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To cite this version:
N. Pelletier-Allard, R. Pelletier. Laser induced fluorescence in Nd\textsuperscript{3+}: LaCl\textsubscript{3}. I. - Hyperfine structures. Journal de Physique, 1980, 41 (8), pp.855-859. 10.1051/jphys:01980004108085500 . jpa-00208906

HAL Id: jpa-00208906
https://hal.archives-ouvertes.fr/jpa-00208906
Submitted on 1 Jan 1980

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Laser induced fluorescence in Nd\textsuperscript{3+} : LaCl\textsubscript{3}

I. — Hyperfine structures

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(Reçu le 18 décembre 1979, accepté le 13 mars 1980)

Résumé. — La technique d'affinement des raies de fluorescence induite par laser a été utilisée pour l'obtention de spectres à haute résolution sur les isotopes enrichis 143 et 145 de l'ion Nd\textsuperscript{3+} dans une matrice de LaCl\textsubscript{3}. Les interactions nucléaires dipolaires magnétiques ont été étudiées sur les transitions \( ^4I_{9/2} \rightarrow ^2H_{11/2} \) et \( ^4I_{9/2} \rightarrow ^4G_{5/2} \) dans des systèmes à deux et à trois niveaux.

Abstract. — The laser induced fluorescence line-narrowing technique has been used to obtain high-resolution spectra of isotopically enriched \(^{143}\)Nd\textsuperscript{3+} and \(^{145}\)Nd\textsuperscript{3+} ions in a LaCl\textsubscript{3} host. Nuclear magnetic dipole interactions have been investigated for the \( ^4I_{9/2} \leftrightarrow ^2H_{11/2} \) and \( ^4I_{9/2} \leftrightarrow ^4G_{5/2} \) transitions in two-level and three-level systems.

1. Introduction. — The selective excitation, by means of a single mode laser, of ions belonging to a definite class of crystal field, enables high resolution crystalline spectroscopy to be obtained, if the technique is applied to transitions whose homogeneous widths are much smaller than the inhomogeneous widths. Its application is in fact limited to the transitions between the lowest crystalline Stark levels of the multiplets. For rare earths ions in ionic crystals, the linewidth corresponding to these transitions can be very small, and in some cases narrower than the jitter of the laser, which then limits the experimental resolution [1, 2].

Lanthanum chloride proved to be a suitable host for hyperfine spectroscopic studies of a substituted rare earth impurity. The particular case of praseodymium has been extensively examined on two-level and three-level systems after excitation of the \( ^1D_2 \) (16 630.5 cm\textsuperscript{-1}) level. The ground doublet and two singlet levels have been investigated, leading to the observation of several second order effects. All spectra are consistent with the assumption that, at low temperature, no relaxation occurs between the degenerate nuclear excited states [3-8].

It appeared interesting to study the behaviour of a Kramers ion for which all levels have a non-zero hyperfine structure. Nd:LaCl\textsubscript{3} has a well known spectrum which possess two levels in the rhodamine spectral region. Therefore we have carried out a study by excitation of the \( ^2H_{11/2} \) and \( ^4G_{5/2} \) levels on enriched odd isotopes. In the absence of any relaxation between the excited nuclear states, the two hyperfine narrowed resonance spectra are related to the ground level structure only. Since interpretation of the experimental spectra implies the participation of the excited level structures, the existence of a relaxation between their nuclear states is demonstrated. This demonstrates the difference between praseodymium and neodymium.

In this paper we present the experimental hyperfine spectra corresponding to the two-level and three-level systems that we were able to observe. We give an interpretation, and deduce the phenomenological parameters when possible. Finally we compare the experimental results with the calculated values.

2. Experimental details. — The experimental arrangement has been thoroughly described in a previous paper [5]. The source is a 375 Spectra Physics CW single mode tunable laser. The beam is focused in the sample by a 0.15 m focal length lens and the power at the dye laser output is 15 to 30 mW according to the wavelength. Under these conditions, the saturation is not reached. This is confirmed by the fact that the intensity of the fluorescence varies linearly with the intensity of the incident light. The fluorescence observed at right angle to the incident beam is analysed by means of a pressure-scanned Fabry-Perot
spectrometer with effective resolution between $10^6$ and $3.8 \times 10^6$, according to the recorded spectra. Calibration is performed by use of a Michelson interferometer. The fluorescence is detected with an RTC XP 1017 photomultiplier. The magnetic field is obtained by means of a Tek-Elek electromagnet.

The cryogenic system is a CF 204 Oxford Instruments continuous-flow cryostat in which the sample is cooled by a static exchange gas. All the spectra presented here were recorded with a sample temperature around 4K.

The crystals contain 0.05 atomic % Nd$^{3+}$. They were grown at the Laboratoire de Physique Cristalline in Orsay, using the Bridgman method. The samples are cut with their faces parallel and perpendicular to the crystallographic axis.

Natural neodymium has seven stable isotopes. The two odd isotopes, of atomic weights 143 and 145, have a 7/2 nuclear spin. Both were studied and the results have been found to be perfectly consistent with the ratio of their respective nuclear moments. The spectra presented in this paper have been obtained from the $^{145}$Nd isotope: they are more accurate as the isotope used is 90% enriched, compared to 75% for the $^{143}$Nd isotope.

3. Bibliographic data. — An energy level diagram was first obtained from the absorption and fluorescence spectra with their Zeeman effects [9]. The data were analysed with the help of intermediate coupling calculations of the energy levels of the 4f$^3$ configuration for various values of the spin-orbit coupling parameter. Calculations, leading to the determination of the values of the three Slater integrals, of the spin-orbit coupling constant and of the four crystal field parameters were subsequently performed [10]. More recently, after an extension of the spectral analysis to higher energies, a new parametric treatment has been given, introducing spin-other-orbit and pseudomagnetic operators, as well as operators for two-particle and three-particle electrostatic configuration mixing interactions [11].

The spin-hamiltonian parameters relative to the Zeeman and hyperfine effects of the ground state were first obtained from paramagnetic resonance absorption experiments [12]. The electron-nuclear double resonance spectra have provided more accurate values of the spin-hamiltonian parameters which are used to deduce the nuclear magnetic moments and the $\langle r^{-3} \rangle$ value of Nd$^{3+}$ [13]. Magnetic dipole transition frequencies were also obtained in the absence of an external magnetic field [14].

The spin-hamiltonian parameters relative to the Zeeman and hyperfine effects of the $^41_{1/2}$ and $^41_{3/2}$ lowest Stark levels were determined from electron paramagnetic resonance experiments on the photoexcited states [15, 16].

4. Hyperfine structures in two-level systems. — The studied spectra have been obtained by excitation of the two Nd$^{3+}$ levels which are in the rhodamine spectral region. These two levels are $^2H_{11/2}$ (15 907 cm$^{-1}$) and $^2G_{5/2}$ (17 095 cm$^{-1}$). So the two resonant spectra presented here are respectively the 6 284.8 Å spectrum and the 5 848 Å spectrum.

4.1 $^41_{9/2} \leftrightarrow ^2H_{11/2}$ system. — 4.1.1 Calculated hyperfine spectrum and selection rules. — The odd isotopes of neodymium have a 7/2 nuclear spin and the nuclear magnetic moments are respectively

$$\mu_N = -1.08 \text{ and } \mu_N = -0.67$$

for $^{143}$Nd and $^{145}$Nd [13].

The electronic wavefunctions have been calculated in the $|xSLJM_j\rangle$ basis, using for the hamiltonian parameters the values determined by Crosswhite [11]. The dipole hyperfine interaction has been introduced as a perturbation on the crystal states. The electric quadrupole moment being nearly zero for both isotopes, it has been neglected in all calculations.

The ground level is a $\mu = 5/2$ level ($\mu$ being the crystallographic quantum number, $\mu = M_j$ modulo 6 in a C$_{3h}$ point symmetry). In the absence of an external magnetic field, the hyperfine matrix leads to nine hyperfine levels with unequal splittings.

The phenomenological parameters of the spin-hamiltonian are known from the EPR experiments. From their $A$ and $B$ values, the parametric

$$(2 \beta \beta N \mu_N/\mathcal{I} \langle r^{-3} \rangle) = a_{df}$$

quantities, relative to all the levels of the 4f$^3$ configuration, are easily deduced

$$^{143}d_{df} = -5.5 \times 10^{-3} \text{ cm}^{-1}$$

$$^{145}d_{df} = -3.41 \times 10^{-3} \text{ cm}^{-1}$$

They can be used in an preliminary calculation of the hyperfine structure of any Stark level of the configuration.

The excited level involved in the 15 907 cm$^{-1}$ transition is a $\mu = 3/2$ level. The consequence is zero matrix elements for the non-diagonal part of the nuclear dipole magnetic interaction and the hyperfine structure is eight equidistant levels. Using the $a_{df}$ values, the calculation gives the following hyperfine splittings

$$^{143}\delta \simeq -16 \times 10^{-3} \text{ cm}^{-1}$$

and

$$^{145}\delta \simeq -10 \times 10^{-3} \text{ cm}^{-1}$$

The number of the possible transitions between the $|0 \text{ cm}^{-1}\rangle$ and the $|15 907 \text{ cm}^{-1}\rangle$ levels is limited. A transition diagram is represented on figure 1. It has been drawn with respect to the two selection rules:

$$\Delta M_J = 0$$

$M_J$ even, relative to an electric dipole transition for an ion in a C$_{3h}$ symmetry. This is verified on the
Zeeman spectrum where only two lines split by \((g^e + g^b) \beta H_||\) are observed.

4.1.2 Experimental spectrum. — The experimental spectrum of the 6284.8 Å line, obtained when excitation and observation are on the same

\[ ^4I_{9/2} \leftrightarrow ^2H_{11/2} \ (15 \, 907 \, \text{cm}^{-1}) \]

This result is exactly opposite to the conclusions drawn from the interpretation of the FLN spectrum relative to the \(^3H_4 (0 \, \text{cm}^{-1}) \leftrightarrow ^1D_2 (16 \, 630.5 \, \text{cm}^{-1})\) transition in \(\text{Pr}^{3+} : \text{LaCl}_3\) [3]. In that case all spectra were perfectly interpreted assuming the absence of any relaxation between the nuclear excited states. It must be noticed however that the hyperfine levels of \(^1D_2 (16 \, 630.5 \, \text{cm}^{-1})\) of Pr are quasi-degenerate, while in Nd the separation of the levels is large with respect to the homogeneous width.

Anyway, under these conditions, the spectrum is easily calculated for each site whose ions are excited by the same laser radiation and a diagram of the allowed \(^4I_{9/2} \leftrightarrow ^2H_{11/2}\) hyperfine transitions can be obtained (such a diagram is represented on Fig. 1). The schematic spectrum is then obtained by a juxtaposition of the lines relative to all the emission transitions with respect to the exciting transition. The spectrum represented on figure 2a perfectly fits the experimental spectra. It has been calculated by using the EPR values for the ground level, and by giving to the excited level splittings the values

\[ ^{143}\delta = -17.8 \times 10^{-3} \, \text{cm}^{-1} \]

\[ ^{145}\delta = -11.2 \times 10^{-3} \, \text{cm}^{-1} \]

The agreement with the previously calculated values given in section 4.1.1 can be regarded as very satisfactory if we take into account the number of approximations involved in the calculation.
4.2 \( ^4I_{9/2} \leftrightarrow ^4G_{5/2} \) SYSTEM. — The excited level involved in the transition has been assigned [9] to a nearly pure \( ^4G_{5/2} \) level with a crystalline quantum number \( \mu = 1/2 \), but the calculated Zeeman splitting \( (g \parallel = 0.6) \) is far from consistent with the experimental result \( (g \parallel = 1.34) \). The question of a misclassification can be raised, and the results of a parametric calculation of the hyperfine parameters may be put in doubt.

Anyhow the symmetry of the level is established and this leads to a structure of nine hyperfine levels with unequal splittings. Besides, in a \( \mu = 5/2 \leftrightarrow \mu = 1/2 \) electric dipole transition for an ion in a \( C_{3h} \) symmetry, all transitions are allowed (leading to a four component Zeeman spectrum).

Under these conditions, and with respect to the \( \Delta M_f = 0 \) selection rule, the number of allowed transitions is easily found. If a thermalization of all the nuclear states is assumed, 400 fluorescence lines at least are expected (the large hyperfine components only being taken into account).

The experimental spectrum of the 5848 Å line, corresponding to the excitation and the observation on the same \( ^4I_{9/2} \leftrightarrow ^4G_{5/2} \) (17 095 cm\(^{-1}\)) transition, has been obtained with an instrumental linewidth of 0.005 cm\(^{-1}\). It has been recorded for various exciting laser frequencies inside the absorption inhomogeneous profile. The example of one pattern, relative to the excitation of the lowest energy side of the transition at 7175 Å, is shown on figure 3a.

As a comparison, a part of the calculated spectrum assuming the excited level is \( ^4G_{5/2} \mu = 1/2 \), relative to a similar excitation, is represented on figure 3b.

The number of the lines of the experimental spectrum — which are not completely resolved — evidently prevents a determination of the structures of the levels involved in the transition being made. Thus it has been impossible to deduce the hyperfine parameters of the excited level. However, this very high resolution study has demonstrated the existence of a thermalization between the hyperfine nondegenerate levels, as assumed in the \( ^2H_{11/2} \) level study.

5. Hyperfine structures in three-level systems. — In three-level systems, the emitting level can be directly excited, and the fluorescence is observed on the transition to the third level. In another kind of system, the emitting level is excited through a cascade process from an upper level, and the fluorescence is observed on the transition to the ground level. In any case, a narrowed fluorescence can be expected only if the three-levels involved in the system are the lowest Stark levels of multiplets as they are the only levels for which the radiative part of the lifetime prevails. As a consequence the homogeneous width is expected to be much narrower than the inhomogeneous width.

Experimentally such fluorescence spectra usually have a very weak intensity. Two of them only appeared to be convenient to a high resolution treatment: they give one example of each model.

5.1 DIRECTLY EXCITED FLUORESCENCE. — In the studied system, the excited level is \( ^2H_{11/2} \) (the laser wavelength is 6284.8 Å) and the fluorescence is observed on the transition at 7175 Å.

The third level implied in this system is a \( \mu = 3/2 \) level. As a consequence, the \( \Delta M_f = \pm 1 \) condition necessary for magnetic dipole transitions being not satisfied, this level is not expected to be observed in EPR experiments. However magnetic resonance transitions were obtained when the magnetic field made a non-zero angle with the crystal axis. It was not possible to determine precisely the \( g \) values. They were only shown to be consistent with the calculated \( g \parallel = 7.8 \) and \( g \perp = 0 \) values [17].

It was thus interesting to study the transition by means of FLN technique. The hyperfine splittings were calculated, using the \( a_{4\ell} \) parameter. But, given the values which have been obtained

\[ ^{143}\delta \sim -9 \times 10^{-4} \text{ cm}^{-1}, \quad ^{145}\delta \sim -6 \times 10^{-4} \text{ cm}^{-1}, \]

the number of allowed transitions and the number of selected sites, a poorly resolved spectrum was expected.

The laser induced fluorescence spectrum which has been obtained is in agreement with this statement, as only a \( \sim 0.05 \text{ cm}^{-1} \) wide line has been recorded. The Zeeman effect of the line has been measured, giving a \( g \parallel = 7.37 \pm 0.03 \) value for the \( ^4I_{11/2} \) (1974 cm\(^{-1}\)) level.

5.2 FLUORESCENCE EXCITED THROUGH A CASCADE PROCESS. — In the studied system, the excited level
is \(^4\text{G}_{5/2}\) (5 848 Å laser wavelength), and the emitting level is \(^2\text{H}_{11/2}\) populated by energy decay from \(^4\text{G}_{5/2}\).

The fluorescence is observed on the transition \((6 284.8 \text{ Å line})\).

The three states concerned in this system have been previously studied. In particular the two levels involved in the fluorescence transition are very well known from EPR and FLN experiments (section 4.1). Moreover the interpretation of the FLN spectrum relative to the \(^4\text{I}_{9/2} \leftrightarrow ^4\text{G}_{5/2}\) system (section 4.2), where no selection rules — except \(\Delta M_I = 0\) — limits the number of allowed hyperfine transitions, has shown that a 5 848 Å laser radiation simultaneously excites ions belonging to a large number of classes of sites. In these conditions the fluorescence spectrum of the 6 284.8 Å line excited through a cascade process is expected to be rather complex.

The recorded spectra exhibit changes according to the excitation conditions but, surprisingly, they sometimes appear very simple: on figure 4a is represented a spectrum obtained when the laser radiation was on the low energy side of the 5 848 Å inhomogeneous profile. Still more striking than its simplicity is the fact that it agrees with the calculated spectrum relative to ions belonging to one class of crystalline sites. This calculated spectrum is displayed on figure 4b. It has been obtained from the allowed \(^2\text{H}_{11/2} \leftrightarrow ^4\text{I}_{9/2}\) transitions (Fig. 1), assuming that all levels are equally populated and using the nuclear parameters which fit the resonant spectrum.

The puzzling problem which appears here (excitation of a large number of sites and relaxation from apparently one site) could not be understood at this stage of the experiment. To investigate this point, information about the effect of the decay process on the linewidths and about the distribution of the sites inside the inhomogeneous profiles of the \(^4\text{G}_{5/2}\) and \(^2\text{H}_{11/2}\) levels was necessary. This has been obtained in the course of an investigation on energy transfer phenomena, and is presented, along with the interpretation of the spectrum of figure 4a, in the following paper [18].

6. Conclusion. — The laser induced fluorescence line-narrowing technique applied to Nd\(^{3+}\) ions in a LaCl\(_3\) host has proved once more to be a powerful means for studying the hyperfine structures of excited levels. Indeed, additional limitation in its application have been shown: when the number of sites involved in the process is high, the spectra may become too complex to permit a quantitative interpretation if no selection rule are present to limit the number of allowed transitions. Nevertheless the work presented here, which gives the values of Zeeman and hyperfine parameters of \(\mu = 3/2\) levels, shows the interest of the method as a necessary complement to EPR experiments. Moreover it shows that, in the case of the nondegenerate hyperfine levels of neodymium, a thermalization occurs among the nuclear states when only one of them is excited.

References