001} plane measured from the [100] direction), the parastriction characteristics take the following form:

$$B(\Gamma_1{}^j)=2\frac{\mu_BH}{v_0g}\langle S_H\rangle[g_\parallel G(\Gamma_1{}^1\Gamma_1{}^j)\cos^2\theta+g_\perp G(\Gamma_1{}^2\Gamma_1{}^j)\sin^2\theta]$$
$$+H^2[C(\Gamma_1{}^1\Gamma_1{}^j)\cos^2\theta+C(\Gamma_1{}^2\Gamma_1{}^j)\sin^2\theta], \quad (16)$$

$$B(\Gamma_2{}^j)=2\frac{\mu_BH}{v_0g}\langle S_H\rangle g_\perp\sin^2\theta[G(\Gamma_2{}^1\Gamma_2{}^j)\cos 2\varphi+G(\Gamma_2{}^2\Gamma_2{}^j)\sin 2\varphi]$$
$$+H^2\sin^2\theta[C(\Gamma_2{}^1\Gamma_2{}^j)\cos 2\varphi+C(\Gamma_2{}^2\Gamma_2{}^j)\sin 2\varphi], \quad (17)$$

$$B_1(\Gamma_3)=2\frac{\mu_BH}{v_0g}\langle S_H\rangle\sin\theta\cos\theta[g_\parallel G_{44}\cos\varphi+g_\perp(G_{44}'\cos\varphi-G_{44}''\sin\varphi)]$$
$$+H^2\sin\theta\cos\theta\cos\varphi C(\Gamma_3\Gamma_3); \quad (18)$$

$$\langle S_H\rangle=-\frac{1}{2}\,\mathrm{th}\frac{g\mu_BH}{2kT}, \quad g=(g_\parallel{}^2\cos^2\theta+g_\perp{}^2\sin^2\theta)^{1/2}.$$

The quantities $C(\Gamma_i^k\Gamma_i^l)$, which determine the contributions to the parastriction from the induced magnetic moment and are calculated from the data in Tables I and III, are listed in Table IV for $i=1,2$ and $C(\Gamma_3,\Gamma_3)=7.7\cdot10^3$ kOe^{-2} N/m^2. $B_2(\Gamma_3)$ is of the same form as $B_1(\Gamma_3)$, with the substitutions $\cos\varphi\to\sin\varphi$ and $\sin\varphi\to-\cos\varphi$.

The spin–phonon interactions constants describe the splitting of the ground-state doublet in second order in the perturbation $\mathcal{H}_Z+\mathcal{H}_d$; in particular,

$$G(\Gamma_2{}^1\Gamma_2{}^j)-iG(\Gamma_2{}^2\Gamma_2{}^j)=-\frac{8g_J{}^2}{\sigma}\langle-|J_x|+\rangle$$
$$\times\sum_{nm}\bar B_n{}^m(\Gamma_2{}^j)\sum_k\Delta_k{}^{-1}\langle+|J_x|k\rangle\langle k|O_n{}^m|-\rangle; \quad (19)$$

here $|+\rangle$ and $|-\rangle$ are the Kramers-conjugate states of the ground state doublet, while $|k\rangle$ and Δ_k are the wave functions and the energies of the excited states of the rare-earth ion in the crystal field. A calculation with formulas of the type in Eq. (19) and the eigenfunctions of the Hamiltonian $\mathcal{H}_0$ within the limits of the ground-state term $^4I_{15/2}$, together with data from Table III, gave the following values for the spin–phonon interaction constants: $G_{44}=-46.4$; $G_{44'}=-00.3$; $G_{44''}=51.6$; the values for the rest of the $G(\Gamma_k^i\Gamma_k^j)$ are given in Table IV.

TABLE IV. Spin–phonon coupling parameters and characteristics of the Van Vleck parastriction in $LiErF_4$.

i	$G(\Gamma_k^i\Gamma_k^j)$				$C(\Gamma_k^i\Gamma_k^j)$			
	$k=1$		$k=2$		$k=1$		$k=2$	
	$j=1$	$j=2$	$j=1$	$j=2$	$j=1$	$j=2$	$j=1$	$j=2$
1	−32.2	−2.38	−43.3	−22.4	−1.74	0.56	−1.31	−0.18
2	10.6	0.33	−32,5	−13.4	6.11	−8,21	−3.62	−3.90

Note. The $C(\Gamma_k^i\Gamma_k^j)$ parameters are given in units of 10^3 $kOe^{-2}N/m^2$.

Replacing the $B(\Gamma_i^j)$ [Eqs. (16)–(18)] the hyperbolic tangents by their arguments, we obtain in the weak-field region a quadratic dependence of the striction on the magnetic field. The proportionality coefficients between $\Delta l/l$ and H^2 calculated from Eqs. (2) and (14) are compared with the experimental data in Table II. Equations (16)–(18), obtained in the spin-Hamiltonian approximation, can be used to estimate the parastriction also in strong fields. In particular, in a field of 30 kOe at $T=4.2$ °K, a rigorous calculation in accordance with Eq. (5), with computer diagonalization of the complete matrix $\mathcal{H}_0+\mathcal{H}_Z$, gives $\Delta l/l=-2.38\cdot10^{-5}$ in the [001] direction, while a calculation according to Eq. (16) gives $\Delta l/l=-2.2\cdot10^{-5}$; the measured value of the longitudinal magnetostriction under the indicated conditions is $\Delta l/l=-2\cdot10^{-5}$.

Despite the obvious approximate nature of the models used for the crystal field and of the lattice dynamics, the theory allows us to correctly predict the sign and magnitude of the parastriction for an arbitrary orientation of the magnetic field. In particular, on the basis of the calculation performed for the electron–phonon interaction constants and the structure of Eqs. (16)–(18), in $LiTRF_4$ crystals, we should expect a significant transverse magnetostriction in the basal plane of the lattice {001}, approximately equal in magnitude and opposite in sign to the longitudinal striction.

The internal lattice strain of the paramagnet, induced by the magnetic field, is determined by the effects of striction and direct interaction of the sublattices with the paramagnetic ions. In $LiErF_4$, these internal strain mechanisms partially suppress one another; most of the sublattice displacements arise in the Γ_2 deformation—in particular, in a field of 30 kOe at $T=4.2$ °K they range from 10^{-3} to $5\cdot10^{-3}$ nm.

The electron–phonon interaction parameters for different rare-earth ions in isomorphic matrices vary insignificantly; the results of a calculation of the parastriction in the Van Vleck paramagnet $LiTmF_4$ with the parameters for the Er^{3+} ion given in Table III agree well with the data measured in Ref. 2 (see Table II).

Theoretical estimates of the absolute value of the striction are 1.5 times too large on the average; nevertheless, considering that we used in the calculations only one empirical parameter (the coefficient of the energy of a $4f$ electron in the electrostatic field of the displaced sublattices), we can hope to obtain results that are sufficiently close to reality by considering, in addition to the parameters found here, also other effects due to electron–phonon interactions and spin–phonon interactions in rare-earth double fluorides (for example, spin–lattice relaxation, magnetoacoustic vibrations,

Zeeman effect on degenerate phonon modes in the Raman spectra). Allowance for magnetic interactions between rare-earth ions does not essentially change the results of this work (in $LiErF_4$, under saturation conditions, the molecular field due to dipole–dipole interactions does not exceed 2 kOe); refinement of the electron–phonon coupling parameters would be facilitated by measurement of the elastic constants of the $LiTRF_4$ crystals [in the numerical estimates, we used the elastic constants for the isostructural crystal $LiYF_4$ (Ref. 7)] and of the transverse magnetostriction.

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[1)]The magnetic ordering temperature (the Néel point) in the $LiErF_4$ crystal is equal to 0.38 °K. (Ref. 9). Thus, $T \gg T_N$ in our investigated temperature interval, and it is valid to neglect magnetic interactions.

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