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Hyperfine structure and Zeeman effect of the $LaBr_3$:Pr^{3+} 6033-Å line using the laser-induced fluorescence-line-narrowing technique

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The ${}^1D_2A_1 \rightarrow {}^3H_4E_2$ transition of $LaBr_3$:Pr^{3+} has been studied using the laser-induced fluorescence-line-narrowing technique. The spectroscopic splitting factor and the hyperfine structure of the ground ${}^3H_4E_2$ level, the radiative lifetime and the nuclear spin relaxation time of the excited ${}^1D_2A_1$ level have been determined.

I. INTRODUCTION

After the first experiments carried out on ruby,[1] the technique of continuous-wave laser-induced fluorescence line narrowing applied to optical crystalline spectroscopy has recently led to a lot of results (see, for instance, Refs. 2–5).

In the particular case of Pr^{3+} in $LaCl_3$, besides measurement of the spectroscopic splitting factor and hyperfine structure of the ground level previously known from conventional spectroscopy and EPR, still smaller effects have been observed: a binary deformation[3] and the pseudonuclear Zeeman splitting.[6] Moreover, the nuclear relaxation time of the hyperfine states of the excited level has been estimated from intensity measurement of transfer lines.

It was interesting to attempt such an investigation in another crystal host, $LaBr_3$, for which very few data are available.

$LaBr_3$ and $LaCl_3$ are isomorphic and have nearly equal lattice dimensions. Therefore, the Pr^{3+} spectra are very similar in both crystals: there is an identical crystal-field quantum-number ordering, the centers of gravity of the multiplets differing by about 10^2 cm^{-1}.[7,8]

The crystal electric field parameters have been obtained from optical data by Wong and Richman,[7] and applied on the ${}^3H_4$ term by Vishwamittar[9] to study thermal and magnetic properties of Pr^{3+} in $LaBr_3$. Finally, a comparative study of radiative and nonradiative transitions of Pr^{3+} has been attempted by German *et al.*[10]

In the present work, we study the ${}^1D_2 \rightarrow {}^3H_4$ fluorescence transition. The experiments are limited to the transitions between lowest crystalline Stark levels, the only ones whose homogeneous widths are small enough to make sense of using a high-resolution technique.[3]

The fluorescence-line-narrowing experiments previously made on the $LaCl_3$: Pr^{3+} 6011-Å resonance line have been carried out on the $LaBr_3$: Pr^{3+} 6033-Å resonance line. Furthermore, the ${}^1D_2A_1$ lifetime—required for an estimation of the nuclear-spin-relaxation time—has been measured.

The experimental data obtained are compared to calculated values deduced from the Wong and Richman crystalline parameters, and also to the results obtained in $LaCl_3$.

II. ENERGIES OF THE LEVELS RELATIVE TO THE 16 570.5-cm^{-1} TRANSITION

In $LaBr_3$, the rare-earth point symmetry is C_{3h}, and the two levels involved in the 16 570.5-cm^{-1} transition are (a) the ground level ${}^3H_4E_2$ of crystalline quantum number $\mu = \pm 2$ modulo 6; (b) the ${}^1D_2A_1$ level of crystalline quantum number $\mu = 0$.

The praseodymium is monoisotopic with a nuclear spin $I = \frac{5}{2}$, and each level has six hyperfine states. The dipole magnetic part of the hyperfine effect leads to energies of the components equal to $A_J \sum_{M_J} (a_{M_J})^2 M_J M_I$ (A_J being the hyperfine constant of the multiplet, and a_{M_J} the wave function's coefficients). Therefore, the ground level is made up of six hyperfine doubly degenerate sublevels; in a pure C_{3h} symmetry these hyperfine components are equally spaced (we call Δ the corresponding splitting). The excited ${}^1D_2A_1$ level is only submitted to the quadrupole electric part of the hyperfine effect and split into three sublevels. Nevertheless, the quadrupole interaction in praseodymium is nearly zero, and will be neglected in all calculations.

The presence of an external magnetic field introduces additional effects: (i) the electronic Zeeman effect splits the ${}^3H_4E_2$ level into two crystalline levels E_+ ($\mu = 2$ mod 6) and E_- ($\mu = -2$ mod 6) by a quantity $g\mu_B H$. Each of these crystalline levels has six equally spaced hyperfine components; (ii) the nuclear Zeeman effect leads to an additional energy equal to $\delta = -(1/I)\mu_I H M_I$ and therefore independent of the level; (iii) the second-order Zeeman hyperfine effect (sometimes called the pseudonuclear Zeeman effect, or the paramagnetic shielding correction). If W_2 is a perturbing crystalline level near the W_1 level, the energy of the W_1 level is given by

$$\frac{\langle W_1 M_I | H_Z | W_2 M_I \rangle \langle W_2 M_I | H_{\rm hf} | W_1 M_I \rangle}{W_1 - W_2} + \text{c.c.},$$

H_Z and $H_{\rm hf}$ being, respectively, the electronic Zeeman operator and the magnetic-dipole interaction operator. This effect has the same form as the nuclear Zeeman effect, but depends on the considered level.

The perturbing levels of ${}^1D_2A_1$ are several thousand cm^{-1} away and then are without any effect. The ground level on the contrary is perturbed by the ${}^3H_4E_2$ (86-cm^{-1}) level. Its hyperfine splittings are then modified by an amount d proportional to the external magnetic field.

In the present case, the nuclear Zeeman effect and the second-order Zeeman hyperfine effect both increase the hyperfine splittings of the ${}^3H_4E_-$ level ($\Delta_- = \Delta + \delta + d$) and decrease the hyperfine splittings of the ${}^3H_4E_+$ level ($\Delta_+ = \Delta - \delta - d$). The Δ quantity is independent of the external magnetic field, whereas δ and d are proportional to the magnetic field. Therefore, these two effects cannot be distinguished in a given level.

III. EXPECTED NARROWED FLUORESCENCE SPECTRA

In spite of the fact that the $\Delta M_I = 0$ selection rule is perfectly verified for all transitions between the ground and excited levels, the laser-induced fluorescence spectra exhibit more than one line due to the fact that ions belonging to several classes of sites are excited. As a matter of fact, the ${}^1D_2A_1$ inhomogeneous level is wider than the ground-level hyperfine structure spread, so that a σ_L transition coming from any of the six hyperfine ground levels (equally populated at 4 K) can excite the ${}^1D_2A_1$ levels of ions belonging to six different classes of sites. In these conditions, a seven-line spectrum is expected: one intense line at the laser wavelength, six equidistant weaker lines split by a 2Δ quantity. The splitting between the σ_L line and the center of gravity of the six other lines is $g\mu_B H$ (in a zero magnetic field the σ_L line is in the middle of the spectrum).

The spectra just described are expected if we assume there is no transfer between the different nuclear states of ${}^1D_2A_1$. This is true at low temperatures. In LaCl_3 above liquid-helium temperature, a relaxation between two next nuclear levels $|{}^1D_2A_1M_I\rangle$ and $|{}^1D_2A_1M_I \pm 1\rangle$ has been put into evidence, and it has been shown that its rate depends in an important way on the temperature.[6] In that case, a simplified model allowed us to determine the order of magnitude of the relaxation time τ as a function of the lifetime τ_0 of the level by means of the relative intensities of the extra lines appearing on account of the transfers.

Figure 1 represents a schematic diagram of the levels and of the transitions in an external magnetic field. The excitation here is from the lower Zeeman group, a similar figure could be obtained by excitation from the upper one.

The six classes of sites excited by the same laser radiation σ_L have been represented. The figure has been drawn so that for any site, all transitions relative to the same frequency are on the same horizontal line.

On the right-hand side of the figure, the expected spectra are schematized, when excitation and fluorescence are on the same Zeeman group (we call it the resonant spectrum) and on different Zeeman groups (we call it the nonresonant spectrum).

This is the case of a temperature such as a $|{}^1D_2A_1M_I\rangle$ state relaxes only to the $|{}^1D_2A_1M_I \pm 1\rangle$ states.

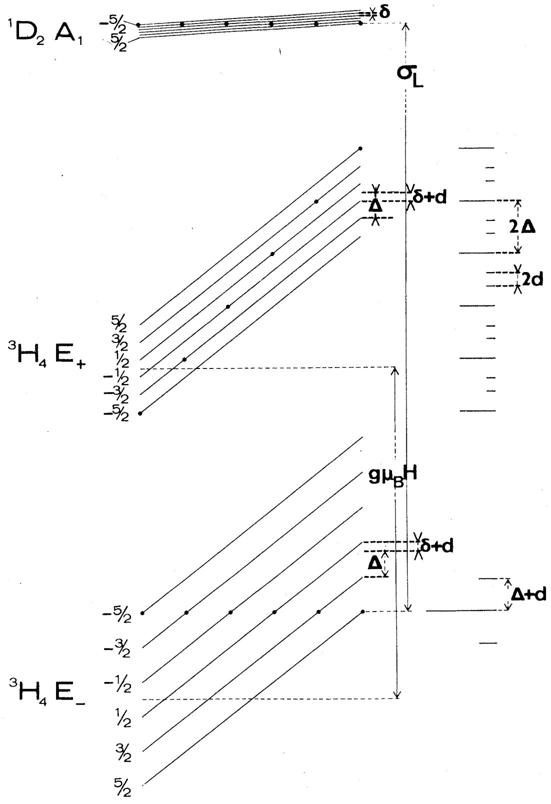

FIG. 1. On the left-hand side: Energy Zeeman levels diagram of excited ions belonging to six classes of site symmetry. Excitation comes from the lower Zeeman group. The figure is drawn so that all transitions relative to the same frequency are on the same horizontal line. On the right-hand side: Schematized resonant and nonresonant spectra.

IV. EXPERIMENTAL METHODS

The crystal sample used in these experiments is anhydrous lanthanum bromide doped with about 0.1-at.% Pr^{3+} ions (this low concentration avoids any interactions between ions). It was grown at the Laboratoire de Physique Cristalline in Orsay, using the Bridgman method. Because of the hygroscopic character of the bromides, the sample is polished and mounted inside the cryostat in a dry box, then kept in vacuum. It is cooled by conduction with liquid helium. Due to its easy cleavage, holding of the sample on the conduction copper is weak. Therefore its temperature is a few degrees higher than 4.2 K.

Lifetime of the $^1D_2A_1$ level has been measured by observation of the time dependence of fluorescence intensity after a pulsed selective excitation. Excitation of the $^1D_2$ multiplet at 5996 Å [transition $|^3H_4\,(0\ \text{cm}^{-1})\rangle \rightarrow |^1D_2E_2(16\,672\ \text{cm}^{-1})\rangle$] is achieved by a $R6G$ dye laser with a grating in the cavity, pumped by a pulsed nitrogen laser with a repetition rate of 10 pulses per sec. Fluorescence lines from the $^1D_2A_1$ level (6033 Å, 6039 Å) are selected by a low-resolution Coderg grating monochromator; their intensity is detected by a S-11 photomultiplier tube and displayed directly on a Tektronix oscilloscope. The traces are photographed by a Polaroid camera.

The fluorescence-line-narrowing experiments have been carried out with the experimental setup described in a previous paper[5]: the source is a continuous-wave single-mode jet-stream dye laser (Spectra Physics 580A), the analyzer is a pressure scanned Fabry-Perot interferometer (The free spectral range was 250×10^{-3} cm^{-1} and the instrumental width 13×10^{-3} cm^{-1}.) The incident beam and the magnetic field are oriented parallel to the crystal axis.

V. EXPERIMENTAL RESULTS AND DISCUSSION

The $LaBr_3$ samples were cleaved, this leading to a very important diffusion of the laser light. To avoid its superposition with the fluorescence light, a modulation technique has been used.[5] However, the laser diffusion was not completely removed, and the observation of the resonant spectra was made very difficult.

A. Hyperfine structure and Zeeman effect of the 6033-Å line

In presence of an external magnetic field and in the case of a nonresonant spectrum, all difficulties due to the laser diffused light are avoided and accurate measurements can be made.

At our experimental temperature, there exists a transfer between the $^1D_2A_1$ nuclear states, but it is small and the presence of extra lines does not reduce the accuracy of the measurements. In these conditions, the data have been found to be

$$\Delta=(17.8\pm0.2)\times10^{-3}\ \text{cm}^{-1},\quad g=0.73\pm0.01$$

(uncertainties being due to inaccuracies in the magnetic field measurements).

As stated before, the resonance spectra are hidden by the diffused laser light. It was then not possible to determine the pseudonuclear Zeeman effect. In a zero magnetic field, only two fluo-

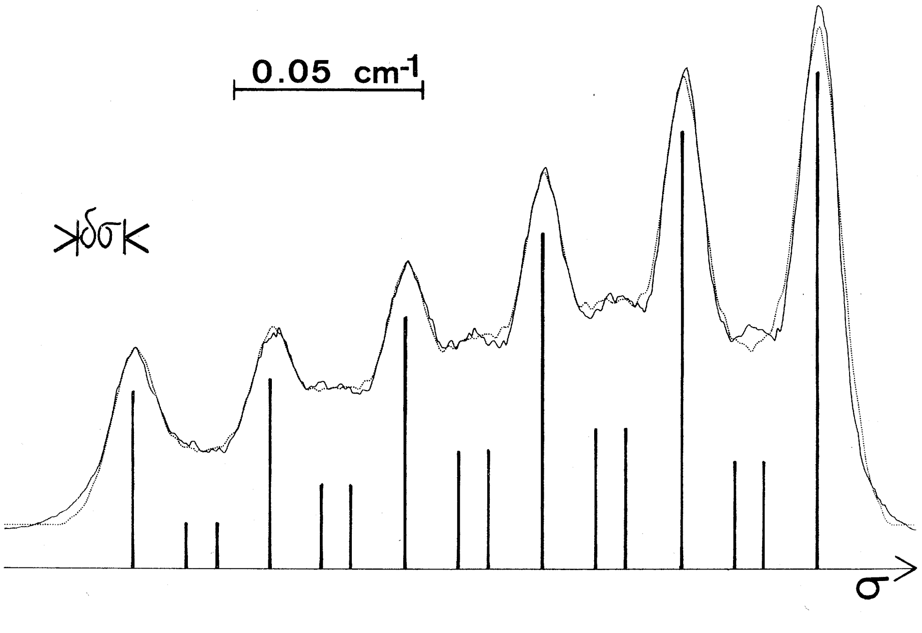

FIG. 2. Nonresonant Zeeman spectrum of the 6033-Å line. Comparison between the experimental spectrum (full curve) and the reconstructed spectrum (dotted curve). Vertical lines represent the intensities of the components. $\delta\sigma$ is the instrumental width.

rescence lines on each side of the resonant line are out of the laser diffusion spectral region. They correspond to different crystalline sites. They are relative to the $|{}^3H_4E_2 \pm \frac{5}{2}\rangle \rightleftarrows |{}^1D_2A_1\rangle \rightleftarrows |{}^3H_4E_2 \mp \frac{5}{2}\rangle$ and to the $|{}^3H_4E_2 \pm \frac{3}{2}\rangle \rightleftarrows |{}^1D_2A_1\rangle \rightleftarrows |{}^3H_4E_2 \mp \frac{3}{2}\rangle$ transitions. The splittings between the symmetric lines are, respectively $(181.8 \pm 2) \times 10^{-3}$ cm^{-1} and $(108.2 \pm 2) \times 10^{-3}$ cm^{-1}. In a pure C_{3h} symmetry, according to the Δ values previously obtained, these splittings should be equal to $(178 \pm 2) \times 10^{-3}$ cm^{-1} and $(106.8 \pm 1.2) \times 10^{-3}$ cm^{-1}. It then can be concluded that the introduction of Pr^{3+} ions in LaBr$_3$ does not modify in an appreciable way the C_{3h} point symmetry of Pr^{3+} ion (in opposition to LaCl$_3$:Pr^{3+}).

The crystal-field parameters have been derived from the experimental spectrum by Wong and Richman[7] and found approximately equal to those of LaCl$_3$:Pr^{3+}.

The $^3H_4$ level being 97.5% pure, it seemed we were entitled to carry out the calculations within the manifold. In this case, the calculated g factor is equal to 0.96,[9] to be compared to the experimental value 0.73. A small change in the A_4^0 parameter (-38.12 cm^{-1} instead of -44.52 cm^{-1}) yields the same average deviation, but fits the experimental g value. We have then made the other calculations using the wave functions derived from this new set of parameters.

The A_J parameter obtained in these conditions is 39.2×10^{-3} cm^{-1}, giving the a_{4f} value 29.8 $\times 10^{-3}$ cm^{-1}. This value is to be compared to the similar value for Pr^{3+} in LaCl$_3$. Wave functions giving the experimental g value 1.035 leads to $A_J = 38.5 \times 10^{-3}$ cm^{-1} ($a_{4f} = 29.3 \times 10^{-3}$ cm^{-1}).

B. Radiative lifetime and relaxation time of the $^1D_2A_1$ states

Although it was not possible to observe the transfer lines on the Zeeman-resonance spectrum and to measure directly their relative intensities, we have been able to estimate them from the nonresonant spectrum by reconstructing it using a simplex method.[11] The $2d$ splitting of two near-transfer lines (not resolved in our experiments) has been calculated. The $|{}^3H_4E_2\rangle$ wave functions giving the experimental g and A_J data lead to a $d \simeq 5\mu_B HM_I \times 10^{-3}$-cm^{-1} value.

Reconstruction has been made with all parameters fixed, the relative intensities only being allowed to vary.

Figure 2 represents the computer trace of the experimental and computed spectra. In these conditions, it has been possible to estimate the transfer rate between the $^1D_2A_1$ nuclear states. At the temperature of the experiment and for an external magnetic field of 17.5 kG it is about 20%.

To convert the transfer rate in a relaxation time, the radiative lifetime of $^1D_2A_1$ has been measured. Including error on oscilloscope base, its mean value τ_0 at the temperature of our experiments is found to be

$$\tau_0 = 162 \pm 8 \ \mu\text{sec} .$$

In these conditions, the relaxation time of a nuclear state is

$$\tau \sim 0.65 \text{ msec} .$$

These values are to be compared to the values obtained in LaCl$_3$ with similar conditions: $\tau_0 = 73.2 \pm 1.9$ μsec,[10] and $\tau \sim 0.20$ msec.[6]

VI. CONCLUSION

The laser-induced fluorescence-line-narrowing technique applied to Pr^3 ions in a LaBr$_3$ host has allowed to determine with great accuracy several data relative to the $^1D_2A_1$ (16570 cm^{-1}) → $^3H_4E_2$ (0-cm^{-1}) transition, such as the hyperfine constant and the spectroscopic splitting factor of the ground level, the radiative lifetime and the nuclear-spin-relaxation time of the $^1D_2A_1$ level.

Calculations are coherent with the experimental results and their validity has been tested by means of a reconstruction of the fluorescence spectrum.

Further experiments, using another cooling system and with a temperature control, will lead to additional results. They will allow to make a more complete comparison between the behavior of Pr^{3+} ions in the two LaCl$_3$ and LaBr$_3$ hosts.

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