Intrinsic fluorescence of an Ising antiferromagnet, DyPO₄, in a magnetic field

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The intrinsic emission of DyPO₄ has been studied under magnetic field above and below the spin-flip transition. A detailed analysis of the behavior of one of the emission lines corresponding to the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition has been performed in the framework of the 3*d* Ising model involving only the nearest-neighbor interactions. The experimental data quite nicely fit this model which was previously proposed by Wright for DyPO₄. We determine the Ising parameter J_0 (exchange and dipolar interactions) for the emitting ${}^{4}F_{9/2}$ level and for the sublevels of the ${}^{6}H_{13/2}$. A calculation of the dipolar field acting on one Dy³⁺ ion allows us to determine the molecular field corresponding to the exchange interaction, which we show to be the same for different sublevels of the $J = \frac{13}{2}$ states. Our measurements, although being much more difficult than absorption studies (short lifetimes, small quantum efficiencies) lead to a different insight in the DyPO₄ model and prove to be very useful in this crystal where we could make a quantitative study from emission spectra.

I. INTRODUCTION

The Ising model has received considerable attention during this past decade. Two essential features are responsible for this interest. First, its idealized simplification allows one to get exact solutions and second, a certain number of real systems were shown to possess, to a good approximation, the basic characteristics of this model.

Among them, the DyPO₄ crystal which has the tetragonal zircon structure has been proven through high-resolution absorption experiments and heatcapacity measurements to nicely fit the threedimensional Ising model.^{1,2} DyPO₄ possesses the useful, if not unique,³ characteristic of displaying a pseudo "superfine" structure on most of its absorption bands, which give rise in polarized light, to five well-resolved bands corresponding to the different spin arrangements of the four nearest-neighbor (NN) ions around the excited Dy^{3+} . This feature has been attributed¹ to Ising interactions restricted to the four NN of a Dy^{3+} ion. However, several difficulties arose when considering certain transitions in certain crystals where it turned out that the optical selection rules were not so well obeved as in others, leading to a more intricate substructure than would give the ideal NN Ising model.²

Compelled by the recent and fruitful progresses

made in the dye laser field as well as in detection and signal processing devices, we decided to tackle this problem from another view point, i.e., starting from emission measurements which were likely to overcome a practical difficulty which arises during the absorption measurements: at low temperature, below 3.4 K which is the antiferromagnetic ordering temperature, the five-line structure evolves into a single line, corresponding to the pure antiferromagnetic (AF) arrangement of all the spins in the lattice. This feature leaves the experimentalist with the possibility to study the behavior (e.g., under magnetic field) of a single transition in the spectrum. This arises because the population equilibrium in the ground state tends to convert all the spin configurations around the central ion into a pure antiferromagnetic or spinflip arrangement.

On the contrary, starting from a conveniently populated excited state, we may hope to get a larger number of allowed transitions (twice more) if the population of the various sites has not had enough time to reach Boltzman equilibrium before the fluorescence decay, or if the pseudosuperfine and Zeeman splittings are very small.

Fortunately one of these conditions (or both) turned out to be fulfilled in this crystal and this proved to be rather fruitful leading to a number of determinations of the same parameters which could,

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in turn, give a reasonable confirmation for the 3d NN Ising model in DyPO₄.

We therefore studied relatively simply structured transitions, generally with two components for a given spin-orbit level. This allowed us to get a complete set of results in the different magnetic phases of $DyPO_4$, since the spectra are never so intricate as they can be in absorption measurements. We shall see that, without any extrapolation we are able to extract a number of parameters.

In Sec. II, we describe briefly the experimental setup which we used in the present study. In particular, we observed that the intrinsic emission of $DyPO_4$ is very low. This gives us information about the processes which tend to destroy the pure excitonic character of the excitations in ordered crystals.

Since we can separate intrinsic emission lines from those related to impurities by time resolving the spectra (Sec. III A) and since the perfect ordering of the $DyPO_4$ crystal is an essential condition in order to get well-defined selection rules for both absorption and emission lines, such a study is relevant to the present problem of checking the NN Ising model for $DyPO_4$.

In Sec. III B we focus our attention to the detailed analysis of the behavior of a particular line (called the *D* line in the following) which displays the interesting property of being both π and σ polarized. From the analysis of the experimental results obtained below and above the critical field $H_{\rm cr}$ we derive a certain number of pertinent parameters and prove definitely the pertinence of the Ising model in explaining the fluorescence experiments, therefore giving strong support to the conclusions of Wright *et al.*¹

In Sec. III C we analyze the results of cw experiments under magnetic field on several other lines observed in the 17 300 cm⁻¹ region. Since they are all either mostly π or σ polarized they cannot bring so much information as the D line and we restricted our attention to their behavior in the ferromagnetic phase. However that study allowed us to estimate J_0 and g for the other sublevels of ${}^6H_{13/2}$.

Moreover (Sec. III D), this study led us to an unambiguous spectroscopic attribution for all the sublevels of ${}^{6}H_{13/2}$. In Sec. III E we report some results concerning the spin-spin interaction in this excited level.

II. EXPERIMENTAL

The very high purity crystal which was used in these experiments was grown at Oxford, in the shape of a small parallelepiped completed with two natural tetragonal pyramids directed along the S_4 axis of the crystal. Its overall dimensions were about 5 mm in each direction and, as we will show later, its particular shape allows us to consider it nearly a sphere for the calculation of the demagnetizing field. This important feature led us to somewhat different results compared to other authors^{1, 2} who used needle-shaped specimens.

In the course of our study, the sample was always mounted in the cryostat so that its S_4 axis lay parallel to the external magnetic field. The exciting beam was perpendicular to the S_4 axis. In that configuration the emitted photons could be analyzed with either π or σ polarization corresponding to emitting dipoles, respectively, parallel and perpendicular to the S_4 axis of the crystal, the emitted light being perpendicular to the S_4 axis.

The experimental setup consisted of a standard liquid helium cryostat containing a split-coil superconducting magnet so that the optical pumping and the collection of the emitted photons could be performed at 90°, which strongly reduced the spurious signals arising from stray diffusion in the sample. The optical pumping could be achieved in two different ways depending on the type of experiment being performed.

A cw argon laser was used for cw measurements adjusted on its blue and uv lines. Time-resolved experiments were performed using a pulsed dye laser (resolution 1 cm⁻¹) pumped by a nitrogen laser.

Since, in all these experiments the quantum yield of fluorescence ranged around 10^{-9} in the spectral region of interest, we were forced to use photon counting techniques both for cw and pulsed experiments. In these studies the emitted photons were collected on the entrance slit of a 1.5-m high-resolution monochromator equipped with a 2500-lines/mm grating, and detected with a very low dark noise photomultiplier. In the cw experiments the photoelectrons issuing from the photomultiplier were counted and time averaged in a microcomputer. In the pulsed experiments, the burst of photoelectrons emitted after each laser pulse was fed into a fast transient digitizer. (Tektronix R 7912) which was specially interfaced in order to allow a digital counting of the photons emitted in a fixed period of time after the laser pulse.⁴ Our detection device was then interfaced to the microcomputer which gave a direct access to the decay times and the time averaging of the emission spectra. As has been shown previously, the gating technique allows one to get information about possible energy transfers during the decay⁵⁻⁸ to impurity traps which might be present in the crystal.

III. RESULTS AND DISCUSSION

A. Intrinsic fluorescence and impurity bands-polarized emission

Due to experimental convenience, we restricted our study to the 17 300 cm⁻¹ region corresponding to the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition where we could detect a larger number of photons. Some other groups of lines, obviously corresponding to the fluorescent decay from the same emitting level to other groundstate multiplets (${}^{6}H_{11/2}$, ${}^{6}H_{9/2}$, ...,) were also detected, but with smaller quantum yields. Figure 1 reports the emission spectra recorded in the 17 300

cm⁻¹ region under cw and pulsed excitation. A straightforward conclusion which can be deduced from our time-resolved experiments is the decay time τ_F (common to all the lines reported in the pulsed spectrum) which was measured as 400 ± 20 ns.

In order to ensure that this rather short decay time was not due to an excessively intense pumping of the ${}^{4}F_{9/2}$ level, we checked, by decreasing, as much as we could, the power of the pumping laser without observing any change in τ_F . As in doped crystals, and considering that all the observed lines decaying to the ${}^{6}H_{13/2}$ level should correspond to transitions with very small oscillator strengths, we conclude that there exists a very efficient nonradiative decay channel, which empties the excited state much faster than would the normal radiative process to the ground state. A tentative explanation for this very fast nonradiative process can be proposed, taking into account the results of Auzel et al.⁹ who found a decreasing nonradiative decay time when increasing the concentration of Eu^{3+} in $[(C_4H_9)_4N]_3Eu_xY_{1-x}(NCS)_6$ from 1 to 100%.

An important consequence of this very short decay time lies in the possibility to observe more lines in emission under magnetic field. Generally, relaxation between Zeeman sublevels occurs before emission. In the case of DyPO₄, the levels split by the magnetic field correspond to different types of Dy^{3+} ions, hav-



FIG. 1. Unpolarized emission spectrum in the 17 300 cm⁻¹ region obtained under cw (upper curve) and pulsed excitation. In the latter case, the counted photons were gated during 2 μ s after the laser pulse. T = 1.5 K and H = 0. The difference in relative intensities of the lines in both spectra should be attributed to different filters used to cutoff the scattered light.

ing different surroundings of nearest neighbors. Then, the relevant relaxation time to the lower Zeeman sublevel is an interionic one, τ_R , which is likely to be much larger than 400 ns, as could be effectively observed under high magnetic fields.

We could also get information about the multiphonon decay in ${}^{4}F_{9/2}$ due to the following feature which was observed when pumping with the $cw Ar^+$ laser: although none of the Ar⁺ line would fall in an absorption line of the DyPO₄ crystal (except the uv line), we obtained, in all cases a relatively strong signal in the 17 300 cm⁻¹ region which did not depend on the excitation wavelength. This feature undoubtedly displays the existence of a relatively important electron-lattice coupling which is responsible for a fast and efficient decay of the pumping energy towards the lowest sublevel of the ${}^{4}F_{9/2}$ state. In order to check that, we performed time-resolved experiments with a blue dye laser pumping well above (750 cm⁻¹) the ${}^{4}F_{9/2}$ level, in a region where no significant absorption could be detected.

This experiment, once more, gave rise to the same fluorescence signal corresponding to the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions with such an intensity that it could not be explained by a resonant pumping of the absorption lines through the small broad-band fluorescence generally emitted together with the sharp laser pulse in dye laser experiments. Another feature demonstrating the existence of a broad multiphonon absorption band was given by the fact that no emission was detected when pumping *below* the resonant line.

The DyPO₄ fluorescence signal appeared immediately after the pumping pulse (in a delay shorter than 10 ns, our photomultiplier time resolution). This result, indicating a very fast multiphonon decay in the excited state of DyPO₄ seems rather surprising when compared to similar experiments performed on doped crystals.¹⁰ At the present time we can only conclude from this feature that there exists a stronger electron lattice coupling in pure DyPO₄ than in diluted systems.

A comparison between both spectra in Fig. 1 shows only a few differences between them: using the gating technique (gate equal to 5 τ_F), we observed that besides a certain number of small lines appearing around 17 280 cm⁻¹ and 17 340 cm⁻¹ a noticeable band appears at 17402 cm⁻¹ which is not detected in the pulsed spectrum. Undoubtedly this band does not correspond to an emitting impurity ion but rather to a perturbed exciton, the decay time of which being much larger than $5\tau_F$. Its splittings in magnetic field confirms this attribution. Another remarkable feature, connected with the existence of this perturbed exciton is that it could be excited only in particular region of the crystal. They have been avoided in the course of the following experiments, where the intrinsic fluorescence was measured with the cw laser, leading to a better signal-to-noise ratio and al-

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lowing a better resolution ($\Delta \sigma = 1.2 \text{ cm}^{-1}$).

Concerning the comparison between the spectra of Fig. 1, it is important to notice the identical width of the cw lines and of those of the pulsed spectrum. Since these widths are larger than our spectral resolution (1.6 cm^{-1}) , we can conclude that in the cw spectrum there are no perturbed exciton lines superimposed to the excitonic ones. This clearly puts in evidence the fact that our crystal exhibits essentially intrinsic fluorescence.

This result can be compared to those obtained for 3d transition in metal magnetic compounds in emission measurements.⁵⁻⁸ It agrees with the fact that Dy^{3+} , being a rare-earth ion is well shielded against perturbations due to impurities. Moreover it indicates the very good quality of our crystal since, even in rare-earth compounds, the impurity bands could appear.¹¹

The five most prominent lines in Fig. 1 can be attributed to the various transitions starting from the lowest sublevel of ${}^{4}F_{9/2}$ of symmetry Γ_{6} or Γ_{7} , down to the various components $(4\Gamma_{6}+3\Gamma_{7})$ of ${}^{6}H_{13/2}$ split by the crystal field in D_{2d} symmetry, which is the symmetry point group of Dy^{3+} in DyPO₄. In the absence of magnetic field, we determine the selection rules in the local symmetry point group D_{2d} . This is correct if we only consider zero-phonon, zeromagnon lines. Then we expect four lines polarized perpendicular to the S_4 axis of the crystal (σ) and three lines polarized both along and perpendicular to this axis ($\pi\sigma$) (Table I).

For sake of simplification we will label these lines as A, B, C, D, and E starting from the low-energy side in Fig. 1. The result of the analysis of the emitted light in π and σ polarizations is reported in Fig. 2. As can be seen from this figure most of these lines show a very clear polarization either in σ or π (except for the D line which is $\pi\sigma$ polarized).

As will be observed in Sec. II B this clearcut polarization extends well over the pseudo "superfine" structure related to the interaction of a Dy^{3+} ion with its four nearest neighbors, each level corresponding

TABLE I. Polarization of transitions in DyPO₄ without applied field (point symmetry D_{2d}).





FIG. 2. Polarized emission spectra in π and σ polarization. T = 1.5 K and H = 0. Monochromator bandwidth $\Delta \sigma = 3$ cm⁻¹.

to a type of Dy^{3+} site being surrounded by a particular arrangement of the spins of its four NN.

Another point, which is worth noticing here, concerns the fact that the emitting level was optically pumped via multiphonon relaxation from a vibronic level situated above the ${}^{4}F_{9/2}$ state. This explains why, although the pumping beam was fully π polarized, both Kramers doublet components are pumped, whether they should be excited by π and σ lights. This is related to the very fast and efficient relaxation which completely destroys the polarization of the pumping beam.

B. Analysis of the results of the Zeeman effect on the D line

As has been mentioned previously, the D line turns out to be both π and σ polarized. As we show in this section, this feature is quite favorable for a complete study of its properties under magnetic field.

1. NN Ising model

In order to understand fully the behavior of the D line in zero field and below or above the critical field which was shown to be¹ $H_{cr} = 5.2 \pm 0.2$ kOe at 1.5 K we must first recall the various fields and interactions which act upon the electronic levels of a Dy³⁺ ion. We will consider here firstly the pure NN Ising model and secondly the corrections to this model which apply both in the antiferromagnetic and in the spin-flip phase. Part of the arguments which we develop here follow those of Wright *et al.*¹ with a few modifications. We will therefore show that they are still valid in the interpretation of the fluorescence experiments.

In the absence of any external magnetic field, at 1.5 K, the system orders in the antiferromagnetic arrangement of the spins. This ordering corresponds to the Hamiltonian acting upon the ions of DyPO₄. In the NN Ising model, the spin Hamiltonian for an ef-

fective spin $S = \frac{1}{2}$ is written¹²

$$H = \sum_{i = NN} \frac{J_0}{S^2} S_{0z} S_{iz} \quad , \tag{1}$$

where the sum is restricted to the four nearest neighbors only.

In the antiferromagnetic phase, we must consider two different sublattices. The first one is made up of all the ions with their spins in the same direction as the concerned Dy^{3+} ion. It will be labeled by the index 1. The second one which involves all the other ions will be labeled by 2.

Considering Levy's work¹³ and since the ground state of the Dy³⁺ ion is a pure $J_z = \pm \frac{15}{2}$ state, we use an Ising Hamiltonian for the ground state of the crystal.¹ We use the hypothesis that the interion interaction is still represented by an Ising Hamiltonian in the excited states. This shall be verified for the studied levels. Then, the scheme we use for DyPO₄ is a molecular field one, which is justified in an Ising model since in this case there is no dispersion of the excitation in the Brillouin zone, which we shall verify later. The Hamiltonian (1) is responsible for the pseudosplitting of all the lines in the polarized absorption spectra into five components corresponding to sites having different arrangements of the four NN spins around the Dy³⁺ ion (Fig. 3).

At low temperature, and as far as the ground state is concerned only the levels of sites having antiferromagnetic or ferromagnetic (above H_{cr}) arrangements are populated.

Corrections to this crude NN Ising model can be introduced by considering the effective fields acting upon the central ion, due to all the other spins (except for the four NN) of both sublattices. If now, we consider both the exchange and the magnetic dipolar interactions (respectively, e and d) we can write the



FIG. 3. Level schemes and selection rules for the emission spectra corresponding to the D line in the antiferro- and ferromagnetic phases (point symmetry group S_4). The discontinuity field has been omitted in these drawings.

correcting field in the antiferromagnetic phase as

$$H^{\rm AF} = H_{1d} + H_{2d} + H_{1e} + H_{2e} \quad . \tag{2}$$

Whereas, in the ferromagnetic (F) phase, the ions of the second sublattice reverse their spins and an additional magnetic field must be introduced:

$$H^{\rm F} = \frac{4}{3} \pi M_0 - M_{D0} \quad , \tag{3}$$

where M_0 stands for the saturation magnetization of the crystal and M_{D0} for the demagnetizing field which arises from the oriented dipoles present on the surface of the crystal. The first term in Eq. (3) takes into account the additional magnetic fields due to the ferromagnetic ordering of all the spins in the lattice. The field H^F is sometimes called "discontinuity field" because it appears rather abruptly at the magnetic phase change and causes the lines to split according to their g factors.

Whereas the demagnetizing field and the field created by all the spins in the spin-flip phase will certainly contribute significantly to the observed effects, the magnitude of the contribution of H^{AF} [Eq. (2)] is expected to be rather small if the crystal behaves according to the NN Ising model. Various calculations¹⁴ have shown that there is a partial cancellation (up to the 5th neighbors) of the dipolar and exchange interactions for other ions than nearest neighbors. This explains why the NN Ising model describes DyPO₄ so well. Nevertheless we will consider these two corrections in the following and see how they influence our experiments.

In order to analyze the results of our experiments on the D line, we must consider Fig. 3 where we have reported the various level schemes involved together with the optical selection rules for the transitions which occur between the different levels of the pseudo "superfine" structure.

2. Spectra under magnetic field

Without any further consideration than the number and the relative intensities of the emission lines which are nearly equal, we must consider that the excited states, being populated in π and σ , do not relax significantly.

Keeping this important feature in mind, we could derive from Fig. 3, the various schemes corresponding to the behavior, under magnetic field, of the various transitions involved in the experiments concerning the D line (Fig. 4).

For DyPO₄ in a magnetic field, the degeneracy of the Kramers doublets Γ_6 and Γ_7 of Table I is lifted. We then consider the perturbed D_{2d} levels, the singlets Γ_6^* (spin up \uparrow and down \downarrow), $\Gamma_7^*(\uparrow$ and \downarrow) for ${}^{4}F_{9/2}$ and $\Gamma_6(\uparrow$ and \downarrow), $\Gamma_7(\uparrow$ and \downarrow) for ${}^{6}H_{13/2}$. In Fig. 3 we report the selection rules for electric-dipole transitions between these sublevels in the case of the



FIG. 4. Predicted behavior of the emissions lines (π, σ) as a function of an external magnetic field applied along the S_4 axis of the crystal. *H* stands here for the effective magnetic field [i.e., including the corrections to the Ising model quoted in Eqs. (2) and (3)]. g and g^{*} stand for the ground and excited state splitting factor and β is the Bohr magneton.

transitions $\Gamma_{6,7}^* \rightarrow \Gamma_{7,6}$ which are $\pi \sigma$ polarized. The case of $\Gamma_{6,7}^* \rightarrow \Gamma_{6,7}$ transitions which are σ polarized can also be deduced from Fig. 3 if we only consider the dotted arrows.

As quoted above, two different features can explain the relative intensity of the emission lines under magnetic field.

The first one corresponds to the fact that the splitting of the excited state is very small, as we observed in absorption and verified in emission. From the excitation spectrum we determine the emitting level, which is the lowest component of ${}^{4}F_{9/2}$ at 20 986 cm⁻¹. The splitting of its absorption band under a magnetic field is shown on Fig. 5. From this and since g = 19.3 in the ground state¹ we deduce that in the emitting sublevel of ${}^{4}F_{9/2}$, g^{*} and J_{0}^{*} are nearly zero (Table II). Then 1.5 K is not a sufficiently low temperature to depopulate one of the concerned levels.

The second feature would involve an interionic relaxation time much longer than the fluorescence decay time τ_F , since the two lines issuing from a single line in zero field correspond to two different types of sites.

Due to some imprecision in the relative intensities of the observed subbands, our experiments do not allow us to know which is the most important of these two processes. Let us mention that, taking into account our signal-to-noise ratio and the very small value of the excited-state g value which we calculate in the following, we estimate that noticeable changes in the relative intensities of the bands would be expected for magnetic fields larger than 80 kOe, which



FIG. 5. Measured splittings under magnetic field above $H_{\rm cr}$ for the *B*, *C*, *D*, and *E* lines. The light was unpolarized and the resolution was 1.6 cm⁻¹. The upper part of the drawing recalls the occurrence of the critical field as observed through the splitting of the ${}^{4}F_{9/2}$ absorption band. We indicate $H_{\rm cr_{1}}$ and $H_{\rm cr_{2}}$ on both sides of $H_{\rm cr}$.

is far above our experimental possibilities.

An answer to this important question could possibly be given by analyzing the intrinsic fluorescence issuing from another emitting level with a large gvalue. Under magnetic field it would then be possible, by considering the ratio of the intensities of two lines corresponding to different ions, to estimate the interionic relaxation time. However, it seems likely that, in this system where both the exchange and the dipolar interactions are so small, the relaxation time τ_R is larger than the observed τ_F . TABLE II. Pertinent parameters resulting from the study of the D line.

 $J_0 = 0.68 \pm 0.03 \text{ cm}^{-1}({}^6H_{13/2})D$

 $J_0^* = 0.03 \pm 0.03 \text{ cm}^{-1}({}^4F_{9/2})$

 $g = 18.5 \pm 0.9 \text{ cm}^{-1}({}^{6}H_{13/2})D$

$$g^* = 0.6 \pm 0.6 \text{ cm}^{-1}({}^4F_{9/2})$$

 $|H_{1d} + H_{1e} + H_{2d} + H_{2e}| \le 0.3$ kOe

 M_0 (calculated) = 1.25 kOe

 M_{D0} (measured) = 4.4 ± 0.6 kOe

 $(M_{D0})_{\rm sph}(\text{calculated}) = 5.23 \text{ kOe}$

Phase change occurring in about 1.5 kOe

H (molecular field) = -5.9 ± 0.5 kOe

 H_d (dipolar field) = -2.36 kOe

 $H_{\rm ex}({\rm exchange field in}^6 H_{13/2}) = -3.5 \pm 0.5 \text{ kOe}$

3. Determination of the g and J_0 factors

In all the cases $(H = 0, H < H_{cr}, H > H_{cr})$, the number of the observed lines agrees with the predicted one in Fig. 3. The zero-field experiments give rise to two doublets either in π or σ polarization as can be seen on Fig. 6. They correspond (Fig. 4) to the sum and the differences of the splittings of the ground and excited states by the J_0 , J_0^* factors and $H^{\rm AF}$. At this point we can get an estimate of the correction which needs be made to the NN Ising model, just by considering the line shape of the zero-field bands. Actually, if we consider that the ions are submitted to the additional field H^{AF} then we turn to the next drawing (right-hand side) which describes the effect of an external magnetic field on the D line. In the case where H^{AF} exists it would give rise to a small splitting of each of these lines, which can be predicted with the help of the g and g^* factors reported in Table II. Now, if we consider the π spectrum, we estimate that the overall splitting of two components under these two lines would be smaller than 0.3 cm^{-1} , which leads us to the equation

$$|H^{AF}| = |H_{1d} + H_{2d} + H_{1e} + H_{2e}| \le 0.3 \text{ kOe}$$
,

which agrees with the value -0.27 kOe proposed by Wright *et al.*¹ derived from the temperature depen-



FIG. 6. (a) Comparison between the observed details of the *D*-line emission under magnetic field below and above $H_{\rm cr}$, with computer calculation using equations in Fig. 4: T = 1.5 K and σ polarization. (b) Observed evolution of the *D*-line emission under magnetic field below and above $H_{\rm cr}$. T = 1.5 K and π polarization. The horizontal units are cm⁻¹.

dence of the lines above the ordering temperature.

Next, we consider the emission lines under a magnetic field $H < H_{cr}$. We found both in π and σ polarization (Fig. 6) that the *D* components split into four bands. We observed that, in the two polarizations, the four bands have the same intensity. This is in agreement with the predictions (Fig. 4).

For higher fields, H > 7 kOe, we observe two bands (Fig. 6) as has been predicted (Fig. 4), both in π and σ polarization.

The pertinent parameters, i.e., J_0 , J_0^* , g, and g^* , have been extracted from the complete set of our experiments. Some of these experimental spectra are sketched in Fig. 6.

We first extract J_0 and J_0^* from the π and σ spectra at H = 0, with a relatively good precision (Table II). For g and g^* we could have used the spectra at particular values of the field like 3.2 kOe (Fig. 6) for which we see four lines issuing from two lines at H = 0. In order to get a better precision we employed another procedure. We tried to reproduce the observed curves in π and σ polarizations for $H \neq 0$ by a computer calculation: we started from the real bands at H = 0 and had them split and move according to the equations reported in Fig. 4, with different values of g and g^* varying by steps. A best fit occurs in the antiferromagnetic phase for both π and σ po-

larization for the g and g^* values given in Table II. We remark that the phase transition shows up as a complicated admixture of both the antiferromagnetic and ferromagnetic spectra [dotted curves in Fig. 6(a)]. It can be observed that the line shapes are strongly distorted in the 4.7-kOe region, i.e., near the critical field at 5.2 kOe. Except for a noticeable enlargement, the 6.9-kOe curve reproduces rather correctly the observed band. This means that, as far as this kind of experiments is concerned, we estimate that the phase change occurs in more than 1.5 kOe. This result agrees with the fact that, in a crystal having a nonzero demagnetizing field (determined by its shape), we do not expect a definite value for the critical field but rather two values H_{cr_1} and H_{cr_2} (Fig. 5) with a superposition of the two magnetic phases between them.

Actually, the computed curves were calculated using a single set of parameters, without introducing any correction due to magnetization or demagnetizing field in the spin-flip phase. The nearly spherical shape of our crystal made us infer that the M_{D0} term in Eq. (3) could exactly cancel out the magnetization of the ferromagnetic lattice.

The difference between the observed and calculated splittings for both the π and σ polarizations in the spin-flip phase allow us to derive numerically the value of the demagnetizing field M_{D0} which critically depends on the crystal shape and therefore is generally estimated within large errors bars. In the present case we use the parameters reported in Table II.

Combining the results in the π and σ polarizations we obtained

$$H^{\rm F} = \frac{4}{3} \pi M_0 - M_{D0} = 0.8 \text{ kOe}$$
.

We calculate M_{D0} as $M_{D0} = 4.43$ kOe.

If our crystal had been of a pure spherical shape, we would have obtained $(M_{D0})_{spher} = 5.23$ kOe.

The introduction of this small "discontinuity field" in the equations allows us to explain the complete set of our experiments in the antiferromagnetic phase as well as in the spin-flip one.

C. Experimental study of the splittings of the A, B, C, and E lines in zero field and under magnetic field $H \ge H_{cr}$

Since the basic features of the NN Ising model have been fully demonstrated through the detailed analysis of the behavior of the D line, we now study a few experimental results concerning the other lines reported in Figs. 1 and 2.

As we already determined the essential parameters $(g^* \text{ and } J_0^*)$ for the ${}^4F_{9/2}$ emitting level, we were not forced to repeat the complete set of experiments for the *A*, *B*, *C*, and *E* lines. Only two measurements were necessary in the case of these transitions. Due to the very small values of the parameters of the excited state we preferred using unpolarized light in order to improve the signal-to-noise ratios. This led to the same results as if we had supposed that g^* and J_0^* were zero in the excited state. Then, by just considering the zero-field splitting of the lines and the magnetic splitting in the ferromagnetic phase we were able to give the results reported in Table III.

The parameters concerning the A band turn out to be very small and could not be measured from this set of experiments. As for the B and C bands the estimate of the J_0 parameters arises from the consideration of the bandwidth in zero field since the splitting cannot be clearly detected.

D. Spectroscopic attribution of the A, ..., E bands

In the preceding we determined the g factors for the various sublevels of ${}^{6}H_{13/2}$. From the g factors and taking into account the polarization of the bands we propose an attribution for the A to E bands.

Firstly, g is the largest (18.5) for the D level of ${}^{6}H_{13/2}$. Then, we deduce that, $|J_{z} = \pm \frac{13}{2}\rangle$ is part of the eigenfunction of ${}^{6}H_{13/2}(D)$ in the D_{2d} crystal field. ${}^{6}H_{13/2}(D)$ must then be a Γ_{7} doublet, and the D band being $\pi\sigma$ polarized corresponds to a $\Gamma_{7} \rightarrow \Gamma_{7}$ transition. We conclude that the emitting level of

TABLE III. Tentative assignment of the various lines observed in the spectra. When a transition is mostly π (or σ) polarized we indicate $\pi + \epsilon \sigma$ (or $\sigma + \epsilon \pi$).

Line	Position (cm ⁻¹)	Observed polarization	Assignment with Γ_7^*	Splitting factors g	$\int_{0}^{J_0} (cm^{-1})$
A	17 252	$\sigma + \epsilon \pi$	Γ ₇	?	?
B	17 221	$\pi + \epsilon \sigma$	Γ_6	2.6 ± 0.3	≤ 0.15
С	17 380	$\sigma + \epsilon \pi$	Γ_7	5.12 ± 0.5	≤0.20
D	17417	πσ	Γ_6	18.5 ± 0.9	0.68
Ε	17 436	$\pi + \epsilon \sigma$	Γ_6	8.4 ± 0.8	0.35

 ${}^{4}F_{9/2}$ is a Γ_{7} doublet.

Since we know the irreducible representation of the emitting state and taking into account the selection rules in DyPO₄ we can attribute the A to E sublevels of ${}^{6}H_{13/2}$ to irreducible representations of the D_{2d} group in an unambiguous way (Table III).

E. Some conclusions concerning the interion interaction

Keeping in mind the molecular-field approximation, it is interesting to estimate the J_0/g values for all the sublevels of the ${}^{6}H_{13/2}$ which correspond to the A to E lines. For the C and B lines we can also determine a maximum value of 0.04 cm⁻¹ for J_0/g .

We propose a conclusion deriving a constant molecular field (exchange + dipole - dipole) for all the sublevels of ${}^{6}H_{13/2}$ which is consistent with our results. This indicates a molecular field equal to

 $8J_0/g + H^{AF} = -5.9 \pm 0.5 \text{ kOe}$.

The minus sign corresponds to an antiferromagnetic ordering, the molecular field being applied to a central ion having an upward spin.

Considering the fact that the spin-spin interaction is the same for all the sublevels of the ${}^{6}H_{13/2}$ state split by the D_{2d} crystal field we may try to get a more precise insight in the molecular-field model. Actually, since the four ions surrounding the excited Dy³⁺, are in the ground state (g = 19.3) we can calculate the dipole-dipole interaction from simple geometrical considerations. Doing that, we found $H_d = -2.36$ kOe for a central ion with an upward spin in the antiferromagnetic ordering. We deduce the nondipolar part which we shall attribute to exchange interaction (in kOe) as

$$H_{\rm ex} = (8J_0/g + H^{\rm AF}) - H_d = -3.5 \pm 0.5$$

which corresponds to an antiferromagnetic interaction.

It is interesting to point out the fact that we get an estimate of the spin-spin interaction for all the components of ${}^{6}H_{13/2}$ since it is generally not possible to reach this interaction for other levels of a J manifold than the lowest doublet.¹⁵ Although the theoretical predictions concerning the value of this interaction in the different components are not clear, at present. our results allow us to conclude that the nondipolar interaction corresponds to a first-order interaction in $S_i S_i$ (S being an effective spin) and that it does not depend on the crystal field. This allows us to eliminate virtual phonon exchange and electric multipole interactions which should be of second order for Kramers ions.¹⁵ That is why we attribute the nondipolar part of the interaction to exchange interaction. Moreover we can remark that the value of -3.5 ± 0.5

kOe which we measured is not very different from the value of $H_{\rm ex}$ in the ground state ${}^{6}H_{15/2}$ [-6.31 kOe (Ref. 2)]. This small difference corresponds to the fact that exchange interaction essentially depends upon the orbital and spin momenta L and S.

IV. CONCLUSION

Polarized fluorescence experiments have allowed us to get a new insight in the three-dimensional NN Ising model proposed for DyPO₄. Despite the very low quantum efficiency of fluorescence (10^{-9}) leading to a much lower signal-to-noise ratio than in the standard absorption experiments, we have been able, through high resolution spectroscopy to fit nicely the Ising model to a complete set of experiments both in the antiferromagnetic and spin-flip phases. The deviation to the pure 3*d* Ising model, which involves the dipolar and exchange interactions with the other ions than NN, could be shown to be very small in agreement with previous studies performed through absorption spectra.

Two circumstances were recognized as very favorable in the course of these experiments: First, the fact that the excited state population did not relax significantly among the pseudosplit sublevels. Second, the fact that our experiments were performed with a very good quality crystal which displayed a very pure intrinsic emission spectrum. These two factors, interplaying together, are probably necessary in order to be able to draw out well-defined information from this kind of experiment.

Under these conditions, we can say that our measurements allowed direct estimate of the pertinent parameters since it is not necessary to make extrapolations. In the absorption experiments the extraction of the parameters requires a temperature high enough to give rise to the quintet structure which may lead to some confusion when the different electronic sublevels lie in a small wavelength range. In our case we had not to choose which are the appropriate bands and consequently our results are unambiguous.

Measurements with the cw laser and time averaging of the spectra allow us to claim reasonably that we do not need the corrections suggested by Ellis *et al.*² to the first model and that we agree with the predictions of Wright¹ for the transitions which we have studied.

Although our emission spectra show a large number of lines, we were unable to attribute definitely any of these lines to magnon sidebands which, in this material, should be found at a few cm^{-1} from the corresponding excitonic bands. Due to the rather intricate spectroscopy of the Dy^{3+} ion and to the complicated behavior of most of the lines under magnetic field, we do not think that a technique similar to

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Belorizki *et al.*¹⁶ could provide a definite answer to the existence of magnon side bands in our crystal. Anyway we observe no line disappearing in the spinflip phase as should have been the case for a magnon side band. This seems to confirm the results of Wright¹ who observed no magnon side band in DyPO₄ absorption spectra. Our results agree also with those of Ellis *et al.*² who claimed that they observed no line disappearing under magnetic field from which we can conclude that they did not observe any magnon sideband in their spectra. **ACKNOWLEDGMENTS**

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- ¹J. C. Wright, H. W. Moos, J. H. Colwell, B. W. Mangum, and D. D. Thornton, Phys. Rev. <u>3</u>, 843 (1971).
- ²C. J. Ellis, M. J. M. Leask, D. M. Martin, and M. R. Wells, J. Phys. C 4, 2937 (1971).
- ³G. A. Prinz, Phys. Rev. 152, 474 (1966).
- ⁴The R 7912 fast transient digitizer (Tektronix) was most simply used as fast digital photon counter by monitoring the output signal corresponding to the eighth bit which changes its value as soon as a signal crosses the median horizontal line on the target of the tube.
- ⁵R. E. Dietz, L. F. Johnson, and H. J. Guggenheim, in *Physics of Quantum Electronics*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill, New York, 1966), p. 361.
- ⁶R. Jacquier, R. Moncorge, and B. di Bartolo, Solid State Commun. <u>31</u>, 693 (1979).
- ⁷D. D. Sell, R. L. Greene, and R. M. White, Phys. Rev.

158, 489 (1967).

- ⁸E. Strauss, V. Gerhardt, and W. Gebhardt, J. Lumin. 18-19, 151 (1979).
- ⁹F. Auzel, G. F. de Sá, and W. M. Azevado, in 2nd Conference on Dynamical Processes in the Excited States of Ions and Molecules in Solids, Madison, Wisconsin, 1979, edited by W. M. Yen (unpublished).
- ¹⁰H. W. Moos, J. Lumin. <u>1-2</u>, 106 (1970).
- ¹¹T. Hufner, IEEE Trans. Magn. <u>8</u>, 151 (1972).
- ¹²J. W. Essam and M. F. Sykes, Physica (Utrecht) <u>29</u>, 378 (1963).
- ¹³P. M. Levy, Phys. Rev. <u>177</u>, 509 (1969).
- ¹⁴C. S. Koonce, B. W. Mangum, and D. D. Thornton, Phys. Rev. B <u>4</u>, 4054 (1971).
- ¹⁵J. M. Baker, Rep. Prog. Phys. <u>34</u>, 109 (1971).
- ¹⁶E. Belorizki, M. J. M. Leask, and K. J. Maxwell, Colloq. Int. C.N.R.S. <u>2</u>, 453 (1970).