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NMR measurement of an ion in an excited state by indirect optical detection: A 1G_4 level of $\text{LiYF}_4:\text{Pr}^{3+}$

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NMR measurements of the 1G_4 excited level (9700 cm^{-1}) of trivalent praseodymium in lithium-yttrium fluoride are reported. They were made by indirect optical nuclear double resonance, where a narrow-band optical excitation, which connects the 3H_4 ground state to the 1D_2 excited state (16741.5 cm^{-1}), pumps individual hyperfine levels. This produces a large polarization of the hyperfine levels, which is preserved as the excitation cascades to the lower crystal-field-split levels. A rf magnetic field induces transitions between the hf states of the longest-lived level (the lowest 1G_4), which are observed through changes in the fluorescence from the lowest 1D_2 level to the ground 3H_4 multiplet. The results may be summarized as parameters in a Hamiltonian: $D = +1.000 \pm 0.001$ MHz, $E < 0.010$ MHz, $\gamma_z = +2.64 \pm 0.02$ kHz/G. From these measurements, the hyperfine constant A_J for the 1G_4 states is determined to be 716 ± 30 MHz. Together with data previously reported for the 1D_2 and 3H_4 states, the interaction between the Pr^{3+} nuclear quadrupole moment and the lattice electric field gradient $P_{\text{latt}} = 0.60 \pm 0.04$ MHz, and the interaction between the $4f$ electrons and the nuclear quadrupole moment are given by $P_{4f} = 0.814 \pm 0.010$ MHz for 3H_4 , 0.028 ± 0.020 MHz for 1G_4 , and 2.027 ± 0.030 MHz for 1D_2 . From these P_{4f} and P_{latt} values, one may obtain $(1-R)\langle r^{-3} \rangle_{4f} = 4.78$ a.u. for the quadrupole interaction, and $A_2^0 = 154\text{ cm}^{-1}$ for the crystal-field interaction, respectively.

INTRODUCTION

Nuclear-resonance measurements in *excited* states require the great sensitivity of optical detection where a radio-frequency-photon event is detected by an optical photon. This increases the sensitivity of the measurement by the ratio of the photon energies. These methods have been demonstrated for both ground and excited states in which the optical excitation terminates on one of the levels studied. In this paper, optical nuclear double resonance of ions in optical crystals is extended to an excited state for which the optical excitation does *not* terminate on the level studied. This process shall be called indirect optical nuclear double resonance (IONDR). This technique is important because it is not always possible to excite resonantly the desired level. For the $\text{LiYF}_4:\text{Pr}^{3+}$ 1G_4 level, a stabilized cw single-mode laser would be required at 9700 cm^{-1} for direct, optically detected NMR. Thus optical nuclear-resonance methods are extended significantly, limited only by the linewidths and the optical pumping rates. In this case the lifetime of the level studied is estimated to be less than $100\text{ }\mu\text{s}$.

In an earlier paper,¹ optical nuclear double resonance (ONDR) of the 1D_2 excited state in $\text{LiYF}_4:\text{Pr}^{3+}$ was reported. It was mentioned in the discussion which identified the level studied that resonances in other levels must be considered as the ONDR did not discriminate between

resonant and nonresonant levels. Level identification must be a part of the process. In that paper, it was concluded that the only other level sufficiently long lived to be observed was 1G_4 . That the 1D_2 (16741.5 cm^{-1}) level was indeed observed was confirmed by the agreement of the calculated and observed magnetic splitting factors for the 1D_2 state, while those of the 1G_4 state were significantly larger. The much longer lifetime of the 1D_2 state was also noted. Subsequently, the Raman heterodyne method of Wong *et al.*² was applied to $\text{LiYF}_4:\text{Pr}^{3+}$ and strong signals were observed³ at the same frequencies as in the ONDR experiments, confirming that it was a direct and not an indirect study of a level not resonant with the laser. No Raman heterodyne signals are expected, nor have been observed at the IONDR 1G_4 frequencies.

THEORY

The energy levels of the praseodymium ion in the S_4 crystal field of the LiYF_4 host crystal are singlets and doublets with the lowest-lying levels for 1D_2 , 1G_4 , and 3H_4 all being electronic singlets. The $I = \frac{5}{2}$ nuclear spin interacts with both the electrons of the ion and the electric field gradient of the host crystal to give a pure quadrupole interaction. In addition a second-order interaction between the electrons and the nuclear spin of the form

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$$\frac{\langle n | \mathbf{J} \cdot \mathbf{I} | 0 \rangle \langle 0 | \mathbf{J} \cdot \mathbf{I} | n \rangle}{E_n - E_0}$$

gives a quadrupolelike interaction.⁴ Another second-order term of the form

$$\frac{\langle n | \mathbf{J} \cdot \mathbf{I} | 0 \rangle \langle 0 | \mathbf{H} \cdot \mathbf{J} | n \rangle}{E_n - E_0}$$

gives the pseudo-nuclear-Zeeman term which produces an anisotropic nuclear Zeeman interaction. All of these can be described by a quadrupole Hamiltonian which has anisotropy added to account for the pseudo-nuclear-Zeeman interaction, and quadrupole parameters which are the sums of those due to the pure quadrupole interaction and the pseudoquadrupole interaction.

This theoretical basis which has been given many times^{5,6} is given by the Hamiltonian

$$H = D[I_z^2 - I(I+1)/3] + E(I_x^2 - I_y^2) - h \sum_i \gamma_i H_i I_i, \quad (1)$$

where

$$\gamma_i / 2\pi = (g_N \beta_N + 2g\beta\Lambda_{ii})/h, \quad (2)$$

$$\Lambda_{ii} = \sum_n \frac{A_J |\langle n | J_i | 0 \rangle|^2}{E_n - E_0}, \quad (3)$$

$$D = D_a + P_{4f} + P_{\text{latt}}, \quad (4)$$

$$D_a = A_J [(\Lambda_{xx} + \Lambda_{yy})/2 - \Lambda_{zz}], \quad (5)$$

$$P_{4f} = -\frac{3e^2Q}{4I(2I-1)} \langle r^{-3} \rangle_{4f} (1-R) \langle J || \alpha || J \rangle \\ \times \langle 0 | 3J_z^2 - J(J+1) | 0 \rangle,$$

$$P_{\text{latt}} = -\frac{3Q}{2I(2I-1)} \frac{B_{20}}{\langle r^2 \rangle} \frac{(1-\gamma_\infty)}{(1-\sigma_2)}.$$

Here $B_{20} = 2A_2^0 \langle r^2 \rangle$; $(1-\gamma_\infty)$, $(1-R)$, and $(1-\sigma_2)$ represent the Sternheimer factors for the lattice-field gradient, $\langle r^{-3} \rangle_{4f}$, and $\langle r^2 \rangle$, for the $4f$ electrons. General formulas for calculating the operator equivalent factors are given by Judd.⁷ A_J is the hyperfine constant for the given J state.⁸ The electronic states $|0\rangle$ used were obtained from calculations of the optical spectra for this system by Esterowitz *et al.*⁹

EXPERIMENT

The measurements, made using the same technique as for the ONDR experiments,¹ are outlined in Fig. 1. A single crystal of $\text{LiYF}_4:\text{Pr}^{3+}$, cooled to 2 K, was illuminated at 16741.5 cm^{-1} with a 50-mW beam of light perpendicular to the c axis. The light was obtained from a stabilized, single-frequency ring laser.¹⁰ Since the light source is narrow ($< 1 \text{ MHz}$ full width at half maximum) compared to the hyperfine splitting (5 MHz), it populates one of the hyperfine levels of the lowest 1D_2 state for each pumped ion. This level relaxes (0.5 ms) to the ground electronic state, primarily through intermediate electronic states. Because of the large number of intermediate crystal-field levels, many optical transitions are seen in the

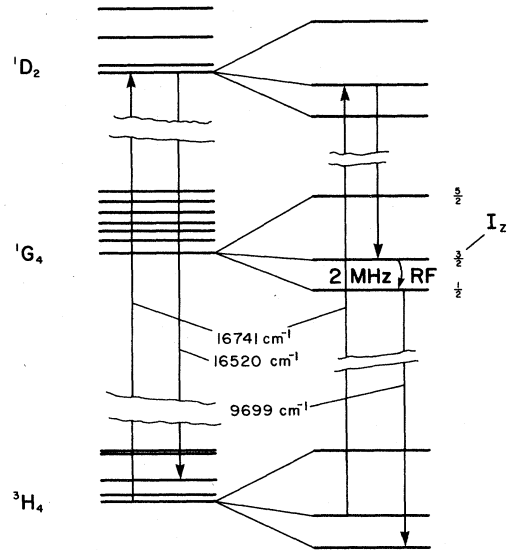


FIG. 1. Indirect optical nuclear double resonance explained. Crystal-field-split energy levels are shown to indicate the optical transitions of interest. The laser pumps the 3H_4 (0 cm^{-1})– 1D_2 (16741 cm^{-1}) transition which relaxes radiatively to the ground state via the intermediate crystal-field levels. While the excitation rests in the lowest 1G_4 level, a rf magnetic field induces magnetic dipole transitions in the hyperfine levels of that state. On relaxation to the ground electronic state, the ion is in a hyperfine level which is inaccessible to the pump laser, reducing the optical absorption. The magnetic resonance is detected by monitoring the optical absorption via the 16520 cm^{-1} luminescence from the crystal as a function of the radio frequency. Only the most direct relaxation channel is shown. Most of the relaxation will proceed by a combination of radiative and nonradiative processes via several levels.

luminescence. The 3H_4 – 1D_2 optical absorption may be monitored by simply observing the luminescence from any of these lines. A rf magnetic field of about 1 G rms, applied to the sample along the light beam, induces magnet-

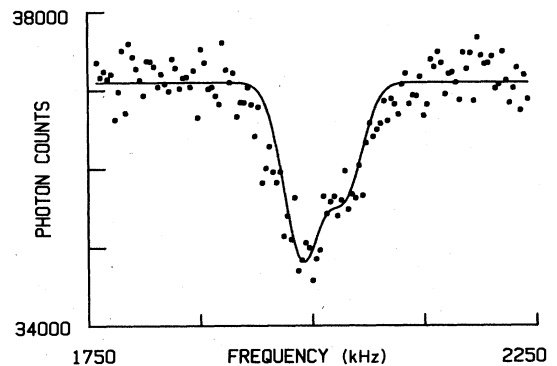


FIG. 2. The $I_z = \frac{1}{2}$ to $\frac{3}{2}$ (1G_4) transition of Pr^{3+} in a LiYF_4 single crystal at 2 K in the absence of an external static magnetic field observed by indirect optical nuclear double resonance. The total dwell time at each point is 4 s. The solid line is drawn to indicate that some structure is evident in the data. No attempt was made to fit the data to two or more peaks. The linewidth is approximately 95 KHz.

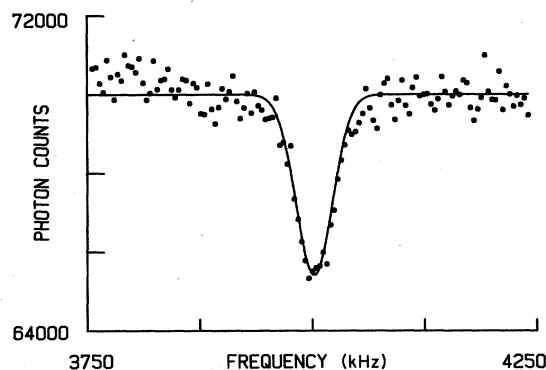


FIG. 3. The $I_z = \frac{3}{2}$ to $\frac{5}{2}$ (1G_4) transition of Pr^{3+} in LiYF_4 single crystal at 2 K in the absence of an external static magnetic field observed by indirect optical nuclear double resonance. The total dwell time at each point is 12 s. The rf-magnetic-field amplitude is one-third that of Fig. 1. The linewidth is approximately 48 KHz.

ic dipole transitions between two hyperfine levels. For an excited-state resonance, the ion returns to a hyperfine level of the ground electronic state which is not resonant with the laser as a result of the rf transition. Consequently the luminescence decreases slightly for both the direct and the indirect process. In addition to the 1D_2 excited-state resonances previously reported,¹ two new dips were observed at 2.000 and 4.000 MHz in the absence of an external magnetic field. These are shown in Figs. 2 and 3. When a magnetic field was applied to the crystal along the c axis, both of these peaks split into two, corresponding to $\gamma_z = 2.64 \pm 0.02$ KHz/G. A typical spectrum is shown in Fig. 4 for the $I_z = \frac{3}{2}$ to $\frac{5}{2}$ transition. As the field direction was rotated away from the z axis, the splitting of the 4-MHz dips decreased as was expected for this $I_z = \frac{3}{2}$ to $\frac{5}{2}$ transition. In order to obtain the transverse-magnetic splitting factors, measurements of the weaker $I_z = \frac{1}{2}$ to $\frac{3}{2}$ transition were required. Unfortunately, as

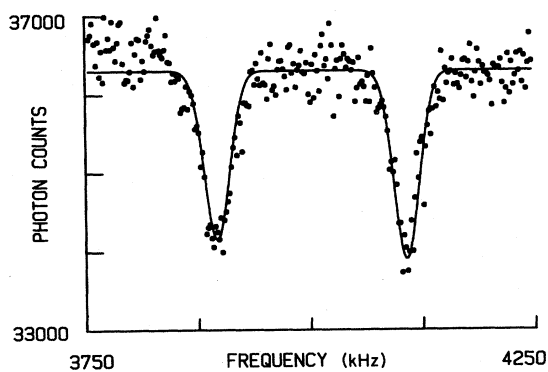


FIG. 4. The $I_z = \frac{3}{2}$ to $\frac{5}{2}$ (1G_4) transition of Pr^{3+} in LiYF_4 single crystal at 2 K, in an external static magnetic field of 40 G along the crystal c axis, observed by indirect optical nuclear double resonance. The total dwell time at each point is 12 s. The rf-magnetic-field amplitude is the same as that of Fig. 2. The linewidth is approximately 34 KHz.

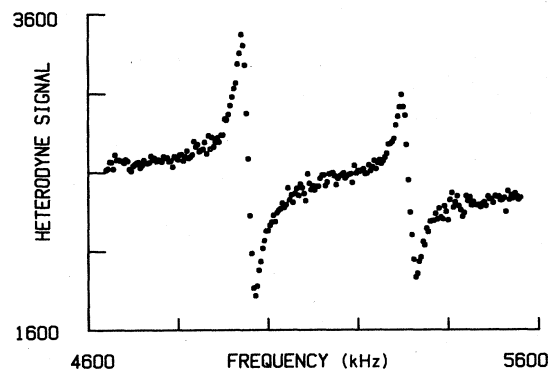


FIG. 5. The $I_z = \frac{1}{2}$ to $\frac{3}{2}$ (1D_2) transition of Pr^{3+} in LiYF_4 single crystal at 2 K, in an external static magnetic field of 80 G perpendicular to the c axis of the crystal, observed by Raman heterodyne spectroscopy. The rf magnetic field is parallel to the light beam which is perpendicular to the c axis of the crystal. The linewidth is approximately 32 KHz. No signals were observed at the 1G_4 frequencies.

the static magnetic field was rotated away from the c axis, the resonance peaks became too weak to many any meaningful measurement of their positions.

In order to confirm the identity of these resonances, Raman heterodyne measurements similar to those reported by Wong² for $\text{LaF}_3:\text{Pr}^{3+}$ were attempted for the excited-state transitions, 1D_2 and 1G_4 . Strong resonances were observed on an oscilloscope when the rf magnetic field was perpendicular to the c axis (but not when parallel), and when the static magnetic field was not parallel to the c axis, for the ground state 3H_4 and 1D_2 but not for 1G_4 . The 50–100-mW weakly focused light beam was along the rf magnetic field. A Raman heterodyne signal obtained using a slowly sweeping rf signal is shown in Fig. 5 for the 1D_2 transition with an 80-G magnetic field perpendicular to the c axis. Since the Raman heterodyne method requires that the optical field terminate on one of the levels studied, the presence of signals at 5 and 10 MHz would confirm that they are from the 1D_2 hyperfine transition as previously reported, while their absence at the 2- and 4-MHz frequencies would indicate that the ONDR transitions are indirect.

RESULTS

The identification of the 2- and 4-MHz dips with a 1G_4 level is not complete with the confirmation that they are indirect resonances. Two other pieces of evidence are considered. First, the lifetimes of the levels lower than the 1D_2 pumped level have not been measured, but estimates can be made from the multiphonon decay studies of Riseberg and Moos¹¹ on the LaF_3 host. The known energy gaps⁹ allow four or fewer phonon processes for all (where the energy gap is less than 1740 cm^{-1}) but the 1G_4 lowest level (energy gap of 2479 cm^{-1}) which should give lifetimes of less than $1 \mu\text{s}$ for those levels. The maximum phonon energy for LiYF_4 is greater than for LaF_3 so that the $100\text{-}\mu\text{s}$ lifetime for LaF_3 should be an upper bound for the 1G_4 lifetime. The $1\text{-}\mu\text{s}$ lifetimes would give resonance peaks much wider than we observe here if they could be

observed at all.¹² One must conclude that the resonances come from 1G_4 once 1D_2 levels are excluded. Secondly, the calculated nuclear Zeeman splitting for 1G_4 approximately matches the observed value for γ_z . Since γ_x could not be measured, no comparison was made.

From the measured magnetic splitting factors and Eqs. (2) and (3), the hyperfine constant for this 1G_4 level can be obtained. From Macfarlane,¹³

$$\gamma_{Pr} = g_N / h\beta_N = 1303.65 \pm 0.15 \text{ Hz/G}.$$

Because of the close proximity of the 3F_4 level, the wave functions are strongly mixed. The g used in Eq. (2) is an effective $g_{\text{eff}} = 1.10$. One obtains $A_J = 716 \pm 30$ MHz compared to a calculated value from Wybourne⁸ of 912 MHz with the intermediate coupling corrections. When γ_x is measured, a confirming value should be obtained. This difference is substantially larger than for the 1D_2 state. In the analysis, three $^{2S+1}L_4$ components were included. No account has been taken for other J contributions which may explain part of the difference. Configuration interaction and relativistic effects are also ignored.

It was noted in Fig. 2 that rather than a single resonance peak observed for the $I_z = \frac{3}{2}$ to $\frac{5}{2}$ transition, structure was evident in the $I_z = \frac{1}{2}$ to $\frac{3}{2}$ transition. This has previously been observed in the ground state 3H_4 in the $\text{LiYF}_4:\text{Pr}^{3+}$ system¹⁴ and was found due to interactions between the nuclear magnetic moment of the host F^- ions with the Pr^{3+} nuclear moments. There is not a sufficiently good signal here to analyze the peak other than to note that it is wider than one for the $I_z = \frac{3}{2}$ to $\frac{5}{2}$ transition. Since we do not have a measured value of the transverse-magnetic splitting factor γ_x , a calculated fit cannot be made. (The calculated value of $\gamma_x = 4.39$ KHz/G.)

The measured hyperfine constant D also gives useful information (and a confirmation of the level studied). Following Sharma and Erickson,¹ "measured" values of P_{latt} and P_{4f} may be obtained from knowing a calculated D_a and the calculated ratios of the P_{4f} :

$$P_{4f} = \text{const} \times \langle J || \alpha || J \rangle \langle 0 | 3J_z^2 - J(J+1) | 0 \rangle.$$

The $\langle J || \alpha || J \rangle$ are given in a formula by Judd.⁷ The second term was calculated with the intermediate coupled wave functions. D_a was obtained from Eq. (5) and the same wave functions. Because the shielding of the lattice-electric-field gradient from the nucleus by the $4f$ electrons is quite small,¹⁵ P_{latt} was assumed to be the same for the three electronic states. The results are summarized in Table I. It should be observed that when combined with the data of Sharma and Erickson, a refined fit of P_{latt} and P_{4f} is obtained which is quite consistent with

TABLE I. Quadrupole interaction parameters for the $\text{LiYF}_4:\text{Pr}^{3+}$ crystal obtained by a linear-regression fit of measured values of the quadrupole parameter D together with the calculated pseudoquadrupole parameter D_a and the calculated ratios of $4f$ -electron part of the pure quadrupole interaction. P_{latt} was assumed to be the same for all three states. The units are in KHz.

	D	D_a	P_{latt}	P_{4f}	Deviation
1D_2	2561	-39	598	2027	-25
1G_4	1000	412	598	28	-38
3H_4	4737	3258	598	814	63

the previous situation. Second, a value of $(1-R)\langle r^{-3} \rangle_{4f}$ may be obtained from P_{4f} and is equal to 4.78 a.u. This may be compared to the values calculated by Sternheimer, $\langle r^{-3} \rangle_{4f} = 5.369$ a.u., and $R = 0.1308$, which give a product of 4.67 a.u.¹⁶ While there is no disagreement over the R values, other $\langle r^{-3} \rangle_{4f}$ values have been calculated by various methods to give values ranging from 4.26 to 5.5 a.u.¹⁷

Finally, the P_{latt} value can be used together with the calculations of Sternheimer for $\gamma_\infty = -80.9$ and $\sigma_2 = 0.60$ to obtain

$$A_2^0 = B_{20} / 2 \langle r^2 \rangle = 154 \text{ cm}^{-1}.$$

This compares to the B_{20} value used by Esterowitz *et al.* in their crystal-field fit of 488 cm^{-1} . ($A_2^0 = 224 \text{ cm}^{-1}$.) The $\langle r^2 \rangle$ value is not given but is assumed to be the 1.089 a.u. as given by Freeman and Watson.¹⁸ The major source of the discrepancy is likely the uncertainty of this $\langle r^2 \rangle$ value.¹⁹

SUMMARY

Optically detected NMR measurements of ion in an excited state have been made where the optical transition does not terminate on the electronic state measured. From a measurement of the zero-field splittings and a magnetic splitting factor in a low magnetic field, combined with the theoretical descriptions of the hyperfine interactions, values of the hyperfine constant A_J , the shielded radial integral $(1-R)\langle r^{-3} \rangle_{4f}$ for the quadrupole interaction, and the crystal-field parameter A_{20} were obtained. These values were compared with those determined from other methods.

This indirect-optical-detection scheme allows study of hyperfine structure of excited states not accessible with stabilized cw lasers, and is limited only by the lifetime and the nuclear-spin relaxation of the state studied. It is estimated that the lifetime of the 1G_4 level studied here is less than $100 \mu\text{s}$.

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³See the Experiment section in this paper.

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