

# Analysis of the fine structure of a ${}^4T_1$ level of a $d^5$ ion coupled to $\epsilon$ vibrational modes from the magnetic-field effect

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The influence of a magnetic field on the fundamental vibronic lines (FVL) of the fluorescent  ${}^4T_1$  level of  $\text{Mn}^{2+}$  in pure cubic ZnS has been studied up to 5 T in order to analyze the fine structure of this level. First, very detailed excitation spectra  $\sigma^+$  and  $\sigma^-$  of the transitions  ${}^6A_1 \rightarrow {}^4T_1$  have been obtained by using polarization modulated laser spectroscopy performed at 1.9 K. Second, the theoretical energies and relative dipole strengths (RDS) of the transitions between the Zeeman levels  ${}^6A_1$  ( $M_S = -\frac{5}{2}$ – $M_S = +\frac{5}{2}$ ) of the fundamental level and the Zeeman levels of the Kramer's doublets  $\Gamma_6({}^4T_1)$ ,  $\Gamma_7({}^4T_1)$ , and spin quartets  $\Gamma'_8/2({}^4T_1)$ ,  $\Gamma'_8/2({}^4T_1)$ , have been analyzed in terms of the Zeeman Hamiltonian  $\mu_B g_e \mathbf{S} \cdot \mathbf{H}$  and in terms of three coefficients that account for the splitting and RDS's of the fundamental vibronic lines in zero magnetic field. Finally, it is shown that the contribution of the term in  $\mu_B \mathbf{L} \cdot \mathbf{H}$  of the Zeeman Hamiltonian is negligible and that the magnetic-field effect permits us to unambiguously determine the nature of the FVL's. [S0163-1829(98)01343-5]

## I. INTRODUCTION

Recent experiments performed on the fluorescent  ${}^4T_1$  level of  $\text{Mn}^{2+}$  in ZnS led us to question both the electronic and vibronic structures previously adopted for this state. A model for the fluorescent  ${}^4T_1$  level of  $\text{Mn}^{2+}$  in ZnS and, more generally, for the orbital triplet states of  $d^5$  ions in II-VI compounds has been elaborated (see Ref. 1).

Concerning the electronic structure, the analysis of the fine structure has shown that the first-order spin-orbit (SO) splitting is strongly reduced with respect to that predicted by the crystal-field (CF) model. This result has been confirmed from a covalent model for the first-order SO interaction. *The fact that the CF model is wrong in predicting the SO interaction has drastic consequences.* First, the previous vibronic models<sup>2</sup> that predicted a strong coupling to  $\epsilon$  vibrational modes are either wrong or at least questionable since they were elaborated from a comparison of the experimental fine structure to the electronic structure as given by the CF model for the SO interaction. Second, the electronic first-order SO interaction is predicted to be very small, so that the second-order SO interactions become very important. Third, since it is very difficult to elaborate a precise covalent model for the second-order SO interactions, it has not been possible to determine with precision the strength of the coupling to  $\epsilon$  vibrational modes. Finally, the nature of the fine-structure lines had to be determined without using the CF model or the covalent model.

In Ref. 1, the nature of the fine-structure lines has been tentatively determined from their relative dipole strengths (RDS's) since these RDS's do not depend on a given model. Unfortunately, two plausible labeling schemes were found for the observed lines (see Fig. 1).

The aim of this paper is to analyze the magnetic-field effect on the  $|{}^4T_1\rangle$  state of  $\text{Mn}^{2+}$  in ZnS in order to unambiguously determine the labeling scheme of the fine-structure lines. (Dichroism experiments performed long ago on this state were of no help since the structure of the quasidegenerate states was not resolved.<sup>3</sup>)

The experiments are reported in Sec. II for selected crystals showing well-defined fundamental vibronic lines (FVL). For conciseness, detailed experimental results are given for  $\mathbf{B} \parallel [001]$  only, since the labeling scheme of the fine-structure lines can be obtained from this orientation of the magnetic field.

The theoretical structure of the  $|{}^4T_1\rangle$  state in zero magnetic field is briefly recalled in Sec. III A. It is shown that the splitting of the studied state and the RDS's of the FVL's are correctly given in terms of three parameters deduced from an analysis of the symmetry of the effective Hamiltonian describing the first- and second-order spin-orbit interaction and the spin-spin interaction. In Sec. III B, a theoretical analysis is made of the magnetic-field-induced splittings of the FVL's and of the RDS's, for polarizations  $\sigma^+$  and  $\sigma^-$ . Two distinct theoretical analyses corresponding to the two proposed labeling schemes of the lines are performed.

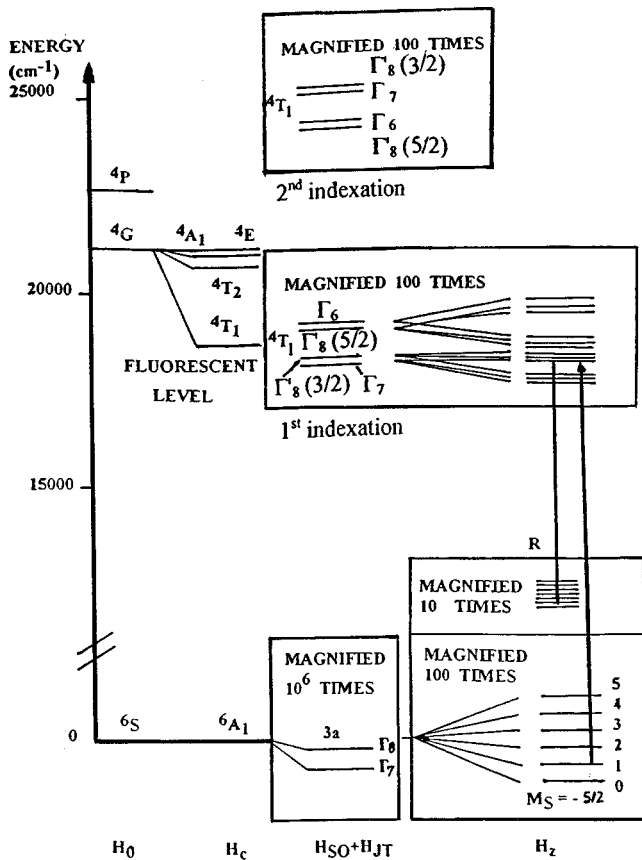


FIG. 1. The spectroscopic terms and the multiplets at lower energy of  $\text{Mn}^{2+}$  in  $\text{ZnS}$  are given to the left. The zero-field splitting, due to the spin-orbit interaction, of the fundamental state is represented, as well as the vibronic structure of the fluorescent  ${}^4T_1$  level due to the spin-orbit and Jahn-Teller interaction. The two labeling schemes of the vibronic lines are from Ref. 1. The transition represented is from the Zeeman state  $|{}^6A_1 M_S = -\frac{3}{2}\rangle$  to one of the 12 vibronic states of the  ${}^4T_1$  level. The arrow  $R$  represents a radiative transition from the excited state to phonon-assisted lines of the fundamental state.

In Sec. IV, the experimental spectra are compared to theoretical spectra corresponding to the two proposed labeling schemes of the FVL's. From an analysis of the energy levels and polarization effects, it is unambiguously shown that the "first labeling scheme" represented in Fig. 1 is the only one that can account for the magnetic-field effect.

## II. EXPERIMENTS

### A. Samples and apparatus

The samples are those that were used in previous Zeeman experiments performed on the  ${}^4E$  level of  $\text{Mn}^{2+}$  in cubic  $\text{ZnS}$ .<sup>4</sup> No excitation line due to stacking faults<sup>5</sup> or Mn-Mn pairs<sup>6</sup> was observed. The linewidths of  $0.6\text{--}0.7\text{ cm}^{-1}$  of the excitation lines of the fluorescent level  ${}^4T_1$  are five times smaller than those observed in previous experiments on this multiplet.

The excitation spectra were obtained from a  $\text{XeCl}^*$  excimer laser pumping a pulsed dye laser synchronized to the phase of a stress modulator transforming the excitation light into right and left circularly polarized light. The degree of

polarization was better than 95%. The linewidth of the laser system was approximately  $0.4\text{ cm}^{-1}$ .

The emission light was selected by a monochromator centered at the maximum of the emission band ( $17240\text{ cm}^{-1}$ ).

The samples were immersed in pumped liquid helium, in a superconducting split coil operating up to 5 T. The experiments were performed at 1.9 K.

### B. Experimental spectra

For  $\mathbf{B}||[001]$ ,  $B=0\text{--}5\text{ T}$ , and  $T=1.9\text{ K}$ , the experimental spectra corresponding to the polarizations  $\sigma^+$  and  $\sigma^-$  are given in Fig. 2(a). For  $B=0$ , two groups of almost superimposed lines are observed. For  $B=0.5\text{--}1\text{ T}$ , for polarizations  $\sigma^+$  and  $\sigma^-$ , each group of lines decomposes into several lines. For  $B=3\text{--}5\text{ T}$  and for polarizations  $\sigma^+$  and  $\sigma^-$ , the amplitude of the group of lines at higher energy strongly decreases with respect to the amplitude of the group of lines at lower energy. For  $B=5\text{ T}$ , for polarization  $\sigma^+$ , only one weak line is observed at higher energy, while one intense line flanked by weak lines is observed at lower energy. For polarization  $\sigma^-$ , the amplitude of all lines strongly decreases when increasing  $B$ .

Experiments were also performed for  $\mathbf{B}||[111]$ . They are not reported here since, as it will be shown in the next section, they did not permit us to determine the labeling scheme of the fine-structure lines.

## III. THEORETICAL MODEL

### A. Structure of the ${}^4T_1$ level in zero magnetic field

Following Ham's method,<sup>7</sup> the first- and second-order spin-orbit interaction and the spin-spin interaction are given by the equivalent operator.

$$H_{\text{eq}} = c_{T1} \mathbf{L} \cdot \mathbf{S} + c_E \frac{2}{3} (1_{\theta} S_{\theta} + 1_e S_e) + c_{A1} \frac{1}{3} \mathbf{L}^2 \mathbf{S}^2 + c_{T2} \frac{1}{2} (l_{\xi} S_{\xi} + l_{\eta} S_{\eta} + l_{\zeta} S_{\zeta}).$$

$\mathbf{L}$  is an orbital operator of rank 1,  $S = \frac{3}{2}$ . The index  $\Gamma$  in the parameters  $c_{\Gamma} S$  indicates that the operators span the representation  $\Gamma$  of Td. The term in  $c_{A1}$  describes the shift common to the fine-structure lines. In the following,  $c_{T1}$ ,  $c_E$ , and  $c_{T2}$  will be considered as three fitting experimental parameters describing the splittings of the fine-structure lines.

For the first labeling scheme as given in Fig. 1, the energy difference  $\Delta$  between the gravity center of the states  $|\Gamma_7\rangle$ ,  $|\Gamma'_8(\frac{3}{2})\rangle$  and the gravity center of the states  $|\Gamma_6\rangle$ ,  $|\Gamma'_8(\frac{5}{2})\rangle$  is  $\Delta = -9.48\text{ cm}^{-1}$ . We can recall that  $\Delta$  is the splitting primarily due to the nonreduced part of the second-order spin-orbit interaction. The fitting of the energy levels gives  $c_{T1} = -0.216\text{ cm}^{-1}$ ,  $c_E = 4.740\text{ cm}^{-1}$ , and  $c_{T2} = -0.094\text{ cm}^{-1}$ .<sup>1</sup>

For the second labeling scheme  $\Delta = +9.48\text{ cm}^{-1}$ ,  $c_{T1} = -0.213\text{ cm}^{-1}$ ,  $c_E = -4.952\text{ cm}^{-1}$ , and  $c_{T2} = -0.049\text{ cm}^{-1}$ .<sup>1</sup>

### B. Magnetic-field effect

The Zeeman Hamiltonian acting on electronic states is

$$H_Z = \mu_B (\mathbf{L} + g_e \mathbf{S}) \cdot \mathbf{H},$$

$\mu_B$  being the Bohr magneton,  $g_e$  the Landé factor of the electron ( $g_e = 2.0023$ ), and  $\mathbf{H}$  the applied magnetic field. The calculations have been performed by taking into account

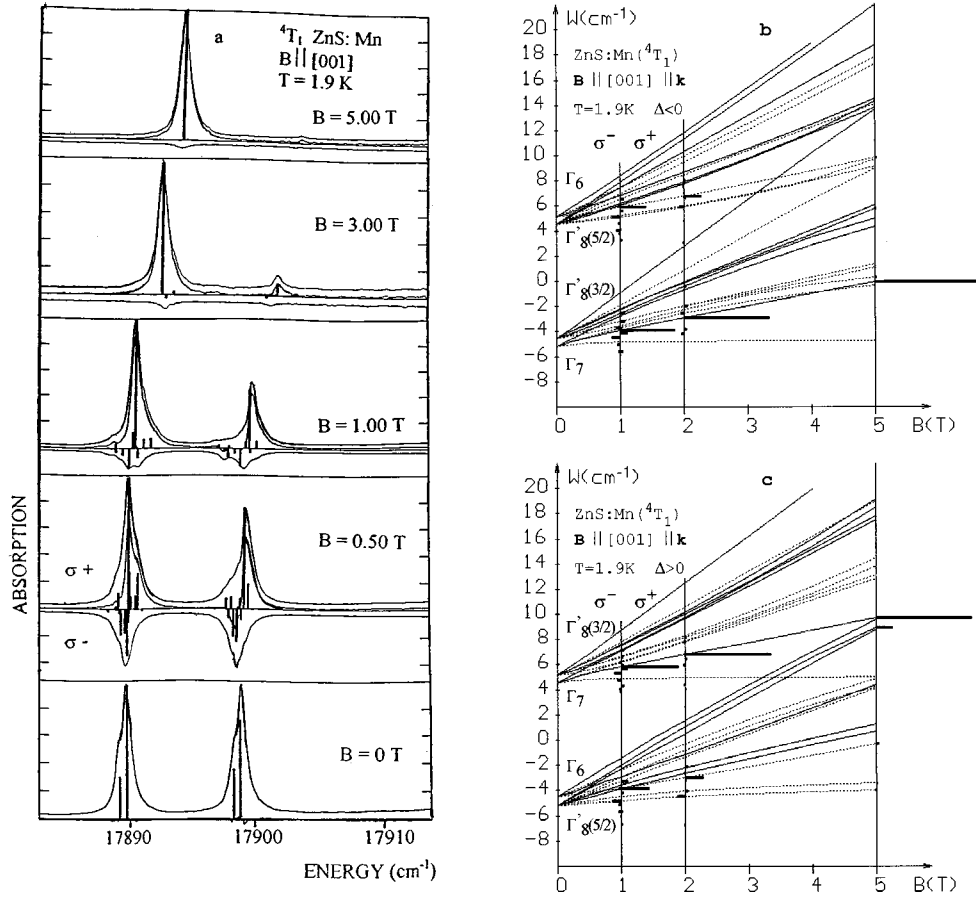


FIG. 2. In (a), the theoretical and experimental polarized excitation spectra are represented for  $B$  extending from 1–5 T,  $\mathbf{B} \parallel [001]$ ,  $T = 1.9$  K. the spectra  $\sigma^+$  and  $\sigma^-$  and the difference between the spectra  $\sigma^+$  and  $\sigma^-$  are represented in each inset. It must be noted that the spectra are normalized so that the most intense excitation line, that is, the line at lower energy in the spectra  $\sigma^+$ , has a constant amplitude. The vertical bars represent the theoretical energies and RDS's obtained from the first labeling scheme. (b) and (c) represent the theoretical energy levels in terms of the magnetic field for the first and second labeling schemes, respectively. The solid and broken lines are associated with transitions from the fundamental states  $|M_S = -\frac{5}{2}\rangle$  and  $|M_S = -\frac{3}{2}\rangle$ , respectively. The RDS's for all transitions from the Zeeman sublevels of the fundamental  $|{}^6A_1\rangle$  state are represented for polarizations  $\sigma^+$  and  $\sigma^-$ , for  $B = 1, 2$ , and  $5$  T.

the nonreduced term in  $\mathbf{S} \cdot \mathbf{H}$  alone. Of course, the influence of the orbital term will be checked *a posteriori* when comparing the experimental and theoretical energy levels and RDS's.

In the calculations, the hyperfine splitting as well as the zero-field splitting [ $3a = 23.61 \times 10^{-4} \text{ cm}^{-1}$  (Ref. 8)] of the fundamental  ${}^6A_1$  level has been neglected.

The matrix elements of  $H_{\text{eq}} + \mu_B g_e \mathbf{S} \cdot \mathbf{H}$  have been calculated by using the parameters corresponding, on the one hand, to the first labeling scheme ( $\Delta < 0$ ), and on the other hand, to the second labeling scheme ( $\Delta > 0$ ). The computation of the energy levels and wave functions of the fundamental and excited states has been performed in Td\*. The basis functions  $|{}^4T_1 J t \tau\rangle$  and  $|{}^6A_1 t \tau\rangle$  were those given by Griffith,<sup>9,10</sup> which correspond to an axis system whose vectors are parallel to the cubic axes  $\mathbf{x} \parallel [100]$ ,  $\mathbf{y} \parallel [010]$ , and  $\mathbf{z} \parallel [001]$ . The matrix for  $\mathbf{S} \cdot \mathbf{H}$  has been calculated in terms of  $H_Z$ ,  $H^+ = H_x + iH_y$ , and  $H^- = H_x - iH_y$ .

The polarization effects are calculated following the method given in Ref. 4. Of course, the Boltzmann distribution in the fundamental state has been taken into account.

The diagonalizations have been performed for  $B$  extending from 0–5 T, for  $\mathbf{B} \parallel [001]$  (and also for  $\mathbf{B} \parallel [111]$ ). In Figs.

2(b) and 2(c), for  $\mathbf{B} \parallel [001]$ , for  $\Delta < 0$  and  $\Delta > 0$ , the energy levels are represented in terms of  $B$  for the transitions  $|{}^6A_1 M_S = -\frac{5}{2}\rangle \rightarrow |{}^4T_1\rangle$  (solid lines) and  $|{}^6A_1 M_S = -\frac{3}{2}\rangle \rightarrow |{}^4T_1\rangle$  (broken lines). All energy levels and RDS's are represented for  $B = 1, 2$ , and  $5$  T. All energy levels and RDS's associated with the transitions from all the Zeeman sublevels of the  ${}^6A_1$  level to all the Zeeman sublevels of the  ${}^4T_1$  level have been represented, for  $\mathbf{B} \parallel [001]$  and for  $\Delta < 0$ , in Fig. 2(a), where the experimental and theoretical spectra are compared.

#### IV. COMPARISON WITH EXPERIMENTS AND DISCUSSION

From experiments performed with  $\mathbf{B} \parallel [001]$ , it will be shown that the first labeling scheme is the only one that permits a good fitting of the experimental results.

The theoretical and experimental spectra for polarizations  $\sigma^+$  and  $\sigma^-$  are compared in Fig. 2(a), for  $\mathbf{B} \parallel [001] \parallel \mathbf{k}$ , at  $T = 1.9$  K, for  $\Delta < 0$ . For  $B = 0$ –1 T, a very complex splitting of the lines that are almost degenerate in zero magnetic field is observed. However, it is clear that the experimental spectra are well accounted for by the theoretical model. For  $B$

$=3-5$  T, the spectra become very simple. For  $\sigma^+$ , they reduce to one intense absorption line at lower energy and one relatively weak line at higher energy, whose amplitude rapidly decreases in terms of  $B$ . For  $\sigma^-$ , weak lines are observed. Of course, the good agreement between the theoretical spectra obtained by taking  $\Delta < 0$  and the experimental spectra is a good argument in favor of the first labeling scheme.

By considering the theoretical spectra for  $\Delta > 0$ , it will now be unambiguously demonstrated that the first labeling scheme is the only indexation in agreement with the Zeeman effect. Figures 2(b) and 2(c) show that the spectra are very different depending on the sign of  $\Delta$ . For  $\Delta > 0$  and  $B > 1$  T, by considering the spectra associated with  $\sigma^+$ , the most intense line appears at higher energy. For  $\Delta > 0$ ,  $B = 5$  T, only two lines separated by approximately  $1 \text{ cm}^{-1}$  appear at higher energy, and two very weak lines appear at lower energy. This result is clearly in disagreement with the experimental spectra.

It can be noted from Fig. 2(b) that for the first indexation, the most intense line in the spectra  $\sigma^+$  can be associated by continuity to the level  $(^4T_1)\Gamma_7$ , and that the transition is from the  $|^6A_1M_S = -\frac{5}{2}\rangle$  state.

For  $\mathbf{B} \parallel [111]$ , a good agreement has been obtained between the experimental and theoretical spectra for the first labeling scheme. However, the theoretical spectra being almost identical for the first and second labeling scheme this orientation of the magnetic field is of no help to determine the correct labeling scheme.

It can be noted that, for the spectra showing well-separated excitation lines, the experimental and theoretical energy levels differ by  $0.2-0.4 \text{ cm}^{-1}$ , that is, differ by less than one linewidth ( $0.6 \text{ cm}^{-1}$ ). This indicates that the contribution of the terms in  $\mathbf{L} \cdot \mathbf{H}$  of the Zeeman Hamiltonian, as well as the second-order interactions involving the excited vibronic states and the excited electronic states are negligible.

### CONCLUSION

A very detailed analysis of the magnetic-field effect has been performed in order to unambiguously determine the indexation of the four fundamental vibronic lines of the fluorescent  $^4T_1$  level of  $\text{Mn}^{2+}$  in cubic ZnS. First, by using

selected crystals showing very small internal strains, very well-defined polarized spectra  $\sigma^+$  and  $\sigma^-$  have been obtained. Then, theoretical analyses of the Zeeman splittings and RDS's have been made by using the term in  $\mathbf{S} \cdot \mathbf{H}$  of the Zeeman Hamiltonian and three parameters describing the zero-field splittings. Two separate theoretical analyses of the Zeeman splittings and RDS's have been performed by using the parameters corresponding to the first labeling scheme and to the second labeling scheme. Finally, by comparing the theoretical and experimental spectra, it has been demonstrated that the *first labeling scheme is the only one that can account for experiments*.

This study has shown that the magnetic-field effect is correctly described by the term  $g_e \mu_B \mathbf{H} \cdot \mathbf{S}$  only, the contribution of the orbital part  $\mu_B \mathbf{L} \cdot \mathbf{H}$  of the Zeeman Hamiltonian and of the second-order interactions involving the spin-orbit interaction being negligible.

Concerning the strength of the Jahn-Teller coupling, it has been shown in Ref. 1 that the fine structure in zero magnetic field could be interpreted by taking  $0 < S < 2$ . It is not possible to give a precise value for  $S$  because we do not know with precision the electronic structure of the fluorescent level either from experiment or from the molecular model. For example, a value for  $S$  near zero would mean that the observed structure represents approximately the electronic structure. This hypothesis cannot be rejected since it has been shown that the electronic first-order spin-orbit interaction is strongly reduced by covalency. It also must be noted that it is not possible to give a precise value for  $S$  from the Zeeman experiments since we do not know whether the electronic contribution of the term in  $\mathbf{L} \cdot \mathbf{H}$  is weak or reduced by the Jahn-Teller effect.

### ACKNOWLEDGMENTS

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