EPR OF Gd$^{3+}$-DOPED La$_{0.9}$Nd$_{0.1}$F$_3$ CRYSTAL:
SPIN–PHONON INTERACTIONS
AND SPIN–LATTICE RELAXATIONS

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The X-band EPR study of Gd$^{3+}$-doped La$_{0.9}$Nd$_{0.1}$F$_3$ single crystal in
the temperature range 4.2–295 K is carried out in order to investigate crys-
tal field effects, the Gd$^{3+}$ spin–phonon interactions, as well as Gd$^{3+}$ and
Nd$^{3+}$ spin–lattice relaxation times. The local distortions at 4.2 K of the po-
sitions of the eight F$^-$ ions surrounding the Gd$^{3+}$ ion in the La$_{0.9}$Nd$_{0.1}$F$_3$
crystal were determined from comparison of the theoretical with the experi-
mental spin-Hamiltonian parameters. The spin–phonon interactions can be
described by the Einstein model, which better characterizes the behavior
of paramagnetic centers in LaF$_3$ and La$_{0.9}$Nd$_{0.1}$F$_3$ crystals than the De-
bye model. It is suggested, from the rotational invariance mechanism for
phonon-induced contributions to spin-Hamiltonian parameters, that the ro-
tational contributions are much smaller than those from the strain.

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1. Introduction

The REFS (RE = Ce, Nd) crystals are expected to serve as heavy, fast, and
radiation hard scintillators for calorimetry at future colliders [1, 2]. These crystals
are also used as laser materials [3, 4].

The electron paramagnetic resonance (EPR) measurements of Gd$^{3+}$-doped
LaF$_3$ and NdF$_3$ single crystals in the temperature range 4.2–295 K were previ-
ously performed by Misra et al. [5, 6]. The EPR linewidths were measured in
Gd$^{3+}$-doped La$_x$Nd$_{1-x}$F$_3$ (0 ≤ x ≤ 1) single crystals in the temperature range
from 77 to 510 K [7, 8], whereas the magnetic susceptibility in the tempera-
ture range 1.5–300 K [9]. A temperature EPR (X-band) study of Gd$^{3+}$-doped
(0.1 mol%) La$_{0.9}$Nd$_{0.1}$F$_3$ single crystal has been carried out presently in order to

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investigate structural and crystal field effects, spin-phonon interactions, and dipolar interactions between Gd\(^{3+}\) and Nd\(^{3+}\) ions. The above sample is the only mixed crystal studied in detail for which well-resolved EPR spectra can be recorded down to liquid-helium temperature.

2. Sample preparation and crystal structure

The La\(_x\)Nd\(_{1-x}\)F\(_3\) single crystals doped with Gd\(^{3+}\) (0.1 mol%) were grown by a modified Bridgman–Stockbarger method [10]. They were transparent and cleft easily in the cleavage planes (001) and (110).

LaF\(_3\) and NdF\(_3\) single crystals have a tysonite structure with the trigonal space-group classification \(P\bar{3}c1\) (\(D\bar{3}d\) trigonal symmetry with a hexamolecular unit cell) [11, 12]. The site symmetry of the La\(^{3+}\) and the Nd\(^{3+}\) ions is \(C_2\). The twofold axis is perpendicular to the threefold axis \(C_3\) in the unit cell. The crystallographic \(a\) axis forms an angle of 30° with respect to one of the three \(C_2\) axes, where the two remaining \(C_2\) axes form an angle of 90° and 150° with respect to \(a\) axis, respectively. The crystallographic \(c\) axis is parallel to the \(C_3\) axis, and perpendicular to the three \(C_2\) axes. There are six molecules per unit cell. The unit cell parameters for LaF\(_3\) are as follows: \(a = 0.7186 \pm 0.0001 \) nm, \(c = 0.7352 \pm 0.0001 \) nm, while for NdF\(_3\) are: \(a = 0.7032 \pm 0.0001 \) nm and \(c = 0.7200 \pm 0.0001 \) nm at room temperature [10]. Since the values of \(a\) and \(c\) and the distances of the rare-earth ions in LaF\(_3\) and NdF\(_3\) are quite close to each other, it is assumed that La\(_x\)Nd\(_{1-x}\)F\(_3\) single crystals also have a tysonite structure, with the \(a\) and \(c\) dimensions scaled in proportion to \(x\) between limit values of lattice constants in LaF\(_3\) and NdF\(_3\) [13].

3. Experimental details

The experimental arrangement has been described elsewhere [14]. The EPR spectra of the Gd\(^{3+}\) ions in La\(_{0.9}\)Nd\(_{0.1}\)F\(_3\) single crystal were recorded with the external magnetic field \(B\) oriented in the \(ZX\) plane. The \(Z\) (\(|| a\)) axis, along which the overall splitting of EPR lines has a maximum, lies in the cleavage plane (001) and is perpendicular to the (110) plane. The \(X\) axis is defined to be the direction of the external magnetic field for which the next-largest extremum occurs. The \(Y\) (\(|| c\)) axis is defined to be the direction for which the minimum splitting of EPR lines is observed.

The angular variation for Gd\(^{3+}\)-doped La\(_{0.9}\)Nd\(_{0.1}\)F\(_3\) in the \(ZX\) plane at 295 K is shown in Fig. 1. These variations in the \(ZX\) plane at room and liquid nitrogen temperatures were found to display three maxima and minima of the three centers placed by 60° from each other. The six ions in the unit cell were found to be magnetically equivalent in pairs, so that there are three magnetically nonequivalent sites of Gd\(^{3+}\) ions forming three observed centers [15]. Thus, EPR spectra are consistent with the rhombic \(C_2\) site symmetry for the Gd\(^{3+}\) ion in the \(D\bar{3}d\) trigonal symmetry with a hexamolecular unit cell. However, only two centers were observed at liquid helium temperature: the Gd\(^{3+}\)(1) center which exhibits the twofold repetition pattern about the \(c\) axis (\(Y\) axis) and the Gd\(^{3+}\)(2) center exhibiting the site symmetry close to monoclinic \(C_2\). It means that the crystal field is changed with lowering the temperature, as a result of the temperature-induced distortion of the crystal lattice [15].
Fig. 1. Angular variation of the EPR lines positions in the ZX plane for Gd$^{3+}$-doped La$_{0.9}$Nd$_{0.1}$F$_3$ single crystal at room temperature. The dots represent the experimental resonant line positions of $\Delta M = \pm 1$ transitions and the solid lines (as a guide for the eye) are smooth curves that connect data points from the same transitions, corresponding to one set (called Gd$^{3+}$(1) center) of magnetically equivalent ions. The circles, which represent the experimental line positions of the Gd$^{3+}$(2) center, are not connected. The transitions are indicated as follows: $A(\frac{7}{2} \leftrightarrow \frac{5}{2})$, $B(\frac{5}{2} \leftrightarrow \frac{3}{2})$, $C(\frac{3}{2} \leftrightarrow \frac{1}{2})$, $D(\frac{1}{2} \leftrightarrow -\frac{1}{2})$, $E(-\frac{1}{2} \leftrightarrow -\frac{3}{2})$, $F(-\frac{3}{2} \leftrightarrow -\frac{5}{2})$, $G(-\frac{5}{2} \leftrightarrow -\frac{7}{2})$.

The average linewidths (peak-to-peak of the first derivative lineshape) $\Delta B_{pp}$ of the seven EPR lines characterizing the rhombic $C_{2v}$ site symmetry of Gd$^{3+}$ in La$_{0.9}$Nd$_{0.1}$F$_3$ (for $B \parallel Z$) are equal to $13.8 \pm 0.8$ mT, $10.8 \pm 0.8$ mT, $9.4 \pm 0.6$ mT, $8.5 \pm 0.6$ mT, and $8.1 \pm 0.6$ mT at 4.2, 22, 50, 77, and 295 K, respectively. In LaF$_3$ average $\Delta B_{pp}$ are about $2.5 \pm 0.3$ mT in the temperature range 4.2–295 K [5].
4. Spin-Hamiltonian parameters (SHP) and superposition model calculations

The spin Hamiltonian describing Gd$^{3+}$ ion in the rhombic $C_{2v}$ symmetry of the crystal field is given as

$$\mathcal{H} = \tilde{g}_B \mu_B B S + \sum_{m=0,2} \frac{1}{3} b_{2}^{m} O_{2}^{m} + \sum_{m=0,2,4} \frac{1}{60} b_{4}^{m} O_{4}^{m} + \sum_{m=0,2,4,6} \frac{1}{1260} b_{6}^{m} O_{6}^{m}. \quad (1)$$

The symbols have their usual meaning as defined by Abragam and Bleaney [16]. The $S (= \frac{7}{2})$ is the electron spin of the Gd$^{3+}$ ion. The eleven SHP's for Gd$^{3+}$ in La$_{0.9}$Nd$_{0.1}$F$_3$ single crystal were evaluated using a least-squares fitting procedure [17] for fitting simultaneously all resonant line positions recorded in the ZX plane (Table I).

**TABLE I**

Values of the spin-Hamiltonian parameters in Gd$^{3+}$-doped La$_{0.9}$Nd$_{0.1}$F$_3$ single crystal at various temperatures. The $b_{i}^{m}$ parameters are expressed in GHz, while $g_{zz}$ and $g_{xx}$ are dimensionless; $n$ represents the total number of line positions simultaneously fitted. $SMD$ [GHz$^2$] = $\sum_j (|\Delta E_j| - h\nu_j)^2$, where $\Delta E_j$ is the calculated energy difference between levels participating in resonance for the $j$-th resonance magnetic field, and $h\nu_j$ is the microwave energy. The coefficient $\alpha$ represents the admixture of state $^6P_{7/2}$ in the state $^8S_{7/2}$.

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>295</th>
<th>77</th>
<th>50</th>
<th>22</th>
<th>4.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_{zz}$</td>
<td>1.993 ± 0.002</td>
<td>1.983 ± 0.003</td>
<td>1.998 ± 0.013</td>
<td>1.991 ± 0.013</td>
<td>1.963 ± 0.013</td>
</tr>
<tr>
<td>$g_{xx}$</td>
<td>1.990 ± 0.002</td>
<td>1.988 ± 0.004</td>
<td>1.971 ± 0.012</td>
<td>1.981 ± 0.012</td>
<td>1.999 ± 0.012</td>
</tr>
<tr>
<td>$b_{2}^{0}$</td>
<td>0.696 ± 0.003</td>
<td>0.698 ± 0.003</td>
<td>0.674 ± 0.011</td>
<td>0.647 ± 0.009</td>
<td>0.652 ± 0.005</td>
</tr>
<tr>
<td>$b_{2}^{2}$</td>
<td>-0.121 ± 0.009</td>
<td>-0.045 ± 0.014</td>
<td>-0.155 ± 0.032</td>
<td>-0.167 ± 0.028</td>
<td>-0.140 ± 0.021</td>
</tr>
<tr>
<td>$b_{4}^{0}$</td>
<td>0.017 ± 0.001</td>
<td>0.017 ± 0.001</td>
<td>0.021 ± 0.004</td>
<td>0.014 ± 0.003</td>
<td>0.022 ± 0.001</td>
</tr>
<tr>
<td>$b_{4}^{4}$</td>
<td>0.045 ± 0.007</td>
<td>0.027 ± 0.009</td>
<td>0.024 ± 0.015</td>
<td>0.018 ± 0.012</td>
<td>0.013 ± 0.012</td>
</tr>
<tr>
<td>$b_{6}^{0}$</td>
<td>0.035 ± 0.011</td>
<td>0.065 ± 0.015</td>
<td>0.070 ± 0.031</td>
<td>0.072 ± 0.025</td>
<td>0.119 ± 0.019</td>
</tr>
<tr>
<td>$b_{6}^{6}$</td>
<td>-0.001 ± 0.001</td>
<td>-0.001 ± 0.001</td>
<td>0.003 ± 0.005</td>
<td>-0.000 ± 0.003</td>
<td>-0.006 ± 0.002</td>
</tr>
<tr>
<td>$n$</td>
<td>125</td>
<td>94</td>
<td>12</td>
<td>34</td>
<td>65</td>
</tr>
<tr>
<td>$SMD$</td>
<td>0.208</td>
<td>0.151</td>
<td>0.098</td>
<td>0.127</td>
<td>0.684</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.19 ± 0.02</td>
<td>0.24 ± 0.02</td>
<td>0.25 ± 0.09</td>
<td>0.24 ± 0.06</td>
<td>0.27 ± 0.03</td>
</tr>
</tbody>
</table>

The crystal-field parameters $b_{i}^{m}$ and the zero-field splittings $\Delta E$ of Gd$^{3+}$ in LaF$_3$ and La$_{0.9}$Nd$_{0.1}$F$_3$ hosts can be fitted in the temperature range 4.2–295 K to the quadratic function, $a + bT + cT^2$, where the values of $a$, $b$, $c$ are included in Table II. A quadratic temperature dependence of $b_{i}^{m}$ was observed for Gd$^{3+}$ in LiY$_{1-x}$Yb$_x$F$_4$ hosts [14, 18], assuming the temperature dependence is due to static distortion. On the other hand, vibrational effects of the crystal lattice cause temperature dependence of $b_{i}^{m}$ which can be fitted to the equation containing terms $\sum_i d_i \coth (\nu_i / 2kT)$, where $\nu_i$ are the lattice vibration frequencies and $d_i$ are
TABLE II
Values of the constants required to fit the spin-Hamiltonian parameters and the zero-field splitting: \((b_1^{m} \text{ and } \Delta E) = a + bT + cT^2\) in the temperature range 4.2–295 K. The \(\chi^2\) values characterizing these fits are also included.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a) [GHz]</th>
<th>(b) [GHz \cdot K^{-1}]</th>
<th>(c) [GHz \cdot K^{-2}]</th>
<th>(\chi^2) [GHz^2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(LaF_3)</td>
<td>(b_2^0)</td>
<td>0.7015</td>
<td>-0.6310 \times 10^{-5}</td>
<td>-1.042 \times 10^{-6}</td>
</tr>
<tr>
<td></td>
<td>(b_2^2)</td>
<td>-0.1110 \times 10^{-1}</td>
<td>-0.5737 \times 10^{-3}</td>
<td>0.1132 \times 10^{-5}</td>
</tr>
<tr>
<td></td>
<td>(b_4^0)</td>
<td>0.1885 \times 10^{-1}</td>
<td>-0.6496 \times 10^{-4}</td>
<td>0.106 \times 10^{-6}</td>
</tr>
<tr>
<td></td>
<td>(b_4^2)</td>
<td>0.5383 \times 10^{-1}</td>
<td>0.1284 \times 10^{-3}</td>
<td>-0.3059 \times 10^{-6}</td>
</tr>
<tr>
<td>(\Delta E)</td>
<td></td>
<td>8.3503</td>
<td>0.1286 \times 10^{-2}</td>
<td>-0.3955 \times 10^{-5}</td>
</tr>
<tr>
<td>(La_{0.9}Nd_{0.1}F_3)</td>
<td>(b_2^0)</td>
<td>0.6412</td>
<td>0.8183 \times 10^{-3}</td>
<td>-0.2146 \times 10^{-5}</td>
</tr>
<tr>
<td></td>
<td>(b_2^2)</td>
<td>-0.1750</td>
<td>0.1516 \times 10^{-2}</td>
<td>-0.4508 \times 10^{-5}</td>
</tr>
<tr>
<td></td>
<td>(b_4^0)</td>
<td>0.1894 \times 10^{-1}</td>
<td>-0.8995 \times 10^{-5}</td>
<td>7.6012 \times 10^{-8}</td>
</tr>
<tr>
<td></td>
<td>(b_4^2)</td>
<td>0.1434 \times 10^{-1}</td>
<td>0.1713 \times 10^{-3}</td>
<td>-0.2285 \times 10^{-6}</td>
</tr>
<tr>
<td></td>
<td>(b_4^4)</td>
<td>0.1063</td>
<td>-0.7255 \times 10^{-3}</td>
<td>0.1658 \times 10^{-5}</td>
</tr>
<tr>
<td>(\Delta E)</td>
<td></td>
<td>7.8387</td>
<td>0.8402 \times 10^{-2}</td>
<td>-0.2156 \times 10^{-4}</td>
</tr>
</tbody>
</table>

The weighting parameters \([19]\). These terms in temperature expansion of \(b_1^m(T)\) will then contain terms in \(T, T^2\), and higher powers.

The SHPs for Gd\(^{3+}\)-doped \(La_{0.9}Nd_{0.1}F_3\) single crystal can be analyzed using the superposition model \([20]\). In this model the \(b_1^m\) are expressed as linear superpositions of single-ligand contributions to the intrinsic parameters \(\tilde{b}_i(R_0)\) which depend on the ligand \(i\) as follows:

\[
b_1^m = \sum_i \tilde{b}_i(R_i)K_i^m(\theta_i, \varphi_i),
\]

where

\[
\tilde{b}_i(R_i) = \tilde{b}_i(R_0)(R_0/R_i)^n.
\]

The \(R_i\)'s in Eqs. (2) and (3) are the distances of the ligand F\(^-\) ions from the Gd\(^{3+}\) ion, \(\theta_i\) is the polar angle of the \(i\)-th F\(^-\) ion with respect to the \(Z\) axis, \(\varphi_i\) is the azimuthal angle of the \(i\)-th F\(^-\) ion with respect to the \(X\) axis and the \(R_0\) is a particular bond length, used as a reference (i.e. the minimum distance F\(^-\)-Gd\(^{3+}\)). The \(K_i^m\) in Eq. (2) are angular functions related to the spherical harmonics \([21]\).

For the \(La_{x}Nd_{1-x}F_3\) single crystals \((x = 1, 0.9, 0.1)\), we consider the nine nearest neighbor F\(^-\) ions to a Gd\(^{3+}\) ion which substitute for La\(^{3+}\), or Nd\(^{3+}\) ion (Fig. 2). The required positions \((R_i, \theta_i, \varphi_i)\) for La\(_3F_3\) and Nd\(_3F_3\) are given in Ref. \([6]\). In order to evaluate the intrinsic parameters \(\tilde{b}_i(R_0)\), the required lattice constants of \(La_{0.9}Nd_{0.1}F_3\) were estimated using Vegard's law \([13]\). The unit cell parameters of La\(_3F_3\) and Nd\(_3F_3\) were measured in the range 87–295 K \([10]\); those parameters at lower temperatures were obtained by extrapolation. The application of the superposition model requires exact knowledge of \(t_i\) intrinsic exponential parameters and positions of ligands around the paramagnetic ion. In our case we assumed that \(t_2 = 9\) and \(t_4 = 14\), which are the same as those for La\(_3F_3\) and Nd\(_3F_3\) hosts \([6]\). The angular coordinations of F\(^-\) ligands were changed independently in the calculations from Ref. \([6]\). We propose to change the angles...
Fig. 2. The projection of F− ions onto the XY plane showing the deformation of the La$_{x}$Nd$_{1-x}$F$_3$ host lattice at room temperature after the Gd$^{3+}$ ion substitute for the La$^{3+}$ or the Nd$^{3+}$ ion. The fluorine ion 1 is above the plane and sets the Z axis. The fluorine ions 6 and 7 lie above the XY plane (connection to the Gd$^{3+}$ ion marked by solid thick lines), whereas remaining fluorides lie below this plane (thin lines).

φ of F− pairs at the coordinates $(R, \theta, \varphi)$ and $(R, \theta, \varphi + 180^\circ)$ by the same values. In our calculations for Gd$^{3+}$-doped LaF$_3$, La$_{0.9}$Nd$_{0.1}$F$_3$ and NdF$_3$ we have attempted a direct fitting to the experimental parameters $b_{l}^{m}$, allowing the angular azimuthal coordinates for eight F− ligands (grouped in pairs) to vary within $\Delta \varphi = \pm 3.5^\circ$ ($\Delta \varphi = \varphi_{\text{final}} - \varphi_{\text{initial}}$). The deformation (rotation) is around the Z-axis; i.e. the F− ions rotate in the XY plane perpendicular to the crystallographic a axis, according to arrows in Fig. 2. Combining Eqs. (2) with (3) we were able to compute angles of local distortions ($\Delta \varphi$) of eight ligands grouped in pairs, intrinsic parameters $\tilde{b}_2$ and $\tilde{b}_4$, and theoretical values of $b_{l}^{m}$ at various temperatures (Table III). There is a good agreement of the calculated theoretical value with the experimental values of the $b_{l}^{m}$, supporting the above mechanism of distortion. There are local distortions (rotations) in opposite directions $\Delta \varphi$ for 2–3 and 4–5 F− pairs in La$_{0.9}$Nd$_{0.1}$F$_3$ (Fig. 2), contrary to those in LaF$_3$ and NdF$_3$ at room temperature, where only 4–5 F− pairs are rotated in direction opposite to other F− pairs. The rotation changes to opposite directions for 4–5 and 8–9 F− pairs are also observed in La$_{0.9}$Nd$_{0.1}$F$_3$ when temperature is lowering down to 4.2 K (see Table III). This confirms our earlier suggestion [15] that the crystal field in La$_{0.9}$Nd$_{0.1}$F$_3$ is changed with lowering temperature, as a result of temperature
TABLE III

The experimental (Exp.) and theoretical calculated from superposition model (Theo.) values of spin-Hamiltonian parameters $b_{ml}^\text{Exp.}$ (in GHz). The intrinsic parameters $b_i$ (in GHz) and the local distortion measured by azimuthal angles $\Delta \varphi_{i,j}$ (in degrees) from Gd$^{3+}$ ion to eight surrounding F$^-$ ions are also included; $R_0$ is the minimum distance between Gd$^{3+}$ -- F$^-$ ions. $\Delta E = E(\pm 7/2) - E(\pm 1/2)$ (in GHz) is the zero-field splitting.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LaF$_3$</th>
<th>La$<em>{0.9}$Nd$</em>{0.1}$F$_3$</th>
<th>NdF$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ [K]</td>
<td>295</td>
<td>295</td>
<td>77</td>
</tr>
<tr>
<td>0.694</td>
<td>0.707</td>
<td>0.696</td>
<td>0.691</td>
</tr>
<tr>
<td>$b_2^2$</td>
<td>-0.083</td>
<td>-0.082</td>
<td>-0.121</td>
</tr>
<tr>
<td>$b_4^2$</td>
<td>0.016</td>
<td>0.016</td>
<td>0.017</td>
</tr>
<tr>
<td>$b_4^4$</td>
<td>0.066</td>
<td>0.072</td>
<td>0.045</td>
</tr>
<tr>
<td>$b_4^6$</td>
<td>0.117</td>
<td>0.108</td>
<td>0.035</td>
</tr>
<tr>
<td>$\bar{b}_2$</td>
<td>-4.616 ± 0.050</td>
<td>-4.547 ± 0.046</td>
<td>-4.622 ± 0.080</td>
</tr>
<tr>
<td>$\bar{b}_4$</td>
<td>0.018 ± 0.001</td>
<td>0.015 ± 0.003</td>
<td>0.015 ± 0.002</td>
</tr>
<tr>
<td>$\Delta \varphi_{2,3}$</td>
<td>2.0 ± 0.5</td>
<td>-3.5 ± 0.5</td>
<td>-3.5 ± 0.5</td>
</tr>
<tr>
<td>$\Delta \varphi_{4,5}$</td>
<td>-3.5 ± 0.5</td>
<td>3.5 ± 0.5</td>
<td>1.0 ± 0.5</td>
</tr>
<tr>
<td>$\Delta \varphi_{6,7}$</td>
<td>3.5 ± 0.5</td>
<td>3.0 ± 0.5</td>
<td>2.5 ± 0.5</td>
</tr>
<tr>
<td>$\Delta \varphi_{8,9}$</td>
<td>2.0 ± 0.5</td>
<td>3.0 ± 0.5</td>
<td>-1.0 ± 0.5</td>
</tr>
<tr>
<td>$R_0$ [Å]</td>
<td>2.4187</td>
<td>2.4133</td>
<td>2.4089</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>8.39 ± 0.10</td>
<td>8.44 ± 0.04</td>
<td>8.36 ± 0.05</td>
</tr>
</tbody>
</table>

induced distortion of crystal lattice which causes the change of the site symmetry of Gd$^{3+}$ ion from $C_{2v}$ at 77 K towards close $C_2$ at 4.2 K. In LaF$_3$ any rotation changes to opposite directions are not observed with lowering temperature down to 4.2 K. The distortions of four fluorine pairs in the same directions as at 295 K only remain.

5. Debye and Einstein models of phonon spectrum

The major part of the temperature dependence of $b_2^2$ is due to the spin–phonon interaction effects [14]. The $b_2^2$ parameter changes its value as much as $\Delta b_2^2 = 0.0073$ GHz (100%) in the temperature range 87–295 K for LaF$_3$. Using the data of lattice constants dependent on temperature [10] and the equation for $b_2$ obtained from Eqs. (2), (3) we evaluate to 0.0024 GHz (about 33%) the contribution of thermal expansion to $\Delta b_2^2$. The remaining part (67%) of the $b_2^2$ change with temperature is due to the modulation of the crystal field by thermally excited phonons. Thus, the temperature dependence of the $b_2^2$ can be ascribed to the spin–phonon interaction. The Debye model in the long-wavelength limit gives [22, 23]:

$$b_2^2(T) = b_2^2(0) \left(1 - C \frac{T^4}{T_D^4} \int_0^\theta_D \frac{x^3}{e^{x/T} - 1} \, dx \right),$$

where $C$ is a constant and $\theta_D$ is the Debye temperature. On the other hand, the Einstein model involving a single oscillator gives

$$b_2^2(T) = b_2^2(0) \left\{1 - C \left[\coth \left(\frac{h\nu}{2kT}\right) - 1\right]\right\},$$

where $h\nu$ is energy of the interacting phonon mode. The parameters for the best fit of the $b_2^2$ to temperature in La$_{0.9}$Nd$_{0.1}$F$_3$ (LaF$_3$) for the Debye model are

$b_2^2(0) = 0.653 \pm 0.063$ GHz ($0.703 \pm 0.070$ GHz),

$C = 0.110 \pm 0.011$ ($-0.003 \pm 0.005$),

$\theta_D = 224 \pm 12$ K ($218 \pm 8$ K),

$\chi^2 = 1.05 \times 10^{-4}$ GHz$^2$ ($1.75 \times 10^{-4}$ GHz$^2$).

On the other hand, the parameters providing the best fit using the Einstein model are

$b_2^2(0) = 0.668 \pm 0.067$ GHz ($0.704 \pm 0.052$ GHz),

$C = -0.071 \pm 0.008$ ($0.022 \pm 0.008$),

$h\nu/k = 434 \pm 16$ K ($406 \pm 15$ K),

$\chi^2 = 1.58 \times 10^{-3}$ GHz$^2$ ($1.01 \times 10^{-4}$ GHz$^2$).

There is a good agreement between the $b_2^2(0)$ values of both models for La$_{0.9}$Nd$_{0.1}$F$_3$ and LaF$_3$ single crystals, confirming the correctness of the fitting. The effective Debye temperatures $\theta_D'$ for La$_{0.9}$Nd$_{0.1}$F$_3$ and LaF$_3$, equal to 224 K and 218 K, respectively, seem to be too low and it is concluded that the errors originate in the use of the Debye model. The energies of single Einstein oscillators $h\nu/k$
used in Eq. (5) are equal to 434 K and 406 K for La$_{0.9}$Nd$_{0.1}$F$_3$(Gd$^{3+}$) and LaF$_3$ (Gd$^{3+}$) respectively, and their values are more close to those 382 K and 387 K reported for LaF$_3$ and NdF$_3$ in Ref. [24]. The ratio of $\theta_D$ to $\hbar/\kappa$ is equal to 0.5 for both samples and means that the Einstein model yields an interaction with somewhat higher-frequency phonons than the Debye model. The ratio is different from that equal to 1.4 determined in LiYF$_4$ [25] and BaTiO$_3$ [23]. It is clear that in La$_{x}$Nd$_{1-x}$F$_3$(Gd$^{3+}$) system are produced higher frequency phonon modes than in LiYF$_4$(Gd$^{3+}$) and BaTiO$_3$(Cr$^{3+}$), presumably due to higher difference of masses of composite ions, as well as to more simple system than in case of LiYF$_4$ and BaTiO$_3$. It is concluded that average phonon spectrum shifts to somewhat shorter wavelength values in La$_{x}$Nd$_{1-x}$F$_3$(Gd$^{3+}$) ($x = 1, 0.9$) than long-wavelength limit described by the Debye model (Eq. (4)). The Einstein model of single oscillator better describes the paramagnetic center behavior, i.e., the temperature dependence of $\beta_2$ parameter, particularly in the case of the presence of one kind of paramagnetic ions (for Gd$^{3+}$-doped LaF$_3$ crystal). Further, the average energy of thermally excited optical phonons is presently determined to be 282 cm$^{-1}$ for Gd$^{3+}$-doped LaF$_3$ and 302 cm$^{-1}$ for Gd$^{3+}$-doped La$_{0.9}$Nd$_{0.1}$F$_3$. The optical phonons of $E_g$ symmetry were observed at 293, 299.8 and 315.1 cm$^{-1}$ in LaF$_3$ [26]. The Stokes vibronic emission lines in Gd$^{3+}$-doped LaF$_3$ at 4.2 K are reported to be 179, 289, 318, 362, and 433 cm$^{-1}$ [27]. Further, in Raman spectra of LaF$_3$ and NdF$_3$ were observed strong "phonon $E_g$ type" bands at 290 cm$^{-1}$ in LaF$_3$, and at 314 cm$^{-1}$ in NdF$_3$ [28]. Taking into account the above comparison, our estimation of optical phonons energy from EPR data is in sufficiently good agreement with those given in the literature.

The average velocity of sound $v_m$ can be estimated from the relation [29]:

$$v_m = \frac{\theta_D}{\hbar} \left( \frac{3qN\rho}{4\pi M} \right)^{1/3},$$

where $\rho$ is the density of LaF$_3$ (5.94 g cm$^{-3}$) or La$_{0.9}$Nd$_{0.1}$F$_3$ (6.16 g cm$^{-3}$), $q$ is the number of atoms in the molecule (4 in these crystals), $N$ is the Avogadro number and $M$ is the molar mass.

The calculated velocities of sound $v_m$ from Eq. (6), using $\theta_D$ ($= \hbar/\kappa$) equal to 406 K for LaF$_3$ and to 434 K for La$_{0.9}$Nd$_{0.1}$F$_3$, are $3.26 \times 10^5$ cm s$^{-1}$ and $3.45 \times 10^5$ cm s$^{-1}$, respectively. The velocity of sound in the XY plane of LaF$_3$ at room temperature was calculated in Ref. [24] as equal to 2.78 $\times 10^5$ cm s$^{-1}$. Schulz and Jeffries [30] measured the velocity of sound in LaF$_3$ single crystal and received in average $3.44 \times 10^5$ cm s$^{-1}$. Our calculated $v_m$'s are quite close to that of measured by Schulz and Jeffries [30] supporting the value of $\theta_D = 406$ K in LaF$_3$ to be more realistic than 382 K calculated in Ref. [24].

Below we consider the successful use of intrinsic parameters to describe the spin-phonon interactions in rare-earth trifluorides. The temperature dependence of $\beta_2$ value is reflected by the change in the value of the intrinsic parameter $\beta_2$ with temperature, because the effect of thermal expansion (contraction) of the lattice on $\beta_2$ is calculated to be rather small. In order to describe the temperature dependence of $\beta_2$ we used the transformed isotropic Einstein model for lattice...
vibration [31], which contains the coupling between Gd$^{3+}$ spin and one localized mode

$$
\bar{b}_2(T) = \bar{b}_2(\text{RL}) + K_2 \coth \left( \frac{h \nu}{2kT} \right),
$$

where $\bar{b}_2(\text{RL})$ is a “rigid lattice” value of $\bar{b}_2$ (i.e. the value of $\bar{b}_2$ at $T = 0$ K minus zero point vibrations) and $K_2$ is the coupling constant describing the magnitude of Gd$^{3+}$ spin–phonon interaction. The $\bar{b}_2(\text{RL})$, $K_2$ estimated from the fitting to Eq. (7) yield values $-4.75 \pm 0.05$, $0.13 \pm 0.02$ GHz for La$_{0.9}$Nd$_{0.1}$F$_3$ and $-4.85 \pm 0.05$, $0.14 \pm 0.02$ GHz for LaF$_3$, respectively.

On the other hand, the Debye model assumes that paramagnetic ions (Gd$^{3+}$) are coupled to the whole phonon spectrum of the crystal lattice. The equation adopted to fit $\bar{b}_2$ to temperature is the following [32]:

$$
\bar{b}_2(T) = \bar{b}_2(\text{RL}) + K_2 \left( 1 + 8 \frac{T^4}{\theta_D^4} \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx \right),
$$

The best fit with $\theta_D = 434$ K and 406 K for La$_{0.9}$Nd$_{0.1}$F$_3$ and LaF$_3$, respectively, yields the following parameters:

- $\bar{b}_2(\text{RL}) = -4.71 \pm 0.06$ GHz, $K_2 = 0.08 \pm 0.04$ GHz (La$_{0.9}$Nd$_{0.1}$F$_3$)
- $\bar{b}_2(\text{RL}) = -4.81 \pm 0.05$ GHz, $K_2 = 0.09 \pm 0.03$ GHz (LaF$_3$).

The above $\bar{b}_2$ (RL) and $K_2$ values derived from the Einstein and the Debye models are equal to each other within errors, confirming the correctness of the fitting.

The coupling between spins and phonons ($K_2$) in LaF$_3$ (Gd$^{3+}$) is about four times greater than in LiYF$_4$ (Gd$^{3+}$) crystal [18]. This statement can be confirmed by optical measurements [33], implying a larger amplitude of zero vibrations of the lattice in LaF$_3$ ($4\delta 9 \times 10^{-3}$ nm) versus LiYF$_4$ ($3.77 \times 10^{-3}$ nm).

6. Rotational invariance and the phonon-induced contributions to SHP

The theory of rotational invariance for the phonon-induced contributions to spin-Hamiltonian parameters developed by Bates and Szymczak [34, 35] gives more precise description of the observed contribution to the $b_0^0$ from lattice dynamics. It is usually difficult to determine magnetoelastic tensor components in low symmetry crystal field, e.g., in REF$_3$ crystals. In order to explain experimentally measured SHP’s by the above mechanism we need to separate the thermal expansion from that of the spin–phonon contributions. In order to separate the spin–phonon contribution we used the $\bar{b}_2$ values determined from superposition model as follows: $\delta D \approx 0.67 \cdot \delta \bar{b}_2 = 0.67[\bar{b}_2(295) - \bar{b}_2(\text{RL})]$. (In Sec. 5 we evaluated to 67% the spin–phonon contribution, the rest part is the contribution from thermal expansion.) Thus, these spin–phonon contributions (δD) are equal to 0.106 ± 0.036 GHz and 0.129 ± 0.034 GHz for Gd$^{3+}$-doped La$_{0.9}$Nd$_{0.1}$F$_3$ and LaF$_3$, respectively.

Further, the anharmonic contributions δD and δDr to D are given by the equations [35]:

$$
\delta D = \frac{-\hbar}{32\pi^2 \rho} (G_{11} + G_{12} + G_{13})(v_1^{-8} + 2v_1^{-5})f(\omega_D, T),
$$

(M.L. Paradowski, L.E. Misiak)
and

$$\delta D_r = -\frac{\hbar}{32\pi^2\rho} Dv_t^{-5} f(\omega_D, T),$$  \hspace{1cm} (10)$$

where $G_{11}$, $G_{12}$, $G_{13}$ are the components of the magnetoelastic tensor, $v_l$ and $v_t$ are longitudinal and transversal velocities of sound, respectively, and

$$f(\omega_D, T) = \omega_D^6 + 8 \left( \frac{kT}{\hbar} \right)^4 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx$$ \hspace{1cm} (11)$$

with $\hbar \omega_D = k\theta_D$.

The values of sound velocities are $v_l = 6.02 \times 10^5$ cm s$^{-1}$, $v_t = 2.31 \times 10^5$ cm s$^{-1}$ for La$_{0.9}$Nd$_{0.1}$F$_3$ and $v_l = 5.69 \times 10^5$ cm s$^{-1}$, $v_t = 2.18 \times 10^5$ cm s$^{-1}$ for LaF$_3$.

The calculation yields the sum values of magnetoelastic tensor components ($G_{11} + G_{12} + G_{13}$) to be $-3.04 \pm 1.00$ and $-3.33 \pm 0.88$ GHz for La$_{0.9}$Nd$_{0.1}$F$_3$ and LaF$_3$, respectively. Further, from Eq. (10) $\delta D_r$ was determined to be $-0.0121 \pm 0.0014$ and $-0.0134 \pm 0.0017$ GHz, as well as the ratio $R_D = \delta D_r/\delta D$ to be $-0.11$ and $-0.10$ for La$_{0.9}$Nd$_{0.1}$F$_3$ and LaF$_3$, respectively. This result is in agreement with those obtained in [35] using the isotropic continuum phonon model for orbital singlet ions in low symmetry crystal field; i.e. the rotational contributions are much smaller than those from the strain. In addition, we determined that the spin–phonon interaction constant $K_2$ given by Eq. (8) could be expressed in terms of the magnetoelastic tensor components as follows:

$$K_2 = \frac{-\hbar \omega_D^4 (v_l^{-5} + 2v_t^{-5})}{21.44\pi^2\rho} (G_{11} + G_{12} + G_{13}).$$  \hspace{1cm} (12)$$

### 7. Nd$^{3+}$ and Gd$^{3+}$ spin–lattice relaxation times

The full linewidth at half peak of a Gaussian distribution due to dipole–dipole and exchange interactions, is given by the expression [36, 37]:

$$\Delta B_{\text{dip-ex}}^2 = \frac{(2.35)^2\hbar^2(\Delta \nu^2)_{\text{av}}}{g^2\mu_B^2}.$$  \hspace{1cm} (13)$$

The dipolar interactions between similar ions can be neglected because the distances between Gd$^{3+}$ ions are sufficiently large in doped crystals. Taking into account dipolar and exchange interactions between dissimilar Gd$^{3+}$ and Nd$^{3+}$ ions the following expression is finally obtained for the second moment [38]:

$$\langle \Delta \nu^2 \rangle_{\text{av}} = \frac{1}{3} S'(S' + 1)h^{-2}$$

$$\times \left[ zJ_p^2 + 2J_p G \sum_{k'}^{z} (1 - 3\gamma_{jk'})r_{jk'}^{-3} + G^2 \sum_{k'}^{z} (1 - 3\gamma_{jk'}^2)^2r_{jk'}^{-6} \right],$$  \hspace{1cm} (14)$$

where $G = gg'\mu_B^2\mu_0$, $h$ is the Planck constant, $g$ and $g'$ are Gd$^{3+}$ and host Nd$^{3+}$ $g$-factor, respectively, $S' (= \frac{1}{2})$ is the effective spin of Nd$^{3+}$ host ion, $\mu_B$ is the Bohr magneton, $\mu_0 = 4\pi \times 10^{-7}$ H m$^{-1}$, $J_p$ is the average host–impurity pair exchange constant, $z (= 1)$ is the number of paramagnetic neighbor Nd$^{3+}$ ions.
to a Gd$^{3+}$ ion in La$_{0.9}$Nd$_{0.1}$F$_3$ (the remaining neighbors are La$^{3+}$ ions), $r_{jk'}$ are the distances between the $j$ and $k'$ ions, and $\gamma_{jk'}$ are the direction cosines of $r_{jk'}$ with the magnetic field $B \parallel Z$. The Gd$^{3+}$-Nd$^{3+}$ average pair exchange-interaction constant $J_p (\mathcal{H}_p = J_p SS')$ is estimated for the paramagnetic host La$_{0.9}$Nd$_{0.1}$F$_3$ to be $J_p = -2.7 \pm 0.5$ GHz [15].

The effective host $g'$ value is determined from the Boltzmann weighting of the $g_i$ value for each of the five Kramers doublets in the $4I_{9/2}$ ground multiplet of Nd$^{3+}$ ion in La$_{0.9}$Nd$_{0.1}$F$_3$ as follows [39]:

$$g' = \frac{\sum_{i=1}^{5} g_i \exp(-\Delta_i/kT)}{\sum_{i=1}^{5} \exp(-\Delta_i/kT)}, \quad (15)$$

where $\Delta_i$ is energy of the $i$-th doublet. The $g_i$ values are taken from Ref. [9]. From Eq. (15), the effective $g'$ values, along the $Z$-axis, have been determined to be 2.40, 2.87, and 3.39 at 4.2, 77, and 295 K, respectively.

The EPR linewidths $\Delta B_{pp}$ (=$\Delta B_{dip-ex}/1.18$) of Gd$^{3+}$ in La$_{0.9}$Nd$_{0.1}$F$_3$ crystal for $B \parallel Z$ are calculated, from Eqs. (13) and (14), to be 370, 438, and 510 mT at 4.2, 77, and 295 K, respectively. The main contribution to these linewidths comes from dipole–dipole interactions whereas contribution from exchange interactions is not larger than 4%. The measured EPR linewidths $\Delta B_{pp}$ in this crystal equal to 13.8, 8.5, and 8.1 mT at 4.2, 77, and 295 K, respectively, are several times narrower than calculated $\Delta B_{pp}$. This strong and temperature dependent narrowing of the EPR resonance lines can be explained with the mechanism of the spin–lattice modulated narrowing proposed by Mitsuma [40]. Finally, the spin–lattice relaxation time of the host Nd$^{3+}$ ions can be determined from the expression

$$\tau_1' = \frac{3}{20 g'\mu_B \Delta B_{dip-ex}^2 \sqrt{2\Delta B_{1/2}}} \quad (16)$$

The EPR lines of Gd$^{3+}$-doped La$_{0.9}$Nd$_{0.1}$F$_3$ (and LaF$_3$) crystals have a Lorentzian shape at all temperatures of investigation ($\Delta B_{1/2} = \sqrt{2}\Delta B_{pp}$). The superhyperfine interactions of Gd$^{3+}$ ion with the neighboring $^{19}$F nuclei cause the increase in the linewidth by 1.4 mT [41] which is subtracted from $\Delta B_{pp}$. Finally, the $\tau_1'$s in La$_{0.9}$Nd$_{0.1}$F$_3$ are evaluated to be $(5.02 \pm 0.3) \times 10^{-13}$, $(1.72 \pm 0.3) \times 10^{-13}$, and $(1.01 \pm 0.2) \times 10^{-13}$ s at 4.2, 77, and 295 K, respectively. The spin–lattice relaxation times of Nd$^{3+}$ ions are dependent on the concentration ($x$) of diamagnetic La$^{3+}$ ions in mixed crystals La$_x$Nd$_{1-x}$F$_3$, being longer for bigger concentration. It can be confirmed for $\tau_1'$s at 295 K, because data for the full range of the concentration are available, i.e. $8.87 \times 10^{-15}$ ($x = 0$), $3.24 \times 10^{-14}$ ($x = 0.1$) and $1.01 \times 10^{-13}$ s ($x = 0.9$). The determined $\tau_1'$s at 145 K are as follows: $3.16 \times 10^{-14}$ ($x = 0$) and $6.30 \times 10^{-14}$ s ($x = 0.1$).

The spin–lattice relaxation time of Gd$^{3+}$ ions ($\tau_1$) can be determined from the EPR linewidth of Gd$^{3+}$-doped LaF$_3$ after subtracting the linewidth equal to 1.4 mT. The estimated $\tau_1$'s using Heisenberg’s uncertainty rule (assuming $h\Delta \nu = g\mu_B \Delta B_{1/2}$) are equal to $3.7 \times 10^{-9}$, $2.8 \times 10^{-9}$, and $2.5 \times 10^{-9}$ s at 4.2, 77, and 295 K, respectively, being longer than $\tau_1'$ of host Nd$^{3+}$ ions. It can be assumed that $\tau_1$ of Gd$^{3+}$ ions in La$_{0.9}$Nd$_{0.1}$F$_3$ is the same, because the Gd$^{3+}$ spin–phonon interaction constant $K_2$ does not differ within experimental errors from that in LaF$_3$ (Gd$^{3+}$) as shown in Sec. 5. The $\tau_1$ increase by 45% with lowering temperature.
from 295 to 4.2 K. This rather small increase is due to weak coupling of Gd$^{3+}$ ions with the lattice, in contrary to strong coupling of Nd$^{3+}$ ions ($\tau_1$ increase by 400% in the same temperature range).

8. Concluding remarks

The small local rotations ($\Delta \varphi = \pm 3.5^\circ$) of the eight fluorine ions (grouped in pairs) surrounding the Gd$^{3+}$ ion, are determined in the Gd$^{3+}$-doped La$_{0.9}$Nd$_{0.1}$F$_3$ when temperature is lowered down to liquid helium. This can induce a slight distortion of the site symmetry of Gd$^{3+}$ ion ($C_{2v}$ to $C_2$) observed at low temperatures (below 77 K).

The energy of single oscillator has been determined to be 302 cm$^{-1}$ for La$_{0.9}$Nd$_{0.1}$F$_3$ and 282 cm$^{-1}$ for LaF$_3$ using the Einstein model of phonon spectrum. These above average values are somewhat higher than values determined from the Debye model in the long-wavelength limit. The determined Debye temperature 406 K for LaF$_3$ is close to the realistic value as discussed in Sec. 5.

The main contribution to the observed EPR linewidths of Gd$^{3+}$ in La$_{0.9}$Nd$_{0.1}$F$_3$ comes from the strong Nd$^{3+}$ spin–lattice and the Gd$^{3+}$–Nd$^{3+}$ dipole–dipole interactions. Contribution from the exchange interaction between Gd$^{3+}$ and Nd$^{3+}$ ions plays a secondary role. The Gd$^{3+}$ spin–phonon interaction constant equal to 0.08 0.13 GHz means that there exist weak interactions of the Gd$^{3+}$ spin with optical phonons at 302 cm$^{-1}$, due to the zero orbital momentum for Gd$^{3+}$ ($^8S_{7/2}$). It is also concluded that there is more stronger Nd$^{3+}$ spin–phonon interaction, i.e. the Nd$^{3+}$ spin with the optical phonons at 302 cm$^{-1}$, because the spin–lattice relaxation time ($\tau_1$) of Nd$^{3+}$ ions is four orders of magnitude shorter than that of Gd$^{3+}$ ions ($\tau_1$).

The sum values of magnetoelastic tensor components ($G_{11} + G_{12} + G_{13}$) are calculated for Gd$^{3+}$ ions to be in the range $-3.33 \div -3.04$ GHz for investigated crystals. Further, the values of $\kappa_D$ in La$_{0.9}$Nd$_{0.1}$F$_3$ and LaF$_3$ crystals show that the rotational contributions to the Gd$^{3+}$ spin-Hamiltonian parameters from phonons are much smaller than those from the strain.

References