Influence of the Jahn-Teller effect on the Zeeman splittings of the 4T2 level of Mn2+ in ZnS

A. Landi, A. Deville, R. Ranvaud

To cite this version:


HAL Id: jpa-00209229
https://hal.archives-ouvertes.fr/jpa-00209229
Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Influence of the Jahn-Teller effect on the Zeeman splittings of the 4T₂ level of Mn²⁺ in ZnS

A. Landi, A. Deville

Département d'Electronique (*), Université de Provence,
Centre de Saint-Jérôme, 13397 Marseille Cedex 4, France

and R. Ranvaud (**) Max-Planck Institut, S.N.C.I.,
avenue des Martyrs, B.P. 166, 38042 Grenoble Cedex, France

(Reçu le 15 mai 1979, révisé le 27 septembre 1979, accepté le 27 septembre 1979)

Résumé. — La structure fine du niveau 4T₂ de plus faible énergie de Mn²⁺ dans ZnS a été analysée par effet Zeeman. Les levées de dégénérescence Zeeman ont été mesurées en utilisant une bobine supraconductrice de 100 kG, pour différentes polarisations. Dans l'interprétation des spectres expérimentaux, on utilise un modèle moléculaire et l'on considère les effets Ham. Un couplage Jahn-Teller intermédiaire avec un mode de vibration E permet d'expliquer les levées de dégénérescence observées en champ fort. On obtient un meilleur accord pour S = 2 que pour S = 0,6, valeur proposée antérieurement à partir d'expériences de pression uniaxiale. Cependant, l'accord entre les intensités calculées et celles observées n'est pas très satisfaisant.

Abstract. — The Zeeman effect has been used to analyse the fine structure of the lowest 4T₂ level of Mn²⁺ in ZnS. We have measured the Zeeman splittings and the relative intensities for different polarizations in a 100 kG superconducting magnet. In order to interpret the experimental spectra, a cluster model is assumed and Ham effects are considered. A medium Jahn-Teller coupling with an E vibrational mode can explain the Zeeman splittings observed in high magnetic field. A better fit is obtained for S = 2 than for S = 0.6, the value previously proposed from uniaxial stress experiments. However the theoretical intensities are not in good agreement with those observed.

1. Introduction. — The ground state of Mn²⁺(3d⁵) ion at substitutional Zn site in tetrahedral symmetry is 6A₁, and the lowest excited states 4T₁, 4T₂, 4E derive from the 4G term of the free ion. Among these levels 4T₁ is the fluorescent one. Langer and Ibuki [1] have studied earlier optical absorption and emission spectra of Mn²⁺ in ZnS, and they have assigned the different bands to transitions from the 6A₁ ground state to the different excited states 4T₁, 4T₂, 4E. The zero-phonon lines associated with each band are narrow enough to allow a detailed analysis of their structure under application of an uniaxial stress or a magnetic field, and a better understanding of the electron-phonon interaction. Uniaxial stress allows an easy determination of the symmetry of the active Jahn-Teller vibrational mode; but in dilute crystals the calculation of the splittings under stress is made with the more or less justified assumption that the relation between stress and strain near the center is that of the bulk material. On the other hand, the Zeeman splittings are more directly related to the strength of the Jahn-Teller coupling. Both experiments are thus complementary, and have been used to explain the fine structure of the 4E [2, 3] and 4T₁ [4] levels. They have shown a strong Jahn-Teller coupling with an E vibrational mode for the 4T₁ state and the absence of Jahn-Teller effect in the 4E level. Uniaxial stress experiments [5] performed on the 4T₂ level suggest a weak coupling to an E vibrational mode.

In this paper, the Zeeman effect on the 4T₂ term is reported. The excitation spectra in zero magnetic field show a fine splitting of 3 cm⁻¹ and, because of linewidth, high magnetic fields up to 100 kG are
necessary to lift the degeneracy of the observed doublet in zero field. Excitation spectra were recorded at low temperature for different orientations of the magnetic field and different polarizations of the excitation light. These experiments are described in section 2.

In section 3 after an analysis in the static crystal field approximation, we take account of a Jahn-Teller coupling to an E vibrational mode. We compare the results obtained in the Ham approximation with $S = 2$ and those obtained in a more realistic treatment in the hypothesis of a weak coupling with $S = 0.6$. In each case the energy levels and the relative intensities are calculated.

2. Experimental. — 2.1 EXPERIMENTAL TECHNIQUE. — A single crystal of ZnS : Mn$^{2+}$ (Eagle-Pitcher) containing approximately $10^{-4}$ Mn$^{2+}$ ions/mole of ZnS is used for these experiments. Its faces are crystallographically oriented, one face is perpendicular to the [111] axis, another one is perpendicular to [110].

In order to avoid complications in experimental spectra and in further theoretical analysis, excitation spectra ($^6A_1 \rightarrow ^4T_2$) were recorded at 1.4 K. The initial ground state $^6A_1$ is split by Zeeman effect with a $g$ factor equal to 2.00 but, at this temperature, when the magnetic field reaches 30 kG, only the $^1A_1$, $M_s = -5/2$, $a_1 >$ ground state is populated, and only transitions originating from this state are to be considered.

Magnetic field up to 100 kG was obtained in a superconducting magnet with field direction parallel to the [111] or to the [110] axis of the crystal. Excitation was provided by a Coherent Radiation CR 490 dye laser pumped by a Spectra Physics 171 U.V. Argon laser. The dye was Coumarin 7, it was pumped by the 4 765 Å line of Argon with a pumping power around 2 W. The excitation linewidth was typically 0.5 cm$^{-1}$ at 20 000 cm$^{-1}$ and the available power was about 10 mW. This dye enabled to vary the excitation light from 4 950 Å to 5 350 Å. Incident light was linearly polarized and excitation spectra were recorded with E polarization parallel to the [111] or [110] axis of the crystal. Detection was obtained by collecting on a cooled Ga-As photomultiplier a large part (typically 100 Å) in the middle of the vibronic band of the fluorescent light ($^4T_2 \rightarrow ^6A_1$). Transverse and longitudinal observations were made.

2.2 EXPERIMENTAL RESULTS. — Figure 1a shows spectra recorded in zero magnetic field. The zero-phonon doublet appears at 19 682 cm$^{-1}$ and 19 685.4 cm$^{-1}$, in agreement with Langer and Ibuki’s spectra. The linewidth of each component is about 5 cm$^{-1}$. Lines located around 19 780 cm$^{-1}$ are attributed to Mn$^{2+}$ ions in stacking faults [6]. A very much weaker line is also detected around 19 717 cm$^{-1}$, with a linewidth about 10 cm$^{-1}$.

Some of the spectra recorded under magnetic field are reported from figure 1b to figure 1e. These spectra were identical for both directions of $H$ ([H/][111] or $H/[/110]$); even for the highest values of the field no measurable anisotropy could be detected. The comparison of the spectra obtained at a given value of the magnetic field $H$ for both orientations of E, the electric field of the excitation light, versus $H$ clearly demonstrates the existence of polarization effects; this is most evident for $H = 100$ kG, as shown in figures 1d and 1e corresponding to $E//H$ and $E \perp H$ respectively. When the intensity of the magnetic field increases, one first observes that the relative intensity of the upper line of the doublet falls down very rapidly and then, for $H > 40$ kG, the lower line of the doublet is split. Figures 2a and 2b show the Zeeman splittings of the $^4T_2$ level for $E//H$ and $E \perp H$ respectively. They were obtained from the experimental spectra after a correction for the Zeeman effect in the $^6A_1$ ground state.

![Fig. 1. — Excitation spectra of the zero phonon lines ($^6A_1 \rightarrow ^4T_2$) of Mn$^{2+}$ in ZnS ($T = 1.4$ K). Polarization effects are observed at $H = 100$ kG.](image)

![Fig. 2. — The observed Zeeman splittings of the $^4T_2$ level of Mn$^{2+}$ in ZnS for different polarizations. The Zeeman shift of the $^6A_1$ sublevel has been subtracted out. The relative intensities of observed transitions are reported in brackets.](image)
2.3 Constancy of the intensity of luminescence. — When the excitation wavelength was kept constant and the intensity of luminescence was recorded as a function of time from the beginning of the excitation, the intensity of luminescence was observed first to decrease weakly, then at a time \( \tau_0 \) to present an important drop and finally to reach slowly a stationary value. The value of \( \tau_0 \) depended on the excitation power and was typically several minutes. This effect will not be discussed here. In all experiments, the time of recording was such that this decrease was negligible.

3. Theoretical analysis. — The static crystal field is first used. It is shown that it fails to explain the zero field spectrum. We thus attempt to interpret the observed positions and intensities of the Zeeman lines in the Ham model. It is finally shown that the value of \( S \) previously proposed from uniaxial stress experiments cannot account for the Zeeman spectra.

3.1 Static crystal field model. — In this approximation all nuclei are assumed in a rigid configuration and interactions of the metal ion with its surroundings are represented by an electrostatic field. A weak field scheme is adopted here. The Racah's parameter \( B \) and \( C \) and the crystal field parameter \( \Delta \) have been deduced by standard methods from the experimental results on the free ion Mn\(^{2+} \), and from Langer and Ibuki's spectra. The chosen value are \( B = 920 \text{ cm}^{-1} \), \( C = 3 \text{ 200 cm}^{-1} \), \( \Delta = -4 \text{ 200 cm}^{-1} \). \( B, C \) have then to be reduced from their free ion values, by an amount of 10\% for covalency.

The \( ^4T_2 \) level considered here is a mixing arising from the \( ^4G, ^4D, ^4F \) free ion terms and is given by the following expression:

\[
| ^4T_2 > = 0.965 | ^4G T_2 > + 0.219 | ^4F T_2 > - 0.141 | ^4D T_2 > .
\]

In the coupling scheme adopted, spin-orbit interaction \( V_{so} = \sum_i \alpha_i s_i \) is treated as a perturbation acting on the Hamiltonian \( \mathcal{H} \) of the ion in the crystal. It lifts the degeneracy of the \( ^4T_2 \) term according to the irreducible representations \( \Gamma_6, \Gamma_7, \Gamma_8 \) of the double point group \( T_d^* \). Its effect up to second order inside the \( ^4T_2 \) level can be described by an effective operator \( [7] \):

\[
\mathcal{H}_{so} = \chi | s > + \mu (l_s^2 s_s^2 + l_s^2 s_s^2 + l_s^2 s_s^2)
\]

where \( l \) is an effective angular momentum transforming as \( T_1 \) with \( l = 1 \) acting in equivalent \( p \) states and \( s \) a spin operator with \( s = 3/2 \). The parameters \( \chi, \mu, \rho \) can be determined by second-order perturbation theory. We use the Griffith notation and represent the spin-orbit adapted states by \( | ^4T_2 J \tau > \) where \( \tau \) is a component of the irreducible representation \( t \) of \( T_d^* \) and \( J = l + s, l + s - 1, ..., | l - s | \). In the calculation of the matrix elements:

\[
\langle ^4T_2 J' \tau' | V_{eff} | ^4T_2 J \tau >
\]

we considered as intermediate states \( \alpha \) all the multiplets originating from the 3d\(^5 \) configuration. The spin-orbit constant \( \zeta \) was reduced by an amount of 10\% from its free ion value because of covalency, and chosen equal to 280 cm\(^{-1} \). The values of \( \chi, \mu, \rho \) are in rough agreement with those reported by Koidl [8] for different values of \( B, C \) and \( \Delta \), in the strong field coupling scheme. They lead to an overall splitting of about 100 cm\(^{-1} \), as reported in figure 3 for \( S = 0 \).

From selection rules for parity and spin multiplicity the transitions \( ^6A_1 \rightarrow ^4T_2 \) are highly forbidden. However perturbation schemes involving the odd

Fig. 3. — Ham effect on the spin-orbit splittings of the \( ^4T_2 \) level versus the strength \( S \) of the Jahn-Teller coupling.

Fig. 4. — Spin-orbit splitting of the \( ^4T_2 \) level calculated in the hypothesis of a weak Jahn-Teller coupling as described in section 3.3.
parity components of the crystal field and the spin-orbit interaction can remove these interdictions. They have been studied by Parrot et al. [5] in order to interpret relative intensities in uniaxial stress experiments on the $^4T_2$ level. It results from their analysis that dipole strengths are described by:

$$
\sigma\left[^6A_1 \ J_{tt} \rightarrow \ ^4T_2 \ J \ ' \ t' \ '\right] = \sum_{(T_2)} \left< ^6A_1 \ J_{tt} \left| V_{so} \right| ^4T_1 \ J_{tt} \right> \left< ^4T_1 \ J_{tt} \left| H_{eq} \right| ^4T_2 \ J \ ' \ t' \ '\right> / \left( E^4A_1 - E^4T_1 \right)
$$

where $^4T_1$ represents intermediate states originating from the $3d^5$ configuration and $E(^6A_1)$, $E(^4T_1)$ are the energies of the $^6A_1$ and $^4T_1$ states respectively.

Here $H_{eq}$ represents the action of the odd parity crystal field terms and the dipolar electric moment [5]. However in relative intensities calculations only symmetry properties of these matrix elements are needed and $H_{eq}$ transforms as the representation $T_2$ of $T_d$.

In zero magnetic field the $^6A_1$ ground state is degenerate and the following relative dipole strengths are obtained:

\[
\begin{align*}
\sigma_{nR}(^6A_1 \rightarrow ^4T_2, ^1/2T_2) & = 0.0 \\
\sigma_{nR}(^6A_1 \rightarrow ^4T_2, ^3/2T_2) & = 0.6 \\
\sigma_{nR}(^6A_1 \rightarrow ^4T_2, ^5/2T_2) & = 1.0 \\
\sigma_{nR}(^6A_1 \rightarrow ^4T_2, ^7/2T_2) & = 0.5 .
\end{align*}
\]

Thus in the crystal field model three lines with comparable intensities and an overall splitting of about 100 cm$^{-1}$ are allowed, in disagreement with the experimental doublet. Moreover the 3 cm$^{-1}$ observed splitting strongly suggests the existence of a Jahn-Teller effect.

3.2 HAM MODEL. — In Ham approximation a cluster model is assumed, and all effects associated with spin are first neglected. This scheme seems justified here since the spin-orbit splitting expected in static crystal field theory is much more greater than the observed splitting of the zero-phonon lines.

A $T_2$ state in tetrahedral symmetry may be coupled to both $E$ and $T_2$ vibrational modes of the cluster. However uniaxial stress experiments have shown that $T_2$ modes are non active ones. So only a coupling with an $E$ vibrational mode is considered, and in this case the vibronic hamiltonian reduces [9] to

$$
\mathcal{H}_{ab} = \mathcal{H}_0 + \frac{1}{2} \mu \left[ P_x^2 + P_y^2 + \mu^2 \omega^2 (Q_x^2 + Q_y^2) \right] x^3 + V Q_x Q_y,$n$

Spin-orbit interaction is then treated as a perturbation acting on the vibronic eigenstates, and this model leads to a partial quenching of spin-orbit coupling.

The spin-orbit interaction within the vibronic triplet is described by an operator [8]

$$
\xi_{ab}^{J_{so}} = \chi_{so} (l_{so}) + \mu_{so} (l_{so})^2 + \rho_{so} \times (l_x^2 s_x^2 + l_y^2 s_y^2 + l_z^2 s_z^2)
$$

with:

$$
\chi_{so} = \left( \chi - \mu \right) \cdot k(T_1) + \frac{\mu}{2} \cdot k(T_2),
$$

$$
\mu_{so} = \mu \cdot k(T_2),
$$

$$
\rho_{so} = (\mu + \rho) \cdot k(E) - \mu \cdot k(T_2).
$$

In these expressions the orbital reduction factors are for $E$ mode coupling [9],

$$
k(T_1) = k(T_2) = \exp \left( - \frac{3}{2} \cdot S \right), \quad k(E) = 1 ,
$$

and $\chi$, $\mu$, $\rho$ are the values derived in the static field approximation. The contribution of the spin-orbit coupling through the excited vibronic states is described [9] by:

$$
\xi_{ab}^{J_{so}} = k_1 (l_{so}) + k_2 (l_x^2 s_x^2 + l_y^2 s_y^2 + l_z^2 s_z^2).
$$

Eigenvalues of $\xi_{ab}^{J_{so}} + \xi_{ab}^{J_{so}}$ have been calculated for different values of $\hbar \omega$, chosen equal to 100, 200, 300 cm$^{-1}$, but the results are weakly dependent on $\hbar \omega$. In figure 3 the spin-orbit splittings of the $^4T_2$ level versus the strength $S (S = E_{JT} / \hbar \omega)$ of the Jahn-Teller interaction is reported for $\hbar \omega = 100$ cm$^{-1}$. We clearly observe a reduction of spin-orbit interaction. In the limit of a strong Jahn-Teller coupling a doublet zero-phonon line is expected with a splitting of 1.5 cm$^{-1}$. In Ham approximation relative intensities are independent of the strength of the Jahn-Teller coupling. They remain the same as in the static crystal field model. Therefore the zero field spectrum may be interpreted in Ham model with a $S$ value greater than 2. For a lower $S$ value a triplet should be observed.

In the presence of an external magnetic field, inside the ground vibronic states the Zeeman interaction is described by the equivalent hamiltonian:

$$
\mathcal{H}_z = \beta \cdot (g_L \cdot l \cdot H + g_S \cdot s \cdot H),
$$

with

$$
g_L = g_L \cdot \exp \left( - \frac{3}{2} \cdot S \right), \quad \beta = \frac{e \hbar}{mc}, \quad g_S = 2.002.3.
$$

Here $g_L$ represents the orbital contribution to Zeeman effect. The $g_L$ value calculated in the crystal field approximation is not sensitive to reasonable variations in $B$, $C$ and $A$ parameters and is equal to 2.33 with the given values of these parameters. So, Zeeman splittings are directly related to the strength of the
Jahn-Teller coupling through the orbital reduction factor. In the calculation of Zeeman effect the second order terms arising from the combined effect of the orbital part of $\mathcal{K}_s$ and the first order spin-orbit interaction with excited vibronic states are described by

$$\mathcal{K}_s^{(2)} = g_1 \beta [(1.s)(1.H) + (1.H)(1.s)] + g_2 \beta [l_2^2 s_z H_x + l_2^2 s_y H_y + l_2^2 s_z H_z]$$

where

$$g_1 = -\frac{\chi g_L}{\hbar \omega} f_s$$
$$g_2 = -\frac{2 \chi g_L}{\hbar \omega} (f_b - f_s)$$

and $f_s, f_b$ as given by Ham in [9].

The second order terms due to excited electronic states have been neglected. Moreover because of the intensity of the magnetic field and of the observed spin-orbit splittings, the Zeeman and spin-orbit interactions are treated on the same equal footing in perturbation.

The Zeeman splittings of the vibronic ground levels have been determined for different values of $S$, and several values of $\hbar \omega$ chosen about 200 cm$^{-1}$. Splittings are not greatly dependent on $\hbar \omega$ and results are reported in figure 5 and figure 6 with $\hbar \omega = 200$ cm$^{-1}$. Figures 5a and 5b corresponding to $E \perp H$ and $E//H$ respectively and $S = 5$, show that in the limit of a strong Jahn-Teller coupling, a high magnetic field lifts the degeneracy of the $^4T_2$ vibronic ground levels as for a fictitious spin $s$, with $S = 3/2$, and a $g$ value sensibly equal to 2. This is a consequence of the quenching of $g_L$ by the Jahn-Teller coupling. Experimental results are also recalled on these figures. A strong Jahn-Teller effect has therefore to be rejected since a doublet is observed experimentally in the high field limit. Figures 6a and 6b show Zeeman splittings

![Fig. 5](image1)

*Fig. 5.* — Theoretical Zeeman splittings of the $^4T_2$ level in the presence of a strong Jahn-Teller coupling. Full and dashed lines represent the $^4T_2$ Zeeman sublevels with non zero and zero relative intensities respectively. Some theoretical relative intensities are reported in brackets. Experimental data (I) are shown for comparison.

![Fig. 6](image2)

*Fig. 6.* — Theoretical Zeeman splittings of the $^4T_2$ level in the presence of a medium Jahn-Teller coupling ($S = 2$) calculated in the Ham approximation. The same representation as in figure 5 is used.
in the hypothesis of a medium Jahn-Teller effect with \( S = 2 \). In this case because of the partial quenching of \( g_L \), the orbital degeneracy within each \( M_e \) sublevel is lifted, and a value of \( S \) around 2 can explain the observed energy levels. We have therefore calculated the relative intensities for this \( S \) value, under the assumption of a high magnetic field. The results are reported in figures 6a and 6b. In both cases only one line is to be observed, whereas for an \( E \) polarization of the excitation light perpendicular to the magnetic field two lines have been observed with a comparable intensity as shown in figures 2a and 2b.

As a conclusion a value \( S = 2 \) gives a reasonable fit for positions, but does not explain the polarization effects. We have therefore tried to interpret the Zeeman experiments using the \( S = 0.6 \) value previously deduced from uniaxial stress studies. However when the strength of the Jahn-Teller coupling is weak, spin-orbit interaction may have the same order of magnitude as the Jahn-Teller energy and the previous approximation is no longer valid.

### 3.3 Weak Jahn-Teller Coupling.

In this section, the Jahn-Teller and spin-orbit interactions are treated on an equal footing of perturbation.

The space dimension associated with the eigenstates of the unperturbed Hamiltonian \( \mathcal{H}_0 + \mathcal{H}_{\text{int}} \) is infinite and diagonalization of the perturbation \( \mathcal{H}_0 + \mathcal{H}_{\text{JT}} \) necessitates that a maximum value \( N \) of the numbers of phonons \( n_0 + n_e \) of symmetry \( E_0 \) and \( E_e \) be chosen [10, 11]. Convergency was tested by observing the eigenstates as a function of \( N \). For \( S \) around 0.5, a good convergency was obtained for \( N = 3 \).

In figure 4 the spin-orbit splittings calculated in this scheme are reported for \( \hbar \omega = 100 \text{ cm}^{-1} \) and \( N = 5 \). The results are very similar to that obtained with the Ham model even for low \( S \) values. However, as previously reported by Parrot et al. [5] there appears a selective intensity transfer from the zero-phonon lines to the one-phonon lines because of the mixing parameters \( \{4T_2, t_J, n, n_0, n_e\} [5] \). The existence of this transfer suggests to assign the weak 19.717 cm\(^{-1} \) line to the \( \{4A_1 \rightarrow 4T_2 \frac{3}{2}F_{8}\} \) transition, the two components of the doublet being associated with transitions to the \( \{4T_2 \frac{5}{2}F_{6}\} \) and \( \{4T_2 \frac{5}{2}F_{8}\} \) levels. However, as reported in figure 7 for \( H = 0 \), this intensity transfer is not sufficient to explain the very weak line observed at 19.717 cm\(^{-1} \).

The determination of the Zeeman splittings and relative intensities has been performed for \( S = 0.6 \) and \( N = 3 \). The results are reported in figures 7a and 7b. There is still a reasonable agreement between calculated and experimental splittings, but we observe a severe discrepancy between the theoretical and experimental relative intensities: we are still unable to explain the polarization effects; moreover a transition to a sublevel of \( \{4T_2 \frac{3}{2}F_{8}\} \) should be observed with an intensity comparable to that of the doublet, even in the high field limit, on the high energy side of the doublet. It does not seem possible to identify such a transition with the very weak line detected around 19.717 cm\(^{-1} \) in zero field.

In order to keep the best \( S \) value, we first evaluated for \( S = 2 \) and \( S = 0.6 \) the quantities:

\[
\Delta E_i = \frac{\sum_i \Delta E_i^2}{\sum_i E_i^2} \quad \text{and} \quad \Delta \sigma_i = \frac{\sum_i \Delta \sigma_i^2}{\sum_i \sigma_i^2}
\]

where \( E_i \) and \( \sigma_i \) are respectively the shift and the relative intensity for a given Zeeman transition, \( \Delta E_i \) and \( \Delta \sigma_i \) the difference between experimental and theoretical values of \( E_i \) and \( \sigma_i \). For \( S = 2 \), we get

![Fig. 7. Theoretical Zeeman splittings of the $4T_2$ level, calculated as described in section 3.3. A weak Jahn-Teller effect ($S = 0.6$) is assumed. The same representation as in previous figures is adopted.](image-url)
\(A_1 = 0.1, A_2 = 0.69\) and for \(S = 0.6, A_1 = 0.16, A_2 = 0.79\). These results reflect the good agreement obtained for position and the discrepancy observed for intensity.

We then verified that the stress experiments could be interpreted in Ham model with an \(S\) value around 2: figure 8 shows the experimental stress results and the fit obtained using a 20 000 cm\(^{-1}\) per unit strain shift for all lines and an \(A\) value [5] of 1 750 cm\(^{-1}\) per unit strain.

We can finally check the convergency of our results since, in the cluster approximation, it is possible to relate \(V\) to \(A\) [12], and then to have an estimate of \(S\). We obtain \(S = 1.3\), in good agreement with our previous \(S = 2\) value. Parrot [5] gets \(S = 4\), to be compared to \(S = 0.6\) (all these results where derived with \(\hbar \omega = 100\) cm\(^{-1}\)).

This discussion shows that the \(S = 2\) value should finally be retained.

**Conclusion.** — The lowest \(^{4}T_2\) excited state of Mn\(^{2+}\) in ZnS has been studied by the Zeeman effect up to 100 kG for different polarizations of the electric field of the exciting light versus the magnetic field. In the Ham approximation, a Jahn-Teller coupling to an \(E\) vibrational mode with \(S = 2\) can account for the observed splittings. Nevertheless it has not been possible to explain fully the observed polarization effects. The discrepancy could be due to the approximation made in relative intensities calculations, as suggested in appendix. This difficulty could also be related to the moderate strength of the Jahn-Teller coupling, since it did not appear in the study of the \(^{4}T_1\) (strong Jahn-Teller effect) and \(^4E\) (no Jahn-Teller effect) levels.

**Appendix.** — We attempt here to discuss possible causes of the discrepancy between the experimental results and the theoretical analysis: in order to analyse the observed spectra we have to take account for perturbations up to second order, and some approximations are needed.

At first in the determination of the energy levels, we calculate the second order matrix elements of spin-orbit interaction within the vibronic ground states:

\[
\mathcal{K}_{ij} = \sum_{k,n} \frac{\langle \psi_i \phi_t | V_{so} | \psi_k \phi_n \rangle \langle \psi_k \phi_n | V_{so} | \psi_j \phi_j \rangle}{E(0) - E(k, n)}
\]

where \(E(0), E(k, n)\) are the energy of the vibronic ground state \(|\psi_i \phi_t\rangle\) and of the intermediate vibronic states \(|\psi_k \phi_n\rangle\) belonging to a different electronic state \(|\psi_k \rangle\).

Assuming that the separation between electronic states is large compared to the vibrational quanta so that the vibrational energy can be neglected in the non-zero terms of the sum, the \(\mathcal{K}_{ij}\) elements reduce by closure to:

\[
\mathcal{K}_{ij} = \sum_{k} \frac{\langle \psi_i | V_{so} | \psi_k \rangle \langle \psi_k | V_{so} | \psi_j \rangle}{E(0) - E(k)} \langle \phi_t | \phi_j \rangle.
\]

In this approximation second order matrix elements are reduced in the same way as first order matrix elements. This approximation was made in section 3.2 in deriving \(\rho_{JT}, \mu_{JT}\). When this approximation is no longer valid, a phenomenological hamiltonian of the same form as that given in section 3 suffices to describe the \(^{4}T_2\) level. It has been verified that reasonable values of \(\rho\) and \(\chi\) chosen around their crystal field values do not lift the discrepancy.

On the same way, in the calculation of the zero-phonon lines intensities we have to evaluate the matrix elements:

\[
\sum_{\Delta T_2, m_{e}, m_{\mu}} \frac{\langle 6A_1, M_6, a_1, n_{ho}, n_{so} | V_{so} | ^{4}T_1, M_6', k, m_{bk}, m_{ak} \rangle}{E(6A_1, n_{ho}, n_{so}) - E(^{4}T_1, m_{bk}, m_{ak})} \times \langle ^{4}T_2, M_6', j, l_{aj}, l_{ij} | H_{eq} | ^{4}T_2, M_6', j, l_{aj}, l_{ij} \rangle
\]

where \(n_{hp}, l_{ij}, m_{ij}\) describe \(E_i\) symmetry oscillators centered in \(Q_j\) and \(n, l, m\) are the occupation numbers.
At low temperature and for the zero-phonon lines of excitation spectra, if no Jahn-Teller effect is assumed in the \( ^4T_1 \) states, the number of phonons \( n, l, m \) are to be equal to zero and these matrix elements reduce simply to

\[
\sum_{\Delta i} \langle \bar{\nu}_1, M_{\bar{\nu}}, a_1 | \nu_o \rangle \langle ^4T_1, M_{\nu}, k | ^4T_2, M_{\nu}', j \rangle \frac{E(\bar{\nu}_1) - E(\nu)}{E(\nu)} \cdot \langle 0_{\nu_0}, 0_{\nu_o} | 0_{\nu_j}, 0_{\nu_j} \rangle = \exp(-S)
\]

so, oscillator strengths are reduced, but the relative intensities remain the same as in the static crystal field approximation.

However if a Jahn-Teller effect is assumed in the \( ^4T_1 \) intermediate states, we have to consider all the vibronic levels deriving from the \( ^4T_1 \) electronic states because of the overlap \( \langle 0_{\nu_0}, 0_{\nu_o} | m_{\nu}, m_{\nu} \rangle \) between vibronic functions, and the relative intensities have the previous form only if the closure relation is valid. From our experimental results it seems that this approximation is not quite justified.

Acknowledgments. — The experiments were done at the Max-Planck Institut-S.N.C.I. in Grenoble. We would like to thank Dr D. Bimberg who gave us the possibility of using his equipment. We are grateful to M. Berger and H. Krath for their expert technical assistance. We are greatly indebted to C. Blanchard for many helpful discussions. We appreciated the help of B. Gaillard for orienting the crystal.

References