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Optically-detected nuclear quadrupole resonance of Eu^{3+} in LaF_3

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Abstract

We report optically-detected nuclear quadrupole resonance (ODNQR) of Eu^{3+} in LaF_3. The anomalous nuclear quadrupole moments of $^{151}Eu^{3+}$ and $^{153}Eu^{3+}$ isotopes have been measured by detecting r.f.-induced quadrupole resonance which enhances the $^7F_0 \leftrightarrow {}^5D_0$ optical transition. Due to significant second-order hyperfine cancellation, the lowest quadrupole splitting in the ground state is only 6.93 MHz. In analysis of the ODNQR spectrum, an effective nuclear quadrupole Hamiltonian is diagonalized and the measured quadrupole splittings are used to determine the quadrupole interaction parameters for the ground state $^7F_0$. For ^{151}Eu, $P^{(151)} = 2.67$ and $\eta^{(151)} = 0.58$, and for ^{153}Eu, $P^{(153)} = 4.80$ and $\eta^{(153)} = 0.49$.

Keywords: Optical–r.f. double resonance; Nuclear quadrupole resonance

1. Introduction

For trivalent europium ion in the ground state $^7F_0$, hyperfine and electronic Zeeman effect vanish in first order. To consider the contribution of higher order hyperfine coupling, the nuclear magnetic moments of $^{151}Eu^{3+}$ and $^{153}Eu^{3+}$ isotopes are anomalously small because the second-order hyperfine coupling with the $^7F_1$ state and the crystal-field induced J-mixing are of opposite sign and comparable magnitude to the intrinsic moment of the Eu nucleus[1,2]. This cancellation is a general phenomenon with some modification depending on the crystalline environment. For this reason, conventional NMR or nuclear quadrupole resonance (NQR) of Eu^{3+} in solids have not been successful. The anomalous nuclear quadrupole moments of trivalent europium ^{151}Eu and ^{153}Eu have only been measured by spectral hole burning and optically-detected nuclear quadrupole resonance (ODNQR) as previously reported for $Eu^{3+}:YAlO_3$ [3, 4], $Eu^{3+}:YLiF_4$ [5] $Eu^{3+}:CaF_2$ [6], and $EuVO_4$ [7].

In this paper, we report an ODNQR study of Eu^{3+} doped into LaF_3. Single crystal LaF_3 doped with trivalent rare earth ions is a laser material and optically-detected magnetic resonance of Pr^{3+} in this host was also reported [8]. To our knowledge, this is the first report of ODNQR work on $Eu^{3+}:LaF_3$. Because of the low site symmetry (C_2), we expect that the Eu^{3+} ions in LaF_3 would have a much greater non-axial quadrupole interaction than in the previously studied systems. Nuclear quadrupole energy levels of the ground-state $^7F_0$ of $^{151}Eu^{3+}$ and $^{153}Eu^{3+}$ have been measured. An effective Hamiltonian combining the contributions of pseudoquadrupole and pure quadrupole interactions is diagonalized to obtained the eigenvalues as functions of the quadrupole interaction parameters. Then, the parameters are determined with the observed splittings. Discussion is given to the differences between the quadrupole interaction parameters obtained in this work and the parameters reported for the two europium isotopes in other systems.

2. Experimental details

A single frequency CW dye laser (linewidth <0.5MHz) pumped by an argon ion laser and a r.f. synthesizer were used in the optical radio-frequency (r.f.) double resonance experiments on a single crystal Eu^{3+}(0.1%):LaF_3. The sample was in the center of a broadband traveling-wave r.f. coil placed in a superconducting magnet cryostat with optical windows. The sample was continuously irradiated at liquid helium

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temperature with the laser at a fixed frequency to saturate the optical excitation between the ground state $^7F_0$ and the excited state $^5D_0$. The saturation or spectral hole-burning effect is a result of redistribution of the ground-state populations by means of optical pumping within the inhomogeneous absorption profile of the $^7F_0 \leftrightarrow {}^5D_0$ transition centered at 17 286.5 cm^{-1}. The inhomogeneous line width for this transition is 3 GHz. The r.f. was amplified by a broad band amplifier to 2–6 W and swept while the sample fluorescence was selected with a monochromator and detected with a photomultiplier and a personal computer or a digital oscilloscope.

Europium has two isotopes with almost equal abundance, 47.77% ^{151}Eu and 52.23% ^{153}Eu. Both isotopes of Eu^{3+} have a nuclear spin quantum $I=5/2$. At zero external magnetic field, the nuclear quadrupole interaction and second order hyperfine coupling split the ground state $^7F_0$ and the excited state $^5D_0$ into three hyperfine levels ($I_z = \pm 1/2, \pm 3/2, \pm 5/2$) separated on the order of 10 MHz. Since the splittings are larger than the laser linewidth, optical excitation is only from one hyperfine level for an Eu^{3+} ion. This level can be easily depleted at low temperature because of the slow nuclear relaxation between the hyperfine levels. At temperatures below 10 K, the spectral hole burning process in Eu^{3+}:LaF$_3$ becomes very efficient for the $^7F_0 \leftrightarrow {}^5D_0$ transition. With a laser power of 100 mW and focused beam size of ~200 μm in the sample, the $^5D_0 \to {}^7F_1$ fluorescence intensity was reduced to 5% of its excitation when the temperature was below 4 K. The r.f.-induced magnetic dipole transitions between the hyperfine levels tend to equalize the populations and result in a large enhancement in the optical absorption and therefore the fluorescence emission.

In Fig. 1, the ODNMR spectrum of ^{151}Eu^{3+} and ^{153}Eu^{3+} in the ground state is shown. The $^5D_0 \to {}^7F_1$ fluorescence at 16 329 cm^{-1} was monitored to obtain this spectrum. The measured r.f. transition frequencies are listed in Table 1. Because ^{151}Eu has a smaller quadrupole moment than ^{153}Eu, the first two lines in the spectrum are assigned to the $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$ transitions in ^{151}Eu. The line at 26.2 MHz is assigned to the $\pm 3/2 \leftrightarrow \pm 5/2$ transition in ^{153}Eu. One line at 17 MHz is due to two transitions. The $\pm 1/2 \leftrightarrow \pm 5/2$ transition in ^{151}Eu and the $\pm 1/2 \leftrightarrow \pm 3/2$ transition in ^{153}Eu coincidentally overlap at the same position. A very weak line at 43.3 MHz for the $\pm 1/2 \leftrightarrow \pm 5/2$ transition in ^{153}Eu was also observed. The slightly asymmetric line shape of the ODNMR spectrum shown in Fig. 1 is due to nuclear relaxation and hole-refilling process. After the r.f. field was swept off resonance with a hyperfine splitting, it took 10 to 100 ms (depending on temperature and laser intensity) for the system to reach its equilibrium. In our experiments this effect was dominated by the nuclear relaxation.

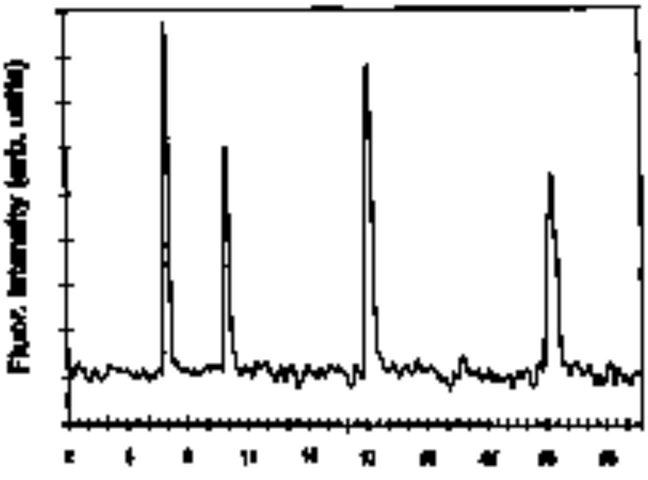

Fig. 1. ODNMR spectrum of ^{151}Eu^{3+} and ^{153}Eu^{3+} in LaF$_3$ at 4 K. The $^7F_0 \to {}^5D_0$ optical transition was at the center of the inhomogeneous profile at 17286.5 cm^{-1}. The $^5D_0 \to {}^7F_1$ fluorescence at 16329 cm^{-1} was monitored while the r.f. field of 1.4 Gauss was swept at 50 kHz s^{-1} and 10 kHz per step. The laser polarization was perpendicular to the crystal c-axis.

Table 1. Quadrupole splittings and interaction parameters of Eu^{3+}:LaF$_3$ in the ground state $^7F_0$ (MHz)

	^{151}Eu	^{153}Eu
$\pm 1/2 \leftrightarrow 3/2$	6.95	17.1
$\pm 3/2 \leftrightarrow 5/2$	9.94	26.2
P	2.67	6.87
η	0.68	0.48

The asymmetric line shape became more significant when the r.f. sweep rate was faster than 1 MHz s^{-1}. The estimated line width for the r.f. transition at 6.95 MHz is 0.3 MHz, and it becomes broader for the higher frequency lines. We believe this is due to the inhomogeneous broadening of the r.f. transitions.

3. Discussion

The hyperfine splitting of a $J=0$ state in Eu^{3+} ions in crystals has contributions from the lattice, from the f-electrons, and from coupling to closed shells whose charge distribution is distorted by the electric field of the lattice. A complete theoretical analysis of quadrupole interaction for Eu^{3+} in general can be found in the literature [1,2]. The present work is focused on experimental measurement of the ground-state quadrupole splitting. A simplified Hamiltonian is used for analysis of the ODNMR spectra of the $J=0$ ground state of the ^{151}Eu and ^{153}Eu isotopes in LaF$_3$. This simplified Hamiltonian combines the nuclear quadrupole interaction and the second order magnetic hyperfine coupling, or pseudoquadrupole interaction, into one framework. At the absence of external magnetic field, the Hamiltonian takes the form [4]

$$H = P\{[I_z^2 - \frac{1}{3}I(I+1)] + \frac{1}{3}\eta(I_x^2 - I_y^2)\} \qquad (1)$$

where P is the effective quadrupole interaction parameter, η the electric field gradient asymmetry parameter. This Hamiltonian is diagonalized on the basis of $|I, I_z\rangle$ to calculate the eigenvalues which we can measure in ODNQR experiments.

First, the eigenvalues of the above Hamiltonian have been calculated as a function of the interaction parameters P and η. Then, the measured quadrupole splittings are used to determine the parameters P and η for both ^{151}Eu and ^{153}Eu. The values of the calculated parameters are listed in Table 1. In comparison of the parameters of Eu in LaF_3 obtained in this work with the parameters of Eu in other hosts, the P value is substantially smaller for both isotopes. This indicates that the ^{151}Eu and ^{153}Eu isotopes in the lattice of LaF_3 have large second order hyperfine interactions which cancel a large part of the quadrupole splitting in the ground state $^7F_0$.

The smaller P for $^{151}Eu^{3+}$ measures the smaller quadrupole moment. The ratio of the quadrupole parameters P for the two isotopes is equal to

$$P^{153}/P^{151} = 2.547 \qquad (2)$$

This compares the ratio of pure quadrupole moments of the two isotopes which has been previously measured by several groups. The average value of Q^{153}/Q^{151} is between 2.55 and 2.58[1–4]. The difference between the ratio of Q and P is due to the contribution of the pseudoquadrupole moment to P. For this reason, the ratio of P's is an indicator of the importance of the pseudoquadrupole effect in various crystalline structures.

The asymmetry parameter η for both ^{151}Eu and ^{153}Eu in LaF_3 are substantially larger than that of the previously studied systems. For Eu^{3+}:$YAlO_3$ [3,4], Eu^{3+}:$LiYF_4$ [5] and Eu^{3+}:CaF_2 [6] the parameter η has a value less than 0.05 for both ^{151}Eu and ^{153}Eu isotopes in the ground state $^7F_0$. This is consistent with the theory of quadrupole interaction. For the non-axial part of the quadrupole interaction, in both the lattice and the electric contribution, one has [7]

$$\eta = 6^{1/2}B_{22}/B_{20} \qquad (3)$$

where B_{22} and B_{20} are the rank 2 crystal field parameters. This simple relation implies that the parameter η is expected to be zero for high symmetry crystal structure in which the crystal-field matrix elements of B_{22} are zero. A small value of η obtained for Eu^{3+} in higher symmetry host suggests that there is local structure distortion surrounding the Eu^{3+} ions. In Ref. [7], ODNQR studies of Eu^{3+} were carried out on a number of defect sites in stead of the intrinsic D_{2d} site. As a result, the parameter η for various defect sites varies from 0 to 0.95. This is a good example of the detailed structure information obtained by high resolution ODNQR. An Eu^{3+} ion in LaF_3 has a C_2 site symmetry. Therefore, nonzero η is expected. Using the crystal field parameters of B_{22} and B_{20} for Eu^{3+}:LaF_3 obtained by Carnall et al. from analysis of optical spectra [9], we have $\eta = 0.56$ in comparison with 0.576 for ^{151}Eu and 0.49 for ^{153}Eu from the present ODNQR work.

In summary, we have studied the ground state quadrupole splitting of Eu^{3+}:LaF_3 by ODNQR. The measurement of zero-field quadrupole energy levels enabled us to determine the interaction parameters of an effective Hamiltonian. In comparison with Eu^{3+} in other system studied previously, the $^{151}Eu^{3+}$ and $^{153}Eu^{3+}$ in LaF_3 have much smaller quadrupole splitting in the ground state $^7F_0$. This implies that the contribution from crystal-field anti-shielding cancels a large part of the contribution from the 4f electrons [2]. The asymmetry parameter η determined with ODNQR characterizes the non-axial crystalline properties and is in general agreement with crystal field analysis. A more detailed analysis of the quadrupole interaction and nuclear Zeeman effect in both the ground state $^7F_0$ and the excited state $^5D_0$ will be published subsequently.

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