VOL. XLVI/XLVII, 30

SECTIO AAA

1991/1992

Institute of Physics, M. Curie-Sklodowska University

L. E. MISIAK

# EPR of Gd<sup>3+</sup>-Doped LiErF<sub>4</sub> and LiDyF<sub>4</sub> Single Crystals: Spin-Lattice Relaxation and Superposition Model Calculation

## INTRODUCTION

LiErF<sub>4</sub> and LiDyF<sub>4</sub> crystals have been recently used as laser materials [1,2]. These crystals were grown by Czochralski and other methods [3,4], as well as the IR spectra were recorded [5]. The EPR experiment in LiREF<sub>4</sub> (RE = Tb, Ho, Er) at submillimeter frequencies have been carried out by Magarino *et al.* [6]. On the other hand, the impurity resonances of ND<sup>3+</sup>, Dy<sup>3+</sup>, Er<sup>3+</sup>, and Yb<sup>3+</sup> were investigated at X band in single crystal samples of LiYF<sub>4</sub> [7], and at millimeter and submillimeter frequencies in LiY<sub>1-x</sub>RE<sub>x</sub>F<sub>4</sub> (RE = Tb, Ho) [8]. NMR spectra for the fluorine and lithium nuclei in LiREF<sub>4</sub> (RE = Tb, Dy, Ho, Er) have been studied at 295 K in Ref. [9], as well as magnetic (in the range 1.3-300 K) and NMR (at room temperature) measurements of LiErF<sub>4</sub> and LiHoF<sub>4</sub> crystals were carried out [10].

The rare-earths being ionic atoms are coupled predominantly by a dipole-dipole interaction. These materials are attractive from the theoretical standpoint because they consist fairly ionic atoms and possess rather high point symmetry  $S_4$  (approximately  $D_{2d}$ ) around a rare-earth ion. EPR lines of  $Gd^{3+}$  resonance transitions in LiErF<sub>4</sub> and LiDyF<sub>4</sub> single crystals are very broad, thus the determined spin-Hamiltonian parameters carry some errors but these parameters are still useful for comparison with other crystals of the same family in the light of the superposition model. Spin-lattice relaxation times can be determined using these linewidths and taking into account the presence of two active ions ( $Gd^{3+}$  and  $RE^{3+}$ ) [11].

It is the purpose to study by EPR of  $Gd^{3+}$ -doped LiREF<sub>4</sub> (RE = Er, Dy) single crystals which have not been investigated yet.

## CRYSTAL GROWTH AND CRYSTAL STRUCTURE

LiErF<sub>4</sub> and LiDyF<sub>4</sub> (LEF and LDF, hereafter) crystals belong to the family of scheelite type structure with the space group classification  $I4_1/a$ , likewise as LiYF<sub>4</sub> and LiYbF<sub>4</sub> [12].

LEF and LDF single crystals have been obtained by a modified Bridgman--Stockbarger method using an induction furnace and using a conventional heated resistance furnace. The technology of crystal growth in the induction furnace can be found elsewhere [13]. The material for crystallization was prepared from components of ErF<sub>3</sub>, or DyF<sub>3</sub> (99.9% purity) and LiF (99.5% purity) produced by Ventron-Alfa Products in USA  $(0.3 \text{ mol } \% \text{ of } \text{GdF}_3 \text{ was used as dopant})$ . LiF was additionally purified by Stockbarger crystallization and REF<sub>3</sub> powders (RE = Er, Dy, Gd) were purified by PbF<sub>2</sub> scavenging procedure prior to crystal growth using the induction furnace. The 2-4 mol % excess of LiF in a starting charge was used, because the vapor pressure of LiF is higher than those of REF<sub>3</sub> fluorides. Graphite crucibles were equipped with covers to lock their upper inlet to reduce to minimum loss of LiF during the heating. The conventional resistance heated Stockbarger furnace controlled to  $\pm 0.5^{\circ}$ C was used. The crucible with mixture of fluorides was placed inside quartz ampoule covered with graphite, next the ampoule was evacuated and sealed. The synthesis and the homogenization of mixture were performed at  $\sim 1050^{\circ}$ C. The temperature at least  $50-100^{\circ}$ C higher than the melting point of a particular compound was used for crystal growth. The crucible lowering rate through a freezing region of 1 mm/h and the temperature gradient of  $60^{\circ} \text{C/cm}$ were used.

Crystals prepared to EPR experiment are generally of a spherical shape, transparent light pink (LEF) and light yellow (LDF). To EPR measurements were selected better crystals, the other ones were crushed in order to obtain X-ray powder diffraction patterns. The X-ray diffraction for LiREF<sub>4</sub> crystals was used to compare the structure and cell dimensions with those of given in references and to select more perfect samples.

The X-ray powder diffraction patterns were taken on crushed material using the Cu K<sub> $\alpha$ </sub> X-ray radiation ( $\lambda = 0.15418$  nm). A computer joined to diffractometer through an interface has collected the data. Diffraction patterns could be indexed on a tetragonal unit cell of scheelite. Spectra were analyzed using computer programs in order to find Miller indices and to calculate lattice constants. The diffraction patterns of crushed LEF and LDF samples are presented on Fig. 1 and the data are exhibited in Table 1. Table 1 shows observed presently additional (224), (107), (321) reflections for LEF crystal, as well as additional (215) reflection and absence of (008) one for LDF crystal (the underlined position in Table 1), comparing with Ref. [14]. Another difference is for (105) reflection of LEF; the presently determined  $2\theta = 45.85^{\circ}(d = 0.1979$  nm), whereas  $2\theta = 44.94^{\circ}(d = 0.2017$  nm) recalculated for CuK<sub> $\alpha$ </sub> (because in Ref. [14] the data are given for Cr X-ray radiation).

The presently determined lattice constants at room temperature for LiErF<sub>4</sub>  $(a = 0.5150 \pm 0.0008 \text{ nm}, c = 1.070 \pm 0.001 \text{ nm})$  and for LiDyF<sub>4</sub>  $(a = 0.5184 \pm 0.0008 \text{ nm}, c = 1.083 \pm 0.001 \text{ nm})$  correspond to the published data as follows:



for LiErF<sub>4</sub> —  $a = (0.5162 \pm 0.0005)$ , 0.516, and 0.515 nm,  $c = (1.070 \pm 0.001)$ , 1.070, and 1.068 nm, for LiDyF<sub>4</sub> —  $a = (0.5188 \pm 0.0005)$ , 0.519, and 0.5185 nm, c = (1.083 + 0.001), 1.081, and 1.084 nm in Refs. [3], [14], and [5], respectively.

## SPIN-LATTICE RELAXATION TIME

EPR linewidths of Gd<sup>3+</sup> ions were investigated at X-band in LEF and LDF single crystals. The EPR experimental arrangement has been described elsewhere [15].

The width of very broad lines (Fig. 2) is in the range 75-86 mT at room temperature because of dipolar and exchange interactions between paramagnetic ions. The lines have a Lorentzian shape due to a narrowing mechanism which influences the dipolar interaction between Gd<sup>3+</sup> and Er<sup>3+</sup> (or Dy<sup>3+</sup>) spins. The each Gd<sup>3+</sup> ion in LiREF<sub>4</sub> crystals has Er<sup>3+</sup> (or Dy<sup>3+</sup>) ions as nearest and next-nearest neighbors because the concentration of Gd<sup>3+</sup> ions is only 0.2%. The magnetic moments of Er<sup>3+</sup>(9.5 $\mu_B$ ) and Dy<sup>3+</sup>(10.6 $\mu_B$ ) are larger than one of Yb<sup>3+</sup>(4.5 $\mu_B$ ) in consistence with the observed linewidths in LiREF<sub>4</sub> crystals. The large effect of the host ions Er<sup>3+</sup> (or Dy<sup>3+</sup>) in the Gd<sup>3+</sup> spectra will be observed if the spin-lattice relaxation time (SLRT) of host ions ( $\tau_1'$ ) approaches to the spin-lattice relaxation time of impurity Gd<sup>3+</sup> ions [16]. This process produces an extra path to rapid transfer of energy to lattice. The fast relaxation of host ions randomly modulates



Fig. 2. EPR spectra of  $Gd^{3+}$ -doped LiREF<sub>4</sub> (RE = Er, Dy) crystals at room temperature ( $\vec{H} \parallel \vec{X}$ )

	LiErF <sub>4</sub>			LiDyF4		
hkl	I(a.u.)	2θ(deg)	d <sub>hkl</sub> (nm)	I(a.u.)	$2\theta(deg)$	d <sub>hkl</sub> (nm)
101	100	19.05	0.4658	100	18.92	0.4690
112	50	29.60	0.3018	70	29.34	0.3044
103	20	30.45	0.2935	10	30.10	0.2969
004	5	33.45	0.2679	10	33.08	0.2708
200	15	34.77	0.2580	5	34.54	0.2597
211	40	39.95	0.2257	30	39.74	0.2268
114	10	41.85	0.2158	10	41.43	0.2179
105	<u>25</u>	<u>45.85</u>	<u>0.1979</u>	5	45.35	0.2000
213	35	46.93	0.1936	25	46.55	0.1951
204	30	49.07	0.1856	20	48.56	0.1875
220	15	50.00	0.1824	10	49.65	0.1836
222	5	53.05	0.1726			_
301	10	54.00	0.1698	5	53.65	0.1708
116	25	57.46	0.1604	10	56.83	0.1620
215	30	<b>58.80</b>	0.1570	<u>5</u>	<u>58.25</u>	<u>0.1584</u>
312	40	59.20	0.1561	20	58.88	0.1568
303	15	59.65	0.1550	10	59.16	0.1562
224	<u>30</u>	<u>61.55</u>	<u>0.1507</u>	5	61.05	0.1518
107	<u>10</u>	6 <u>3.40</u>	<u>0.1467</u>	5	62.75	0.1481
321	<u>5</u>	<u>65.90</u>	<u>0.1417</u>	10	65.45	0.1426
008				<u>5</u>	—	—
323				5	70.35	0.1338
400				5	72.86	0.1298

Table 1. The values of relative intensity I,  $2\theta$ , and the distances between (hkl) planes  $d_{hkl}$  determined from X-ray diffraction patterns at 290 K. The differences between Ref. [14] and present data are underlined

dipolar and exchange interactions between host and impurity Gd<sup>3+</sup> ions, observed as the spin-lattice narrowing.

According to Van Vleck's calculations [17] the expression is finally obtained for the mean square power frequency deviation:

$$\overline{\langle \Delta \nu^2 \rangle} = \frac{1}{3} S(S+1) h^{-2} \sum_k B_{jk}^2 + \frac{1}{3} S'(S'+1) h^{-2} \sum_{k'} C_{jk'}^2, \tag{1}$$

where coefficients  $B_{jk}$  and  $C_{jk'}$  of terms  $\vec{S}_{zj} \cdot \vec{S}_{zk}$  and  $\vec{S}_{zj} \cdot \vec{S}_{zk'}$ , respectively, are defined as follows:

$$B_{jk} = -\frac{3}{2}g^{2}\mu_{B}^{2}r_{jk}^{-3}\left[3\gamma_{jk}^{2}-1\right],$$
  

$$C_{jk'} = \tilde{A}_{jk'} + (1-3\gamma_{jk'}^{2})gg'\mu_{B}^{2}r_{jk}^{-3}.$$
(2)

The symbol  $\bar{A}_{jk'} = -2z_1 z_2 J_{jk'}$   $(z_1, z_2 \text{ are the numbers of electrons in 4f shell of interacting ions, <math>J_{jk'}$  is the exchange integral) embodies the effect of exchange alone, whereas  $C_{jk'}$  contains also a dipolar contribution,  $B_{jk}$  is purely dipolar in origin. The primed and the unprimed letters are used to distinguish two varieties of ions, the unprimed component is responsible for the resonance.

The first term of Eq. (1) can be neglected, because of the large distances between impurity ions, usually 0.1-0.5 mol % of these ions are used.

The full width at half peak of a Gaussian distribution is given by expression [18]

$$\Delta H_{dip-ex} = (2.35)^2 h^2 \overline{\langle \Delta \nu^2 \rangle} / g^2 \mu_B^2. \tag{3}$$

Taking into account rapid motion of host spins which narrowing impurity resonance lines, Anderson and Weiss [19] and next Mitsuma [20] showed that EPR linewidths are given by the expression:

$$\Delta H_{1/2} = \frac{10}{3} 2\Delta H_{dip-ex}^2 / H_{mod},$$
 (4)

where  $H_{mod} = h/g' \mu_B \tau'_1$  (The factor 10/3 is assumed for extreme narrowing and the factor 2 is due to Loretzian shape of a narrowed resonance line.).

The combination of (1), (2), (3), and (4) gives the equation to calculate SLRT of host ions (for an external magnetic field being along  $\vec{z}$  axis [17] and if two different paramagnetic ions are present) taking into account a crystal environment [11]

$$\tau_{1}^{\prime} = \frac{9g^{2}\mu_{B}hf\Delta_{p}H_{p}}{110.45g^{\prime}S^{\prime}(S^{\prime}+1)} \times \frac{1}{NA_{p}^{2}+G^{2}\sum_{k^{\prime}}^{N}(1-3\gamma_{jk^{\prime}}^{2})^{2}r_{jk^{\prime}}^{-6}+2A_{p}G\sum_{k^{\prime}}^{N}(1-3\gamma_{jk^{\prime}}^{2})r_{jk^{\prime}}^{-3}},$$
(5)

where the primed components are used for host ions, whereas the unprimed ones for impurity ions,  $G = gg' \mu_B^2 \mu_o$ , g, g'are g-factors, S, S' are effective spins,  $r_{jk'}$ are distances between the j and k' ions,  $\gamma_{jk'}$  are direction cosines of  $\vec{r}_{jk'}$  with an external magnetic field,  $A_p = z_1 z_2 J_p$  ( $J_p = 0.53$  GHz is the pair exchange constant. The exchange constants for LEF and LDF [10] are experimentally determined to be in agreement with 4.2 GHz for LiTbF<sub>4</sub> [21].), N(= 8) is a number of nearest and next-nearest neighbors,  $\Delta H_{pp}$  is an experimental value of EPR peak-to-peak linewidth, and f is the factor equal to 1.73 for a Lorentzian lineshape and to 1.18 for a Gaussian lineshape.

A calculation of  $r'_1$  using (5) requires very precise crystal-structure data, which are determined for the I4<sub>1</sub>/a tetragonal symmetry of LiREF<sub>4</sub> crystals using crystal data of Ref. [14]. Fig. 3 shows nearest (1-4) and next-nearest (5-8) neighbor RE<sup>3+</sup> ions of a impurity Gd<sup>3+</sup> ion. The distances from Gd<sup>3+</sup> to 1-4 nearest and to 5-8 next-nearest neighbor RE<sup>3+</sup> ions are  $r_{1,2,3,4} \equiv R'_1 = 0.3717$  nm and  $r_{5,6,7,8} \equiv R'_2 = 0.5160$  nm for LEF, whereas 0.3747 nm and 0.5190 nm for LDF, respectively. The g' = 3.137 and 1.112 for Er<sup>3+</sup> and Dy<sup>3+</sup> in LiYF<sub>4</sub>, respectively [7], whereas g's can be found for Gd<sup>3+</sup>-doped LEF and LDF in Table 2 and for LiYbF<sub>4</sub>(Gd<sup>3+</sup>) in Ref. [15]. The energy levels of ground state of Er<sup>3+</sup>(<sup>4</sup>I<sub>15/2</sub> level splits to doublets placed at 0, 27, 44, 95, 452, 517, 572, and 613 cm<sup>-1</sup>) [10] in LiErF<sub>4</sub> and Dy<sup>3+</sup>(<sup>6</sup>H<sub>15/2</sub> splits to doublets placed at 0, 42.3, 61.8, 110.9, 154.9, 210.7, 272.3, and 468.5 cm<sup>-1</sup>) [22] in DyF<sub>3</sub> (assumed



Fig. 3. The configuration of four nearest (k' = 1 - 4) and four next-nearest (k' = 5 - 8) neighbor RE<sup>3+</sup> ions around the impurity Gd<sup>3+</sup> ion in a half-unit cell of LiREF<sub>4</sub> crystal (RE = Er, Dy)

that energy level values for DyF<sub>3</sub> are close to those for LiDyF<sub>4</sub>) were used to evaluate effective spins S' = 7/2 and 9/2, respectively (related to the highest energy level which the population is in excess of 10% as determined from a Boltzmann distribution of population of energy levels). The Yb<sup>3+</sup> doublets of  ${}^{2}F_{7/2}$  ground term in LiYbF<sub>4</sub> crystal [23] are at 0, 235, 366, and 456 cm<sup>-1</sup>. SLRT's have been presently calculated from (5) to be  $2.7 \times 10^{-15}$ ,  $1.0 \times 10^{-15}$ , and  $2.2 \times 10^{-15}s$  using the room-temperature linewidths of 86, 82, and 24.5 mT (transition of  $5/2 \leftrightarrow 3/2$ ;  $\vec{H} \parallel \vec{z}$ ) for LDF, LEF, and LiYbF<sub>4</sub> [11], respectively. SLRT's calculated from equation which is valid only for cubic lattice with one kind of paramagnetic ions, to be  $2.9 \times 10^{-11}$ ,  $0.16 \times 10^{-11}$ , and  $2.5 \times 10^{-11}s$  for LDF, LEF, and LiYbF<sub>4</sub>, respectively, are different by four orders of magnitude (longer) from SLRT's calculated using (5). The determined SLRT of Gd<sup>3+</sup>-doped NdF<sub>3</sub> crystal [24] (N = 12) to be  $\tau'_1(Nd) = 1.73 \times 10^{-15}s$  is slightly different from those of LiREF<sub>4</sub> and lead to the conclusion that interactions are as strong as in the former. The spectroscopic properties of  $RE^{3+}$  ions influence also SLRT.

### SPIN-HAMILTONIAN PARAMETERS AND SUPERPOSITION MODEL

Angular variation of EPR lines for  $Gd^{3+}$ -doped LiREF<sub>4</sub> crystals in zx plane (Fig. 4) at room temperature are similar to those of  $LiY_{1-x}Yb_xF_4(Gd^{3+})$  [15], however, because of very broad lines in the former, the spin-Hamiltonian parameters are determined with greater errors than in the latter. The spin-Hamiltonian was used to be the same as in Ref. [15]; fitted values of spin-Hamiltonian parameters are presented in Table 2.

Table 2. The values of spin-Hamiltonian parameters for Gd<sup>3+</sup>-doped LiREF<sub>4</sub> crystals (RE = Er, Dy) at room temperature. The parameters  $b_n^m$  are expressed in GHz,  $g_{zz}$ ,  $g_{xx}$  are dimensionless,  $\overline{N}$  represents a total number of line positions simultaneously fitted, and  $\chi^2$  is in GHz<sup>2</sup>

	LiDyF4	LiErF <sub>4</sub>
g 2 2	$1.923 \pm 0.042$	$1.934 \pm 0.042$
gss	$2.018 \pm 0.042$	$2.016 \pm 0.042$
62	$-2.325 \pm 0.061$	$-2.331 \pm 0.053$
60 B	-0.055 ± 0.025	$-0.037 \pm 0.022$
b4	$0.182 \pm 0.074$	0.256 ± 0.081
6 <sup>0</sup>	-0.010 ± 0.033	$-0.024 \pm 0.025$
6	$-0.013 \pm 0.182$	-0.026 ± 0.183
ทั	75	81
$\chi^2$	3.4	3.8

The z axis coincides with the [001] crystal axis, where the spectrum shows the maximum of overall splitting. The x and y axes are assumed to be in the perpendicular plane to the z axis in correspondence to equivalent positions of the maximal splitting in the xy plane. Considering positions of the minimal splitting in the xy plane and fitting the experimental data, the same absolute values (in error bars), but the opposite signs [25] should be obtained for the  $b_4^4$  and  $b_6^4$ , as compared to positions of the maximal splitting in the xy plane. The fitting of the experimental data, e.g., for the minimal splitting in LEF crystal, gives the  $b_4^4$  (= -0.45±0.14 GHz) and  $b_6^4$ (= 0.40±0.19 GHz) ( $\chi^2$  = 4.4 GHz<sup>2</sup>).

In order to understand a nature of crystalline field in scheelite crystals and a deformation due to an introduction of  $Gd^{3+}$  ion in a host lattice, it is necessary to analyze the obtained data using a point-charge or a superposition model. The point-charge model gives for LiYF<sub>4</sub>(Gd<sup>3+</sup>) the value of  $b_2^0 \simeq 6.1457$  GHz [26], which is 2.5 times greater than the experimental  $b_2^0$  value and has the reverse sign. On the other hand, the calculation following the superposition model requires the exact crystal structure data, i.e., the exact knowledge of ligand positions  $F^-$  around rare-earth ion, and one requires to take into account the lattice distortion, because the lattice as a whole protects changes produced by the substitution for smaller host lattice ions (Yb, Er, Y, Dy) by larger Gd<sup>3+</sup> ions.

Fig. 4. Angular variation of the EPR line positions for  $Gd^{3+}$ -doped LiErF<sub>4</sub> single crystal in the zx plane at room temperature. The various transitions ( $M \leftrightarrow M -$ 1) have been indicated as follows: A ( $-5/2 \leftrightarrow -7/2$ ), B ( $-3/2 \leftrightarrow -5/2$ ), C (-1/2 $\leftrightarrow -3/2$ ), D ( $1/2 \leftrightarrow -1/2$ ), E ( $3/2 \leftrightarrow 1/2$ ), F (5/2 $\leftrightarrow 3/2$ ), G ( $7/2 \leftrightarrow 5/2$ ), I (DPPH). The continuous lines connect data points belonging to the same tran-

sitions



The longer distance of four  $F^-$  ions to rare-earth ion ( $R_2 = 0.2321$  nm) and the vertical angle  $\theta_2(= 142^{\circ}22')$  calculated from the conventional neutron-diffraction structure analysis data given by Als-Nielsen *et al.* [27] for LiTbF<sub>4</sub> crystal are only greater by 0.2 and 0.05% respectively, than those of calculated for this crystal using lattice constants ( $R_2 = 0.2317$  nm and  $\theta_2 = 142^{\circ}18'$ ). This strongly support the property of presently evaluated crystal data (used to calculations under superposition model), given in Table 3 for other LiREF<sub>4</sub> crystals.

From the condition of  $\overline{b}_4 = \overline{b}'_4$  it is possible to calculate directly  $t_4$  (the anomalous low mean over considered crystals value of  $t_4 \simeq -60$  is calculated without taking into consideration any distortion) and to evaluate the degree of vertical angles decrease of eight neighboring  $F^-$  ions  $\theta_1^i$  and  $\theta_2^{i+4}$  (i = 1 to 4). The  $t_4(=-9)$  parameter is assumed for all crystals, which is the mean value of  $t_4$  determined from stress experiments in MeF<sub>2</sub>(Gd<sup>3+</sup>) (Me = Cd, Ca, Sr, Pb, and Ba) crystals [28], where environment is similar to presently studied;  $t_4(= 14)$  for REF<sub>4</sub>(Gd<sup>3+</sup>) (RE = La, Ce, Pr, Nd) [29], where environment is different.

Taking into account, that the difference between ionic radii of Gd<sup>3+</sup> and Er<sup>3+</sup>

	LiYbF4	LiErF	LiYF	LiDvF	LiTbF	LiGdF
	[4]	[3]	[30]	[3]	[27]	[3]
radius of						
RE <sup>3+</sup> (nm)	0.0858	0.0881	0.0896	0.0908	0.0923	0.0938
c/a	2.0630	2.0740	2.0780	2.0880	2.0950	2.1020
R <sub>1</sub> (nm)	0.2218	0.2231	0.2246	0.2249	0.2253	0.2267
$\theta_1$ (deg)	67°07'	67°00'	67°05'	66°50'	66°46'	66°40'
$\phi_1$ (deg)	-32°58'		-33°00'		(-48°00')	
$\chi_1$ (deg)	1°42'		1°30'		(2°07')	
$R_2$ (nm)	0.2269	0.2288	0.2293	0.2313	0.2321	0.2339
$\theta_2 \; (deg)$	141°52'	142°01'	142°03'	1 <b>42°14'</b>	142°22'	142°28'
$\phi_2$ (deg)	-37°29'		-36°59'		-53°37'	
$\chi_2$ (deg)	-2°49'		-2°29'		(-3°30')	
$R_o$ (nm)	0.2244	0.2260	0.2270	0.2278	0.2287	0.2298
62 (GHz)	-2.4812	-2.3310	-2.4863	-2.325		-2.2100°
a	-1.0928	-1.0844	-1.0900	-1.0740		-1.0632
ad	-0.5106	-0.9289	-0.6412	-0.9971		-1.0632
Ь	1.7122	1.7274	1.7310	1.7462		1.7655
bd	0.9860	1.5226	1.1622	1.6443		1.7655
с	-0.3680	-0.3814	-0.3720	-0.3982		
d	-1.0817	-1.0648	-1.0610	-1.0435		
e	12.5190	12.4781	12.5260	12.4271		
ſ	2.4953	2.4623	2.4660	2.4218		

Table 3. The structural data of LiREF<sub>4</sub> crystals determined, or cited from the data given in literature. The values in parentheses are only roughly estimated. The asterisk for  $b_2^0$  of LiGdF<sub>4</sub> marks the extrapolated value. The dimensionless  $a_d$  and  $b_d$  coordination factors are calculated using  $\theta_1$  and  $\theta_2$  for a distorted host lattice. For the definition of symbols see Ref. [15]

is 0.0057 nm, we can compute that, if this substitution increases the distances RE<sup>3+</sup> -  $F^-$  about 0.003 nm, then  $t_4$  parameter is changed by 1.3% only. The absolute value of  $t_4$  decreases by 50% for  $R_1 \equiv R_1 - 0.003$  nm and  $R_2 \equiv R_2 + 0.003$  nm, however, such a distortion is impossible in case of substitution of greater Gd<sup>3+</sup> ion for smaller rare-earth host lattice ion ( $t_4$  increases in reverse case, i.e., for  $R_1 + 0.003$  nm and  $R_2 \equiv R_2 - 0.003$  nm). The horizontal angles  $\phi_1$  and  $\phi_2$  contribute to  $t_4$  not much, in calculations under superposition model are used  $\chi_1$  and  $\chi_2$  angles (equal to a few degrees). The increase of the  $\chi_1$  absolute value by 0.5° and  $\chi_2$  one by 1°, which is the rule [30], change  $t_4$  by ~5%. The similar situation takes place for  $t_2$  parameter which is mainly influenced by the change of  $\theta_1$  and  $\theta_2$ , because the increase of  $R_1$  and  $R_2$  by  $(r_{Gd} - r_{Dy}) = 0.003$  nm changes  $t_2$  parameter maximally by 0.5% [the increase of  $R_1$  and  $R_2$  by  $(r_{Gd} - r_{Yb}) = 0.008$  nm changes  $t_2$  by 1.3%].

The conclusion from above discussion is the following: it is sufficient to take into account the prevailing part of the distortion produced by the decrease of  $\theta_1$  and  $\theta_2$  vertical angles. The determined (from superposition model) decrease of vertical angles  $\theta_1$  and  $\theta_2$  of eight fluorines around  $\mathrm{Gd}^{3+}$  ion are as follows:  $\Delta \theta_{RE} = 7.5^\circ, 5.5^\circ, 2^\circ, \text{ and } \simeq 1^\circ$  for RE = Yb, Y, Er, and Dy, respectively. The values of  $\Delta \theta_{Yb} = 7.5^\circ$  and  $\Delta \theta_Y = 5.5^\circ$  are determined more exactly because of smaller errors of experimental spin-Hamiltonian parameters.

Table 4 shows the calculated values of  $b_2(R_o)$  intrinsic parameters in case of an

				-	
t2	LiYbF4	LiErF <sub>4</sub>	LiYF4	LiDyF	LiGdF4
-6	-3.0557	-2.7209	-3.0419	-2.5464	-2.2760
	-4.2948	-2.9895	-3.9272	-2.6667	
-4	-3.3196	-2.9694	-3.2789	-2.7939	-2.5096
	-4.5660	-3.2494	-4.1750	-2.9194	
-2	-3.6315	-3.2657	-3.5544	-3.0922	-2.7936
	-4.8715	-3.5568	-4.4544	-3.2223	
0	-4.0058	-3.6256	-3.8788	-3.4591	-3.1468
	-5.2184	-3.9261	-4.7721	-3.5925	
1	-4.2226	-3.8362	-4.0635	-3.6761	-3.3579
	-5.4101	-4.1402	-4.9479	-3.8102	
2	-4.4636	-4.0721	-4.2663	-3.9215	-3.5985
	-5.6158	-4.3785	-5.1366	-4.0552	
3	-4.7333	-4.3383	-4.4899	-4.2011	-3.8753
	-5.8372	-4.6452	-5.3400	-4.3331	
4	-5.0370	-4.6412	-4.7378	-4.5229	-4.1971
	-6.0760	-4.9459	-5.5594	-4.6509	
5	-5.3816	-4.9888	-5.0140	-4.8972	-4.5762
	-6.3345	-5.2875	-5.7972	-5.0181	
6	-5.7760	-5.3920	-5.3239	-5.3380	-5.0292
	-6.6152	-5.6791	-6.0558	-5.4471	
7	-6.2321	-5.8652	-5.6740	-5.8650	-5.5805
	-6.9212	-6.1326	-6.3379	-5.9551	
8	-6.7655	-6.4287	-6.0728	-6.5062	-6.2659
	-7.2562	-6.6641	-6.6470	-6.5663	
9	-7.3978	-7.1110	-6.5312	-7.3036	-7.1416
	-7.6244	-7.2955	-6.9873	-7.3160	
10	-8.1595	-7.9543	-7.0636	-8.3222	-8.2997
	-9.0211	-9.0591	7 2627	-9 2572	

Table 4. The calculated values of  $\bar{b}_2(R_o)$  for LiREF<sub>4</sub> crystals in case of the undistorted (upper value) and the distorted (lower value) host lattice. The distortion of  $\theta_1^i \equiv \theta_1 - \Delta \theta_{RE}$  and  $\theta_2^{i+4} \equiv \theta_2 - \Delta \theta_{RE}$  (i = 1 to 4 for fluorine ions) is introduced using the evaluated values of  $\Delta \theta_{Vb} = 7.5^\circ$ ,  $\Delta \theta_V = 5.5^\circ$ ,  $\Delta \theta_{Fr} = 2^\circ$ ,  $\Delta \theta_{Du} \simeq 1^\circ$ , and  $\Delta \theta_{Gd} = 0^\circ$ 

undistorted and a distorted environment of Gd<sup>3+</sup> ion. The decrease of the intrinsic parameter  $\overline{b}_2$  absolute values for LiREF<sub>4</sub>(Gd<sup>3+</sup>) along the rare-earth series relates to their differences between Gd<sup>3+</sup> and RE<sup>3+</sup> ionic radii. Values of  $\overline{b}_2(R_o)$  are more consistent for  $t_2 = 5.5$  and 8 (Table 4) in case of an undistorted and a distorted lattice, respectively. In addition, in order to determine  $t_2$  parameter the procedure from Ref. [29] was followed. The -2.210 GHz value for LiGdF4 was extrapolated from the linear dependence of  $b_2^0$  on difference between Gd<sup>3+</sup> and RE<sup>3+</sup> ionic radii [31] for LiYbF<sub>4</sub>, LEF, and LDF crystals. A Gd<sup>3+</sup> ion in LiGdF<sub>4</sub> is in an undistorted environment, whereas in LiREF4 crystals there are some distortions. Following the procedure from [29] one can evaluate  $t_2(=5)$  as the mean value for an undistorted lattice, and  $t_2 = 7.5, 6.5, 7.5$ , and 7.0 for RE = Yb, Er, Y, and Dy, respectively, therefore  $t_2(=7\pm 1)$  as the mean value for a distorted lattice. These  $t_2$  values are greater than those assumed by Newman and Urban [32]  $(t_2 = 1)$  accounted for cancellation effects, and by Vishwamittar and Puri [33]  $(t_2 = 2.5)$  for scheelite type crystals MeWO<sub>4</sub>, MeMoO<sub>4</sub> (Me = Ca, Sr, Ba, Pb). The values of  $b_2^0$ in MeWO<sub>4</sub> and MeMoO<sub>4</sub> are almost the same as in LiREF<sub>4</sub>(Gd<sup>3+</sup>). The  $\overline{b}_2(R_o)$  for  $t_2 = 5$  (Table 4) are consistent with those in the range from -4.7 to -5.6 GHz determined for scheelite MeWO<sub>4</sub> and MeMoO<sub>4</sub> crystals [33]. For the same crystals N e w m a n and U r b an [32] gives somewhat greater values of  $\bar{b}_2$  in the range from -6.3 to -5.6 GHz which are consistent with those calculated presently for  $t_2 = 7$  (see Table 4). On the other hand, the values of  $\bar{b}_2(R_o)$  for REF<sub>3</sub>(Gd<sup>3+</sup>) (RE = La, Ce, Pr, Nd) [29], are in the range from -4.5 to -5.3 GHz, whereas  $b_2^0$ 's are in the range 0.7-0.8 GHz (for LiREF<sub>4</sub>  $b_2^0$ 's are in the range from -2.3 to -2.5 GHz). The  $t_2 = 8 \pm 1$  is determined for Fe<sup>3+</sup> ion substituted for Ti<sup>4+</sup> in BaTiO<sub>3</sub> under superposition model analysis [34]. Concluding, presently are determined  $t_2 = 7 \pm 1$  and  $t_4 = -9 \pm 2$  for LiREF<sub>4</sub>(Gd<sup>3+</sup>) crystals.

#### CONCLUSIONS

In the light of the present study on LiREF<sub>4</sub>(Gd<sup>3+</sup>) crystals there is the distortion produced by an incorporation of the larger Gd<sup>3+</sup> ion into a host lattice. The distortion consists mainly in the decrease of vertical angles of eight fluorines  $F^$ around Gd<sup>3+</sup> ion. The series of three — four crystal lattices analyzed presently constitute too small sample for a more reliable test, however, the distortion effect now can be understood. It would be very helpful to determine  $t_2$  and  $t_4$  parameters directly from a stress experiment.

#### REFERENCES

- Jones D. A., Cockayne B., Clay R. A., Forrester P. A., J. Cryst. Growth, 30 (1975), 21.
- [2] Cockayne B., Lloyd K. H., Abell J. S., Harris I. R., Jones D. A., J. Cryst. Growth, 36 (1976), 205.
- [3] Keller C., Schmutz H., J. Inorg. Nucl. Chem., 27, (1965), 900.
- [4] Thoma R. E., Brunton G. D., Penneman R. A., Keenan T. K., Inorg. Chem., 9 (1970), 1096.
- [5] Ivanova I. A., Morozov A. M., Petrova M. A., Podkolzina I. G., Feofilov P. P., Izv. Akad. Nauk SSSR, Neorgan. Materialy, 11 (1975), 2175; Inorg. Materials (USA), 11 (1975), 1868.
- [6] Magarino J., Tuchendler J., Beauvillain P., Laursen I., Phys. Rev., B21 (1980), 18.
- [7] Sattler J. P., Nemarich J., Phys. Rev., B4 (1971), 1.
- [8] Tuchendler J., Phys. Rev., B33 (1986), 6054.
- [9] Hansen P. E., Nevald R., Phys. Rev., B16 (1977), 146.
- [10] Hansen P. E., Johansson T., Nevald R., Phys. Rev., B12 (1975), 5315.
- [11] Misiak L. E., Misra S. K., Orhun U., Phys. Stat. Sol., B154 (1989), 249.
- [12] Gmelin Handbuch der Anorganischen Chemie Seltenerdelemente, Bergmann H., (ed.), Teil C3, 39, Springer-Verlag, Berlin-Heidelberg, New York 1976.
- [13] Misiak L. E., Mikolajczak P., Subotowicz M., Phys. Stat. Sol., A97 (1986), 353.
- [14] McClune W. F., Powder Diffraction File, Inorganic Compounds, Published by the Joint Committee on Powder Diffraction Standards — International Center for Diffraction Data, (Managing ed.), Pennsylvania 1978.
- [15] Misiak L. E., Misra S. K., Mikolajczak P., Phys. Rev., B38 (1988), 8673.

- [16] Abragam A., Bleaney B., Electron paramagnetic resonance of transition ions, Clarendon Press, Oxford 1970.
- [17] Van Vleck J. H., Phys. Rev., 74 (1948), 1168.
- [18] Misra S. K., Orhun U., Phys. Rev., B39 (1989), 2856.
- [19] Anderson P. W., Weiss P. R., Rev. Mod. Phys., 25 (1953), 269.
- [20] Mitsuma T., J. Phys. Soc. Jpn., 17 (1962), 128.
- [21] Als-Nielsen J., Holmes L. M., Guggenheim H. J., Phys. Rev. Lett., 32 (1974), 610.
- [22] Xu L. W., Crosswhite H. M., Hessler J. P., J. Chem. Phys., 81 (1984), 698.
- [23] Kupchikov A. K., Malkin B. Z., Natadze A. L., Ryskin A. I., Sov. Phys.-Solid State (USA), 29 (1987), 1913; trans. Fiz. Tverd. Tela (USSR), 29 (1987), 3335.
- [24] Korczak W., Paradowski M. L., Misiak L. E., Phys. Stat. Sol., B165 (1991), 203.
- [25] Amoretti G., Giori D. C., Varacca V., Spirlet J. C., Rebizant J., Phys. Rev., B20 (1979), 3573.
- [26] Vaills Y., Buzaré J. Y., Gesland J. Y., Solid State Commun., 45 (1983), 1093.
- [27] Als-Nielsen J., Holmes L. M., Krebs Larsen F., Guggenheim H. J., Phys. Rev., B12 (1975), 191.
- [28] Kuriata J., Pastusiak W., Acta Phys. Pol., A66 (1984), 627.
- [29] Misra S. K., Mikolajczak P., Lewis N. R., Phys. Rev., B24 (1981), 3729.
- [30] Vishwamittar, Puri S. P., J. Phys. C: Solid State Phys., 7 (1974), 1337.
- [31] Sharma V. K., J. Chem. Phys., 54 (1971), 496.
- [32] Newman D. J., Urban W., Adv. Phys., 24 (1975), 793.
- [33] Vishwamittar, Puri S. P., J. Chem. Phys., 61 (1974), 3720.
- [34] Siegel E., Müller K. A., Phys. Rev., B19 (1979), 109.