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# Crystal field study of $Gd^{3+}$ -doped $La_xRE_{1-x}F_3$ (RE = Ce, Pr, Nd) single crystals

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## ABSTRACT

The mixed  $La_xRE_{1-x}F_3$  (RE = Ce, Pr, Nd) single crystals doped with  $Gd^{3+}$  (0.1 mol%) were grown by a modified Bridgmann-Stockbarger method. The crystal field was investigated using electron paramagnetic resonance technique. The angular dependencies of  $Gd^{3+}$  ( $^8S_{7/2}$ ,  $f^7$ ) line positions with magnetic field oriented in (001) plane were measured in the temperature range 4.2 – 295 K. The surroundings of  $Gd^{3+}$  ions were investigated analyzing spin-hamiltonian parameters in the light of the superposition model. The small distortion of the  $D_{3d}^4$  trigonal symmetry has been observed in  $LaF_3$ ,  $La_{0.9}Ce_{0.1}F_3$  and  $La_{0.9}Nd_{0.1}F_3$  below 150 K. The local structure deformation of the site symmetry of  $Gd^{3+}$  ions induced by temperature starts at about 150 K becoming larger at 4.2 K. In  $PrF_3$  the distortion was not observed in the temperature range 4.2 – 295 K. The results were compared with those of  $Gd^{3+}$ -doped  $LiYF_4$  crystals.

**Keywords:** rare-earth trifluorides, electron paramagnetic resonance (EPR), spin-hamiltonian parameters, zero-field splitting, distortions, magnetic ordering.

## 1. INTRODUCTION

The  $La_xRE_{1-x}F_3$  (RE = Ce, Pr, Nd) single crystals are utilized as laser materials and radiation hard scintillators for calorimetry at future colliders.<sup>1-4</sup> The mixed  $La_xCe_{1-x}F_3$  single crystals can also be used as the filters for the vacuum ultraviolet.<sup>5</sup> The single crystals doped with  $Gd^{3+}$  (0.1 mol%) were grown by a modified Bridgmann-Stockbarger method described elsewhere.<sup>6,7</sup> The  $^8S_{7/2}$  ground term of the  $Gd^{3+}$  ion in these single crystals is split by the crystalline electric field into four Kramers doublets. It is important to know how the crystal field splits this term at various temperatures. The small distortion from the  $D_{3d}^4$  trigonal space group, caused by the strong influence of the crystalline field, was observed in  $La_xCe_{1-x}F_3$  and  $La_xNd_{1-x}F_3$  single crystals using magnetic susceptibility method.<sup>8,9</sup> A small change of the crystal field in  $La_{0.9}Nd_{0.1}F_3$  with lowering temperature, as a result of temperature induced distortion of the crystal lattice (which caused a change in site symmetry of  $Gd^{3+}$  ions from  $C_{2v}$  at 77 K towards  $C_2$  at 4.2 K) was observed in our most recent works.<sup>7,10,11</sup>

The purpose of the present paper is to study the crystal field in all samples at different temperatures using Electron Paramagnetic Resonance (EPR) technique and superposition model, because they are very sensitive to the distortion of the crystal lattice. Therefore surroundings of  $Gd^{3+}$  ions in the trigonal symmetry  $D_{3d}^4$  with a hexamolecular unit cell were investigated. The spin-hamiltonian parameters (SHP) are analyzed in the light of the superposition model. Previously we studied local deformation in  $La_{0.9}Nd_{0.1}F_3$  single crystal.<sup>7,11</sup> Further, we extended the EPR measurements to temperatures covering the range 4.2 – 295 K in all chosen samples. The negative  $g$  shift of  $Gd^{3+}$ -doped  $La_{0.9}Ce_{0.1}F_3$  and  $La_{0.9}Nd_{0.1}F_3$  from that in the isostructural diamagnetic host  $LaF_3$  indicates the antiferromagnetical ordering of  $Gd^{3+}$ - $Ce^{3+}$  and  $Gd^{3+}$  -  $Nd^{3+}$  pairs.

## 2. CRYSTAL FIELD STUDY

The crystal field study has been performed by analyzing SHP's for  $Gd^{3+}$ -doped  $LaF_3$ ,  $La_{0.9}Ce_{0.1}F_3$ ,  $La_{0.9}Nd_{0.1}F_3$  and  $PrF_3$  single crystals in the temperature range 4.2 – 295 K, using the superposition model.<sup>7,11</sup> The above samples are the only crystals studied in detail for which well-resolved EPR spectra can be recorded down to liquid-helium temperature. Details of EPR measurements can be found elsewhere.<sup>11</sup> typical example of the spectrum and magnetic splitting of four Kramers

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doublets are presented in Fig. 1. The zero-field splitting (ZFS) of  $Gd^{3+}$  is defined as  $\Delta E = E(\pm 7/2) - E(\pm 1/2)$  at magnetic field  $B = 0$ . The ZFS was determined on the basis of nine SHP's and plotted in Fig. 2. It can be seen that ZFS depends on the temperature as a parabolic function. The ZFS reaches maximum value at about 150 K for  $LaF_3$ ,  $La_{0.9}Ce_{0.1}F_3$  and  $La_{0.9}Nd_{0.1}F_3$ , whereas for  $PrF_3$  the ZFS is increasing monotonically with lowering temperature down to 4.2 K. In  $Gd^{3+}$ -doped  $LiYF_4$  crystal the ZFS also increased with decreasing temperature down to 4.2 K.<sup>12</sup> In order to explain such behavior of ZFS, the intrinsic parameter  $b_2$  ( $m = 0$ ) should be taken into consideration.<sup>11</sup> The ZFS and SHP varied linearly with the intrinsic parameter as determined from the superposition model. The intrinsic parameters  $b_2$  for  $Gd^{3+}$ -doped samples in the temperature range 4.2 – 295 K are plotted in Fig. 3. The  $b_2$  reaches minimum of negative values at about 150 K for  $LaF_3$ ,  $La_{0.9}Ce_{0.1}F_3$  and  $La_{0.9}Nd_{0.1}F_3$ , whereas for  $PrF_3$  and  $LiYF_4$  its negative values are continuously decreasing with decreasing temperature. The intrinsic parameter depends only on  $R_0$  (the minimum distance between  $Gd^{3+} - F^-$  ions corresponding to the 2-3  $F^-$  pairs<sup>7,11</sup>). The  $R_0$ 's depend on temperature similar to lattice constants<sup>6</sup> and reach minimum value at liquid-nitrogen temperature for  $Gd^{3+}$ -doped  $LaF_3$ ,  $La_{0.9}Ce_{0.1}F_3$  and  $La_{0.9}Nd_{0.1}F_3$  (Fig. 4). On the other hand, for  $PrF_3$  and  $LiYF_4$  the  $R_0$  is decreasing with decreasing temperature from 295 K to 4.2 K. Since the intrinsic parameter depends only on the  $R_0$ , it can be plotted versus  $R_0$  (Fig. 5). The slightly change of  $R_0$  with decreasing temperature causes drastic increase of  $b_2$  in the temperature range below 150 K. Such behavior of the intrinsic parameter explains changes of SHP and ZFS. On the other hand, in  $PrF_3$  and  $LiYF_4$  there are not any drastic changes of the intrinsic parameter  $b_2$  with  $R_0$ . Generally, the behavior is due to monotonic decrease of  $R_0$  with temperature down to liquid-helium. We think that different behavior of the investigated samples is caused by critical temperature of the intrinsic parameter. The critical temperature of the intrinsic parameter does not depend on the structure of crystal lattice but individual character of lattice – the site symmetry of  $Gd^{3+}$  ion that is changed with temperature, as a result of temperature induced distortion of crystal lattice.

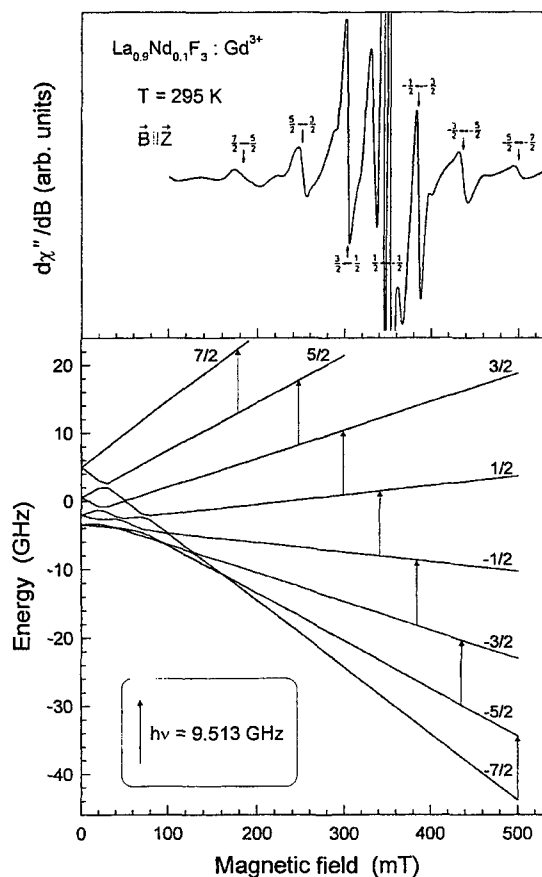


Fig. 1. EPR spectrum and energy levels of  $Gd^{3+}$ -doped  $La_{0.9}Nd_{0.1}F_3$  single crystal at  $T = 295$  K with  $B \parallel Z$  ( $a$ -axis).

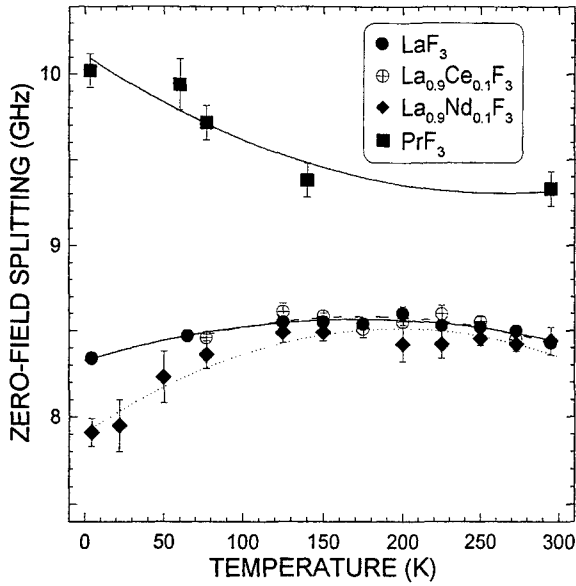


Fig. 2. Temperature dependence of ZFS for  $Gd^{3+}$ -doped  $LaF_3$ ,  $La_{0.9}Ce_{0.1}F_3$ ,  $La_{0.9}Nd_{0.1}F_3$  and  $PrF_3$  single crystals.

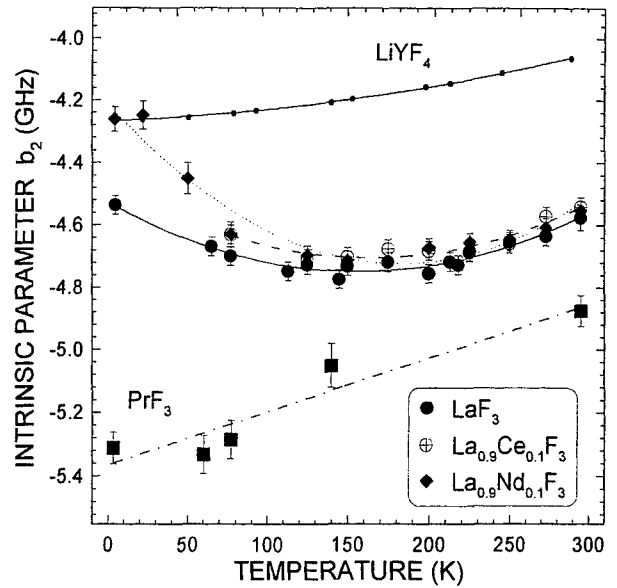


Fig. 3. Temperature dependence of the intrinsic parameter  $b_2$  for  $Gd^{3+}$ -doped  $LaF_3$ ,  $La_{0.9}Ce_{0.1}F_3$ ,  $La_{0.9}Nd_{0.1}F_3$ ,  $PrF_3$  and  $LiYF_4$ <sup>12</sup> single crystals.

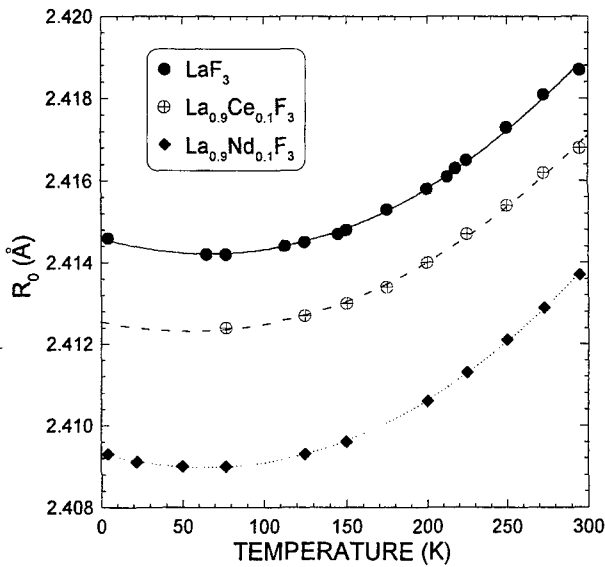


Fig. 4. Temperature dependence of the minimum distance  $R_0$  between  $Gd^{3+} - F^-$  ions corresponding to the 2-3  $F^-$  pairs<sup>7,11</sup> in  $LaF_3$ ,  $La_{0.9}Ce_{0.1}F_3$ ,  $La_{0.9}Nd_{0.1}F_3$  single crystals.

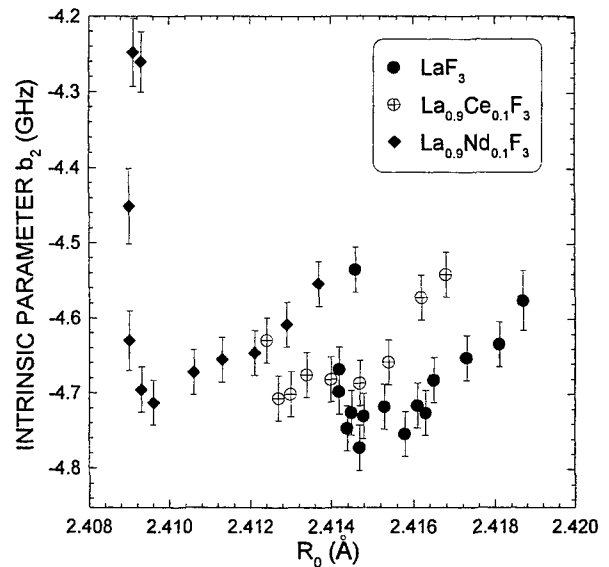


Fig. 5. The plot of the intrinsic parameter versus  $R_0$  for  $Gd^{3+}$ -doped  $LaF_3$ ,  $La_{0.9}Ce_{0.1}F_3$  and  $La_{0.9}Nd_{0.1}F_3$  single crystals.

### 3. CONCLUSIONS

New insight into the intrinsic parameter  $b_2$  has been performed using superposition model. The critical temperature for intrinsic parameter has been proposed. The intrinsic parameter is very sensitive to the distortion of the site symmetry of  $Gd^{3+}$  ions. Although the variation of the distortion is small, it has a drastic effect on the intrinsic parameter  $b_2$ . The small distortion of the  $D_{3d}^4$  trigonal symmetry has been observed in  $LaF_3$ ,  $La_{0.9}Ce_{0.1}F_3$  and  $La_{0.9}Nd_{0.1}F_3$  below 150 K. Further, the distortion of the local site symmetry of  $Gd^{3+}$  ions from  $C_{2v}$  towards  $C_2$  starts at 150 K and continuously increases with temperature decreasing down to 4.2 K, whereas in  $PrF_3$  the distortion was not observed in the temperature range 4.2 – 295 K.

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