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TITLE: Gd[3+]-Yb[3+] Exchange Interactions in LiYb[x]Y[1-x]F4 Single Crystals

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Gd^{3+}-Yb^{3+} exchange interactions in $LiYb_xY_{1-x}F_4$ single crystals

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ABSTRACT

The evaluated Gd^{3+} -Yb^{3+} exchange interactions over the nearest and the next-nearest neighbors in $LiYb_xY_{1-x}F_4$ are found to increase in parabolic manner with x, the concentration of Yb^{3+} ions. The Gd^{3+} -Yb^{3+} exchange interactions are sensitive to x in the range x = 0.6 - 1.0, while they are almost constant in the range x = 0.1 - 0.5. The estimated Gd^{3+}-Yb^{3+} exchange interaction constants ($J = J_{nn} + J_{nnn}$) are in the range 0.5 – 2.8 GHz for x from 0.1 to 1, respectively. These exchange interaction constants are increased with lowering temperature. The results are comparable to those of estimated using the molecular-field model. The average Gd^{3+} -Yb^{3+} pair exchange interaction constant is determined to be 0.33 GHz in paramagnetically diluted $LiYb_xY_{1-x}F_4$ crystals.

Keywords: lithium rare-earth fluorides, electron paramagnetic resonance (EPR), exchange interactions, spin-hamiltonian parameters, exchange interaction constant.

1. INTRODUCTION

$LiYF_4$ is the most-used fluoride laser host crystal, generally doped with trivalent rare-earth ions.[1] The $LiYF_4$ crystals are also used for preparation of infrared and laser windows,[2] to convert infrared excitation to green emission,[3] as well as neutron scintillation detectors.[4] The $LiYb_xY_{1-x}F_4$ crystals have scheelite ($CaWO_4$) structure with the space group $I4_1/a$ (C^6_{4h}) and the S_4 local symmetry at Y^{3+} or Yb^{3+} sites, the same as those of $LiYF_4$ and $LiYbF_4$.[5,6] The $LiY_{1-x}Yb_xF_4$ (x = 0 – 1) single crystals doped with Gd^{3+} were grown from the melt by a modified Bridgmann-Stockbarger method.[6]

X-band (~9.5 GHz) EPR studies of Gd^{3+} -doped $LiYF_4$ and $LiYbF_4$ have been reported.[7,8] A detailed X-band EPR study has been performed in Gd^{3+} -doped $LiYb_xY_{1-x}F_4$ crystals, for various values of x and at variable temperatures, in the range 4.2 - 290 K.[9] Further, the molecular-field model[10] was used to estimate the Gd^{3+} -Yb^{3+} exchange interactions at 4.2 K. For the host crystals with x > 0.1, it was not possible to record EPR spectra at temperatures much lower than room temperature, because of increasing line broadening. Detailed Gd^{3+} EPR-linewidth studies have also been reported.[11]

The EPR spectrum of Yb^{3+} ions was not at all observed, due to the rather short spin-lattice relaxation time of Yb^{3+}, which broadens out the Yb^{3+} EPR lines substantially at temperatures above 4.2 K; Yb^{3+} EPR spectrum was observed only for the host crystals with x < 0.2. This consisted of a broad line corresponding to the 69% non-magnetic, even-mass isotopes in natural ytterbium with nuclear spin I = 0 (^{168}Yb, ^{170}Yb, ^{172}Yb, ^{174}Yb and ^{176}Yb), at about 4960 G, without any superhyperfine structure. (The Yb^{3+} superhyperfine structure was observed[12] in $LiYF_4$ host crystal, doped by Yb^{3+} ions (0.1 at. %) at X-band, for the magnetic field orientation only within 2° from the *c* axis.) The spectrum of ^{171}Yb (I = ½), with nonzero nuclear magnetic moment in scheelite crystal hosts occurs at X-band in the magnetic field range 8.5 – 10 kG.[13] In $LiYb_{0.1}Y_{0.9}F_4$ crystal at 4.2 K only one line was observed at about 9.5 kG. [9]

The nearest-neighbor (nn) Gd^{3+} pair spectrum in $EuCl_3$ have been recorded[14] for the direction of **H** along the *c* crystal axis, and the next-nearest neighbor (nnn) Gd^{3+} pair spectrum with **H** parallel to the calculated nnn bond direction. In $LiYb_xY_{1-x}F_4$ crystals, the pair spectrum was not at all observed, neither for **H** parallel to the *c* axis, nor for **H** in the XY plane, which contains the bond direction of the nnn Gd^{3+} pair. This can be explained to be due to the rather small concentration of the Gd^{3+} ions (0.1 - 0.2 mole %) in $LiYb_xY_{1-x}F_4$,[9] compared to that in $EuCl_3$ (0.5 - 1.0 mole % of Gd^{3+}).[14] The g shift of Gd^{3+} ion in a paramagnetic $LiYb_xY_{1-x}F_4$ host, from that in the isostructural diamagnetic $LiYF_4$ host, is dependent upon the magnetic interactions of the Gd^{3+} ion with the Yb^{3+} paramagnetic neighbors. These exchange interactions can be estimated from the g shift values of the Gd^{3+} ion in the isostructural paramagnetic and diamagnetic hosts.[8,14]

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2. ESTIMATION OF Gd^{3+} -Yb^{3+} EXCHANGE INTERACTIONS

The exchange-interaction constant due to the nearest and next-nearest Gd^{3+} -Yb^{3+} neighbors in the paramagnetic hosts $LiYb_xY_{1-x}F_4$ can be evaluated using the shift of the isotropic part of the single-ion g-tensor of a Gd^{3+} ion, from that in the isostructural diamagnetic host ($LiYF_4$): [8,14]

$$(\delta g_{zz} + \delta g_{xx}) = (g_{zz} + 2g_{xx})_p - (g_{zz} + 2g_{xx})_d = -\frac{96}{\Delta_{av}}(J_{nn} + J_{nnn}). \tag{1}$$

In eq. (1), J_{nn} and J_{nnn} are respectively the exchange-interaction constants of Gd^{3+} with the nearest and next-nearest Yb^{3+} neighbors, the subscripts p and d refer to the isostructural paramagnetic and diamagnetic hosts $LiYb_xY_{1-x}F_4$ and $LiYF_4$, respectively, and Δ_{av} is an average energy difference between the first excited levels and the ground state of Yb^{3+}. The multilevel spacings, Δ_{av}, of these levels from the ground state can be taken into account by averaging.[15]

$$\Delta_{av} = \sum_i \Delta_i \exp(-\Delta_i/k_B T) \Big/ \sum_i \exp(-\Delta_i/k_B T). \tag{2}$$

The uncertainty, caused by the averaging, is less than that associated with the experimental measurements.[15] The separations (Δ_i) of the energies between the ground level and the next-three excited states of Yb^{3+} ion in $LiYF_4$ crystal[16] are determined to be 212, 364, 455 cm^{-1}, respectively. The average energy separation, to be used in eq. (1) is 294 cm^{-1}. (The other higher-lying levels do not contribute as they are separated from the ground state by large energies,[16] e.g., $\sim 10^4$ cm^{-1}.)

2.1. Estimation of g_{zz} and g_{xx}

The spin hamiltonian for the Gd^{3+} ion, occupying a site of local symmetry S_4 in the tetragonal $LiYb_xY_{1-x}F_4$ host lattice, can be found elsewhere.[9] For the estimation of the Gd^{3+} -Yb^{3+} exchange-interaction constant it is necessary to have very accurate values of g_{zz} and g_{xx}. These values were usually obtained from least-squares fitting of all the spin Hamiltonian parameters in which a large number of EPR line positions (obtained for several orientations of the external magnetic field) were simultaneously fitted.[9] More precise values of g-factor can be calculated by the use of the experimentally observed line positions for the 1/2 ↔ -1/2 transition (for $\mathbf{H} \| \mathbf{Z}$ and $\mathbf{H} \| \mathbf{X}$). The calculation to second order using perturbation method, gives[17]

$$g\beta H^{(2)} = h\nu + E\left[\frac{90}{(1-9y^2)} - \frac{120}{(1-y^2)}\right], \tag{3}$$

where,

$y = b_2^0/g\beta H^{(2)}$, $E = (b_2^2)^2/18g\beta H^{(2)}$.

One can calculate from eq. (3) for $LiYb_xY_{1-x}F_4$:

$$g_{zz} = h\nu/\beta H_z^{(2)} \text{ and } g_{xx} = h\nu/\beta H^{(2)}(1-A), \tag{4}$$

where,

$$A = \frac{9(b_2^0)}{72g_{xx}^2\beta^2(H^{(2)})^2}\left\{\frac{90}{1-\left[\frac{9(b_2^0)^2}{4g_{xx}^2\beta^2(H^{(2)})^2}\right]} - \frac{120}{1-\left[\frac{(b_2^0)^2}{4g_{xx}^2\beta^2(H^{(2)})^2}\right]}\right\}. \tag{5}$$

This A value at room temperature can be estimated fairly reasonably by using the g_{xx} and b_2^0 values, specific to each $LiYb_xY_{1-x}F_4$ host, determined from least-squares fitting. Thus, when the determined values of A for the various hosts are used in eq. (4) for the evaluation of g_{xx}, they do not cause significantly large errors. The values of g_{zz} and g_{xx}, so computed from eq. (4) for the various hosts, are listed in table 1.

2.2. Estimation of the Gd^{3+} -Yb^{3+} exchange interaction constant

The values of the exchange-interaction constant (J), computed using the g shift in eq. (1) are given in table 1. It is seen from Fig. 1 that, as the amount of paramagnetic Yb^{3+} ions increases for x in the range 0.1 - 1.0, the Gd^{3+} -Yb^{3+} exchange-interaction constant J also increases in parabolic manner.

Table 1. The room-temperature values of g_{zz}, g_{xx}, A, and J (the exchange-interaction constant) in Gd^{3+} -doped $LiYb_xY_{1-x}F_4$ single crystals. The x is the mole fraction of Yb^{3+} ions, z is the number of nearest and next-nearest neighbors and J_p (= J/z) is the average Gd^{3+} -Yb^{3+} pair exchange-interaction constant.

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.8	0.9	1.0
g_{zz}	1.9956(5)	1.9953(5)	1.9947(5)	1.9947(5)	1.9941(5)	1.9935(11)	1.9920(11)	1.9864(11)	1.9788(11)	1.9738(11)
g_{xx}	1.9908(8)	1.9885(8)	1.9866(8)	1.9894(8)	1.9860(8)	1.9855(14)	1.9862(14)	1.9882(14)	1.9863(14)	1.9864(14)
A	-0.1165	-0.1173	-0.1188	-0.1171	-0.1188	-0.1186	-0.1185	-0.1161	-0.1165	-0.1169
J (GHz)		0.5(0.30)	0.9(0.30)	0.4(0.3)	1.0(0.3)	1.2(0.6)	1.2(0.6)	1.3(0.6)	2.4(0.6)	2.8(0.6)
z	0	1	2	2	3	4	5	6	7	8
J_p (GHz)		0.5	0.45	0.20	0.33	0.30	0.24	0.22	0.34	0.35

In $LiYbF_4$ the number of each of the nearest-neighbors and the next-nearest neighbors (z) is four.[5] As for the $LiYb_xY_{1-x}F_4$ single crystals, the number of z can be scaled in proportion to x, to estimate the average number of Yb^{3+} neighbors to a Gd^{3+} ion, and further to calculate the average pair exchange-interaction constant J_p (= J/z). The values of J_p, so calculated, are included in table 1. It is seen that all the J_p values are the same (on average 33 GHz), within errors of estimation.

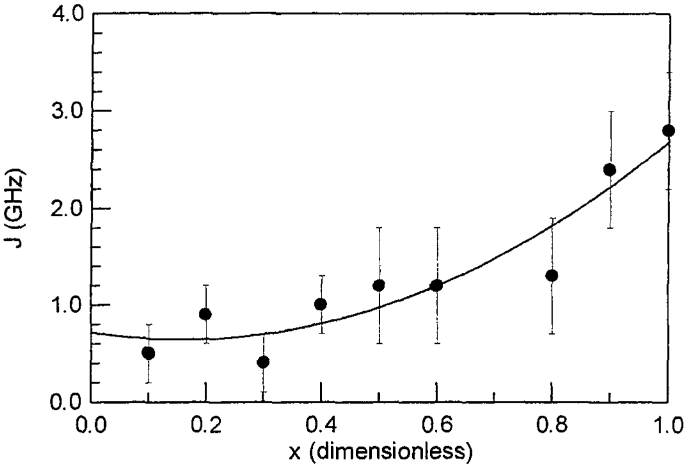

Fig. 1. The exchange-interaction constant (J) as a function of the mole fraction of Yb^{3+} ions (x) in Gd^{3+}-doped $LiYb_xY_{1-x}F_4$ single crystals.

3. DISCUSSION AND COMPARISON OF RESULTS

The calculation of Gd^{3+}-Yb^{3+} exchange interactions was made previously, using the molecular-field model for $LiYb_{0.1}Y_{0.9}F_4$ at 4.2 K,[9] because this is the only crystal containing Yb^{3+} ions, which exhibits well-resolved spectrum at liquid-helium temperature. The values of the Gd^{3+} -Yb^{3+} exchange-interaction constants J, at 4.2 K, were clculated to be 3.8 GHz from the molecular-field model[9] and 4.9 GHz in the present calculations. These two values can be considered to be in reasonably good agreement, taking into account the experimental errors and the approximations made in the calculation of J. The value of J was estimated to be 6.24 GHz and 2.32 GHz at 77 K and at room temperature, respectively, for Gd^{3+}-Eu^{3+} exchange interactions in $Eu(OH)_3$ single crystal.[15] The room-temperature value of Gd^{3+}-Eu^{3+} exchange interactions (2.32 GHz) is not much different from that of 2.8 GHz, the Gd^{3+} -Yb^{3+} exchange interactions in $LiYbF_4$ at room temperature. From the values of Gd^{3+}-Yb^{3+} exchange interaction constants at room temperature and at 4.2 K in $LiYb_{0.1}Y_{0.9}F_4$, and those of estimated for Gd^{3+}-Eu^{3+} exchange interactions in $Eu(OH)_3$,[15] it is seen that the strength of the exchange interactions increases with decreasing temperature in these hosts. As the temperature decreases, the distances between the ions in the lattice become smaller, thereby enhancing the exchange-interaction constant. This is to be expected, because the exchange interaction constant is determined to be dependent upon an interionic distance R as R^{-12},[18] or as $e^{-3.55R}$; [19] the latter provides a better agreement to the experimental values of exchange interactions. The exchange interactions between the Gd^{3+} -Yb^{3+} ions in $LiYb_xY_{1-x}F_4$ are effected mostly through the ligand F^- ions.

4. CONCLUSIONS

The Gd^{3+} -Yb^{3+} exchange-interaction constant J (= $J_{nn} + J_{nnn}$), as estimated for Gd^{3+} -doped $LiYb_xY_{1-x}F_4$ single crystals, are in the range 0.5 - 2.8 GHz at room temperature. On the other hand, at liquid-helium temperature, the calculated value of J for $LiYb_{0.1}Y_{0.9}F_4$ is 4.9 GHz. Thus, the exchange-interaction constant is strongly dependent upon temperature, and upon the mole fraction x (in the range x = 0.5 - 1.0). However, J is almost independent of the mole fraction (x) for $x < 0.5$. The average Gd^{3+} -Yb^{3+} pair exchange interaction constant in paramagnetically diluted $LiYb_xY_{1-x}F_4$ crystals is determined to be 0.33 GHz.

The values of the Gd^{3+}-Yb^{3+} exchange-interaction constants as estimated in $LiYb_xY_{1-x}F_4$, are consistent with those of evaluated using the molecular-field model[9] and are comparable in magnitude to those for Gd^{3+} -Eu^{3+} exchange constant in $Eu(OH)_3$ host.[15] Reasonable agreement between the exchange-interaction constants in $LiYb_xY_{1-x}F_4$ as estimated presently with those of estimated using the molecular-field model, is expected, since the latter is an approximation of the former.

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